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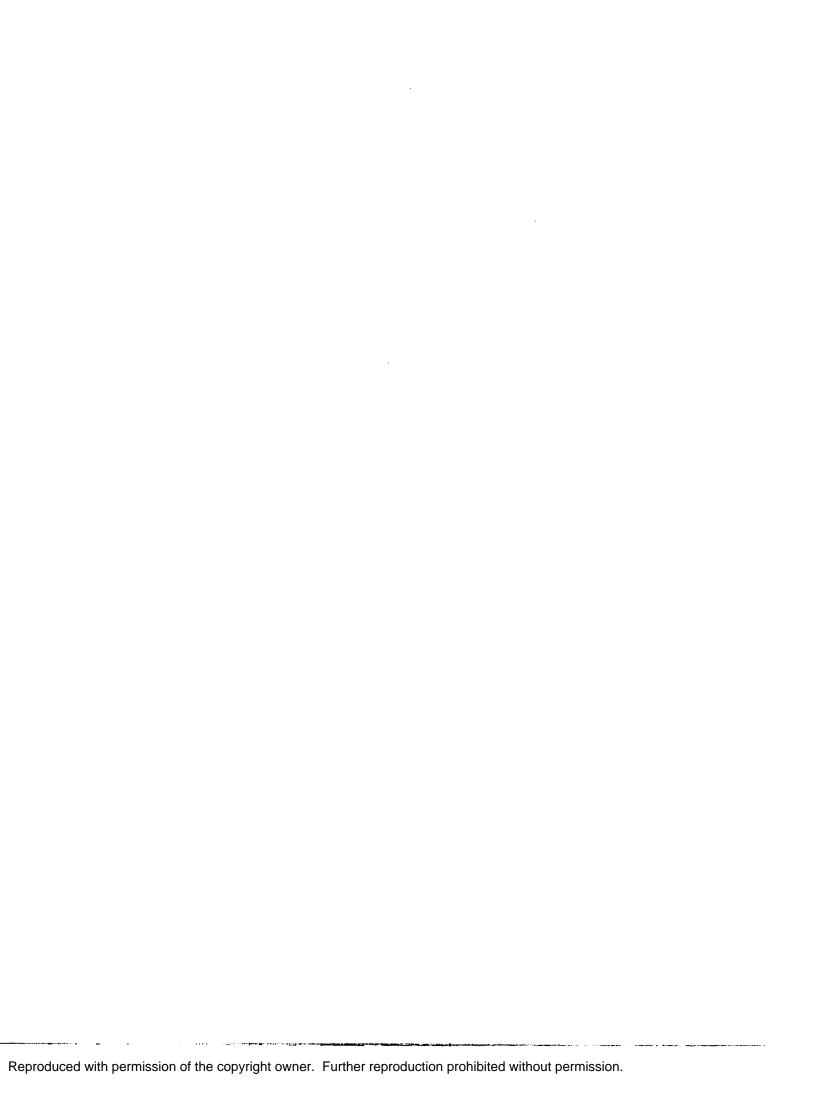
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Options for management of soil contamination problems at Superfund sites: A proposed approach to setting soil cleanup levels

Schumann, Paul Blane, D.Env.
University of California, Los Angeles, 1989

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# UNIVERSITY OF CALIFORNIA

Los Angeles

# Options for Management of Soil Contamination Problems at Superfund Sites: A Proposed Approach to Setting Soil Cleanup Levels

A dissertation submitted in partial satisfaction of the requirements for the degree

Doctor of Environmental Science and Engineering

by

Paul Blane Schumann

1989

The dissertation of Paul Blane Schumann is approved.

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University of California, Los Angeles
1989

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1989

#### **DEDICATION**

This work is dedicated to three important women. First, to the memory of my grandmother, Marie, whose vision inspired me to pursue this goal; and whose years of sacrifice set me well along its road. Second, to my mother, Elaine. Finally, to Judy, who stood by me through so much.

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#### LIST OF ACRONYMS AND ABBREVIATIONS

Aquifer Finite Element Model AQUIFEM **ARARS** applicable or relevant and appropriate requirements **BDAT** Best Demonstrated Available Technology BOD biological oxygen demand BTU British thermal unit C degrees Celsius CAA Clean Air Act CDM Camp, Dresser and McKee, Inc. CEC cation exchange capacity CERCLA Comprehensive Environmental Response, Compensation and Liability Act **CFR** Code of Federal Regulations cm centimeter Cancer Potency Factor CPF CWA Clean Water Act (also Federal Water Pollution Control Act) СУ cubic yard DRE destruction/removal efficiency Enforcement Decision Document EDD **EDTA** ethylene diamine tetraacetic acid EP Extraction Procedure (for the RCRA toxicity characteristic) **EPA** United States Environmental Protection Agency F degrees Fahrenheit FDM finite difference method FEM finite element method FS Feasibility Study ft foot FWOC Federal Water Quality Criteria (promulgated under CWA) **HAWAMAX** Hazardous Wastes Management Expert HELP Hydrologic Evaluation of Landfill Performance model Hazardous Materials Control Research HMCRÍ Institute HRS Hazard Ranking System **HSWA** Hazardous and Solid Waste Amendments IFDM integrated finite difference method IGWMC International Ground Water Modeling Center in inch IRM Initial Remedial Measure kq kilogram 1b pound

MARS	Model Annotation Retrieval Database
	(IGWMC)
MCLG	Maximum Contaminant Level Goal
-	(promulgated under SDWA; synonymous
	with RMCL)
MCL	Maximum Contaminant Level
	(promulgated under SDWA)
MEI	Maximum exposed individual
mg	milligram
ml	milliliter
MOC	method of characteristics
MRI	Midwest Research Institute
MSL	Mean Sea Level
MTV	mobility, toxicity, volume
NASA	National Aeronautics and Space
Ad	ministration
NCP	National Contingency Plan
NDD	Negotiation Decision Document
NOAEL	No Observed Adverse Effect Level
	(for systemic toxicants)
NPL	National Priorities List
NRC	National Research Council
O&M	operation and maintenance
OAT	Office of Apropriate Technology
	(California)
OSW	Office of Solid Waste (EPA)
OTA	Office of Technology Assessment
	(U.S. Congress)
PA	Preliminary Assessment
PAH	polycyclic aromatic hydrocarbon
PCB	polychlorinated biphenyl
PCE	perchloroethylene
рН	log hydrogen ion concentration
PL	Public Law
ppb	parts per billion
PPCL	Preliminary Protective Concentration
	Limit
mqq	parts per million
PRP	Potentially Responsible Party
RA	Remedial Action
RCRA	Resource Conservation and Recovery
	Act
RD	Remedial Design
RF	radio frequency
RfD	Reference dose (for systemic
	toxicants)
RI	Remedial Investigation
RIDAM	Risk and Decision Analysis Module
NA VALI	(HAWAMAX)
RMCL	Recommended Maximum Contaminant
KHOU	Level
	TIE A ET

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ROD	Record of Decision
RPM	Remedial Project Manager
RSD	Risk Specific Dose (for carcinogens)
RTI	Research Triangle Institute
SARA	Superfund Amendments and
·	Reauthorization Act
SI	Site Investigation
SITE	Superfund Innovative Technology
	Evaluation program
SOCEM	Soil Contaminant Evaluation
	Methodology
TCA	1,1,1-trichloroethane
TCE	trichloroethylene
TCLP	Toxicity Characteristic Leaching
	Procedure
TOC	total organic carbon
TSCA	Toxic Substances Control Act
USC	United States Code
USGS	U.S. Geological Survey
VOC	volatile organic compound
VHS	Vertical and Horizontal Spread
	model

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1985-1989	Environmental Engineer Environmental Protection Agency Washington, D.C.

# PUBLICATIONS AND PRESENTATIONS

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#### ABSTRACT OF THE DISSERTATION

Options for Management of Soil Contamination

Problems at Superfund Sites:

A Proposed Approach to Setting Soil Cleanup Levels
by

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Contaminated soil cleanups at uncontrolled or abandoned hazardous waste sites historically have been complex and difficult to accomplish, due to a variety of technical and institutional factors. The consequences have been inconsistent soil cleanups from site to site, and inconsistent selection of cleanup levels.

Site-specific risk assessments are necessary to determine the most effective cleanup, and to set soil cleanup levels based on the most limiting exposure pathway at each site, for each compound of concern. For the purposes of this study, soil leaching and ground water ingestion is assumed to be the most limiting pathway at most CERCLA sites. EPA needs to apply a

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similar decision making process from site to site for selecting and applying models to assess risks from soils, and to estimate soil cleanup levels by back-calculating soil levels from "safe" ground water concentrations. The Soil Contaminant Evaluation Methodology (SOCEM) is proposed as a candidate modeling decision process, incorporating decision analysis principles to semi-quantitatively estimate and track the uncertainties associated with each decision in the model selection process.

At the McKin Superfund site in Gray, Maine, one of EPA's first sites with a published, numerical soil cleanup target, the author applied many of the SOCEM principles to advise EPA analysts and contractors in selecting and using a model to back-calculate the soil cleanup level, based on potential ground water exposure to trichloroethylene. Other SOCEM principles were applied after the McKin decision was made, as the responsible parties challenged the model choice and EPA rebutted.

Results of the analysis, and the implications of adopting a SOCEM approach on a national scale, are discussed. Recommendations for future testing, improvements, and research needs for SOCEM are given in the text.

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#### 1.0 INTRODUCTION

Since 1980, the United States Environmental

Protection Agency (EPA or "the Agency") has proceeded

with cleanups of uncontrolled hazardous waste sites

under the authority of the Comprehensive Environmental

Response, Compensation, and Liability Act (CERCLA), also

commonly referred to as "Superfund." Response actions at

hazardous waste sites have involved many different

approaches to reduce the threats of uncontrolled wastes.

Within the framework provided by Superfund's

implementing regulations in the National Contingency

Plan (NCP), response actions must employ a cost
effective alternative that is technologically feasible

and that provides adequate protection of public health

and the environment.

EPA constantly has been confronting the need for safer and better methods for determining both the appropriate cleanup alternative for a given site, and the optimum extent of remedy. This report will outline the nature of this problem, with special focus on the question of how to more accurately and consistently determine the appropriate extent of remedy when the chief concern is with contaminated soils at a Superfund site. To do this involves examining the technical problems associated with soil contamination at

Superfund sites, as well as understanding the institutional framework of the Superfund program within which these problems are addressed.

#### 1.1 CERCLA and SARA

CERCLA was passed in 1980 as Public Law (PL) no.96-510 (codified as amended in Title 26 of the United States Code (USC) at 26 USC Sections 4611 through 4682 and 42 USC Sections 6911a, 9601-9657, 1982). It gave broad authorities to the President, and in turn to EPA, for cleanup of abandoned hazardous waste disposal sites and spills of hazardous substances that threaten public health and the environment.

This authority was sorely needed. The Solid Waste Disposal Act, as amended by RCRA, the Resources Conservation and Recovery Act of 1976 (42 USC 6901-6991(i), 1982 and 1984) established Federal and State hazardous waste management frameworks regulating the generation, transport, storage, treatment, and disposal of newly created hazardous waste. However, RCRA did not provide general authority for responding to long-term threats posed by past improper disposal practices and abandoned, uncontrolled hazardous waste sites prior to its reauthorization in 1984. Likewise, under Section 311 of the Clean Water Act (PL 97-117; 33 USC 466 et seq.), the Federal government had some authority to

respond to spills and accidents involving oil or some 300 hazardous substances when they threatened navigable waterways, but no authority to respond to releases elsewhere into the environment (EPA, 1983A; Brown, 1984).

Sections 211(a) and 221-223 of CERCLA created a \$1.6 billion revolving fund called the Hazardous Substance Response Trust Fund or "Superfund", created largely from taxes on petroleum and chemical feedstocks, to finance these actions. The Fund could be replenished by suing the responsible parties to recover costs and damages.

Two sections provided the primary authority for cleanup actions: Section 104, which authorized the government to undertake Fund-financed responses to protect public health and the environment from releases or threatened releases; and Section 106, which provided enforcement authorities allowing EPA to sue the responsible parties to abate the site threats, or to issue administrative orders requiring the responsible parties to undertake cleanup, when releases or threatened releases pose imminent and substantial endangerment of public health and the environment. These authorities are similar to the emergency enforcement powers of other environmental statutes such as the Clean Air Act, Clean Water Act, Toxic Substances Control Act, Safe Drinking Water Act, and RCRA (Brown,

1984). A third Section, 107, provided for cost recovery from responsible parties for cleanups undertaken under the authority of Section 104. Actions taken under CERCLA authority were required to provide adequate protection of public health and the environment and to be cost-effective.

Superfund was enacted as a five-year program. Its funding authority expired in 1985. The law was reauthorized by the Superfund Amendments and Reauthorization Act of 1986 (SARA; PL 99-499), which added a new requirement and an important new preference to the requirements that remedial actions be protective of public health and the environment and cost-effective. SARA's cleanup standards provisions in Section 121 also require that remedial actions attain the applicable or relevant and appropriate requirements of other Federal statutes, and those of promulgated State requirements that are more stringent than their Federal counterparts.

Additionally, SARA expressed a Congressional preference for the use of permanent solutions and alternative treatment or resource recovery technologies to the maximum extent practicable. In another passage of the law this is interpreted to be best achieved through permanent and significant reductions in the mobility, toxicity, or volume of the hazardous substances at the site. This is a significant shift

from the original Superfund program's attainment of the statutory goals largely through reduction or prevention of exposure. The new focus is on reduction of the hazard itself through destruction or detoxification to enhance the long-term effectiveness of the remedy and, where possible, to achieve a "permanent solution" at the site.

## 1.2 The "How Clean is Clean?" Issue

The decision on extent of remedy or degree of cleanup, popularly termed the "How clean is clean?" issue, has been and remains a controversial issue among Federal and State agencies, potentially responsible parties, legislators, citizen groups, environmentalists, and others involved in addressing uncontrolled hazardous waste sites (Frost, 1984; Brown, 1984; Keystone Center, 1985; Office of Technology Assessment, 1985; Smith, 1988; Wolf and Warren, 1988). Stated simply, the problem is in determining how much contamination to treat or remove from a Superfund site or, conversely, what ambient levels of contaminants, if any, are safe to leave in soils, air, surface water, and/or ground water at the site following the cleanup without causing unacceptable threats to public health and/or the environment.

Superfund sites typically vary widely in terms of

size, facility type, waste mixture, and site
hydrogeologic setting, and often contain an identifiable
contaminant source such as a landfill, industrial
facility, abandoned dump, or mine. In some cases, there
may be a less discrete source area such as a field,
marsh, unpaved lot or road, or woodland contaminated
with sprayed pesticides or industrial wastes, or a dirt
field contaminated by runoff or wind-borne pollutants,
now itself a potential contaminant source area.

Often one or more plumes of released contaminants are migrating away from the source in surface water, ground water, air, river or harbor sediments, etc.. In some cases, such as several contaminated municipal well field sites, the plume cannot be traced back to any identifiable source. Complex mixtures of wastes and multi-media contamination are frequent.

The "how clean is clean?" issue is a critical one for several reasons: (1) the cleanup criteria employed ultimately determine whether adequate protection of public health and the environment is achieved, and address the extent to which the selected remedy will satisfy the new statutory preference for permanent solutions; (2) the cleanup criteria ultimately define the scope and cost of each individual cleanup and of the overall Superfund program; and (3) the cleanup criteria should promote public trust in and support for the

program (Frost, 1984; Edelson, 1988; Wolf and Warren, 1988). The extent of remedy issue has arisen because the CERCLA statute did not set substantive health- or environment- based cleanup standards for sites, nor did it establish a clear means for choosing among the remedial alternatives available for a given site (Keystone Center, 1985).

#### 1.2.1 The National Contingency Plan

All Section 104 cleanup actions must be consistent with the revised National Contingency Plan (NCP). The NCP was originally promulgated in 1968 as a set of regulatory guidelines for oil and hazardous substance spill cleanups under the authority of Section 311(c)(2) of the Federal Water Pollution Control Act. However, in Section 105(8)(A) of CERCLA, Congress recognized the limitations imposed by the size of the Fund relative to the national scope of the problem. They directed the EPA to revise the NCP to contain the general specifications and guidelines for performing cleanups under the broad CERCLA authorities. The revisions were to focus on the following (Brown, 1984):

- (1) "criteria for determining priorities among releases or threatened releases ...for the purpose of taking remedial action,"
- (2) "methods and criteria for determining the appropriate extent of removal, remedy, and

other measures" (CERCLA Section 105(3); and

(3) "means of assuring that remedial action measures are cost-effective over the period of exposure or potential exposure to the hazardous substance or contaminated materials" (CERCLA Section 105(7)).

Thus, the NCP was to contain guidelines for determining which sites should be cleaned up, which should be cleaned up first in terms of their relative risks, when site conditions warrant initiation of responses under CERCLA/SARA authority, and when the response taken is sufficient under the law (i.e., "how clean is clean"). These requirements were partially satisfied via the publication and updates of the Hazard Ranking System and the National Priorities List (Brown, 1984), and by Subpart F of the NCP.

The revisions to the NCP were promulgated in July, 1982, and revised in November, 1985, as Part 300 of Title 40 of the Code of Federal Regulations (40 CFR 300). The NCP sets forth the analytical and decisionmaking framework for response actions under Superfund in stages, from the initial discovery of a site or a potential release through the design and implementation of a final solution at the site (EPA, 1982A, 1985A). The NCP criteria require remedies to be selected that are cost-effective, technologically feasible and reliable, and protective of public health

and the environment.

### 1.2.2 The CERCLA Compliance Policy

According to the Agency's policy on compliance with other statutes, which was appended to the NCP preamble (EPA, 1985A), protectiveness is to be assured via the remedy's attainment of "applicable or relevant and appropriate Federal and State requirements" (ARARs) that have been identified for the site and the response action in question. Exceptions may occur only when one of five specific circumstances described in 40 CFR 300.68 (i)(5) exists. EPA must document all analyses of these circumstances, which it does in its Record of Decision (ROD) for the site remedy.

The compliance policy memorandum interpreted the terms "applicable or relevant and appropriate." It included preliminary lists of regulations that are potentially applicable to CERCLA cleanups, and other Federal requirements, advisories, criteria, and guidance that could be considered, to the extent that they are relevant and appropriate, when formulating Superfund remedies. Under SARA, promulgated State requirements may be found applicable or relevant and appropriate as well. Limited direction for implementing this approach at Federal Superfund sites is found in the Superfund guidance for feasibility studies (EPA, 1985B), a guidance

for preparing Records of Decision (EPA, 1985C), and in several other EPA draft documents (EPA, 1985D, 1986A).

In the past, this often resulted in selection of site remedies encompassing some type of containment of wastes, either at the original site, or at a commercial off-site hazardous waste land disposal facility regulated under Subtitle C of RCRA. However, these practices might not meet the permanence preference in the reauthorized statute, and EPA has received continued criticism that the NCP guidelines are too general to provide clear, unambiguous direction for selecting appropriate remedies or for determining the appropriate extent of their application, i.e. "how clean is clean" for the site. Additional discussion of this issue is given in the preamble to the NCP (EPA, 1985A).

#### 1.3 The Soil Contamination Problem

Contamination of surface and subsurface soils is one of the most complex and pervasive problems encountered at Superfund sites. This contamination typically results from a broad range of mismanagement or release situations including leaks from drums, tanks, impoundments, or other waste management units; direct discharges of wastes to pits or to the ground surface; spills, fires, explosions, or other catastrophic releases; and leaching to soils from pits, ponds, piles,

tanks, landfills, or solid residues. Likewise, it may result from indirect contamination by pollutants carried to soils by surface runoff, volatilization from the subsurface, tracking of wastes across surfaces of a site, or wind or airborne transport, as will be discussed further in Sections 3.1.2 and 4.2.

whether measured in terms of numbers or types of sites, or of volumes of contaminated soil. A recent analysis of volumes of contamination at 272 National Priority List sites indicated that an average of approximately 37,900 cubic yards of contaminated soil is found at a "typical" site (Table 1; Camp, Dresser and McKee, 1985A). Over the next five years, remedial actions will be undertaken at some 400-plus sites, requiring the containment, treatment and/or disposal of some 15,242,000 cubic yards of contaminated soil. If large municipal landfills are included in the universe of sites to receive action, the volume estimates range as high as 120 million cubic yards (Camp, Dresser and McKee, 1985A).

In this analysis, 272 sites were grouped into eight categories based on type of past and present site use, which to some extent also correlated with the types and distributions of contaminants found. Contaminated soils are found in virtually every one of the eight National Priorities List site categories other than contaminated

Volumes of Contaminated Soils at National Priorities List Sites (Source: Camp, Dresser and McKee, 1985A) TABLE 1

		3	Contaminated Source Material	. Material	
Site Category	Lagoons (gallons)	Sludges (cubic yds)	Tanks (gallons)	Orums (55 gal/drum)	Soils (cubic yds.)
Commercial/Industrial Landfill (8)(e)	44,000,000 (5,500,000)(b)	21,000 (2,600)	0	25,000 (3,100)	484,800 (60,600)
Municipal Landfill (5)	10,500 (2,100)	175,000 (35,000)	350 (0/)	69,000 (13,800)	10,100
Manufacturing (12)	3,374,000 (281,000)	259,500 (24,590)	112,600 (10,236)	2,300 (206)	65,500 (5,000)
Recycling/Recovery (15)	55, 360, 000 (3,690, 000)	148,500 (9,900)	2,584,000 (172,000)	22,400 (1,500)	176,500 (12,400)
Refinery (4)	10,200,000 (2,550,000)	132,000 (33,000)	c	75 19	184,500 (46,100)
Uncontrolled Chemical Dumpsite (12)	1,060,000 (91,500)	18,500 (1,550)	•	129, 900 (1,800)	353,000 (29,500)
Mood Ireatment (2)	•	46,000 (23,000)	•	•	58,000 (29,000)
Defense (4)	0	0	0	•	(292,500)
Total Sites 62(a)					
TOTALS	114,000,000	800,500	2,697,000	138,000	2,502,000

TABLE 1 (Continued)

37,917	15,242,000
2, 101	844,602
40,864	16,427,326
12,127	4,875,054
1,727,270	694, 360, 000
Overall Average/Site	Projection for 402 Sites (d)

FOOTNOTES:

for these sites are in waste classes (Groundwater & Total Contaminated Volume) not reviewed in this summary. However, 66 sites are used to calculate the overall site averages shown in this table. (a) 4 sites and 2 site categories (Mining & Contaminated Wellfield) are not listed in this table because the volume estimates

(b) Average per site in parentheses. Calculated by dividing the total volume of source material by the number of sites in each category.

(c) Number of sites in each site category in parentheses.

(d)<sub>Calculated</sub> by multiplying Overall Average/Site by 402.

well fields. The distributions of contaminants highlight the complexity of contaminant mixtures in the contaminated soil at these sites, as follows:

- o Large landfills on the National Priorities List tend to contain primarily volatile (83%) and nonvolatile (50%) organics, polychlorinated biphenyls (PCBs; 32%), and metals (52%), reflecting local disposal practices and typical municipal waste composition.
- o Recycling and recovery facilities on the National Priorities List contain metals (68%), volatile organics (68%), nonvolatiles (56%), and PCBs (48%), mirroring historical industrial waste streams.
- o Manufacturing sites on the National Priorities List contain volatiles, especially trichloroethylene (TCE; 51%), and heavy metals (40%), but low levels of PCBs (10%).
- o Refinery sites on the National Priorities List contain primarily volatiles and nonvolatiles (100%) due to their receipt of acid asphaltic sludges from refinery processes. However, metals (40%) and PCBs(40%) are also relatively common. Very few National Priorities List sites are in this category.
- O Uncontrolled dumps on the National Priorities List have been found to contain mainly volatiles (64%) and metals (41%), but also dioxins (18%), pesticides (18%), and PCBs (27%).
- O Defense sites on the National Priorities List often contain predominantly metals (80%) and volatiles (43%), but they may also have complex wastes such as explosives, nerve gases or biological agents, and typically are situated on large land areas.
- o Wood treatment sites are contaminated with nonvolatile organics such as pentachlorophenol, polycyclic aromatic hydrocarbons (PAHs), and creosote (82%) as well as metals such as copper and arsenic (46%), and occur increasingly on the National Priorities List.

- o Mining sites universally, and predominantly, contain metals.
- Contaminated well fields are a rapidly expanding National Priorities List category although, as mentioned above, they rarely contain contaminated soil. Sometimes the source of contamination cannot even be identified (e.g., the Charlevoix site in Michigan). Typically they are contaminated with volatile organics such as TCE (83%).

To protect public health and the environment, response actions must mitigate or prevent direct or indirect exposure to contaminated soil, and control the threat of migration of hazardous substances from the site.

#### 1.3.1 <u>Problems in Selecting Appropriate Soil</u> Remedial Actions

The choice of remedial options for contaminated soils depends greatly on the context in which the choice is made. Most site remedies to date have considered soils as a medium in which pollutants are stored and subsequently transformed and transported to human and environmental receptors. In this context, the resource being protected is the eventual receptor or receiving medium, i.e., human health, surface or ground water, air, wildlife, and terrestrial or aquatic habitats. The soil itself traditionally has not been protected as a resource, unlike ground water, for which the existing regulatory framework clearly favors restoration. Some contaminated soils remedies might be altered

significantly by a strong preference to restore soils for specific productive uses.

The second context relates to the remedy selection criteria in the NCP and SARA--adequate protection of public health and the environment, cost-effectiveness, satisfaction of applicable or relevant and appropriate requirements, and the preference for permanent solutions. The overall site remedy, and the soils remedy or remedies at a site, must strike the best balance available to satisfy these often conflicting objectives. The extent of cleanup decision must balance such factors as the uncertainty in the available data; the time and cost of supplemental analyses; the volumes and types of soil and contaminants requiring containment, treatment, and/or redisposal; the degree of hazard of the contaminants via the exposure pathways present at the site; the relative long-term effectiveness and cost-effectiveness associated with different cleanup levels; and the perceived value of each resource.

#### 1.3.2 <u>Problems in Selecting Appropriate Soil</u> Cleanup Levels

Past "how clean is clean" decisions for Superfund soil remedial actions are summarized in Appendix I.

They have ranged from no action, to containment of all

contaminated materials, to cleanup to the limits of visible contamination, to the removal and/or treatment of all soils with pollutant levels above detection limits (i.e., cleanup to "background") (EPA, 1987F).

Many factors have contributed to this wide range of levels, one important factor being the lack of available standards. Aside from a handful of concentration levels developed under the RCRA land treatment regulations, EPA standards presently do not exist for safe (or acceptable) health- and environment-based ambient levels of contaminants in soils. Regulations promulgated under other Federal environmental statutes provide only limited direction on levels of cleanup for contaminated soil. Few states have soil standards.

The lack of soil standards derives partly from the fact that Federal environmental regulation traditionally has focused largely on the fate and transport of pollutants through single media other than soil. A limited set of criteria and standards have been created under environmental laws such as the Clean Water Act (CWA), Safe Drinking Water Act (SDWA), and the Clean Air Act (CAA), establishing safe ambient levels for pollutants in these other media, for example Maximum Contaminant Levels (MCLs), Federal Water Quality Criteria (FWQCs), worker exposure standards developed by the Occupational Safety and Health Administration

(OSHA), and National Ambient Air Quality Standards.

Other statutes such as the Toxic Substances Control Act (TSCA) and RCRA provide ambient levels only indirectly, such as RCRA's "background" standards for "clean closure" of surface impoundments and for ground water protection beneath regulated hazardous waste disposal facilities, as will be described in Chapter 3. Instead they focus on performance standards for regulating certain types of treatment or disposal actions, for example TSCA regulations for management of polychlorinated biphenyls at 40 CFR Parts 760-765, RCRA design and operating standards for new land disposal facilities (40 CFR Parts 264 and 270), and RCRA treatment standards promulgated under the land disposal restrictions program (40 CFR Part 268).

Because of the tremendous diversity of
environmental conditions and exposure routes present at
Superfund sites, until recently these criteria and
standards have been applied to contaminated soils
problems on an ad hoc, site-by-site basis. No clear
distinction has traditionally been made between the use
of health-based ambient concentration standards provided
by other statutes and the action-specific or
performance-based determinations provided by RCRA and
TSCA to set soil cleanup levels, with the end result
being the diversity of cleanup targets previously

described.

# 1.3.3 <u>The Need for a Consistent Decisionmaking Approach</u>

Specific guidance concerning how and to what extent the criteria and standards for other media should be used for contaminated soils, as well as methods for setting cleanup levels for pollutants that lack published standards, has not been developed by the Superfund program or by other Agency programs to date. Very few Superfund Records of Decision signed through 1984 allowed contaminants to be left unmanaged in the soil above background levels, or the boundary of visible contamination, except where the site was capped and closed in accordance with RCRA landfill closure regulations (40 CFR 264 Subpart G). Guidance is needed on how to choose a soils cleanup remedy and on how to define the extent of cleanup at a given site.

#### 1.4 Purpose of the Study

In this dissertation the author proposes a methodical approach for the site-specific determination of acceptable cleanup levels for contaminated soil at Superfund sites. The approach has several objectives:

- 1. It must retain sufficient flexibility to work over the wide range of soil contamination situations typically encountered at Superfund sites;
- 2. It must provide the maximum degree of consistency attainable in approaching different sites in a systematic, consistent fashion;
- It must be accessible to a broad range of users including the EPA, States, and private parties undertaking cleanups; and
- 4. It must lead to decisions that conform to the requirements of SARA and the NCP, including protectiveness, technical feasibility, cost- effectiveness, and the preference for permanent remedies.

The proposed approach was tested at a Superfund site, and the initial results of these tests are discussed in the form of a case study in Chapter 5.

The focus of this document is on establishing appropriate "how clean is clean" levels for contaminated soils, with a special emphasis on the use of risk assessment, fate and transport models, and decision analysis concepts to help make this determination.

While all potential pathways of exposure to soil contamination will be discussed, the analysis will focus on soils' threats to ground water, and estimation techniques for fate and transport of pollutants via this exposure pathway.

A detailed discussion of the problems and uncertainties inherent in the toxicological components of risk assessment, i.e., hazard identification and

dose-response relationships once the contaminant has entered the body of the receptor, is outside the scope of this report and will not be presented.

#### 1.5 Overview of the Report

The remainder of this report is structured into six main chapters. Chapter 2 describes the process for remedial actions taken under Superfund, current technologies used to remediate soil contamination, and problems encountered in using these methods.

Chapter 3 describes the multi-media exposure problems caused by contaminated soil, and describes different approaches considered in establishing soil cleanup standards. It then discusses in more detail the role of other environmental laws and requirements in formulating Superfund contaminated soil remedies, and issues in how these affect the extent of remedy decision.

chapter 4 focuses on the soil-to-ground water exposure pathway, and the processes affecting the transport, transformation and fate of pollutants in soils. It then reviews the fundamental concepts of flow and transport models, and describes how models can be used to simulate key processes of contaminant migration at a Superfund site. It then presents new decision approaches for selecting and using models, and key factors affecting their development and use.

Chapter 5 presents the McKin Superfund site in Maine as a case study to illustrate the author's and EPA's initial attempts to apply the concepts of the SOCEM decision approach at a site. It presents an analysis of the results and subsequent refinements made during implementation of the selected soils remedy.

Chapter 6 discusses some of the technical and institutional problems and constraints realized in applying the decision approach, and presents generally how the analysis might have been conducted at other sites, or at the same site under different constraints and uncertainties. Chapter 7 presents the conclusions of this report, and provides some recommendations concerning the full-scale implementation of such a soils cleanup decision approach by the Superfund program.

#### 2.0 SOILS CLEANUP METHODS

This chapter sets the stage for examining appropriate ways of setting soil cleanup levels by providing an overview of the types of Superfund responses in Section 2.1, and then of the remedial process by which Superfund sites are identified and studied, showing how cleanup alternatives are identified and evaluated. A remedy is then selected and implemented, as discussed in Section 2.2.

A review of currently available soils cleanup methods is given in Section 2.3. Problems encountered by the Superfund program to date in selecting and implementing soils remedies are discussed in Section 2.4, to provide an introduction to the discussion of options for setting soil cleanup levels in succeeding chapters.

### 2.1 Types of Response Actions Under Superfund

Under the most recent revisions to the National Contingency Plan (EPA, 1985A), Superfund response actions were divided generally into two main categories:

Removal actions, taken when immediate responses are necessary for spills, threats of fire or explosion, or direct contact of persons or sensitive environments with acutely toxic substances, or other emergencies (Clean Water Act Section 311(a)(8); CERCLA Section 101(23)). Removal actions, undertaken at both National Priorities

List and non-National Priorities List sites, may include cleanup of surface spills, excavation or removal of drums and tanks, emptying of lagoons, sampling and analysis, installation of security fencing or discharge control barriers, provision of alternate water supplies, or evacuation of threatened populations (EPA, 1984A; 1985A,E). They are intended to be temporary responses to abate imminent, relatively well-defined hazards. A removal may not necessarily abate all threats to public health and the environment at a site (Brown, 1984); removal actions were limited to 6 months duration and \$1 million in cost under CERCLA, and are similarly limited under SARA.

Remedial actions, the focus of this report.
These are longer-term actions, generally much costlier than removals, that are consistent with the attainment of a permanent remedy at the site (CERCLA 101(24); EPA, 1985A). In contrast to removals, remedial actions generally are performed to minimize or eliminate significant long-term threats or potential threats to public health and the environment. They are undertaken by EPA in partnership with the State (either agency may have the lead) under Section 104, or by private parties in consultation with the EPA under Section 106. Fund-financed remedial actions may be taken only at National Priorities List sites.

A third category, <u>Planned Removals</u>, also termed interim remedial measures or, more recently, expedited response actions, was included in the 1982 National Contingency Plan to describe short-term responses sharing some characteristics of both removal and remedial actions but intermediate between the two. They addressed short-term but non-emergency risks that nevertheless merited expedited response. They were occasionally selected in situations where continuation of an ongoing removal activity was the most cost- effective

overall response to complete a site. This category was considered to be redundant to removals and it was eliminated from the 1985 revision of the National Contingency Plan.

Remedial responses may include any of the actions described above as "Removals," plus others such as the containment, removal, and/or treatment of wastes, sludges, sediments, and contaminated soils; and other measures resulting in containment, removal, and/or treatment of any other sources of contamination (often referred to as "source control" measures). They may also include containment, removal, and/or treatment of contaminated ground or surface water (often called "management of migration" measures).

Examples of removal and remedial site problems are discussed by the Office of Technology Assessment (1983, 1985); Epstein et al. (1982); and Brown (1979).

Actions may include installing caps, slurry walls, and other engineered containment structures or barriers; treating wastes through physical, chemical, or biological methods such as land treatment, oxidation processes, precipitation reactions, solidification, air stripping, or incineration. As stated previously, remedial actions must be protective of public health and the environment and cost-effective (considering also other potential needs and uses of the Fund--EPA, 1985A;

Brown, 1984). They must also conform to those Federal and State requirements found to be applicable or relevant for the site, and preferably should use permanent solutions and alternative treatment/ destruction or resource recovery technologies to the maximum extent practicable (SARA Sections 121(b)(1) and (d)(1)). Remedial actions are performed in a series of stages given in Subpart F of the National Contingency Plan.

#### 2.2 Overview of the Remedial Process

One can distinguish three main phases of the remedial response process described in the National Contingency Plan: (1) definition of the problem, (2) planning and selection of the remedial response, and (3) implementation of the remedial action (EPA, 1983A).

These phases are depicted in Figure 1. (1) Definition of the problem involves discovery and screening of the site, evaluation via the preliminary assessment (PA) and site inspection (SI), and ranking of the site on the National Priorities List. (2) Remedial response planning for sites that become listed on the National Priorities List occurs in the Remedial Investigation and Feasibility Study (RI/FS). 40 CFR 300.68 outlines EPA's process for evaluating the nature and extent of contamination in the Remedial Investigation, developing

3 Superfund Removal and Remedial Response Processes (Source: EPA, unpublished data) 3] ŀ ıį Į § 5 FIGURE 1: ]: [0]

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and evaluating remedial technologies and alternatives in the Feasibility Study, selecting the remedy, and documenting its selection in the Record of Decision.

(3) The selected remedy is implemented in the Remedial Design (RD) and Remedial Action (RA) phases. Completed sites may be deleted from the National Priorities List when the threats prompting their original assignment to the National Priorities List have been abated. These process steps will be described briefly in the following sections.

# 2.2.1 <u>Definition of the Site Problem: Preliminary</u> <u>Assessment, Site Investigation,</u> and Hazard Ranking System

The primary goals of the problem definition activities are to screen sites according to their magnitude of threat and to establish priorities for remedial action among the worst sites. Remedial actions that satisfy the statutory goals to provide protective and permanent solutions will be enormously costly at many sites (Office of Technolgy Assessment, 1983, 1985, 1988). As discussed in Chapter 1, Congress and EPA recognized that the scope of the problem far exceeded the limited resources of the Fund. Thus, the preliminary assessment and site inspection are limited, relatively low-cost field and literature investigations that provide information sufficient to rank the site for

the National Priorities List using the Hazard Ranking System model.

The Preliminary Assessment and Site Investigation identify the types (and estimate the quantities) of hazardous substances present; potential population risks through especially the air, surface water, and ground water pathways; and potential for contamination of drinking water supplies, other potential exposure pathways, or sensitive ecosystems. Fire, explosion, and direct contact potential are estimated to assess the need for removal actions (EPA, 1983, 1985A). The Hazard Ranking System model then combines scores of hazard, migration potential, and exposure potential for the three pathways. Sites whose cumulative score does not exceed 28.5 (on a scale of 100) are ineligible for Fundfinanced remedial actions under Section 104 unless designated by the State as its top priority site. Sites scoring above 28.5 may be listed on the National Priorities List through formal rulemaking procedures following public notice and comment. The National Priorities List has been updated several times and currently contains about 1175 listed or proposed sites.

The Hazard Ranking System currently is being revised in response to several criticisms. It does not constitute a risk assessment, since it addresses potential risks and neglects actual exposures and effects

(Office of Technology Assessment, 1985; EPA, 1985A).

Limited data are used. Empty data points are scored zero, and scores can also be increased or decreased by actual observations of releases, large quantities of tanks or drums, or smaller or greater migration distances to receptors. Moreover, the current model does not provide for inclusion of additional knowledge about the site into its score, for example more detailed hydrogeologic data affecting fate and transport, or local land-use patterns that increase or decrease the likelihood of population exposures (Office of Technology Assessment, 1985; EPA, 1985A).

The Hazard Ranking System was not designed to determine extent of cleanup. It is not so used by EPA, and currently it would be inadequate for that purpose (Office of Technology Assessment, 1985).

#### 2.2.2 <u>Remedial Response Planning: The Remedial</u> Investigation/<u>Feasibility Study</u>

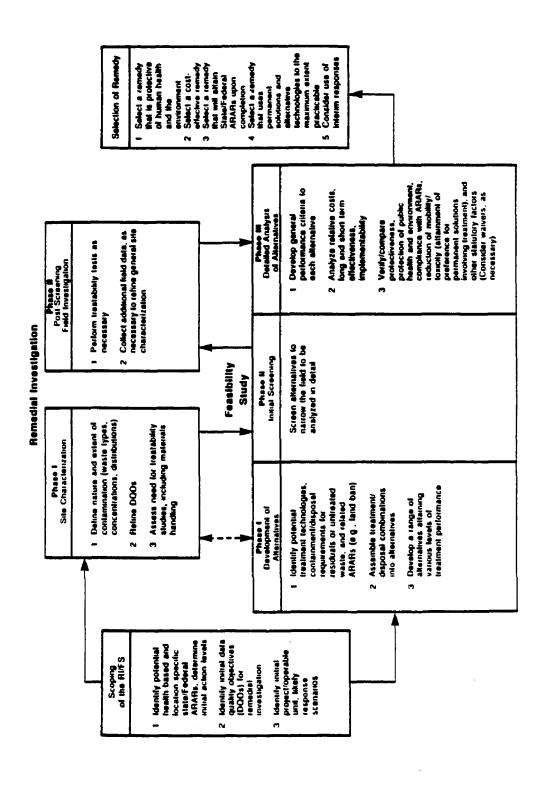
The Remedial Investigation and Feasibility Study are the major analytical components of the remedial planning and design process. In the Remedial Investigation, the site problem is defined more thoroughly as data about site and waste characteristics, their hazards, and actual and potential routes of exposure are collected and analyzed. Data about

treatability of wastes are assembled and treatment processes are tested as necessary. In the Feasibility Study, candidate remedial technologies are developed, assembled into alternatives, and screened, and the most promising subset of potential alternatives is thoroughly evaluated based on the Remedial Investigation data. The final draft Remedial Investigation/ Feasibility Study report is then presented for public review and comment, and the Regional Administrator (or the Assistant Administrator) selects the remedy in accordance with Section 300.68(i) of the National Contingency Plan. The selected remedy and the rationale for its selection are described in a public document called the Record of Decision (ROD; see Section 2.2.3). In most cases the State concurs on the selected remedy.

The major components of the Remedial Investigation/
Feasibility Study process are shown in Figure 2. The
Remedial Investigation and the Feasibility Study are
performed concurrently and are interdependent. As the
Feasibility Study progresses, more sophisticated data is
required to assess the feasibility of some alternatives,
sometimes necessitating collection of additional site
data or bench- or pilot-scale testing of a treatment
technology.

The Remedial Investigation (40 CFR 300.68(e))

Superfund Remedial Investigation/Feasibility Study Process : FIGURE



focuses on defining the nature and extent of contamination through intensive field sampling and laboratory analyses that characterize waste types, mixtures, the media in which they occur, concentration ranges and profiles, and interface zones between media.

The public health evaluation is conducted to characterize and assess risks, routes of fate and transport, and likely human and environmental receptors (EPA, 1986A; Schultz et al., 1987). The public health evaluation is discussed further in Section 3.4.3. Potentially applicable or relevant and appropriate Federal requirements (ARARs) are identified, and EPA may receive initial notification of potential state requirements, focusing at this phase primarily on those representing health-based requirements or ambient concentrations in various media, and on those applicable or relevant and appropriate requirements related to the site's location (e.g., floodplain or wetland limitations, historic lands, high-hazard areas, etc.) (EPA, 1985D). These institutional requirements are discussed further in Section 2.2.

Based on the alternatives being formulated, the need for treatability studies on one or more technologies is assessed, and laboratory-scale tests may be conducted in this phase to answer questions about potential treatment performance, materials handling

requirements, residuals characteristics, and the need for subsequent field- or pilot-scale testing prior or handling requirements, residuals characteristics, and the subsequent to completion of the Remedial Investigation/ Feasibility Study. Treatability testing was performed relatively infrequently in earlier Remedial Investigations due to the strong bias toward what were considered proven, available containment technologies in earlier years of the Superfund program.

Recently, emphasis has been placed on making the Remedial Investigation into a progressively more phased process wherein the data quality objectives (DQOs) are tailored to the need for additional site, waste, and technology performance information at a given time. They are refined in an iterative fashion throughout the phases of the Remedial Investigation and Feasibility Study as the understanding of the site and of the potential remedial alternatives become progressively more sophisticated. Collection of data in a phased manner thus enhances the effectiveness and the costeffectiveness of the Remedial Investigation effort. A more detailed description of the Remedial Investigation's elements is given in EPA (1985F).

The <u>Feasibility Study</u> begins concurrently with or slightly after the initiation of site characterization. It consists of three major steps: (1) Development of

Alternatives (NCP at 40 CFR Section 300.68(f)), (2) Initial Screening of Alternatives (NCP at 300.68(g)), and (3) Detailed Analysis of Alternatives (NCP at In phase (1), potential treatment and 300.68(h)). containment technologies are identified and the containment or disposal requirements for residuals or untreated wastes are assessed. Technologies are considered for suitability as elements of remedial alternatives in terms of their engineering feasibility, their implementability, the likely long-term management requirements for any residuals or wastes left untreated, prior performance (or potential) in achieving the desired remedial results, likely long-term effectiveness, and level of long-term operation and maintenance (O&M) required.

A preliminary identification is made of the potential action-specific (i.e., technology-based) applicable or relevant and appropriate requirements related to each technology being considered, for example RCRA design and operating requirements related to various types of containment or land disposal options, treatment or surface water discharge limits for liquids, or Best Demonstrated Available Technologies (BDATs) and treatment levels for wastes restricted under the Land Disposal Restriction regulations (EPA, 1986B). The land ban regulations were promulgated under the 1984 Hazardous

and Solid Waste Amendments to RCRA.

Technologies or combinations of technologies are then assembled into candidate remedial alternatives. According to the existing National Contingency Plan, a range of alternatives currently is developed according to their degree of attainment of "ARARS", having some that attain ARARS, some that exceed ARARS, and others that do not attain ARARS, as well as a no action alternative. Difficulties associated with this scale for development of alternatives are discussed in Section 2.2.

In phase (2), the alternatives are screened to narrow the field to be analyzed in detail, with the objective being to eliminate alternatives offering equivalent performance in all significant respects other than cost. Major portions of the Remedial Investigation, such as the initial site characterization and risk assessment, may be available to facilitate the screening such that the relative feasibility, implementability, and promise of various alternatives in assuring long-term protection, minimizing short-term impacts, can be assessed. Remaining uncertainties must be resolved in a series of decisions to either collect additional information to reduce the uncertainty or to eliminate an alternative from further consideration. The role of cost at this stage typically has been to

eliminate alternatives that outpriced the field without affording superior protection, to the extent this is possible given the preliminary, order-of-magnitude cost information generally available at this stage.

A limited subset of alternatives is carried through the initial screen for detailed evaluation in phase (3). The performance of each alternative in attaining its treatment or containment targets, ease of implementation, effectiveness in attaining its associated ARARS, likely public acceptance, effectiveness in achieving long- and short-term protection, and other factors, is evaluated in detail. Capital and long-term costs are analyzed for each alternative, including a sensitivity analysis using several discount rates between 3 and 10 percent in some cases.

In a few instances, a qualitative evaluation of the potential failure and replacement characteristics of the containment/ land disposal components of each alternative has been performed as part of the long-term effectiveness analysis. However, the attention given to this analysis has varied highly from site to site and no definitive guidelines for its conduct currently are available. This may improve under SARA, as the long-term effectiveness assessment will be required to

address seven statutory factors listed in Section 121
(b)(1) therein (see discussion in Chapter 1).

The relative effectiveness and costs of each alternative can then be arrayed and compared for key evaluation factors as described in EPA (1985A, B).

The draft final Remedial Investigation/ Feasibility Study report is then prepared and provided to the public for review and comment. It documents all sampling and analyses performed and arrays the alternatives for the decision maker, the public, and all other parties involved.

## 2.2.3 Selection of Remedy: The Record of Decision

Administrator (or the Assistant Administrator) selects the remedy based upon the criteria in Section 300.68(i) of the National Contingency Plan, which specify that the appropriate extent of remedy is determined by "selection of a cost- effective remedial alternative that effectively mitigates and minimizes threats to and provide adequate protection of public health and welfare and the environment. Except as provided under one of five exceptional circumstances described in 40 CFR 300.68(i)(5), this will require selection of a remedy that attains or exceeds applicable or relevant and appropriate Federal public health and environmental

requirements that have been identified for the specific site", considering "cost, technology, reliability, administrative and other concerns, and their relevant effects on public health and welfare and the environment." Additionally, future Records of Decision must conform to both Federal and State applicable or relevant and appropriate requirements and to the statutory preference for permanent solutions to the maximum extent practicable, per Section 121 of SARA.

The selected remedy and the rationale for its choice are described in the Record of Decision. In the case of sites addressed under CERCLA Section 106, negotiations with responsible parties may in some cases lead to a negotiated settlement in which the remedy will be implemented (and sometimes the Remedial Investigation/ Feasibility Study will be performed) by one or more responsible parties. The agreement is described in a confidential Negotiation Decision Document and the selected remedy is then documented in a Enforcement Decision Document that is essentially the equivalent of the Record of Decision.

## 2.2.4 <u>Implementation of the Selected Remedy:</u> Remedial Design/RA

In these phases, the selected alternative is designed and constructed. The State assumes

responsibility for any ongoing O&M required beyond the first year following completion of construction.

Remedial design and construction on activities at Federal-lead sites are overseen by the U.S. Army Corps of Engineers, and at State-lead sites by the State's contractors. The Remedial Design and the Remedial Action processes are described in more detail in EPA (1986C). Following the completion of the remedy, the site may be eligible for deletion from the National Priorities List.

Sometimes, field- or pilot-scale testing of a selected alternative has been deferred to the Remedial Design stage. In other cases, selection of the final extent of remedy (for example, determination of exact volumes and concentrations to be excavated for off-site disposal), or refinement of the cleanup level through additional field sampling, was deferred to the Remedial Design stage (or to actual construction, as in the case of the Acme Solvents site (EPA, 1985M).

Sometimes, response actions at a site are broken up into several "operable units" representing fairly distinct and separable actions. For example, removals might be considered separate operable units from source control or management of migration measures. Generally each operable unit (except a removal) has its own Remedial Investigation/ Feasibility Study and Record of

Decision. In many cases, complex sites are thus subdivided for ease of overall site management or to expedite certain activities that will alleviate a significant portion of the overall hazard, such as surface cleanup, drum and tank removal, or installation of alternate water supplies. More difficult decisions requiring more detailed analysis, such as ground water remediation or final "how clean is clean" levels for soil contaminants, frequently have been deferred to later operable units in this fashion. Each must be consistent with attainment of a cost- effective, permanent overall site solution, however (NCP Section 300.68 (c)).

#### 2.3 Current Soils Remedies

As discussed in Sections 2.2 and 3.5.1, general response objectives are developed for each site cleanup. They are roughly conceptualized in the early scoping stages of the Remedial Investigation/Feasibility Study, and then refined at the beginning of the Feasibility Study based on site investigation data. As stated in Section 3.2, they may be viewed in terms of mitigation or abatement of the risks posed by the site. Soil contamination response objectives are generally developed in terms of prevention of exposure to contaminated soils posing air, surface water, ground

water and direct contact threats, for example.

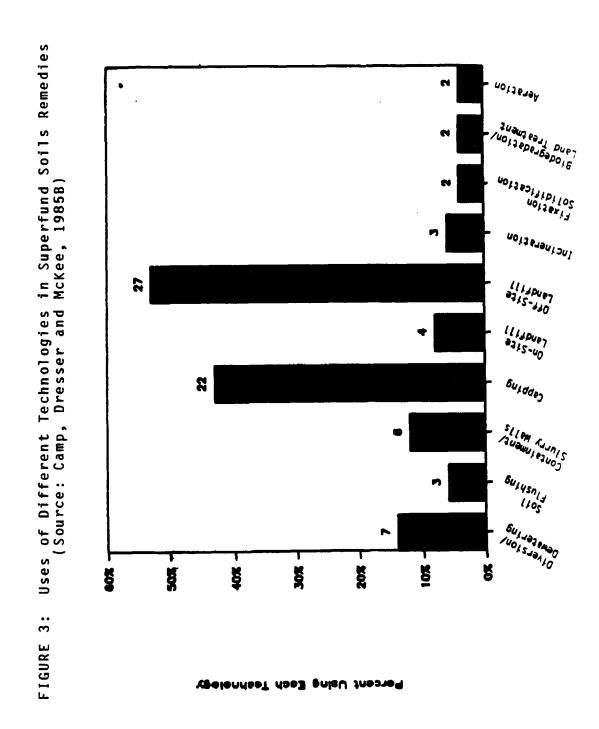
The alternatives addressing these are often termed source control alternatives, as contrasted with management of migration alternatives that would address a ground water plume or surface run-off or air releases moving beyond the site boundaries. The various remedial options are then compared in the Feasibility Study in terms of how effectively each technology, or combination of technologies, achieves these response objectives in light of the National Contingency Plan selection criteria in 40 CFR 300.68(i). Source control remedies may achieve response objectives of exposure prevention in two general ways, each addressing one of the two components of soil risk identified in Section 3.2:

- 1. They may reduce the intrinsic hazard of the wastes or contaminated soils, i.e., reducing the source strength term available to release to other environmental media by destroying or detoxifying the contaminated soils (for example by incineration or other treatment/destruction technologies); or
- They may prevent exposure but may not reduce the criginal hazard, for example by capping the wastes in place, or by excavating them and disposing of them, untreated, at an off-site land disposal facility.

Prior to the passage of SARA, containment remedies may have been given equal consideration with treatment-based remedies in terms of their effectiveness at achieving response objectives, or preferred over

treatment due to the relatively untried status of most treatment /destruction technologies on hazardous wastes and especially on contaminated soils (Camp, Dresser and McKee, 1985B; EPA, 1985A; Office of Appropriate Technology, 1981). Recent years have seen increased emphasis on selection of treatment over containment technologies to increase the "permanence" of remedies, as the uncertainties regarding the actual long-term protection of land disposal have become more widely known (as discussed in SARA floor statements and in HSWA; see Figure 3).

Thus, the decision maker must consider the tradeoffs between exposure reduction, for example by containment, which reduce soil exposures (and thus risks) to zero until the containment system fails; and hazard reduction, for example through incineration or treatment, which may be initially more costly and uncertain due to innovativeness, but which removes the hazard and has little or no uncertainties as to longterm effectiveness. As a general rule, assuming relatively homogenous soil/waste mixtures, the more the overall source strength (hazard) is reduced through removal or destruction, the more the long-term effectiveness of the remedy is increased, and the less will be the need for long term monitoring or maintenance to assure the continued long term effectiveness of the remedy (i.e.,



the greater its overall "permanence").

Additionally, the complex mixture of contaminants and soil matrices at most sites may not be effectively contained or treated by a single technology alone. Most remedies evaluated and selected are combinations of several technologies that are believed to optimally satisfy the remedy selection criteria of SARA and the National Contingency Plan. Some technologies, such as incineration, may require pretreatment or "conditioning" of the waste stream to enhance latent heat content or susceptibility of some contaminants to degradation; or the residues may require post-treatment, for example if organics were destroyed by incineration, but metals in the ash must still be stabilized to reduce mobility and/or toxicity.

#### 2.3.1 Traditional Approaches

As described previously, most site remedies prescrib, a to date have considered soils only as a medium in which pollutants are stored, transformed, and/or transported to human and environmental receptors (Dragun, 1988A,B,C). In this context, the resource ultimately being protected is the eventual human or environmental receptor. The soil itself traditionally has not been protected as a resource, unlike ground water, for which the existing regulatory framework clearly

favors restoration.

Four generic types of remedial actions traditionally have been used to address contaminated soils problems:

- No action—this may mean no action at all if soil contaminant concentrations or types do not pose significant health risks, or if they do not exceed local background levels. Depending upon site conditions, the no action decision may still require some long-term monitoring and (in some cases) possibly land or aquifer use restrictions to verify the effectiveness (or "permanence") of this remedy.
- Closure by containment— soils are not moved or managed beyond minimal consolidation of released material into one area (or waste management unit) prior to placement of a cover over the area, as is done to close hazardous waste land disposal facilities in accordance with Subtitle C of RCRA (40 CFR 264 through 270). Protection is accomplished primarily by preventing exposure to the hazardous substances through capping and ground water monitoring (and corrective action if releases are detected). This approach would be used at the conclusion of any onsite redisposal into a newly constructed disposal cell as well.
- Excavation--Removal of soils from their original location for treatment or redisposal. Superfund wastes traditionally have been redisposed either into a newly constructed landfill cell on-site, or, more commonly, off-site into a commercial land disposal unit constructed and operated in accordance with RCRA Subtitle C design and operating standards (40 CFR 264-270; EPA, 1985A).
- o <u>Treatment</u>--several physical, chemical, and/or biological methods are available that destroy, detoxify, stabilize, or fix contaminants in soils. Treatment of excavated materials can be performed on or off the site. On-site, some methods may be used either on excavated soils, or in situ. In-situ methods are available for some materials that treat the contaminants in place, requiring varying degrees of disturbance to, or management of, the

contaminated material.

A fifth category, recycling, will be mentioned only briefly, since it is not considered by EPA program officials to be a viable alternative for the vast majority of contaminated soils at this time. For industrial waste streams, recycling is considered to be increasingly viable from the standpoint of technological availability (Office of Technology Assessment, 1983; National Research Council, 1984). Some have been in use in certain industries for a number of years and are relatively well proven (Campbell and Glenn, 1982; Office of Technology Assessment, 1983); however their application to contaminated soils is relatively untried and likely would not satisfy SARA cost-effectiveness requirements at most sites. Thus, recycling of soil contaminants will not be discussed further here.

EPA (1985B,H) contain lists of remedial technologies in terms of the media they address or control (i.e., surface water, ground water, subsurface gas, atmospheric emissions, direct waste/soil treatment, etc.) A cursory review of these categories of technologies is provided in the following sections. Detailed descriptions and discussions of these technologies are beyond the scope of this report. For more information on a particular source control technology, the reader is referred to the Office of

Technology Assessment (1983, 1985); EPA (1985H);
Ehrenfield and Bass (1983); Camp, Dresser, and McKee
(1985B, 1986); and Repa and Kufs (1985); among others.

#### 2.3.2 No Action

The current National Contingency Plan requires that the "no action" alternative be among the final set of alternatives evaluated in the Feasibility Study and presented to the decision maker. This is required for several reasons discussed in the National Contingency Plan preamble, chief among them being that CERCLA actions must by law remain consistent with the requirements of the National Environmental Policy Act of 1970. In so doing, the baseline site risk evaluation performed in the Remedial Investigation presents the "no action" alternative as a baseline against which the effectiveness of the various remedial alternatives may be compared.

As discussed previously, this alternative may consist of no action whatsoever, for example at sites where residual contamination is minimal, there is little or no possibility of exposure, and EPA believes the contamination (e.g., a ground water plume) will meet health based levels within a reasonably rapid time frame through natural attenuation mechanisms. This could occur at sites where an initial removal or remedial

action resulted in prior reduction of soil contaminant source strength to low levels.

Alternatively, "no action" may be defined to include limited monitoring, and/or access restrictions for example to prevent direct contact exposures to soil contaminants at sites where natural or enhanced biodegradation and chemical attenuation processes (discussed in Section 4.3.3) are expected to immobilize or destroy soil contaminants within a reasonably rapid time frame.

# 2.3.3 Closure by Containment

containment methods, used singly or in combination, generally reduce source strength by exposure prevention rather than reduction of the intrinsic hazard posed by the contaminated soils although in some cases, soils have been treated prior to land disposal. However, this was done generally to help stabilize them or support the final cover, rather than to reduce toxicity or mobility. As stated previously, containment has been the traditional method of choice for addressing contaminated soils problems (see Appendix I and Figure 3). At some sites, contaminated soils were excavated and taken off site for containment in land disposal facilities, as shown in Appendix I. These off-site containment remedies will be discussed further in Section 2.3.4.

Containment technologies generally are intended to prevent human and environmental contact with wastes and soils, and atmospheric release of dusts and gases; minimize infiltration through the source; prevent flooding; control erosion through the source area; and collect, transfer, store, discharge, control, or redirect surface run-on and run-off from the contained area (Ehrenfield and Bass, 1983). As with other alternatives, containment remedies generally consist of a combination of passive or active technologies to achieve the stated performance goals. Passive systems comprise two general categories:

- o <u>Passive source control or containment measures</u> for the contaminated soils themselves, including caps; liners; low-permeability barriers such as slurry walls, grout injections or curtains, vibrating beam barriers, or sheet piling; and
- o <u>Passive liquid and gas control measures</u> such as subsurface drains, leachate collection systems; run-on, run-off, and infiltration diversion and collection systems; grading, revegetation and dust control measures; and vapor collection and treatment systems.

Active systems include measures such as leachate or ground water pumping or withdrawal to dewater a contaminated soils source; to adjust ground water levels near or beneath a contaminated soils site; to actively control rates, directions, or levels of infiltration or leachate entering or exiting the contaminated soils

site; or to contain or remove contaminated leachate or ground water (Repa and Kufs, 1985). These categories are reviewed below.

# 2.3.3.1 Passive Source Control Methods

Chief among these methods is <u>capping</u>, which involves placement of a cover consisting of soil, clay or synthetic membrane layers (singly or in combination) over the contaminated soils /waste source. A variety of designs has been used, but in most cases final CERCLA covers have been designed in accordance with the RCRA Subtitle C landfill closure performance standards at 40 CFR 264.111 and 264.310. They require minimization of migration of liquid through the source material, minimal long-term maintenance, resistance to settling or subsidence, efficient site drainage, and cover permeability equaling or exceeding that of underlying soils (or synthetic liners, if present).

These requirements are often satisfied with a multimedia design as specified in 40 CFR 264.310, consisting of an upper vegetative layer, underlain by a drainage layer (often composed of geotextile materials) over a low permeability layer of compacted clays, a synthetic membrane, or both; but waste- and site-specific circumstances may warrant simpler or varied designs (EPA, 1985H, 1987B).

The selection of design and materials is based on site, climate, waste, soil and hydrogeologic factors affecting the likely movement of contaminants from the capped soil source to ground water, as discussed in Sections 4.2 and 4.3; as well as design factors.

These design factors include the desired functions and effectiveness of the cover; the need to prevent direct contact or control vapor release; availability and costs of materials; and expected future maintenance requirements and uses of the site (EPA, 1985H).

Alternative cover designs are discussed in EPA (1985H, 1987B); Matrecon (1983); Cope et al. (1984); and Lutton (1982), among others.

The effectiveness of the cap nearly always requires long term monitoring of ground water to detect releases of contained wastes or soils, and proper maintenance of the cap coupled with site access restrictions to ensure that its integrity is not breached during its design life. Often this effectiveness is enhanced by combining the cap with additional measures such as pretreatment or stabilization of the wastes/soils (see Sections 3.2.5 and 3.2.6), and other active or passive control measures. Examples of other passive source control measures include passive liquid and gas control measures such as vapor collection and treatment systems beneath the cover; dust control measures; grading, scarification,

terracing, and compaction; revegetation; and various passive measures for control of run-on, run-off, and infiltration through the cap (discussed in Section 2.2.3.2). A more detailed review of these design and construction measures is found in EPA (1985H).

# 2.3.3.2 Passive Liquid/Gas Control Measures

These include measures such as subsurface drains; low permeability barriers such as slurry walls, sheet piling, and grout curtains; gas collection systems; and other measures to divert liquids or gases before they enter a contaminated soils source area; or collect them afterwards before they can escape to other media such as air or ground water. Several common technologies are described briefly below.

Subsurface drains are used at shallow depths (less than 40 to 100 feet) and include any type of buried channel or conduit which collects and conveys discharge by gravity flow. They function much like an infinite line of extraction wells (see Section 3.2.3.3) and can perform many of the same functions, including containment or removal of a shallow leachate plume, or lowering of the ground water table in the immediate site vicinity to prevent contact of water with the contaminated soils source (EPA, 1985H). They may be preferable to active systems where subsoils have low or

variable hydraulic conductivities, or where ground water elevation control is required over very long time frames.

At several sites they have been used in conjunction with barrier walls to intercept plumes hydraulically downgradient from the source, as given in Appendix I. circumferential drain system may be used in conjunction with a cap and a barrier wall as a total containment system. Subsurface trenches may also be used to collect and divert subsurface gases by altering convective flow paths through the waste or soil source area and the surrounding soils (EPA, 1985H). Limitations of this technology include depth, ambient conditions favoring carbonaceous or iron- manganese precipitates, and highly viscous soil contaminants or sludges which could clog the drain system (EPA, 1985H). A discussion of design, location, spacing, materials, gradient determination, design discharge, filters, pumps, and construction methods is given in EPA (1985H); Soil Conservation Service (1973); Bureau of Reclamation (1978); and Repa and Kufs (1985).

Low-permeability barriers are used to contain, redirect, or capture leachate or infiltration (or ground water flow) in the immediate vicinity of a site, when used in the vertical dimension; or to seal off the base of a soil contaminants site through injection of gels, grouts or other sealants (Repa and Kufs, 1985; EPA,

1985H). They may be of several major types, chiefly soil-bentonite or cement-bentonite slurry walls, grouts, and sheet piling. These categories are described briefly below.

Slurry walls comprise a broad category of barriers that are constructed in a vertical trench excavated under a slurry. The slurry hydraulically prevents collapse of the trench sidewalls while it forms a filter cake on the walls which, upon curing, prevents movement of fluids into surrounding soils, much in the same manner as drilling fluids (EPA, 1985H). The trench is then backfilled with low-permeability materials, which are placed continuously within the trench behind the advancing excavation front. Slurry walls are perhaps the most commonly used type of subsurface barrier due to their relatively low cost compared to the other types. They are identified according to the composition of backfill materials:

o <u>Soil-bentonite</u> slurry walls, composed of blended engineered soils, bentonite, and water. This type has the lowest permeabilities, the broadest chemical compatibility range (although it is not compatible with strong salt solutions, strong acids and bases, and some organics; D'Appolonia, 1980A,B), and the lowest installation cost among the slurry wall types.

Disadvantages of this type are the requirement for a large working space, least strength, highest compressibility, and potential for slurry and backfill to flow. Thus, its applicability is limited to nearly level sites (Spooner et al., 1984A; EPA, 1985H).

- Cement-bentonite slurry walls, consisting of 0 mixtures of Portland cement, bentonite, and water. Very deep trenches may sometimes be excavated with a normal bentonite slurry which is then replaced by the cement-bentonite (EPA, 1985H). Since this type sets into a semisolid, fairly rigid material, it is less restricted by topographic variations than the soilbentonite wall, and is used in settings where where less elasticity can be allowed. It requires less working space as well. Limitations include its higher costs, higher permeabilities (typically 10-8 cm/s compared with a potential 10-8 cm/s permeability for a well-engineered soil-bentonite wall; Spooner et al., 1984A), and greater incompatibilities with sulfates, strong acids and bases, and highly ionic contaminants (Spooner et al., 1984B).
- Diaphragm walls, constructed of precast or cast-inplace concrete panels placed in the trench and surrounded by soil-bentonite or cement-bentonite slurry. These are used only in rare instances where considerable load-bearing strength is required, for example where slurry walls must cross roads or railroad beds (EPA, 1985H). Limitations are similar to those of cement- bentonite walls, and design permeabilities may be comparable, provided interfaces between individual panels are joined properly. Their use at hazardous waste sites is extremely rare (EPA, 1985H; Spooner et al., 1984A).

Several configuration options are available for slurry walls, depending on site conditions and the intended use of the barrier, as shown in Spooner et al. (1984A). They may be keyed vertically into a confining layer or competent bedrock, or "hang" suspended from grade level downwards several feet below the ground water table. The latter application may divert or contain a layer of low density contaminants such as

petroleum hydrocarbons ("floaters") atop the ground water table, or migrating gases (Spooner et al., 1984; EPA, 1985H; Repa and Kufs, 1985). Slurry walls may be placed circumferentially around the contaminated soils source, or in an up- or downgradient position relative to ground water flow. Upgradient walls would divert uncontaminated infiltration from the soil source area, slowing (but not halting altogether) leachate generation. Downgradient placement could contain floating contaminants and gases such as methane, but compatibility testing is more crucial to its effectiveness than to an upgradient placement.

A circumferential wall is considered the commonest and most effective design, when coupled with a cover, an upgradient infiltration barrier, and a system for reducing the hydraulic head within the wall (EPA, 1985H; Spooner et al., 1984A).

The use of these systems, and their effectiveness, depends highly on soil and contaminant conditions, the site hydrogeologic characteristics, compatibility of contaminants with the proposed barrier materials, thorough monitoring of water and leachate levels and compositions, and the intended role of the barrier system in the overall response alternative being designed. More details on design, construction,

placement, limitations, selection criteria, and monitoring and maintenance of slurry walls can be found in EPA (1985H); D'Appolonia (1980 A,B); Spooner et al. (1984 A,B); Repa and Kufs (1985); and others.

Grouting refers generally to the process of injecting a fluid into a rock or soil mass, where upon curing, the grout reduces or diverts water or leachate flows and strengthens the formation. Grouted barriers generally are more expensive and more permeable than slurry walls, and thus are typically used in rock formations, especially to expand or seal bedrock fractures, fissures, solution openings, or joints, rather than in unconsolidated materials (EPA, 1985H).

Rock grouting applications are highly site specific and require specialized skills and very thorough, expensive geotechnical site characterization in order to locate and contact all significant rock fissures, voids, or channels of concern surrounding the contaminated soils source of interest. Grout curtains can be applied in some subsurface materials in partial or fully circumferential configurations, much like slurry walls. They may be more sensitive than the slurry wall designs to permeability increases, through gaps in the curtain, and to incompatibilities with contaminants (Spooner et al., 1984B).

Grout curtains are constructed by pressure

injection of the grout through a pipe into the stratum to be sealed. Injections are made in staggered fashion through a triple series of holes spaced typically at 20-40 foot intervals, such that secondary holes are injected once the primary series has set. Construction is performed by four basic methods (Guertin and McTigue, 1982; Hayward Baker et al., 1980):

- o <u>Stage-up method</u>, in which the borehole is fully drilled, and grout is injected gradually as the drill is slowly withdrawn from the hole;
- o <u>Stage-down method</u>, in which the borehole is partly drilled (e.g., through the topmost zone to be injected, then the drill is withdrawn and the section is grouted. The hole is then redrilled through the grout to the next deeper zone, and so on;
- o Grout port method, in which a slotted injection pipe is sealed into the borehole using a brittle mortar/Portland cement jacket. Each zone to be injected is isolated with a double packer, then high pressure water is briefly pulsed through the pipe to rupture the jacket. Grout is then pumped through the ruptured jacket to seal the zone, then the process is repeated vertically in each zone of interest; and through the pipe to rupture the jacket.
- vibrating beam method, in which an I-beam is vibrated into the soil to the required depth, then slowly withdrawn. As it rises, grout is pumped into the opening left by the beam through ports in its base. The beam is then moved to an adjacent, overlapping location and the process is repeated.

Grout curtains require little or no maintenance, but compatibility testing is critical. Several types of grouts are available. Selection of the appropriate type depends on

site factors, contaminant compatibility, and intended design and operation of the wall or injection system. A critical design criterion is matrix pore size and/or grain size of the matrix to be sealed by grouting.

Grouts include hydraulic cements which set, cure, and retain structural integrity in water (Kirk-Othmer, 1979; Bowen, 1981); various swelling clays, bentonite, and bentonite-chemical mixtures (Guertin and McTigue, 1982); alkali silicates; and various organic polymers including acrylamide-, phenolic-, urethane-, urea-formaldehyde, epoxy-, and polyester-based grouts (Spooner et al., 1984B; EPA, 1985H).

Sheet piling, consisting of wood, steel, or precast concrete, can be used to form leachate or ground water barriers. Generally, wood is considered ineffective at preventing liquid migration, and concrete plates tend to be used only where great load-bearing strength is necessary (as discussed for diaphragm walls previously). Steel sheet piling may be used as a barrier in much the same fashion and with the same placement options as slurry walls and grout curtains. Due to high costs and unpredictable integrity, they are employed primarily for temporary dewatering during construction of structures and for erosion protection of some other barrier contacting flowing water (EPA, 1985H). Sheet piling consists of interlocking sections driven into soils by

drop or vibrating hammers. They initially allow water movement until fine particles "seal" the interlocking connections; however, boulders and other subsurface heterogeneities can distort the sheets and reduce the wall's integrity, as can extreme soil pHs or resistivities. Precoating, galvanizing, or cathodic protection may prolong the effective life of the structure in electrically or chemically corrosive settings (EPA, 1978).

Passive gas control measures may include subsurface drains or other high-permeability conduit systems, as well as barrier structures and synthetic membranes that serve as a low-permeability barrier to direct and contain the gas, as discussed previously for leachate and infiltration. Often conduits and barriers might be combined as part of the containment remedy to collect and divert gas as it is generated within the waste/soil source (SCS Engineers, 1980). Many of the design, application, and construction characteristics of these systems are similar to those described above, and a given barrier/drain network may be designed to apply to both gas and leachate transport within the site. More information on these systems can be found in SCS Engineers (1980); Repa and Kufs (1985); and EPA (1985H).

## 2.3.3.3 Active Liquid/Gas Controls

Active systems can be used for control of liquids or gases entering or exiting the waste/soil source.

Active systems for liquids are based on pumps and/or well systems which may be used for ground water level adjustment, plume or leachate containment, or plume/leachate removal (Repa and Kufs, 1985).

extraction wells to dewater a waste/soil mass by creating a cone of depression beneath it, or by using injection wells to create ground water mounds, for example to redirect or contain leachate or contaminated ground water to prevent its reaching supply wells (EPA, 1985H; Repa and Kufs, 1985). These can remove liquids from the soil source area or change speed and directions of leachate and ground water flow in the vicinity of the source.

They may also be used in conjunction with passive barrier systems to control fluids as they accumulate on the upgradient side of the barrier, to prevent contact of incompatible materials and to control hydraulic pressures within the design limits of the passive structures. Active and passive leachate collection and extraction systems are also used within and between underliners of both municipal and hazardous waste

landfills, and such systems are required in any newly constructed land disposal units regulated under RCRA (40 CFR Parts 264 through 270) pursuant to the 1984 Hazardous and Solid Waste Amendments, as will be discussed in Section 2.3.4.

Plume containment alternatives may employ either extraction or injection wells or a combination. Containment differs from removal in that it may be employed temporarily where the source has not yet been addressed, thus the soil continues to contaminate ground water (Repa and Kufs, 1985). Extraction systems, commonly referred to as "pump and treat," are used to remove contaminated portions of the ground water, which may or may not be treated prior to discharge. Design and operational considerations regarding pumping and treating of contaminated ground water, and other aspects of aquifer restoration, are outside the scope of this document and will not be discussed. Further information can be found in Repa and Kufs (1985); Javandel et al. (1985); Barcelona et al. (1987); Office of Technology Assessment (1984); National Research Council (1984B); EPA (1986D); Johnson Division UOP Inc. (1975); and Keely et al. (1986) among others.

Gas migration may be controlled using active as well as passive systems, the technology for which has become very advanced in recent years for purposes of

recovering methane and other gases generated within municipal landfills (EPA, 1985H). Detailed discussions of design, construction, and operating considerations are found in EPA (1985H).

Both liquid and gas active systems require operation and maintenance, as well as having ongoing requirements for energy and for treatment and disposal capacity of the extracted fluids and gases. These concerns must be addressed during the technical feasibility and cost-effectiveness analyses in the Feasibility Study.

#### 2.3.4 Excavation

Excavation of wastes and contaminated soils has been the most commonly used method of reducing source strength at Superfund sites addressed by Records of Decision prior to about 1986 (see Appendix I). It has been undertaken in one or both of two general circumstances:

- o The most contaminated wastes and/or soils may be removed as part of an emergency removal or an interim remedial measure, designed to abate imminent hazards to public health and the environment; or
- o Remaining liquid and solid wastes, debris, drums, and contaminated soils are removed during the source control operable unit of the remedial action. In this phase, chronic, long-term threats to public health and the environment are considered in selecting the appropriate cleanup level or

determining total amounts, types, and distributions (and eventual fate) of excavated materials.

In most instances, the excavated wastes and soils were taken to a commercial land disposal facility offsite, and disposed in an engineered landfill cell meeting the design and operating requirements of Subtitle C of RCRA, or to an approved off-site treatment facility such as a commercial hazardous waste incinerator, in compliance with the Off- Site Policy in SARA. In other cases, excavated material was placed into an existing or newly constructed land disposal unit on the site itself. As with other technologies discussed throughout Section 2.3, remedial alternatives employing excavation will often combine it with other technologies such as on- or off- site treatment or disposal, ground water pumping, secondary containment barriers such as slurry walls, insitu treatment, etc.

Excavation, hauling, and removal of wastes and contaminated soils is generally accomplished using standard heavy construction equipment and techniques (EPA, 1985H). These methods are well known in constructing engineered land disposal units.

As described in Section 2.4, problems with reduced availability of acceptable off-site land disposal capacity, costs and difficulties in transportation of Superfund wastes and soils, and public opposition in

communities receiving the transported wastes have affected use of the excavation alternative for Superfund soils. Impacts are heightened by the restrictions on land disposal of untreated hazardous wastes under RCRA's land ban regulations, which gave a 2-year exemption to Superfund soils and debris, and a statutory requirement in SARA that off- site land disposal of untreated Superfund wastes is the method of last resort.

It is not in full conformance with the preference for permanent solutions, since the original hazard of the waste is not reduced; risks are reduced only at the site itself. Total environmental risks are unchanged.

Excavation may lead to redisposal/ containment of either untreated soils or treatment residuals in an engineered land disposal cell meeting the design and operating requirements of 40 CFR Parts 264 through 270, which specify limits on locations in high-hazard terrain such as floodplains and seismic zones; an underliner composed of a double, multimedia liner/leachate collection system with specified hydraulic conductivity not exceeding 10<sup>-7</sup> cm/sec. Compatible materials, and additional design, operation, and construction requirements are discussed by several authors (e.g., Cope et al., 1984; Office of Technology Assessment, 1983; and EPA, 1985H).

At the conclusion of the unit's operating life, it

is capped and closed as discussed in Section 2.3.3. It requires long-term maintenance, access restrictions to ensure the integrity of the closed unit, and monitoring of ground water to detect any inadvertent release of contaminants from the "closed" soil source area.

Additional information concerning design, construction, operation, and limitations of existing land disposal technologies is given in the aforementioned sources.

# 2.3.5 <u>Treatment Technologies</u>

As stated previously in this section, Congressional intent expressed in both HSWA and SARA is leading to increased emphasis on evaluation and selection of treatment technologies. They reduce soils risks by directly reducing the hazard posed by the soil contaminants themselves, through destruction or immobilization to reduce their toxicity and/or their mobility in the soils (Camp, Dresser, and McKee, 1985A, B; Office of Technology Assessment, 1983, 1985; EPA, 1985A, 1986E,F).

Treatment alternatives may be designed and selected in several sizes and configurations, depending on whether physical, chemical, or biological treatment is required; the types, mixtures, and physical and chemical forms of contaminants in the soil matrix; and the variability of the soil matrix in which the contaminants

are distributed.

Many treatment technologies may be applied to contaminated soils either in situ (with little or no physical disturbance to the contaminated soils mass) or in a separate treatment unit following their excavation. These treatment units may be located either on or off the Superfund site. On-site units may be constructed as either permanent, stationary structures (that may or may not remain on site following completion of source control actions), or mobile units may be brought to the site during the duration of the soil remediation process, then transported elsewhere. Factors affecting the selection of these technology configurations are discussed further in EPA (1985E; Camp, Dresser and McKee, 1986, 1988). In-situ treatment is discussed further in Section 2.3.6.

In the following subsections, treatment technologies applicable to contaminated soils will be described briefly. They can be divided generally into broadly overlapping categories of physical, chemical, and biological processes. Physical processes can be further subdivided as thermal (defined here as high temperature) processes, other "nonthermal" (ambient— to moderately—elevated—temperature) processes, and stabilization/ solidification processes. These are shown in Table 2.

# TABLE 2 TREATMENT TECHNOLOGIES FOR CONTAMINATED SOILS

#### Thermal Processes

Incineration -- Rotary Kiln

Liquid Injection

- Boilers

- Cement Kilns Fluidized Bed

Infrared

Pyrolysis--

Plasma Arc

Advanced Electric

Wet Oxidation--Supercritical Water Oxidation

Wet Air Oxidation

# Other Physical Processes

Air stripping

Steam Stripping

Mechanical Aeration/Extraction--

Mechanical rototilling

Enclosed mechanical aeration

Pneumatic conveyor systems
Low temperature thermal stripping

Vacuum Extraction

Distillation

Evaporation

Activated Carbon

Soil Wash/ Flushing

Filtration/ Membrane Processes

Phase separation --

Oil separation

Centrifugation

Dissolved Air Flotation

#### Flocculation

# Solidification/Stabilization/Immobilization

Cement Based

Pozzolanic -- Fly ash/ Lime Based

Thermoplastic--Asphalt Based

Thermoset

Macroencapsulation

(Continued)

# TABLE 2 (Continued)

# Chemical Processes

Reduction-Oxidation
Precipitation
Chelation
Polymerization
Neutralization
Chemical Dechlorination
Ion Exchange-Clays
Resins
Zeolites

# Biological Processes

Aerobic Treatment--

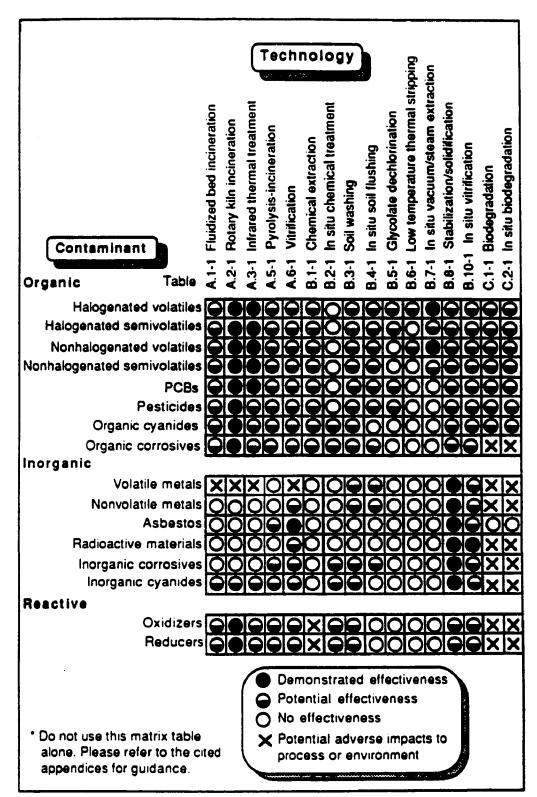
Activated Sludge Sequential Batch Reactors Rotating Biological Contactors Trickling Filters Fixed-film Processes

Land Treatment/ Landfarming Anaerobic Digestion Composting Facultative Lagoons A brief summary of the applications and design considerations of each technology is provided below for many of the technologies discussed in this section. However, a detailed discussion of all technologies currently in use or under consideration for treatment of contaminated soils would be outside the scope of this document. Further details can be found in the references cited in this chapter.

Different technologies will be effective on different contaminants, as shown in the applicability matrix in Figure 4. The complex soil— contaminant mixtures at Superfund sites may not be effectively immobilized or destroyed by a single technology. As with other remedial technologies discussed in Section 3.2, treatment methods may often be combined to form treatment trains of unit processes that address different contaminants, or that provide conditioning or pre-or post-treatment processing of the contaminated soils. Depending on the degree of treatment achieved (i.e., threat posed by the treatment residuals and by the levels that were left untreated), long-term monitoring and some containment or land disposal technology may be part of a given remedial alternative.

Needs for long-term management, as well as for pilot-and bench-scale testing, are also related to the relative newness of many of these technologies. Some

FIGURE 4: Technology/Contaminant Appplicability Matrix (Source: Camp, Dresser and McKee, 1988)



have been used in other industrial process applications and are now being considered for use on contaminated soils (Office of Appropriate Technology (OAT), 1981; Camp, Dresser and McKee, 1985B, 1986, 1988). Previous Superfund experience with treatment is limited, as shown in Table 3. Many technologies are so innovative as Superfund applications that they have not yet been evaluated beyond the bench or pilot scale.

Thus, considerable effort is being devoted within the EPA Superfund program to advancement of new technologies, and to determining methods by which site managers can select and evaluate new, relatively untested technologies, in the Superfund Innovative Technology Evaluation (SITE) Program (EPA, 1986F). Many states are pursuing similar efforts (Office of Technology Assessment, 1983, 1985; OAT, 1981).

# 2.3.5.1 Thermal Processes

Thermal treatment refers in this context to the use of high temperatures to destroy or detoxify hazardous substances in soils. Elevated—temperature treatment methods not involving extremely high temperatures, such as hot air or steam stripping methods, are discussed in Section 3.2.5.2). It can provide volume reduction (limited for contaminated soils), material or energy recovery, and detoxification through destruction of

TABLE 3
Treatment Technologies Selected at Superfund Sites
(Sources: EPA, 1987F; Camp, Dresser and McKee, 1986)

TECHNOLOGY	SITE/STATE	COMMENTS
Incineration	Baird & McGuire, MA	See Appendix I
	Hyde Park, NY	10
	Drake, PA	••
	Westline, PA	10
	Coleman Evans, FL	10
	Mowbray Engineering,	AL "
	Arrowhead Refinery, M	
	Fields Brook, OH	11
	LaSalle Electric, IL	<b>11</b>
	Metamora Landfill, MI	. 11
	Spiegelberg Landfill,	MI "
	Sikes Disposal, TX	91
	Bog Creek Farm, NJ	99
	Swope Oil, NJ	11
	MOTCO, TX	<b>11</b>
	Triangle Chemical, TX	<u> </u>
	Woodbury Chemical, CC	
	Bridgeport, NJ	11
	Acme Solvents, IL	· 11
	Berlin & Farro, MI	11
	Laskin/Poplar, OH	t1
	Western Processing, WA	Infrared incin. o
	Peak Oil, FL	Infrared incin. o
	Tibbett's Road, NH	Infrared incin. dioxin soils
	Mimor Beach WO	Rotary kiln incir
	Times Beach, MO	of dioxin soil
Solidification	Mowbray Engineering,	See Appendix I
	Pepper's Steel, FL	85
	Sapp Battery, FL	11
	Burrows Sanitation, M	MI "
	Fields Brook, OH	11
	Forest Waste, MI	11
	Queen City Farms, WA	11
Stabilization/	Bruin Lagoon, PA	11
Neutralization	Wide Beach, NY	***
	Davie Landfill, FL	••
	Bioecology, TX	21
	D100001097, 22	

74 (Continued)

TABLE 3 (Continued)

TECHNOLOGY	SITE/STATE	COMMENTS
Stab./Neutr. (Cont.)	Denver Radium, CO Sylvester, NH	See Appendix I Sludge dewatering, encapsulation
Soil Washing	Goose Farm, NJ South Tacoma/Well 12A WA Tinkham Garage, NH United Chrome, OR Bridgeport, NJ Chem-Dyne, OH Montana Pole, MT	See Appendix I  " " " " Potassium/poly- ethylene glycol deg. of dioxins, pentachlorophenol
Biodegradation	Old Inger, LA Byron/Johnson, IL Leetown, WV Burlington, MN Tinkham, NH Sylvester, NH	See Appendix I  " " " " Tertiary biotrt. ground water
Land Appli- cation/Compost	Tinkham, NH	See Appendix I
Soil Aeration	McKin, ME Tinkham, NH Caldwell Trucking, NJ Metaltec, NJ Hollingsworth, FL Verona Wellfield, MI Triangle Chemical, TX Outboard Marine, IL	See Chapter 5 See Appendix I  " " " " Aeration of sediments w/PCB

organic compounds. Destruction and removal efficiencies of commercially available thermal treatment systems can reach 99.99% for some wastes ("four nines," as is required under the RCRA regulations), and some can achieve 99.9999% for certain materials ("six nines," required under RCRA and TSCA regulations for substances such as PCBs and dioxins), though treatment efficiency data for contaminated soils is limited.

In addition, these processes may produce solid, liquid, and/or gaseous residuals. Liquid residuals are generated by wet oxidation systems and by wet scrubbers used for air emissions control. Solid residuals include uncombusted portions of the influent stream (including large for air emissions control. Solid residuals include heterogeneous solid debris, soil particles and metals) that form bottom and fly ash. Gases are generated by most of the processes and are generally discharged through stacks after passage through air emissions treatment trains (Camp, Dresser and McKee, 1988). Residuals may require post treatment or longterm management as described previously, depending on type and extent of intrinsic hazard presented by the residuals.

Three categories of thermal treatment are considered applicable to contaminated soils at this time (Office of Technology Assessment, 1985; EPA, 1985H;

Camp, Dresser and McKee, 1985B, 1988). These are incineration (including rotary kiln, liquid injection, fluidized bed, and infrared methods); pyrolysis (including plasma arc and electric reactor methods); and wet oxidation (supercritical water and wet air methods).

<u>Incineration</u> refers generally to controlled combustion of organic materials in an oxidizing environment, as a positive partial pressure of oxygen exists after combustion. Types include rotary kilns, liquid injection systems, and infrared systems. Rotary kilns may be fixed or mobile. Contaminated soils are introduced into the high end of a cylindrical, refractorylined kiln. Contaminants are substantially oxidized to ash and gases at temperatures of 1200 to 1800 F over residence times ranging from seconds to hours, depending on solids content, latent heat content or BTU value of the contaminated soils, amount of supplementary fuel provided, feed and kiln rotation rates, and kiln design (Camp, Dresser and McKee, 1986; EPA, 1985H). Exhaust gases are passed through an afterburner chamber (1400 - 2400 F) and an air emission control train, where acid gases and particulates are removed before release.

Rotary kilns can treat many heterogeneous liquid, solid, and gaseous wastes and soil contaminants, including halogenated organics such as PCBs, dioxins,

and pesticides, and many nonhalogenated organic contaminants. High levels of metals or inorganic salts can cause problems with air emissions and degradation of the kiln refractory material, respectively (Camp, Dresser and McKee, 1988; EPA, 1986F).

Liquid injection units are in relatively widespread use in various industrial applications. Two types are considered potentially applicable to soil contaminants, industrial boilers and industrial kilns (lime, cement, aggregate, or clay), since no mobile units are currently available for contaminated soils applications (Camp, Dresser and McKee, 1986; EPA, 1986E; OAT, 1981). Liquid injection involves introduction of liquefied wastes (or soils) into a refractory-lined combustion chamber (boiler or kiln) in the form of atomized droplets vigorously mixed with air, where they are combusted in excess oxygen (at 2000 F in clay kilns and 3000 F in lime kilns), and exhaust gases are quenched and scrubbed prior to discharge, similarly to the rotary kiln (EPA, 1986E; Camp, Dresser and McKee, 1986). Many industrial boilers currently use regulated hazardous wastes and PCB liquids as supplemental fuel under RCRA Subtitle C and TSCA regulations. Use of wastes as fuels in cement, lime, and clay kilns is more limited at this time (OAT, 1981; EPA, 1986E).

Soil materials thus require much pretreatment

(maceration, slurrying by liquid and supplemental fuel addition, etc). Contaminant applicability and limitations are similar to rotary kilns with the added requirement that input materials be pumpable and atomizable. High moisture and chlorine contents may cause problems in some instances as well (Camp, Dresser and McKee, 1986). Drawbacks include high feed liquids requirements and potentially high liquid effluent production (as well as some ash) when soils are treated in this process.

Fluidized bed incinerators and related units, using circulating bed combustion, are available in fixed and They consist of refractory-lined chambers mobile form. with a bed of inert, graded material such as silica sand. Heated bed materials expand when hot combustion air is forced upward through the materials. Feed streams of contaminated soils or wastes are injected through the sidewalls and mix with the bed materials, thereby becoming heated and dried. As they combust, heat is transferred back to the bed. Operating temperatures are lower than other incinerators (1300 -2100 F) due to efficient heat transfer, residence times are relatively long (2 seconds for gases; minutes to hours for solids), and little ash agglomeration occurs (EPA, 1986E). However, solids must be pretreated to achieve uniform, small particle size, and large,

homogeneous solids cannot be treated. Inorganic residuals become trapped in the bed material, requiring its constant removal and replacement. Wastes can be treated in solid, liquid, sludge and slurry form, and include halogenated and non-halogenated organic soil contaminants, phenolics and solid, liquid, sludge and slurry form, and include PCBs, and pharmaceutical wastes. Considerable industrial process experience with this technology exists in oil refinery, coal, paper, and wastewater treatment applications (for paper mill and wastewater treatment sludge destruction, respectively; Camp, Dresser and McKee, 1986).

Infrared incinerators are commercially available (Shirco, Inc., 1986; Camp, Dresser and McKee, 1986) that pass wastes and contaminated soils along a metal conveyor belt under infrared heating elements within a ceramic-lined furnace for long, carefully controlled residence times (10-180 minutes at 500-1850 F). Ash residue is discharged from the end of the primary furnace, while gaseous residuals are passed through a secondary combustion chamber (1000 - 2300 F) and air pollution control train prior to discharge. Contaminated soils, PCBs and dioxins, and activated carbon are treatable using this method. Limitations include a minimum solids requirement (22 percent) and preprocessing requirements, as large, heterogeneous

solids will not be combusted.

In <u>pyrolysis</u>, wastes and soils are thermally decomposed in a hypoxic environment, generating primarily gases and some ash. Types include plasma arc systems and advanced electric reactors. Plasma arc systems consist of a plasma generator and a reaction vessel with atomization and equilibration zones. Finely divided, fluidized wastes or soils are introduced to the atomization zone, wherein collinear electrodes generate a plasma or electric arc. Low pressure air is ionized as it passes through the arc, generating heat. As activated molecules return to lower energy states, intense ultraviolet light is emitted. The light and heat energy (temperatures exceed 10,000 F) degrades feed waste and soil materials in the air stream to elemental forms (residence time 0.005 seconds). In the equilibration zone, they cool and recombine as simpler, less toxic species (temperature 1700 - 2700 F, residence time 1-2 seconds) prior to passage through air pollution treatment trains.

This technology is currently reached only pilot and bench scale (Camp, Dresser and McKee, 1986), but is potentially effective for chlorinated organic contaminants with few of the chlorine restrictions of the other high-temperature methods. However, it is highly energy intensive and requires slurrying and

atomization of input materials, limiting its utility for contaminated soils.

Advanced electric reactors (also called high temperature fluid wall reactors) are being developed as both mobile and fixed units specifically for application to contaminated soils (Camp, Dresser and McKee, 1986), but it can be used for liquids and gaseous wastes as well. Contaminants processed include halogenated organics such as PCBs and dioxins, nerve gases, pesticides, etc, which reportedly are degraded to carbon monoxide, carbon, hydrogen, and their other elemental constituents by thermolysis at approximately 4000 F (Bailey and Lobnitz, 1983).

This is done in a reactor containing a porous carbon core, surrounded by carbon electrodes which are heated electrically. Incoming wastes are introduced through the reactor top by a metering screw, and heated through direct radiative heat transfer. Residual solids and gases are passed through two post-reactors, ensuring complete combustion. Residuals include solids and gases from the process, and liquids from cooling and air pollution systems. This technology is currently available only at the pilot scale, although it is undergoing extensive development for widespread commercialization (Bailey and Lobnitz, 1983).

Wet oxidation is the third category of high-temperature

thermal treatment discussed in this section. It refers to the decomposition of organic contaminants in a water solution or suspension under high temperature (above 700 F) and pressure (above 3200 pounds per square inch). Air is mixed with aqueous waste or soil materials in a high pressure pump, then heated to supercritical conditions in a feed/effluent heat exchanger. Large organic molecules are degraded to low molecular weigh compounds, then oxidized in a stream of high pressure Bases such as sodium hydroxide are introduced to neutralize inorganic acids formed in the oxidation Inorganic salts tend to precipitate out of reactions. the supercritical liquid phase at temperatures above approximately 930 F (Camp, Dresser and McKee, 1986), and excess heat is generated by many of the exothermic reactions occurring.

Amenable soil contaminants include solvents, still bottom and tank bottom contaminants and sludges, halogenated contaminants such as dioxins and PCBs, and many pesticides. Limitations include control of the heat content of influent material in the 1800 BTU/lb range, and the requirement that feed streams be pumpable, requiring some pretreatment of soil materials.

Wet air oxidation is a closely related process in relatively broad use in waste treatment. Fixed units are operating in Southern California at the Orange

County advanced wastewater treatment plant and at the Casmalia Resources commercial hazardous waste treatment facility in San Luis Obispo County, as well as in industrial applications such as chemical manufacture (Camp, Dresser and McKee, 1986; Zadonick, 1984). Mobile units currently are being developed.

In this process, liquefied wastes are mixed with compressed air, then preheated in a heat exchanger before introduction to the main reactor vessel, wherein primarily exothermic oxidation reactions occur.

Effluent residuals are then passed through the heating coils of the heat exchanger prior to separation of spent vapors (primarily air and carbon dioxide) and liquid residuals. Residence time, temperature, pressure, and use of catalysts depend on contaminant specific conditions.

Applicability is similar to the supercritical water process but somewhat more limited in maximum and minimum concentrations (Camp, Dresser and McKee, 1986). Because of the requirement to liquefy influent waste streams, the wet oxidation processes should be considered only marginally potentially applicable to contaminated soils at the present time, although these methods are being refined in terms of pretreatment requirements, however they are highly applicable to leachates and ground water generated by contaminated soils. Therefore, they may

form important components of a contaminated soils treatment train.

## 2.3.5.2 Other Physical Processes

Physical treatment processes generally separate the contaminants in a soil or waste stream by applying physical forces or by changing the physical form of the soil or waste (Camp, Dresser and McKee, 1986; EPA, 1985H). Generally, the chemical composition of the contaminants is unchanged by these processes, therefore their intrinsic hazard may not be reduced. However, physical processes may often be used in a treatment train to remove contaminants from the soils for subsequent mobility or toxicity reduction by another process. Processes currently used or believed appropriate for use on contaminated soils are listed in Table 2. Examples of Superfund sites where these processes were selected as part of the remedial alternative are listed in Table 3 and Appendix I, and include the McKin site used as a case study in this report (see Chapter 5).

These processes are summarized briefly below. More comprehensive descriptions and design information can be found in EPA (1985H); Office of Technology Assessment (1983, 1985); EPA (1986E); Camp, Dresser and McKee (1985B, 1986); and Metcalf and Eddy, 1979; among others.

Air stripping systems allow mass transfer of contaminants from liquid to gas phase. Such designs are used commonly in industrial applications, and for removal of relatively volatile, less water-soluble contaminants from ground water plumes at many Superfund sites, including Triangle Chemical, Texas; Tyson's, Pennsylvania; and Verona, Michigan, among others. It is especially applicable to chlorinated hydrocarbons such as trichloroethylene (TCE) and aromatics including toluene. Practical tower dimensions range to 12 feet in diameter and 50 feet in height, based on design factors such as pressure, temperature, surface area for mass transfer, and air to water ratio (EPA, 1985H, 1986E).

Limitations include volatiles concentrations

(approximately 100 ppm), minimization of suspended

solids, and temperature dependence of removal

efficiencies. Soils can be aerated directly as well, as

discussed below under mechanical aeration.

Steam stripping systems use steam to volatilize organic contaminants from soils or aqueous wastes. Contaminants treated include halogenated hydrocarbons, ketones such as methyl ethyl ketone or acetone, aromatics such as xylenes, alcohols, and chlorinated organics with high boiling points such as pentachlorophenol. A packed or tray tower is used to carry out essentially a continuous fractional distillation

process. The tower is heated with clean steam rather than reboiled bottoms. Residuals include contaminated steam condensates, recovered solvents and other contaminants, and "stripped" residual liquids. The technique is confined primarily to liquid or liquefied streams, and can treat a broader range of contaminants than can air stripping in terms of their volatility, water solubility, and concentration (EPA, 1986E).

Mechanical aeration involves physical mixing or agitation of soils, sometimes augmented with heat, to extract volatile contaminants, as was done at the McKin site (see Chapter 5); Triangle Chemical, Texas; and South Tacoma/Well 12A, Washington. See Appendix I for more information on these sites and others.

Contaminated soils are mixed with air to transfer volatile contaminants from the soil to the air.

Removal efficiencies and rate constants for selected volatile organic contaminants were estimated by Camp, Dresser and McKee (1985B) using a volatilization rate model developed by Dow Chemical researchers (Bonazountas and Wagner, 1984), as shown for a hypothetical contaminated soils scenario as shown in Table 4. Key parameters for aeration methods include soil moisture and organic carbon content, contaminant characteristics including water solubility and vapor pressure, and sorption characteristics (as discussed in

TABLE 4
Removal Efficiencies of Selected Volatile Organic
Compounds From Soil by Mechanical Aeration
(Source: Camp, Dresser and McKee, 1985B)

(Assume Final Clean-up Criteria to be 99.99% Removal with base level of 500 mg/kg)

		• • •	
Compound	*K. (day-1)	t (day)	t (min)
Chloroform	17,600	5.24 x 10 <sup>-4</sup>	0.75
Carbon Tetra- chloride	9,970	9,25 x 10 <sup>-4</sup>	1.33
Bromoform	1,667	5.53 x 10 <sup>-3</sup>	7.96
Methylene chloride	118,462	7.78 X 10 <sup>-5</sup>	0.11
1,1-Dichloroethane	228,800	4.03 X 10 <sup>-5</sup>	0,06
Trichloroethylene	67 <b>,</b> 15B	1.37 X 10 <sup>-4</sup>	0.20
1,1,1-Trichloroethane	36,125	2.55 x 10 <sup>-4</sup>	0,37
1,1,2-Trichloroethane	2,572	3.58 X 10 <sup>-3</sup>	5.16
Benzene	24,775	3.72 X 10 <sup>-4</sup>	0.54
Chlorobenzene	1,019	9.05 x 10 <sup>-3</sup>	13.02
1,4-Dichlorobenzene	110	8.40 x 10 <sup>-3</sup>	120.70
2-Butanone	2,284	4.04 x 10 <sup>-3</sup>	5.80

Section 4.3), and environmental conditions including ambient pressure and temperature, wind velocities, etc. (Camp, Dresser and McKee, 1985B).

The method can be applied to soils in situ, or soils can be excavated and aerated in various treatment units. Excavation and treatment in units offers more opportunities to control volatile releases to the atmosphere off the site by passing volatiles-laden exhaust gases through secondary extraction systems such as fume incinerators, activated carbon units, or conventional air pollution control trains (EPA, 1986E; Camp, Dresser and McKee, 1895B, 1986). Nonvolatile contaminants generally are not removed from soils using these methods. Extraction efficiency depends on heterogeneity of soil type, particle size, and contaminant distribution, as well as ambient or operating temperatures and feed or aeration rates (EPA, 1985J, 1986E; Webster, 1986). Several different methods have been used:

- o <u>Mechanical rototilling</u>, wherein shallow surface soils are tilled in place, as is done in conventional land treatment processes, discussed briefly in Section 2.3.5.5;
- Enclosed mechanical aeration, wherein contaminated soils are mixed in a pug mill or rotary drum system such as a cement mixer. Induced air flow is used to enhance volatiles release from soils and to capture air emissions for treatment prior to discharge (Camp, Dresser and McKee, 1985B, 1986);

- Pneumatic conveyor systems, consisting of induced draft fans forcing air through long ducts at high velocity. Solids are introduced to the air stream by feeders and collected by cyclone separators at the effluent end of the duct. Some units heat influent air to approximately 300 F to enhance volatilization of contaminants from the solids. These systems are widely used to dry solids in several conventional manufacturing processes (Camp, Dresser and McKee, 1986), and allow high air/solids ratios (much like the air/liquid ratio of air strippers);
- Low temperature thermal stripping, similar to the enclosed aeration system with the addition of heat transfer surfaces and/or heating of the induced air inflow, such as in an asphalt batch facility. A combustion afterburner may be used to destroy contaminants in the effluent air. This type of system was part of the treatment train eventually used at McKin; and
- o <u>Vacuum extraction</u>, usually performed on soils in situ. The system consists of a network of wells or boreholes penetrating the contaminated soils mass, connected by a pipe network to a high volume vacuum pump which draws air from the margins of the treatment zone through the contaminated soils, enhancing release of contaminants from soil pore spaces and surfaces. Secondary trains can be used to recover free hydrocarbon products by condensation, or to remove contaminants prior to discharge of the effluent gases. Such systems have been used to recover hydrocarbon and chemical free product layers floating on the ground water table after releases from underground storage tanks (Camp, Dresser and McKee, 1986).

<u>Distillation processes</u>, widely used as a unit operation in petroleum refining, chemical manufacturing, and metal finishing applications, separate components of liquid mixtures by partially vaporizing them. The process is applicable to acetone, alcohols, ketones, and halogenated and non-halogenated hydrocarbons, and is not

applicable to inorganics, polyurethanes, and liquids with high solids concentrations or with high viscosity at high temperatures (Camp, Dresser and McKee, 1986). Thus, use for contaminated soils, especially for the variable chemical and physical contaminant compositions at Superfund sites, would be very limited, except as part of a treatment train addressing a complex site problem.

Evaporation can be used, similarly to distillation, to vaporize part of a mixture or suspension of contaminated soils (or sludges) and liquids while concentrating the solid components, as is regularly done in commercial hazardous waste and wastewater treatment using solar evaporation impoundments (Camp, Dresser and McKee, 1986; Meredith/ Boli and Associates, 1983; Metcalf and Eddy, 1979). Other processes used in many conventional industrial applications include thin-film evaporation, kettle methods, tubular evaporation, scraped surface methods, and the Carver Greenfield process, which use enclosed vessels in varying configurations (Camp, Dresser and McKee, 1986). Evaporation could be used as a treatment or pre- or post- treatment step for removing liquid contaminants or water from contaminated soils.

Activated carbon commonly is used in wastewater and contaminated ground water treatment, and in a variety of

industrial manufacturing processes. It can sorb and collect relatively water soluble (and water insoluble) metallic ions and organic compounds through surface attraction mechanisms. A general discussion of sorption as a subsurface fate and transport phenomenon is provided in Section 4.3.2.1. Becker and Wilson (1978) summarized the effectiveness of granular activated carbon in removing various organic contaminants from liquids and gases.

Stationary units are in use at several Superfund sites including Stringfellow, California, and EPA has used a mobile system to treat spilled liquid contaminants and contaminated surface and ground water at several sites (EPA, 1986E). Spent, fully sorbed carbon can be regenerated in a special incinerator, but few regeneration facilities are currently available (Traver, 1983).

Soil Washing involves extraction of contaminants from soils using water or other solvents, surfactants, oxidizing or reducing agents, acids or bases (for inorganics), chelating agents, or detergents. Soil washing or flushing may be done in situ, or soils may be excavated and treated in an enclosed unit or a lined waste pile. This technology has been used for many years by the mining industry for metal leaching or solution mining, and by the oil industry for tertiary petroleum

recovery, as well as in agriculture to leach accumulated salts, pesticides and other soil contaminants. However, use for contaminated soils at Superfund sites has been limited (EPA, 1986E).

Use will be limited in dry or organic-rich soils, or where hydraulic conductivity is limited or soil pores become blocked by precipitates, microparticles, etc. Choice of washing fluid is highly dependent on soil conditions and types and forms of contaminants present. Ground water pump and treatment systems sometimes may be combined with soil washing (especially in situ) in recirculating systems where extracted ground water is treated and reinjected to enhance contaminant removal (Repa and Kufs, 1985). Recyclability of flushing media is limited for certain surfactants (Camp, Dresser and McKee, 1986; Barcelona et al., 1987).

In situ systems have more limitations due to uncertainties of site hydrogeology, lack of close process control, post-treatment limitations in high-clay-content soils, and the potential to enhance, introduce, or alter ground water contamination by the process. Thus, much effort is focused on development of effective washing agents that are intrinsically nontoxic and/or biodegradable (Camp, Dresser and McKee, 1986; EPA, 1986E). Types of washing fluids considered for different contaminants are discussed in Camp, Dresser

and McKee (1986). Several Superfund sites using soil washing methods are described briefly in Table 5.

Filtration using porous media or selectively permeable membranes is a conventional technology used frequently in a variety of industrial applications to selectively remove solids or specific contaminants from a liquid suspension by passage through a porous granular filter material, using pressure, vacuum, or gravity to achieve separation. This technology is described by Metcalf and Eddy (1979); Camp, Dresser and McKee (1986); and EPA (1985H, 1986E), among others. Most processes are designed to have optimal feed rates and optimal influent solids contents and particle size distributions. Their application for contaminated soils treatment would be as part of a train for liquid removal. Flocculants may be added in a pretreating step to enhance separation, as in some wastewater treatment processes (Metcalf and Eddy, 1979).

Membrane technologies may be considered a special category of filtration for purposes of this report.

They separate solids or chemical contaminants from a liquid suspension or solution by of filtration for purposes of this report. They separate solids passage through a semi-permeable membrane that is selective based on ionic state or valence, particle size, or coprecipitation to yield volume reduction; concentration

TABLE 5
Superfund Sites Using Soil Washing
(Source: Camp, Dresser and McKee, 1985B, 1986)

SITE	SOIL/WASTE	WASH MEDIUM	COMMENTS
Bridgeport, NJ	Lagoon sludges, subsoils w/ PCBs, metals	Recirculated ground water	See Appen- dix I
South Taco- ma/Well 12A, WA	Soils w/TCE	Water	1st alter- tive to aeration (selected)
Volk Air Base, WI	Soils w/ volatile organics	Water, 2% surfactant	Wash fluid reused after air stripping
Lee's Farm, WI	Soils w/ lead, acid	Water, 5% EDTA	Wash fluid regen. by electro- lysis
Celtor, CA	Ore tailings w/Cd, Cu, Zn	See Appendix	I
Battery Pit, Leeds, AL	Soils w/ lead	Water, 2% EDTA	Wash fluid regen. by sulfide precip.

or purification of contaminants, recoverable solvents, or washing fluids; or concentration of separated soil contaminants (Camp, Dresser and McKee, 1986). Methods include hyper- and ultra-filtration, electrodialysis, and reverse osmosis. Reverse osmosis processes have been used effectively on leachates, ground water, and other liquids. Contaminants removed include PCBs, chlorinated organics, inorganics, pesticides, and solvents including benzene and acetone. Landfills and wood preserving sites in Canada have been treated using mobile reverse osmosis systems (Camp, Dresser and McKee, 1986).

<u>Phase separation</u> is accomplished by applying force to remove contaminants having different densities than water from a water solution or suspension. Several processes are used, for example:

- Oil <u>separation</u>, which removes oil from water suspensions using a variety of equipment configurations such as coalescing chambers;
- Centrifugation, which separates contaminants on the basis of specific gravity and density differences (Camp, Dresser and McKee, 1986; Metcalf and Eddy, 1979); and
- Dissolved air flotation, used in commercial oil refining and other industrial applications involving wastewater treatment, used to separate oils from aqueous fluids by emulsifying the oils, dissolving air into the suspension under high pressure, then reducing the pressure, generating fine air bubbles throughout the water phase. Oils accumulate at the air/water interfaces, rise to the surface, and are skimmed from the chamber.

Specific design factors include oil concentrations, retention times in the unit, surface area, removal rates, and other site-specific factors. Phase separation processes are particularly applicable to contaminated soils remedies where the alternative includes removal and separation of immiscible hydrocarbon products released in relatively pure states, or where other combined soils/aquifer remediation techniques are to be used for separate-phase contaminants (Camp, Dresser and McKee, 1986; Barcelona et al., 1987).

## 2.3.5.3 Stabilization/Solidification

For the purposes of this report, stabilization or solidification processes can be grouped under general titles such as "fixation" and "immobilization" as well. They refer collectively to the addition of substances to wastes or contaminated soils (fixatives) that combine with them chemically and/or physically to decrease the mobility of the contaminants present, especially by water related transport processes.

Stabilization may be done for several purposes: (1) to retard further contaminant migration by immobilizing highly soluble contaminants; (2) to solidify or immobilize liquid or sludge matrices; (3) to reduce mobility by minimizing surface area of the waste or

contaminated soils particles available for contact with infiltrating leaching fluids; or (4) to stabilize certain wastes (such as unconsolidated, noncohesive soils or sludges) to enhance their structural support capacity, for example prior to placement of final cover over landfilled or consolidated wastes or soils (as was done, for example, at the Bruin Lagoon, site in Pennsylvania; see Appendix I). Stabilization of wastes or soils, or immobilization processes can be performed in situ or on excavated materials.

Many stabilization processes are not fully irreversible. Therefore, as a sole remedy they may not comply fully with the SARA "permanence" preference in Section 121, as discussed in previous chapters of this report. However, as with other technologies discussed in this section, they may form one component of a remedial alternative, and have many applications as post-treatment steps following other processes, as was the case at the McKin site discussed in Chapter 5. Specific technologies reviewed briefly in this section include cement-based, lime- and fly ash-based (pozzolanic), thermoplastic (including asphalt-based), and thermoset methods, and macroencapsulation.

Several chemical treatment methods such as precipitation, chelation, and polymerization may to some extent be considered immobilization methods as well, as

they may have the effect of making certain contaminants insoluble in water and preventing their leaching from soil matrices, especially when applied in situ (EPA, 1985H). However, since this is achieved by chemically altering the soil contaminants or the contaminant -soil associations, precipitation, chelation, and polymerization will be discussed in Sections 2.3.5.4 and 2.3.6, respectively.

Stabilization/solidification processes have been applied primarily to aqueous inorganic wastes such as metalcontaining sludges and radioactive wastes (see Table 3 for examples). Much of the data on stabilization is derived from the development of radioactive waste stabilization methods (Camp, Dresser and McKee, 1985B). Organic wastes (concentrations exceeding 10-20 percent organic contaminants) traditionally have not been considered amenable to stabilization for two reasons: first, because the organic contaminants tend to interfere with some of the physical and chemical binding processes; and second, because other treatment processes (e.g., biodegradation or incineration) have been selected more frequently for wastes having higher organic contents (Camp, Dresser and McKee, 1985B, 1986; Cullinane et al., 1986).

Fixatives used may be inorganic or organic mixtures.

They can be characterized as follows (Camp, Dresser and

McKee, 1985B; Cullinane et al., 1986):

- O <u>Inorganic fixatives</u> include sorbent clays, Portland cement, and pozzolanic materials (with or without lime or cement). They have relatively low costs, are simple to process at ambient pressures and temperatures, are readily available, experience with their use is extensive, and they are relatively stable against physical and chemical degradation.
- Organic fixatives include polyethylene, urea-0 formaldehyde, asphalt, other polymers, and various thermoplastics. They are often supplemented by additives that sorb various contaminants or enhance the structural integrity of the solidified mass. They have a greater potential to fix contaminants chemically than the inorganic fixatives, and have higher fixative/waste ratios and lower overall solidified volumes (due to dewatering before treatment). They tend to be more equipment- and process-intensive, and less well demonstrated, than many inorganic fixative processes. For purposes of this discussion, these organic processes can be grouped into the general categories of thermoplastic, thermoset, and macroencapsulation processes (Camp, Dresser and McKee, 1985B).

Cement-based processes commonly use one of the five types of Portland cement, primarily Type I common construction cement. Sometimes it is supplemented with additives such as clay and vermiculite to absorb excess liquids, sodium silicate to precipitate interfering ions, or soluble silicate to enhance contaminant binding to the cement matrix. Contaminated soils or wastes are mixed into a slurry of anhydrous powdered cement and water. Calcium silicate and water form hydration products with the contaminants and matrix particles, and the mixture swells forming a stable matrix of interlocking

calcium silicate fibers, with hydroxides of calcium and metallic contaminants and other contaminant hydration products forming in the matrix interstices. As the mass cures and sets, a rigid mass is formed (Camp, Dresser and McKee, 1985B).

Vendors have reported overall waste/soil volume increases ranging from 5 to 60 percent, depending on contaminant and soil characteristics and types of additives used. This process is generally effective for most inorganic contaminants, including oxidizers and acidic materials, depending on the neutralization capacity provided by the cement mixture. Organic contaminants are not as effectively stabilized because of degradation of the contaminants in the matrix during and after curing, which decreases structural integrity and increases permeability of the solidified mass.

Other interferences include sulfates (which form calcium sufoaluminate hydrates, which retard setting and exacerbate swelling); soluble salts of some metals (e.g., lead, zinc, copper, tin, manganese, and sodium salts of sulfide, arsenate, borate, and phosphate, which retard setting and reduce final structural integrity); and fine organic particulates (e.g., lignite, fine clays, etc., which can coat larger contaminant particles, interfering with cement- contaminant bonding; Camp, Dresser and McKee, 1985B). Special injection

equipment and process controls may be required for in situ applications of these processes (Camp, Dresser and McKee, 1986), as will be discussed in Section 2.3.6.

Pozzolanic processes use fine-grained silecious (pozzolanic) materials such as cement kiln dust, ground blast furnace slag, and power plant fly ash, in combination with lime as the fixatives. These are mixed with contaminated soils or wastes and water to form a concrete-like mass. In some cases these fixatives have been used in combination with asphalt to fix complex chlorinated organics such as dioxins (Camp, Dresser and McKee, 1985B). Process and equipment requirements, and key operating parameters, are similar to cement-based processes. These processes are commonly used to stabilize power plant emissions control residuals, such as flue gases, flue gas desulfurization sludges, and fly ash, metal smelting sludges, and thickened coal fines (Camp, Dresser and McKee, 1985B), and may be especially effective on more acidic inorganic contaminants in soils.

Thermoplastic processes use organic fixatives such as bitumen, asphalt, nylon, polyethylene, polypropylene, and asphalt. Wastes or contaminated soils are heated, dried, dispersed through the thermoplastic fixative in liquid or semi-liquid form at elevated temperatures (130-230 C, depending on the characteristics of the contaminated soils to be treated and the type of

fixatives). The mixture is allowed to cool in containers. The process requires waste/soil pre-processing and specialized equipment.

Advantages include more predictable and reliable reactions than inorganic fixatives (due to less sensitivity to pH, water content, and contaminant chemistry); lower final volumes (due to the pre-fixation dewatering); lower levels of free liquids or unsolidified contaminants in the product; less potential for contact of leaching fluids with contaminants; and greater effectiveness for many organic contaminants (Camp, Dresser and McKee, 1985B). Limitations include containerization requirements, due to product plasticity; high input energy requirements; greater air emission potential than inorganic fixation methods; and more safety concerns with flammable contaminants and fixatives.

Thermoplastics such as asphalt and bitumen have been used widely to stabilize organic wastes containing radionuclides. They may show limited effectiveness on contaminated soils or wastes with high water contents, organic concentrations above 30% by weight, organic contaminants with high vapor pressures and low molecular weights, or that dissolve the fixative, or with inorganic contaminant such as anhydrous salts (which can rehydrate if exposed to water and cause asphalt

fixatives to physically degrade), aluminum salts or iron tetraborates (which prematurely harden bitumen fixatives), or strongly oxidizing salts (e.g., chlorates or nitrates, which can slowly degrade the organic matrix when present in high concentrations; Camp, Dresser and McKee, 1985B).

Thermoset processes are innovative and have been applied primarily to radioactive wastes, although as described in Section 2.3.6, some hazardous waste plumes in ground water have been treated in situ using polymers (EPA, 1985H). Fixatives include organic polymers such as phenolics, polyesters, and urea-formaldehyde. Unlike thermoplastics, they solidify when heated, and remain solid in subsequent heating and cooling cycles. Wet or dry contaminated soils or wastes are mixed in batches with the polymer and an acidic catalyst, and heated to facilitate solidification. The resultant mass is spongy and less dense than cement and must be containerized for ultimate disposal (Camp, Dresser and McKee, 1985B).

The process is less sensitive to liquid content than the others described in this subsection, and does not depend on high temperatures for solidification. The acid conditions cause metals to dissolve prior to fixation in the polymer matrix, however, and thus they are not immobilized. The resin is not flammable, but is very susceptible to chemical degradation (by oxidizers)

and to biodegradation (especially the urea-formaldehyde resins; Camp, Dresser and McKee, 1985B). Acidic "weep water" and gaseous residuals are generated in this process, which will require post-treatment.

Reversibility and "permanence" concerns are involved also. Since no chemical binding of contaminants to the matrix occurs, any degradation of the fixed material can cause contaminant release.

Macroencapsulation involves the containment of contaminated soils or wastes within coatings of asphalt and asphalt emulsions, vinyl, and polyethylene (sometimes reinforced with fiberglass). Often the coatings are applied to the surfaces of stabilized contaminant masses or containers as a post-treatment step following one of the other immobilization processes for purposes of containing weep fluids, or minimizing contact potential of solidified materials with leaching fluids following disposal (Camp, Dresser and McKee, 1985B). Encapsulation processes are expensive, energy-intensive, and are in the early stages of development. They have not been used at full scale on contaminated soils at Superfund sites.

## 2.3.5.4 Chemical Processes

The following section provides an overview of the primary chemical treatment processes considered applicable

as source control technologies for contaminated soils at Superfund sites. For purposes of this discussion, chemical treatment will be defined as chemical alteration of the contaminants or the soil matrix in which they are held, producing less mobile and/or less toxic daughters or residuals. Clearly, many of the physical treatment methods and stabilization processes discussed previously in this Section, as well as many of the biological processes to be discussed in Sections 2.3.5.5 and 2.3.6, involve chemical modification of the contaminants or of the waste or soil matrix being treated. Many chemical treatments particularly involve chemical modification of the contaminants or of the waste or or uniquely applicable to contaminated surface water or ground water, either in situ or following extraction, will not be discussed in this section. Chemical processes discussed below include oxidationreduction processes, neutralization and precipitation reactions, chelation, dechlorination, and ion exchange processes. Polymerization is discussed in Sections 2.3.5.3 and 2.3.6.

Many of these processes have been in traditional use in industrial waste treatment and pretreatment, and general reviews of these processes can be found throughout the industrial process literature. Further, many of these phenomena occur naturally in the subsurface

and affect the fate and transformation of soil contaminants as they migrate to ground water.

Additional discussion is provided in that context in Section 4.3.

Redox processes use oxidation-reduction reactions to detoxify organic contaminants and metals by changing the oxidation states of reactants in the matrix. These reactions have been applied typically to treat aqueous industrial wastes and sludges bearing heavy metals, typically in tanks or enclosed vessels wherein reactants may be mixed rapidly under close pH and reagent concentration control. Applications to soils or soil slurries are more recent (Camp, Dresser and McKee, 1986).

Soils treatment will require special consideration, for example to ensure thorough contact of reactants with soil contaminants, and to ensure complete reaction in soils of high natural organic carbon content. In situ applications may affect soil permeability and hydraulic conductivity, for example if hydroxide precipitates form and clog soil pores, or may affect contaminant mobility in unexpected ways as soil sorption capacity is affected by oxidation and reduction of soil organics. Thus, combination of this technology with others such as soil washing may provide a more controlled and more effective treatment process for some contaminated soils.

Complex contaminant mixtures may also complicate the reaction process, and must be evaluated in selecting this technology. For example, if soils containing both organics and metals are oxidized (e.g., oxidizing solvent-contaminated soils also containing chromium III), the more toxic, mobile chromium VI may be generated (Camp, Dresser and McKee, 1985B).

Contaminants amenable to oxidation include most organic contaminants, cyanide, arsenic, iron, and manganese. Reducible contaminants include Chromium VI, mercury, silver, lead, chlorinated organics (discussed separately below), and many unsaturated hydrocarbons (Camp, Dresser and McKee, 1986). Oxidizing agents are used more frequently than reducing agents due to the high reactivity of many reducing agents. Typically used industrial agents are discussed in Camp, Dresser and McKee (1986).

Neutralization refers to pH adjustment (typically of an aqueous mixture or suspension or a gas) by addition of bases to strongly acidic mixtures, and acids to strongly basic contaminant mixtures. This is typically done in numerous industrial process applications and in municipal wastewater treatment (Metcalf and Eddy, 1979; Camp, Dresser and McKee, 1985B, 1986; EPA, 1985H). Lime, sulfuric acid, and sodium hydroxide are commonly added reagents. Specific

selections depend on types and concentrations of the contaminants, buffering capacity of the matrix in which they occur, and other factors. Applicability to contaminated soils is primarily as a pretreatment or post-treatment step in a multiple treatment train.

Precipitation is a conventional, well understood process for treatment of many industrial process wastes and municipal wastewaters (Metcalf and Eddy, 1979), which is often applied in combination with sedimentation and flocculation, particularly for detoxification of heavy metals and their removal from aqueous solutions and suspensions. Efficiency of the process is highly dependent on concentrations, pH, and presence of interfering contaminant species, as discussed by Camp, Dresser and McKee, (1985B, 1986); EPA (1985H, 1986F); Metcalf and Eddy, (1979); and others.

The process is especially well developed for liquids, although it can be applied to contaminated soils, either excavated or in situ, especially in more homogeneous and permeable subsoils such as coarse sands (EPA, 1985H). Interferences and side effects on subsurface transport and transformation are discussed further in Section 4.3.

Chelation by addition of specific chelating agents may either enhance or retard the mobility of specific contaminants, as discussed in Section 4.3. For example,

the agent Tetran sorbs strongly to clays and thus may immobilize contaminants with which it forms complexes (EPA, 1984D). Commonly used chelating agents include ethylenediamine tetraacetic acid (EDTA), citric acid, and diethylenetriamine pentaacetic acid (Rogoshewski and Carstea, 1980). Chelating agents may be especially appropriate for use in soil flushing or solution mining, either in situ or after excavation of contaminated soils, to remove metals from the soil matrix. They may be part of a train of processes for immobilization or recovery of the metals.

Dechlorination processes have been developed as mobile and fixed treatment processes, initially for treatment and/or reconditioning of PCB-containing oils in contaminated electrical transformers pursuant to TSCA regulations (OAT, 1981; Office of Technology Assessment, 1983, 1985; EPA, 1986E; Camp, Dresser and McKee, 1986). The process has been extended for use on Superfund soils contaminated with chlorinated organics such as PCBs and dioxins.

Dechlorination is accomplished using reagents containing an alkali metal (generally sodium or potassium) and polyethylene glycol, which react with the chlorinated contaminants via nucleophilic displacement of the chlorine atoms to form substituted organic polymers and alkali metal chlorides (KCl or NaCl), with

polymers, salts, and heavy metals (if present) as byproducts. Limitations include moisture content and contaminant concentration. For example, soils require dewatering, since the reagents are water sensitive, and PCB concentrations should not exceed 5000 ppm (Camp, Dresser and McKee, 1986). Reagents are also airsensitive, therefore, dechlorination is more effective under nitrogen atmospheres. Thus, at its current stage of development, dechlorination is likely to be less effective for in situ treatment of contaminated soils.

Ion exchange using clays, zeolites, or synthetic resins can also be an effective separation method for contaminants in soils (EPA, 1984D; Camp, Dresser and McKee, 1986). As with other fundamental physical and chemical processes discussed in Sections 3.2 and 4.3, many basic texts provide detailed discussions of the process; a cursory overview will be provided here for the purposes of this discussion. Certain minerals and resins will exchange either anions or cations preferentially for other anions and cations in aqueous solutions or suspensions. Use of ion exchange columns to remove heavy metals and hazardous ions from dilute solutions is a well established practice in industrial processes and some wastewater treatment applications, especially to remove carboxylic and sufonic acids and phenols under sufficiently alkaline conditions, and

organic amines under sufficiently acidic conditions sufficiently alkaline conditions, and organic amines (De Renzo, 1978; Ghassemi et al., 1981).

Both inorganic and organic contaminants can be treated by ion exchange, however, it is most effective in aqueous environments where the surface area of contaminant bearing particulates is maximized and/or contaminants are in solution or suspension directly in the aqueous phase. Thus, soils would have to be liquefied, or these processes would be used on liquid influents or effluents from other treatment processes as a separation step in a multi- component remedial alternative. Limitations for cation exchange involve interferences by other cations in complex contaminant mixtures, especially if interfering contaminants are present at higher concentrations than those to be preferentially treated (EPA, 1984D). For heavy metals, basic pHs may limit ion exchange compared to precipitation (Bonazountas and Wagner, 1981).

Clay minerals in soil will remove cations in exchange for equimolar amounts of calcium. Clays and humic materials have the greatest capability for ion exchange, measured as cation exchange capacity (CEC) in milliequivalents per 100 grams dry weight of soil.

Brady (1974) measured CEC in natural soils ranging from 2 to 60 milliequivalents per 100 g, and up to 150 and

200 meg/100 g for montmorillonite and humus, respectively. Considerable research exists on the ion exchange properties of bentonite and other clays for immobilizing chlorinated hydrocarbon pesticides (Coffey and Warren, 1969; Weber et al., 1965; Bailey et al., 1968).

Synthetic resins are available as either anion or cation exchangers. They consist of networks of hydrocarbon radicals bearing ionic functional groups, crosslinked in three dimensions. The resin is insoluble in water and individual resins can be synthesized to select specific ionic species (EPA, 1984D), since the ion enters the pore of the resin in order to be exchanged, as determined by the crosslinking of the molecules. They tend to be relatively expensive, and effectiveness in contaminated soils may be limited by competition for ion exchange sites by naturally occurring soil ions (EPA, 1984D), thus their large-scale application to Superfund soils likely will be limited.

Zeolites are a family of crystalline-hydrated aluminosilicates. Certain species are highly selective and capable of sorbing heavy metal cations, sometimes offering stability and capacity superior to other ion exchangers (EPA, 19084D). They do not biodegrade and are stable over broad alkaline pH ranges, though they will degrade in acidic environments. Metal sorption

abilities are affected primarily by pH, choice of solvent, presence of competing cations or complexing agents, and ionic strength of the solution (EPA, 1984D). They have been used for removal of heavy metals from wastewater, but have not been used at field scale to treat contaminated soils. Further information on their chemical and physical properties can be found in Breck (1974), Sherman (1978), and Coffey and Warren (1969).

## 2.3.5.5 <u>Biological Processes</u>

A variety of degradation processes occur naturally in soils and ground water that are initiated or mediated by macro- or microorganisms indigenous to the subsurface environment, as discussed in Section 4.3.3.

Additionally, several technologies using aerobic or anaerobic biodegradative processes have been developed to treat liquids, sludges, and solid wastes and contaminated soils. Biological treatment can occur in tanks or other treatment vessels, or may be conducted on contaminated soils and ground water in situ, to treat a broad range of organic and inorganic contaminants.

Many basic texts are available that discuss the fundamental chemical and biological processes involved, and the design and operating considerations for the various types of treatment processes that have been or could be applied to treat contaminated soils. A

detailed discussion is outside the scope of this study.

A brief description of the more applicable and available aerobic and anaerobic methods is given in this subsection.

Aerobic treatment of aqueous contaminants can be accomplished using conventional activated sludge processes, sequential batch reactors, rotating biological contactors, trickling filters, and fixed-film reactors. Many of these processes can be conducted in mobile-tank-based units as well as in fixed facilities such as conventional and advanced wastewater treatment plants (Metcalf and Eddy, 1979; Camp, Dresser and McKee, 1986).

They can treat low to moderate concentrations of many nonhalogenated and halogenated organic compounds and mixtures, and may remove small amounts of heavy metals through adsorption to the biological material (Camp, Dresser and McKee, 1986). Addition of activated carbon in powder form can enhance removal of many halogenated organic contaminants such as pesticides and some solvents. Effectiveness of treatment depends on factors including nutrient availability, pH between 6 and 8, adequate dissolved oxygen, alkalinity, and careful process control of suspended solids levels and retention times, as well as many other factors (Camp, Dresser and McKee, 1986; Metcalf and Eddy, 1979;

Barcelona et al., 1987; Keely et al., 1986; Repa and Kufs, 1985; EPA, 1984D, 1985H). Biological treatment of contaminated ground water in situ is discussed in Section 4.3.

Most variations of the activated sludge process involve aeration of the contaminant materials in an open tank for a 6-24 hour period, in which aerobic biodegradation occurs, enhanced and facilitated by suspended active microorganisms maintained by period, in which aerobic biodegradation occurs, enhanced and recycling sludge. New biomass is produced during treatment, followed by solids separation in a clarifier or using other separation processes discussed in this section. Loading rates may vary from 10 to 180 pounds BOD applied per 1000 cubic feet, depending on site- and contaminant-specific factors (EPA, 1986E).

Trickling filters use rock beds, wood, or synthetic filter media over which contaminants are sprayed in aqueous solution. Microorganisms form slime layers on the filter surfaces, oxygenated by air flowing countercurrent to the liquid spray and downflow, and degrade the organic contaminants in the liquid (EPA, 1985H; Canter and Knox, 1985; Metcalf and Eddy, 1979).

Rotating biological contactors consist of rotating discs on a common shaft, rotating in a basin in which

approximately 40 percent of their surfaces are submerged at a given time. Contaminated liquids flow through the basin, wherein they are degraded by microorganisms in films on the disc surfaces (Canter and Knox, 1985; Metcalf and Eddy, 1979).

Applications and limitations of various conventional aerobic biological treatment processes are discussed by EPA (1985H), Metcalf and Eddy (1979), and others. Biological treatment processes particularly applicable to soils in situ are discussed further in Section 2.3.6.

Anaerobic digestion has had broad applications in treatment of concentrated municipal wastewater treatment sludges and some industrial process wastes, typically using an enclosed reactor system having a minimum recycle of biomass, often using a two stage process. Sludge is heated and digested in the first stage, and stored and concentrated in the second (Camp, Dresser and McKee, 1985B). Retention time varies from 10 to 30 days, depending on system design and wastes handled.

Two groups of bacteria are believed to accomplish biodegradation: acid-forming facultative anaerobes, which hydrolyze and ferment complex organic contaminants to acetic and propionic acids, and strict anaerobes (e.g., methanogens), which convert these organic acids to methane and carbon dioxide. Growth rates generally

are much slower than aerobes. Suflita et al. (1982), and Barcelona et al. (1987), among others, indicated the utility of anaerobes in degrading many halogenated organic contaminants by reductive dehalogenation.

Anaerobic degradation may be carried out in situ as well as in enclosed treatment units, as will be discussed in Section 2.3.6. Excavation and treatment of contaminated soils in enclosed units may offer opportunities for use of enhanced exogenous or bioengineered microorganisms (Camp, Dresser and McKee, 1985B), however, most aerobic and anaerobic biodegradative processes use resident microbial populations, and treatment process control is focused on optimizing the supply of nutrients.

Conventional land treatment of hazardous and nonhazardous wastes and soils has been practiced for many years, coming into more widespread use in recent years as an alternative for treatment of hazardous wastes as well as of municipal and industrial wastewater treatment sludges, especially from food processing and oil refining (Loehr, 1986; Overcash and Pal, 1979; Loehr et al., 1979; EPA, 1983B; American Petroleum Institute, 1983). It involves management and enhancement of naturally occurring photolytic and biodegradation mechanisms (primarily aerobic, but some anaerobic degradation also occurs) in surface soils through controlled application of wastes or soil contaminants by

tilling or direct injection.

Many reviews discussing performance, design, operation, and limitations of conventional land treatment processes are available (Loehr, 1986; EPA, 1983B; Overcash and Pal, 1979; Huddleston et al., 1986; Sims, 1986; and others). Land treatment has been used at several Superfund sites, including Old Inger, Louisiana, Burlington Northern, Minnesota, and Picillo Farm, Rhode Island (Appendix I), primarily for treatment of oily wastes and soils contaminated with wood treatment residuals and phenols.

Composting offers potential for treatment of
Superfund contaminated soils because the biodegradative
processes, and the microorganisms performing the
degradation, are similar to those involved in land
treatment, especially the pseudomonads (Camp, Dresser
and McKee, 1985B). Composting allows stricter process
control, however. It typically is performed using one
of three methods: turned windrow systems, static windrow
systems, and reactor vessel systems. Composting piles
are based on structurally firm, biodegradable material
such as livestock feed or chopped hay, with small
amounts of waste or contaminated soils added (i.e., less
than 10% of the total mass; Doyle and Isbister, 1983;
Camp, Dresser and McKee, 1985B). Composting processes
all have a thermophilic stage in which temperatures may

exceed 80 C.

In open windrow systems, materials to be treated are stacked in elongated open piles. The windrows are aerated in turned systems by turning over and rebuilding the stacks periodically, while in static systems, they are aerated by air forced through the stacks. In enclosed systems, materials are placed in a reactor unit and aerated by tumbling, mechanical agitation, or forced air induction.

Aeration, temperature, pH, moisture content, nutrients, and substrate composition are carefully controlled to optimize biodegradation. Aeration rates are critical to the process, depending on the structural integrity of the composting substrate and the types and concentrations of contaminants present. For example, chlorinated hydrocarbons will undergo reductive dehalogenation only under anaerobic or cyclically aerobic/anaerobic conditions, as discussed in Section 4.3.

Temperature and moisture content are likewise controlled closely, as moisture contents above 40% and temperatures between 55 and 60 C are required for optimal microbial activity. Solid, liquid, and gaseous emissions are much more carefully controlled than in conventional land treatment systems, which may be especially critical for highly toxic soil contaminants

(Camp, Dresser and McKee, 1985B; Savage et al., 1985). Composting of Superfund contaminated soils has not yet been performed at field scale.

#### 2.3.6 In Situ Treatment Processes

Many of the treatment processes described in Section 2.3.5 can be applied to contaminated soils or ground water in situ. Many physical, chemical, and biological processes are particularly suited to in situ applications, as listed in Table 6. As with other processes discussed throughout Section 2.3, many of these techniques are most effective when used in combination with containment or other above-ground treatment techniques to form a remedial alternative for source control of the contaminated soils.

Cursory descriptions of several of these techniques were given in the preceding section. Detailed descriptions of each process as applied to Superfund contaminated soils in situ are given by EPA (1984D, 1985H, 1985K, 1986E); Amdurer et al. (1986); Repa and Kufs (1985); Cullinane et al. (1986); and Camp, Dresser and McKee (1985B). EPA (1984D) categorized the in situ processes considered applicable to contaminated soils at Superfund sites according to their principal functions: extraction, immobilization, degradation, attenuation, and reduction of volatilization.

## TABLE 6 IN SITU TREATMENT PROCESSES FOR CONTAMINATED SOILS

## Physical/Chemical Processes

Air stripping Steam Stripping

Mechanical Aeration/Extraction--

Mechanical rototilling

Low temperature thermal stripping

Vacuum Extraction

Activated Carbon

Soil Wash/ Flushing

Solidification/Stabilization/Immobilization

Cement Based

Pozzolanic -- Fly ash/ Lime Based

Thermoplastic--Asphalt Based

Vitrification RF Destruction Block Displacement

#### Chemical Processes

Reduction-Oxidation
Precipitation
Chelation
Polymerization
Neutralization/Hydrolysis
Nitrification
Chemical Dechlorination
Ion Exchange-Clays

Resins

Zeolites

Permeable Treatment Beds

#### Biological Processes

Aerobic Treatment--Land Treatment/ Landfarming Anaerobic Digestion In general, in situ processes are not as well developed or understood as other treatment methods, and experience in their application is limited, especially with respect to Superfund sites. Uncertainties relate to EPA's limited knowledge of subsurface hydrogeology and geochemistry at the time of Record of Decision, and to the difficulties of maintaining control of all key process parameters, of ensuring thorough delivery and mixing of reactants, and of controlling the spread of contaminants or reagents beyond the treatment zone in heterogeneous subsurface environments. Appendix I lists several Superfund Records of Decision wherein in situ treatment processes were selected.

#### 2.3.6.1 Physical/Chemical Processes

A number of techniques are currently under development that involve manipulation of the soil matrix in place to modify its physical properties affecting contaminant transport, and/or to remove, mobilize, detoxify, or immobilize the contaminants themselves.

Extraction of contaminants can be performed via aeration, vacuum extraction, air or steam stripping, insitu heating, or soil washing/solution mining methods.

Immobilization can be effected via fixation/stabilization techniques, vitrification, ground freezing, block displacement, chemical precipitation,

polymerization, and sorption of contaminants on activated carbon or ion exchange media.

Radio frequency (RF) heating has been proposed for in situ heating to volatilize and decompose many organic soil contaminants. The method has been under development since the 1970s and has been pilot tested for recovery of hydrocarbons from a landfill. A row of horizontal conductors is laid on the ground surface to be treated, and connected to an RF generator through a matching network. Soil temperatures are raised to 300-400 C, assisted with steam. Residence time is two weeks. A vapor recovery system such as a negative pressure fume hood with air pollution controls is used on the land surface. This method may be approximately one-half to one-quarter the cost of excavation and incineration (Dev et al., 1984).

Artificial ground freezing is accomplished by inserting refrigeration loops beneath the ground surface into the soil surrounding the contaminant mass. The frozen soil is virtually impermeable, however the method is costly and energy intensive. It has been used to date primarily as a temporary containment or stabilization measure in civil construction projects (Sullivan et al., 1984).

In situ vitrification was developed originally for containment of nuclear wastes and radionuclide

contaminated soils, but the technique has been tested with some success on PCB contaminated sandy soils as well (Fitzpatrick et al., 1984; UCLA, 1981; EPA, 1986E; Sanning, 1984). Battelle Northwest Laboratories and the Electric Power Research Institute are working toward development of a full-scale unit.

This technique uses joule heating of soils by passing electric current through the contaminated soils mass. The mass melts and forms a durable obsidian-like glass upon cooling, with its inorganic contaminants trapped or crystallized within the mass. Most organic contaminants are volatilized or pyrolyzed during the process, therefore vapor recovery and treatment systems are required on the ground surface being vitrified. As with the RF process, effectiveness is limited by depth and homogeneity of the soil being treated, as well as other factors. The process is highly energy intensive, and its long term effectiveness for hazardous wastes and contaminated soils is still under study.

As discussed in Section 2.3.5, precipitation may be very useful for immobilization of certain soil contaminants, especially many dissolved metals such as lead, cadmium, iron, and zinc, as well as some forms of arsenic, mercury, chromium, and some organic fatty acids (EPA, 1985H; Huibregtse and Kastman, 1979). Sulfides or phosphates are the most promising for precipitation of

divalent metal cations, especially sulfides due to their low solubility product and the broad pH stability of the resultant metal sulfides. Sodium sulfate used together with sodium hydroxide has been broadly effective for many metals. Precipitation occurs at neutral or slightly alkaline pHs, and little resolubilization occurs. Sodium hydroxide acts to increase pH and to minimize sulfide gas formation (EPA, 1985H).

The effectiveness of precipitation techniques will be strongly dependent on site physical and chemical conditions, and will be greatest in sands and coarse silts. Limitations of precipitation include pH dependence of reversibility and the potential for precipitates to clog soil pores and alter hydraulic conductivity and preferential flow paths for subsurface liquids, as discussed in Section 4.3.

Polymers have been applied in situ to abate ground water plumes following monomer spills (EPA, 1984D, 1985H). Williams (1982) described the remediation of a 4200 gallon acrylate monomer leak from a corroded pipeline into a glacial sand and gravel aquifer. Catalysts, activator, and wetting agent were injected into the ground water, and soil borings showed polymerization of up to 90 percent of the spilled materials. Applications of this technology are limited primarily to organic monomers such as styrene, vinyl

chloride, isoprene, and methacrylate, and effectiveness is limited by the ability of polymerizing agents to mix thoroughly with the released contaminants (Huibregtse and Kastman, 1979).

Use of conventional solidification methods described in Section 3.2.5.3 in situ has been limited primarily by difficulties in obtaining complete mixing described in Section 3.2.5.3 in situ has been limited of contaminants with the stabilizing agents, leading to incomplete stabilization which may break down rapidly (EPA, 1982C, 1985H; Truett et al., 1982).

soil flushing methods may be effective in extracting certain contaminants from soil pores and matrices (also termed soil washing, solution mining, solvent flushing) for subsequent removal and treatment or disposal. Repa and Kufs (1985), EPA (1984D, 1985H), and Barcelona et al. (1987) describe in situ soil washing methods that use couplets of injection and extraction wells or treatment beds to recirculate washing fluids through a contaminated soils mass or contaminated aquifer. Flushing solutions include water, acids and bases, chelating agents, surfactants, and certain reducing agents.

Several Superfund sites and other waste sites have used these methods. The Goose Farm site in New Jersey used water flushing of contaminants using a wellpoint

collection and recharge system (EPA, 1984D). Truett et al. (1982) described a 6-year cleanup of an herbicide factory site using water flushing. A German site with soils contaminated by a perchloroethylene spill was remedied by water flushing which effected a 50 percent reduction in contaminant levels over an 18 month period. spill was remedied by water flushing which effected a 50 Problems and limitations related to these methods are discussed in Section 4.3. Surfactants have been used primarily for tertiary oil recovery and other industrial applications, and have not been tested at field scale at Superfund sites.

#### 2.3.6.2 Chemical Processes

Chemical methods have been discussed generally in Section 2.3.5, and may act to extract, immobilize, destroy, or detoxify soil contaminants when used in situ. As with other in situ methods, they will affect the soil matrix, and the physical and chemical properties of the subsurface as well, in ways which are not well understood at the present time. Extraction methods were discussed above in the context of soil flushing, and chemical immobilization by precipitation, polymerization, and chelation were discussed above as stabilization techniques. EPA (1984D) and Repa and Kufs (1985) provided brief synopses of in situ chemical methods

for organic and inorganic contaminants.

#### 2.3.6.3 Bioreclamation

In situ bioreclamation of contaminated soils and ground water is currently the subject of intense research in EPA and elsewhere (EPA, 1985H; Keely et al., 1986; Barcelona et al., 1987; Wilson et al., 1986A,B). It has developed rapidly in recent years and may be the most widely applicable and the most promising of the in situ treatment categories. As discussed in Sections 2.3.5.5 and 4.3, both aerobic and anaerobic biodegradation can and does occur in most natural subsurface environments.

In most cases, in situ bioremediation is conducted most effectively by optimizing physical conditions and nutrient and oxygen delivery to the naturally occurring microbial population, rather than introducing exotic microbial species (Wilson et al., 1986A,B; Barcelona et al., 1987).

Overcash and Pal (1979) and Mills et al. (1985)
listed organic contaminants susceptible to aerobic
biodegradation. Contaminated sites where in situ
bioreclamation methods have been used are described
briefly in Table 7. Most systems used to date are
modifications of the original method used by Raymond,
Jamison, and others at Suntech in the early 1970s to

TABLE 7 Contaminated Sites Using In Situ Biodegradation (Source: EPA, 1985H)

Lorat ion	Cont erinent	Waste Site Characteriatics	Trestarnt	Comment a
Ambler, PA 1972	Gasoline spill	Soil and groundustre contemination in a dolomite aquifer	Physical recovery followed by in- situ restment. Matrient solu- ten delivered: sir apropel through wells. Froducing wells controlled groundwater flow.	To gasoline left in aquifer 10 months after treatment: estimated from 744 to 444 barrels degraded
Hillville, MJ 1976	Gasoline spill	Soil and proundester costaninstion in a sendy aquifer	Physical recovery followed by in- aica treatment. Mutrient colu- tion delivered; air aperged through velle. Producing welle controlled groundwater flow.	the free product detected at end of program; phenol concentrations reduced to acceptable levels
LaGrange, OR	Gasoline leat	Soil and grounduster contamination in a aballow, highly permeable aquifer	Physical recovery followed by insite treatment. Matrient addition; groundwater recycled through site. Air supplied at bottom of injection trench with diffuers.	System operated one year after which no free product detected
Biocraft Laba Malduick, MJ 1981	Methylene chloride, butamol, dimethyl miline, acetone	Soil and groundwater contamination in a layer of glacial till	Physical recovery followed by surface biological treatment with indigenous airrorrganism; reinjection and in-situ treatment using seration wells. Producing wells controlled groundwater flow.	Concentrations reduced from 100 to 100 mg/l down to 0.1 mg/l or less in ground-uster effor two year program
Karlarube, West Germany 1982	Petroleum producta, cyanide	Soil and groundwater contamination in a mandy/gravelly aquifer	Groundwater pumped to surfere, treated with asone, then reinfiltrated.	Drinking water quality produced
Feankenthal, Heat Germany	Armstic and alighstic hydro- carbons including bensene, styrene, tollone, niese, and napthelene	Soil and groundwater contemination in a sandy, high permeability aquifer	Chysical recovery followed by in- situ treaternt. Mitrate respiration enhanced by the addition of mitrate. Recirculated flushing water arrisped and filtered before reinjection. Mater temperature	in I months are acted to and alighetics reduced to 1/1 initial concentrations

TABLE 7 (Continued)

	fament a	Program evaluation not yet evallable	Trestment to commence Reving 1985
	Trestment	Physical recovery followed by in- Program evaluation not yer and treatment. Hydrogen granioble permite as oxygen mourer and natrients added in-line to recycled water.	Meantdown waste diaposal in-aitu trestment plemmed. site; soil and ground- Matrints and hydrogen peroxide water contamination in will be added to recytled claye, low permeability groundwater.
	Maste Alte Characteristics	Soil and groundwater contamination in a sendy aquifer	Massrdows waste disposal site; soil and ground- water contamination in clayer, low permeability
•	Cont = inent	Gasol ine lesk	carbons, halo- genated altanes and arosatics.
	Location	ranger, IN	elly Air Force lane, TX 1985

treat hydrocarbon contamination using indigenous microbial populations enhanced by delivery of oxygen (in the form of air, gaseous oxygen, or hydrogen peroxide) and appropriate nutrients (EPA, 1985H; Wilson et al., 1986A,B).

Design considerations for effective delivery and recovery systems are focused on (1) providing adequate contact between microorganisms, nutrients, cometabolites, and contaminated substrate materials (soil or ground water), and (2) effecting hydrologic control to minimize release of reactants or products beyond the treatment zone and to maximize recovery of contaminants and spent treatment fluids as necessary. They require a thorough understanding of site and subsurface physical and geochemical properties, as will be discussed in Sections 4.3 through 4.7.

### 2.4 Problems With Traditional Soils Remedies

At a few sites where the volume of contaminated soils is relatively small and its boundaries are well-defined and readily identified in the field, complete excavation to background, with subsequent treatment of excavated materials and/or secure disposal of any unsafe residuals, has sometimes provided the simplest and most straightforward remedy. The majority of sites are more complex, and require a combination of several

approaches to meet the multiple goals of SARA and the National Contingency Plan.

Two types of problems generally have been encountered in performing contaminated soils remedies: problems with implementing the selected remedy and difficulties in determining appropriate cleanup levels. Implementation problems have included the following (EPA, 1983; Office of Technology Assessment, 1985, 1988; Keystone Center, 1985; Edelson, 1988):

- Costs of off- site transportation and disposal, especially of large volumes. Cost-effectiveness problems with high-volume, low-hazard waste may need special attention;
- 2. Limited availability of off-site disposal facilities, in terms of capacity shortages, community opposition, legal blocks, and lag time until disposal is possible, e.g., at the McColl site in Fullerton, California;
- Risks of excavation, transportation, redisposal, as for example, if accidents occur during any of these stages;
- 4. Need for long-term O&M of containment system components, including periodic replacement;
- 5. Potential for failure of containment systems, either by long-term erosive or degradation mechanisms or by catastrophic events, resulting in recontamination problems that may differ from or exceed the original environmental hazard at the site as, for example, at the Butler Tunnel and Bruin Lagoon sites in Pennsylvania;
- 6. Releases of contained materials through mobilization by percolating infiltration, surface run-off, volatilization, or air entrainment of particulates;
- 7. Leakage and mixing of contained incompatible wastes

(e.g., via corrosion of landfilled drums), potentially leading to violent reactions, fires, or explosions;

- 8. Locational problems with in-place containment; and
- 9. Engineering problems with containment in place, for example, difficulties in installing effective caps, slurry walls, etc. at some sites or on certain wastes, as at the Charles George Landfill in Maine.

The most pervasive and difficult problems

generally have been in the form of continued slow or

episodic releases of contaminants to ground water from

ineffective containment, or due to recontact of

contained wastes with ground water moving vertically or

laterally through the waste mass. This is sometimes due

to source control actions that did not address a

continued ground water problem, or that were not

coordinated with the ground water remedy at the site.

As described earlier, most contaminated soils remedies selected to date involve removal or excavation followed by off- site disposal, typically to a RCRA-regulated disposal facility. The Office of Technology Assessment (1985) asserted that since the RCRA regulations do not provide adequately for detection and prevention of ground water contamination, and that since containment without prior treatment does not assure long-term protectiveness, this type of remedy results only in transfer of the risks to another location. Typically, these risks associated with the receiving

facility have not been considered in the risk assessment for the site. The McColl site is a notable exception where, due to local opposition, EPA revisited a signed Record of Decision when prompted by a court action.

The Office of Technology Assessment also asserted that off-site removal actions do not address ground water already contaminated at the site, and that ground water remedies sometimes have been limited to source control or containment measures, or to provision of alternate water supplies (taking no action to remedy the aquifer itself), all methods which are low-cost in the short term, but which lack significant long-term effectiveness. Brown (1984), Smith (1988), and the Office of Technology Assessment (1985, 1988) stated that many such remedies may have to be revisited in the future.

A recent review of 51 completed Records of
Decision confirmed the tremendous emphasis on selecting
remedies relying on excavation of soils or containmentbased systems to isolate contaminants from potential
receptors in the Superfund program to date (Camp,
Dresser and McKee, 1985B). As shown in Figure 3, of the
51 sites examined in the study, 22 (43 percent) used
capping to reduce mobility and/or exposure, sometimes in
conjunction with slurry walls or other secondary
containment systems. Excavation to an off-site landfill
was selected at 27 sites (53 percent), and excavated

soils and wastes were redisposed in an on-site landfill at 4 sites (8 percent). Since several technologies were used at some sites, this total exceeds 100 percent.

Several factors have been responsible for this avoidance of alternative treatment/disposal technologies, including their higher costs relative to land disposal, uncertainties of the technologies including their relatively unproven performance or effectiveness on Superfund -type waste streams, and the Superfund program's operational interpretations of the protectiveness and cost- effectiveness requirements in the CERCLA statute and the current National Contingency Plan as discussed in Chapter 3. For a detailed discussion of these factors, see Camp, Dresser and McKee (1985B); National Research Council (1984); and the Office of Technology Assessment (1983, 1985, 1988); among others.

As stated in Chapter 1, this emphasis on what were considered "proven" containment/ disposal technologies, combined with discoveries of releases at several offsite facilities that had accepted Superfund wastes, increased public and legislative interest in destroying or detoxifying hazardous wastes rather than land disposing them, and other factors, have led to the statutory preference for treatment/ destruction- based remedies and "permanent solutions" recently expressed in

the cleanup standards provisions found in Section 121 of SARA.

The difficulties experienced in selecting remedies relate directly to the problem of establishing soil cleanup levels, since the amount and type of analysis necessary depends on the type of remedy selected. For example, if all soil contaminants will be removed, the cleanup level is straightforward. If they are all to be left in place and capped, the problem is also straightforward, but in a different way. The focus is shifted to assessing the effectiveness of the cap in preventing exposures, and the types and magnitudes of exposures if and/or when the system fails. Approaches that could be applied to the problem of selecting cleanup levels will be the focus of the remaining chapters of this report.

#### 3.0 SETTING SOIL CLEANUP LEVELS

The soil cleanup level problem has two key components: difficulties in selecting the appropriate remedy for the site problem, and difficulties in determining "how clean is clean" for the selected remedy. Chapter 2 provided an overview of the Remedial Investigation/ Feasibility Study process and of the remedial technologies currently being selected or developed to address current Superfund contaminated soils problems. CERCLA's conceptual approach traditionally has focused on protection of public health and the environment by preventing these exposures, but only recently included a structured consideration of the permanence of the selected soils remedy. Therefore, some technical problems were seen in earlier cleanups, where "permanence" was not an up-front concern.

This chapter focuses on the second component, the difficulties for the Superfund program created by the lack of soil standards or consistent approaches to set cleanup levels for soils. The multi-media nature of the soils problem is described in Section 3.1 in terms of the problem presented by soils as a source of human and environmental exposure to soil- borne contaminants, pointing out how cleanup levels must account for these exposures. Section 3.2 presents the institutional

options for setting soil cleanup levels: either to create new soil standards on a generic or site-specific basis, to modify existing standards or criteria for other media to fit the soil situation, or to mix and match these approaches. Institutional issues raised by these options are discussed in Section 3.3.

Section 3.4 proposes a conceptual approach for selecting the soil remedy and cleanup level on a site by site basis. This approach could be used and, to a limited extent as discussed in subsequent chapters, has been used to analyze Superfund soils problems within the existing Remedial Investigation/ Feasibility Study framework. Problems in setting soil cleanup levels using both traditional methods and the proposed approach are discussed in Section 3.5.

These discussions are intended to provide the rationale for choosing the site-specific approach to setting cleanup levels, given the options presented in Section 3.2. It lays the foundation for discussion in Chapter 4 of the intended focus of this report, which is to propose a method for setting soil cleanup levels, based on the use of site-specific risk assessments, when concerns focus on ground water exposures.

## 3.1 Relationship of Soils to Other Media

The relationship between soils and other media--

including air, surface water, and ground water—is extremely complex. Soils may function as a source or a sink for contaminants in other media, depending on concentrations and their gradients in each medium, and on the physical, chemical, and biological processes available at a given contaminated soils site. As discussed in the following sections, these processes may function singly or in combination to transform the contaminant species, shift its physical or chemical state, or promote intermedia transfers. Further, the equilibria between media concentrations of a given pollutant, and their phases of occurrence in each medium, may shift as conditions change within the contaminated soils mass.

The source area at a Superfund site may consist of the original wastes and the units or areas in which they were contained, and soils contaminated by release of these contaminants. Alternatively, as mentioned previously, contaminated soils may represent the entire source area to be addressed by CERCLA response actions. Contaminated surface and subsurface soils pose both direct and indirect threats to human and environmental receptors, as illustrated in Table 8. The following discussion will consider soils primarily as a source of releases to other environmental media.

Gardening
Construction
Occupational exposures
Recreational exposures
(e.g., off-road vehicles) See dermal contact above Residential/commercial future site use See ingestion above EXAMPLE Soil consumption by children Children playing CONTAMINATED SOIL EXPOSURE SCENARIOS entrainment Surface runoff, air entrainment Tracking Windblown dust Volatilization INTERNEDIATE TRANSPORT
MEDIUM
MECHANISM Same n/a n/a Table 8 Surface runoff Surface soil Air Same n/a n/a Air Ingestion/inhalation of contaminated particulates released from soils off-site Dermal contact with contaminated particulates released from soils off-site INDIRECT EXPOSURE PATHWAYS Ingestion of soil on-site DIRECT EXPOSURE PATHWAYS Dermal contact with soil on-site Inhalation of vapors released from soils **EXPOSURE PATHWAY** 

Table 8 (Continued)

EXPOSURE PATHWAY	INTERMEDIATE TRANSPORT NEDIUM	TRANSPORT MECHANISM	EXAMPLE
Ingestion of contaminated ground water	Ground water	Leaching from soil, transport	Residential/commercial use on-site/downgradient
Inhalation of contaminants released from ground water	Spane	OS BEC	Washing, showering, Irrigation, commercial uses of pumped ground water Direct volatilization to surface from aquifer
Dermal contact with contaminated ground water	Same	Spane	Washing, showering, irrigation, commercial uses of pumped ground water
Ingestion of contaminated surface water	Surface runoff	Leaching from soil, transport to surface water Overland transport of contaminated particulates to	Use as public water supply Incidental ingestion during recreational activities
	Ground water	Surface water soil, transport to surface water	
	Sediments	Sediment contamination yia above surface water, ground water mechanisms; release of contaminants to surface water	

#### 3.1.1 <u>Direct Exposure Scenarios</u>

Direct exposures occur through dermal contact with soil contaminants and through ingestion of soils containing contaminants. The contribution of exposure via these pathways to the overall risk posed by the contaminated soils to the exposed individual varies site-by-site; however, in most cases, ingestion has been considered the predominant direct exposure pathway of concern in most investigations to date.

Considerable controversy exists currently concerning both of these pathways, not only within the scientific literature, but also within the EPA and other agencies responsible for risk assessments, such as the Agency for Toxic Substances and Disease Registry of the Centers for Disease Control. For dermal contact, there is disagreement about what "standard" exposure assumptions are appropriate for estimating how much skin is typically exposed; whether and how this varies by age, occupation, season, and site conditions; whether different substances sorb differentially across the skin, and whether different skin areas sorb compounds differently (EPA, 1986A,H; Anderson et al., 1984; Brown et al., 1984; Schultz et al., 1987).

For soil ingestion, controversy is more marked concerning how soil ingestion rates vary by age and

occupation, and whether different compounds, particularly carcinogens versus noncarcinogens, require different ingestion rate assumptions, as well as how dose-response relationships vary by age, absorption rates into the body, target organ affected, etc. (Kimbrough et al., 1984; Rabinowitz et al., 1985; EPA, 1986H; Binder et al., 1986; Sedman, 1987). Researchers generally agree that soil ingestion is strongly age dependent. Over 90 percent of the total lifetime intake of a contaminant by this pathway occurs between ages 18 months and six years. However, some children exhibit "pica" behavior, an abnormally high rate of ingestion of inert materials including soil, sometimes at several times the "normal" rate. The scientific community and the agencies have not yet reached consensus on the frequency of occurrence of this condition, termed "pica" behavior, nor on whether it represents a "worst case" ingestion rate that should be adopted as a standard assumption for all risk assessments involving this pathway. These problems greatly compound the uncertainties attendant in performing quantitative risk assessments involving these direct exposure pathways for soil contaminants.

#### 3.1.2 Indirect Exposure Pathways

Indirect exposures to contaminated soils can occur through a variety of mechanisms (see Table 8). These

include inhalation of vapors released from the soils to the atmosphere either on or off the site; ingestion of or dermal exposure to dusts and particulates bearing sorbed contaminants, either on or off the site; and leaching of soil contaminants to ground water and subsequent exposure of receptors to contaminated ground water via ingestion or inhalation of volatilized contaminants when the water is used for cooking, washing, or showering. Other indirect exposure pathways for contaminated soils include ingestion or dermal contact with surface water that has received soil contaminants. Soil contaminants may reach surface waters via surface runoff transporting contaminated soils, or via influx of contaminated ground water to the surface water body, either of which may also cause sediment contamination.

Plant, animal, and human receptors also may be exposed to contaminants that may be taken up from soils by plants or animals and bioaccumulated in terrestrial ecosystems. Contaminants transported from soils similarly may be taken up from contaminated surface waters or sediments and bioaccumulated in aquatic ecosystems, subsequently reaching human receptors when the fish or shellfish are consumed (Schultz et al., 1987). Little research exists upon which to reliably estimate risks to public health and the environment

through the bioaccumulation pathway for terrestrial systems. In the past this pathway seldom has been evaluated formally, unless called for owing to unique site circumstances.

To base soil cleanup levels on a site-specific risk assessment requires that one be able to quantitatively assess the risk through each of the actual or potential exposure pathways that exist for soils at a given site. The exact nature of the pathways at a given site, and the extent to which each of the exposure mechanisms described above exist at that site, and contribute to the total human and environmental risk which each of the exposure mechanisms described above exist from the contaminated soils, will vary greatly from site to site. This is evaluated in the site exposure assessment, as will be discussed in Section 3.4.4. Overall risk to public health and the environment includes all applicable direct and indirect pathways from the contaminated soils. All contributions to overall risk via other pathways, such as existing or likely future contamination of air, surface water, or ground water. must be considered and added into the overall risk calculation (EPA, 1986A).

The question then arises as to whether, and how accurately, each pathway can be identified and quantified. This must be examined in two ways: in terms

of (1) the state of scientific understanding in describing and quantifying these various exposure pathways, and (2) for those that can be quantified successfully, the amounts and kinds of site data that must be collected during the Remedial Investigation to perform an adequate, and accurate exposure assessment. That is, the tradeoff between the level of detail, cost, and time of the site investigation and the level of precision in the resultant understanding of overall site risk. This issue of level of scientific uncertainties about both the direct and indirect soils exposure pathways will be discussed further in Sections 3.4 and 4.9. The issue of data/ precision tradeoffs will be discussed in Chapters 4 and 6.

For most of the indirect soils exposure pathways mentioned, there is disagreement among the scientific community as well as the agencies on the relative importance of contributions of each to the overall site risk. Therefore, many pathways were ignored in the exposure assessments other than the ground water route, and the surface water route at certain sites.

At most Superfund sites, soil ingestion and exposure to contaminated ground water are considered the most critical pathways for direct and indirect exposure to contaminated soils, and past cleanup levels have

generally focused almost exclusively on these pathways.

Other exposure routes have been assumed to be less critical for soils at most sites, though this assumption generally has been based more on qualitative assessments or best engineering judgement than upon critical, quantitative analysis of other potential exposure routes.

Likewise, the scientific and regulatory communities lack consensus regarding the appropriate methods and assumptions to employ when assessing exposure (National Research Council, 1983; Schultz et al., 1987). The latter issue is more complex for the indirect pathways than for the direct pathways because fate and transport mechanisms and multimedia transfers are involved in bringing contaminants from the soil source to the eventual receptor, as shown in Table 8. Controversy surrounds the appropriate analytical methods to use, since modeling is required in order to estimate future exposures. This is discussed further in the context of the conceptual approach in the next subsection.

# 3.2 <u>General Approaches for Establishing How Clean Is Clean</u>

In Chapter 1, the concept was introduced that successful implementation of the remedial process depended largely on successful determinations of both the appropriate type of remedy and the appropriate

extent of remedy (the degree of cleanup). Cleanup goals are established in the remedial process as overall site response objectives, as discussed in Section 2.2.2.

Response objectives for Superfund sites
traditionally have been cast in terms of prevention of
exposure to unacceptable pollutant concentrations via
the potential exposure pathways that exist at a
particular site. Typically, one or more response
objectives will be set for each medium of actual or
potential exposure at a given site. Examples include
the maintenance of adequate supplies of safe drinking
water for populations potentially affected by
contaminated ground water; prevention of exposure of the
public by inhalation to harmful levels of airborne
contamination, prevention of hazardous dermal contact
with contaminated soils by the public; and protection of
state-designated uses of—and aquatic life in—a nearby
wetland or surface water body.

Response objectives, then, are premised on actual or potential risks to public health and the environment at a given site. In their simplest terms, these risks may be expressed as (Starr, 1969; National Research Council, 1983; Shih and Bernard, 1988a):

Risk = (Hazard) x (Exposure)

that is, the risk each compound poses to a given receptor is a combination of the inherent hazard posed by the compound and the level and duration of exposure to it. Inherent hazard is a combination of its mass or concentration at the source and its intrinsic toxicity based on chemical state, mode of entry into the receptor, absorption into the target tissue, etc. The level of exposure to the compound is the fraction of the original hazard available to the receptor at the point of exposure, or the probability of exposure by the receptor to the original hazard at the point of exposure.

The purpose of the Remedial Investigation/
Feasibility Study is to identify and evaluate remedial actions that attain the response objectives by reducing these site risks, either by elimination of the hazard through destruction or removal of the pollutants to safe levels, or by prevention of exposure through containment or access control measures. They may address both components of the overall risk.

Cleanup targets or levels define ambient concentrations or residual levels of contamination that may be left in a given medium (air, surface water, ground water, soils) at the site without further management at the completion of the remedial action; thus, they define "how clean is clean." They will affect the volume of wastes and contaminated soils to be

treated and/or disposed, which in turn directly affects the overall cost of the response and the feasibility of various technologies (EPA, 1985G).

The choice of cleanup goals and targets is dependent on a variety of complex technical issues including, for example, the limitations of available technologies, the uncertainties in available toxicity data, the exposure pathways present, the risks through each pathway, and the uncertainties in the risk estimates and in the conduct of risk assessments. As discussed in Sections 1.2.2 and 3.3, the decision maker must also consider the role of applicable requirements in setting cleanup targets.

The difficulties posed by the consideration and selection of applicable requirements are intensified by the problem of multiple and sometimes conflicting standards and criteria for some compounds in certain media, especially water, and the lack of available standards for other media, especially contaminated soils. Ultimately the establishment of cleanup targets is a national policy decision (Office of Technology Assessment, 1985), constituting risk management as well as, or sometimes in lieu of, involving risk assessment (EPA, 1984C; National Research Council, 1983). The purpose of the ensuing discussion in this section is to review the range of conceptual approaches available for

setting cleanup standards in any medium. This will provide a background against which to examine a possible approach for contaminated soils cleanup levels in subsequent chapters of this report.

Many alternative approaches are possible for establishing national goals for the extent of cleanup at Superfund sites or, alternatively, nationally consistent methods for determining how clean is clean. Several have been suggested by Brown (1984) and the Office of Technology Assessment (1985), among others. Several states also have approaches that could be adapted for use at a national level. They can be grouped into five general categories (see Figure 5):

- Health-based approaches, based on scientific information on public health or environmental risk;
- 2. Technology-based approaches, such as RCRA's design and operating requirements and the BDAT levels in the land ban regulations, as discussed in Section 2.3.5;
- Cost-benefit-based cleanup approaches;
- 4. Site or land-use classification systems; and
- 5. Best engineering judgement. As defined below, this is similar to the "ad hoc" approaches discussed by Office of Technology Assessment (1985).

A representative sample of the range of potential approaches is briefly presented in the following discussion.

FIGURE 5: Standard Setting Approaches

39	GENERIC	SITE- SPECIFIC
HEALTH-BASED		
- Background	•	0
<ul><li>National Standards</li><li>Site-Specific Risk Assessments</li><li>Delisting Levels</li></ul>	•	•0
TECHNOLOGY-BASED	•	0
COST-BENEFIT	0	•
SITE/LAND USE CLASSIFICATION	•	0
BEST ENGINEERING JUDGEMENT	0	•

#### 3.2.1 <u>Health-based Approaches</u>

Health-based approaches focus on specific risks to public health and the environment posed by the wastes present at a particular site. Therefore, they constitute the broadest and the most contentious category. Several options are possible:

- o Cleanup to background or to "pristine" levels;
- Cleanup to generic health-based levels by establishing national soil cleanup standards;
- o Cleanup to safe levels as determined by sitespecific risk assessments;
- o Cleanup to levels that would no longer be considered hazardous wastes under RCRA. This is the RCRA delisting process, which is both generic and site-specific; and
- o Cleanup using the current "ad hoc" approach, relying on applicable standards and requirements from other laws to provide sufficient information to establish cleanup levels (see NCP in EPA, 1985A; and Office of Technology Assessment, 1985). This approach combines elements of the other options.

## 3.2.1.1 Cleanup to Background

This approach calls for the excavation and/or treatment of contaminated source material (wastes and contaminated liquids, sludges, and soils), or contaminated ground water, either to levels statistically indistinguishable from local or regional background levels or, alternatively, to "pristine" levels as defined by the Office of Technology Assessment

(1985). This standard has a programmatic history. It is consistent with the RCRA ground water protection standard for regulated hazardous waste facilities in 40 CFR 264 and 265 Subpart F, which states that ground water beyond the downgradient unit or facility boundary, or otherwise-defined "point of compliance," must not contain levels of contaminants in excess of local background levels of those compounds or their MCLs under the Safe Drinking Water Act. Likewise, the proposed closure standard for storage surface impoundments at 40 CFR 265.228 (EPA, 1982B) suggested that for those units, cleanup or decontamination of source materials to background was required in order to "walk away" from the unit without further management requirements.

Cleanup to background contains elements of technology-based as well as health-based approaches. Its use avoids extensive time and resource expenditures in the performance of a detailed, complete risk assessment, including exposure modeling and site-specific exposure and toxicity assessments.

Cleanup to a background standard would not take into account the inherent toxicity or mobility of site contaminants, and thus it bypasses the expensive, time-consuming, and politically difficult process of setting standards for contaminants. Rather, it incorporates an implicit risk management decision that all exposures

above background levels pose unacceptable risks to public health and the environment. As such, however, the background standard has the advantages of allowing unrestricted future land or water use at the site, and of consistency with RCRA requirements. Note, however, that cleanup of ground water to local background levels may not attain all applicable requirements.

However, it requires a determination of local background levels of the pollutants at the site. For synthetic compounds, background generally is initially assumed to be zero, or in practice, below the detection limits of the measurement methods in use for that medium at that site. For naturally-occurring compounds and metals, background may initially be assumed to be the level historically present in soils (or ground water) in the site vicinity. This will be a site-specific determination that may be technically quite difficult at many sites. Often there may be great vertical and lateral variability in soil types and characteristics on the site itself; the problem is compounded when local or regional background must be determined.

Historical background levels for soils have been notoriously hard to establish even for naturally occurring compounds, and become more difficult and complex when past and present regional land-use practices are factored in. How should the site vicinity

or "region" be defined if, for example, the site is located in a highly industrialized neighborhood where background concentrations may far exceed the national average, for example as found in studies of lead, dioxin, and PCB levels in urban residential soils (Stark et al., 1982; Kimbrough et al., 1984; Gallacher et al., 1984; Rabinowitz et al., 1985; Binder et al., 1986)? What if the levels exceed average levels in rural soils (Carey and Gowen, 1976)? In such a case, the costs and efforts required to define what the "region" is for purposes of establishing background, and to determine what fraction of an area-wide contamination problem should be attributed to a particular Superfund site, may be substantial.

For the Superfund program, attainment of the statutory protectiveness requirement, if defined as cleanup to a background standard, traditionally has been considered to conflict with the statutory cost-effectiveness requirement. Compliance with a background standard has been traditionally difficult to establish at most Superfund sites, where migration of contaminants from their original source or point of disposal has led to highly complex vertical and lateral distributions of contaminants in the soils surrounding the source itself.

It also may require removal and/or treatment of

very large volumes of soils in proportion to the fraction of the site threat they may represent (see Section 2.3 for a detailed discussion), substantially increasing cleanup costs compared with costs where safe levels above background could be established.

Limitations on the size of the Fund could cause relatively few sites to be cleaned up to a strict background standard; the Fund might be depleted after addressing only a few large, complex sites. Site-specific differences in background levels would lead to different levels of cleanup from site to site (Office of Technology Assessment, 1985). Finally, the background standard may not be protective at sites where local or regional backgrounds are high, for example, in TCE-contaminated ground water in the Santa Clara and San Gabriel valleys in California, and in soils surrounding metal smelters such as Bunker Hill in Idaho or the New Jersey Zinc smelter in Palmerton, Pennsylvania. Office of Technology Assessment (1985) suggested the use of "pristine" levels in such circumstances; however, local sources could repollute such an area following its cleanup, bringing the cost- effectiveness of cleanups to pristine levels, and the appropriateness of such uses of the Fund, into doubt.

### 3.2.1.2 Cleanup to National Standards

The Office of Technology Assessment (1985)
discussed the establishment of national goals, or
generic cleanup levels, yielding residual ambient soil
concentrations above background that could be left onsite without further management requirements. Under
this approach, the same concentration of a given
compound would be used as its cleanup target at all
sites in the country, irrespective of site-specific soil
or waste characteristics, or the location or composition
of potential receptor populations. These concentrations
would ideally be set at safe levels such that no
constraints on future land or water use would be
required at sites attaining these standards.

Theoretically, standards could be set strictly on the basis of the inherent toxicity of each compound, or they could incorporate risk management considerations such as cost or cost-effectiveness of treatment or management, constraints on the Fund's resources, the limitations of available treatment technologies, or adjustment factors for different land or resource uses This is similar in concept to the setting of existing Federal ambient standards for pollutants in air or water, e.g., National Ambient Air Quality Standards under the Clean Air Act, MCLs promulgated under Safe

Drinking Water Act, or Water Quality Criteria under the Clean Water Act.

Site-specific risk assessments would not be performed under this approach. Rather, amounts excavated and/or treated in site cleanups would be based only on assessments of the composition and distribution of wastes and contaminants in various media. Thus, problems and uncertainties inherent in site-specific risk assessments (see Sections 3.2.1.3 and 2.4) are avoided, and residual concentrations ideally would be similar nationally among sites. Ambient standards might be above or below local background levels for a given compound at a given site.

As described in Section 1.2, no Federal standards now exist for ambient concentrations of contaminants in soils. Their nearest approximations are maximum cumulative annual soil loading levels for two pollutants, cadmium and polychlorinated biphenyls (PCBs), in RCRA's land treatment regulations (40 CFR 257.3). Simply applying existing standards developed for air and water to soils would be largely inappropriate and of limited value (Office of Technology Assessment, 1985), since they generally were developed for a single medium and a single exposure pathway, not the multiple exposure pathways possible for soil contaminants (see Section 3.1). Nor do they

address the interactions among several compounds or the multimedia exposures to which a given receptor might be subjected at some Superfund sites.

The toxicological data base upon which existing standards are based would be essential to the soils standard-setting effort; however, it requires supplementation. Reliable data and standards do not yet exist in the other media, air and water, for all compounds encountered at Superfund sites (National Research Council, 1983; Office of Technology Assessment, 1985). Conflicting values exist for some compounds in certain media. Research adequate to develop these standards in soils for all compounds commonly encountered at Superfund sites, that would be protective in all foreseeable combinations of soil type, waste mixture, and interactions, and for all potential human and environmental receptors, would require many years to complete and resources not available within the Fund. Thus, development of Federal nationwide soil standards would be a long, politically difficult, resource intensive process. In the meantime, some sites require attention to mitigate imminent and substantial threats to public health and the environment.

As mentioned in Section 1.1, a provision was added to the cleanup standards in Section 121 of SARA requiring the consideration of promulgated state

standards when they are more stringent than their
Federal counterparts, or when no Federal standard
exists. A few states are developing generic soil
standards, such as California's Applied Action Levels
(Sedman, 1987; Marshack, 1985), or New Jersey's cleanup
standards for industrial sites developed under that
state's Environmental Corporate Responsibility Act (Dime,
1987). A survey by Garnik (1986) showed 22 states with
established soil cleanup levels. Of these, only 5
states had formal cleanup levels. Only Alabama and
New Mexico had numerical soil standards, and these were
available only for a few petroleum constituents.

## 3.2.1.3 <u>Cleanup Using Site-specific Risk</u> <u>Assessments</u>

This approach presumes that (1) at many sites, a "safe level" of residual contamination above background levels can be established for all contaminants that is protective of public health and the environment for all routes of exposure existing or possible at the site; (2) any soils or wastes with concentrations exceeding these safe levels are hazardous substances that require destruction, treatment, containment, or some form of long-term management; and (3) these safe levels and cleanup amounts can be determined on a site-by-site basis using risk assessments explicitly. Cleanups to

this safe level may involve excavation and/or treatment of differing quantities of wastes or soils, and differing final residual concentrations, from site to site.

Thus, at a given site, these residual concentrations, and the resultant quantities of excavated/ treated soils that would require management as hazardous, might differ from those yielded by cleanup to a generic national standard or by cleanup to background. Uniformity or national consistency in the residual risk level would be established by basing the site-specific soil concentrations on uniform national residual risk levels within a single risk range, and by using the same methodology to assess risks at all sites to the extent possible.

The general process for using site-specific risk assessments to determine site-specific cleanup levels will be discussed in detail in Section 3.4. As will be discussed in Chapter 4, the same analytical approach may not apply to all sites, requiring that consistency be achieved by standardizing the procedure to select and use the analytical approach rather than the approach itself.

Two significant challenges must be met in order to maintain this desired national consistency: (1) uniform, standardized methods for performing the risk

assessments must be agreed upon; and (2) a single set of health-based concentration values or toxicity values must be established and agreed upon for all constituents and compounds of concern at Superfund sites. These would provide the baseline values that, when applied to the site soils, would be manipulated to address each pathway of exposure that may be encountered at that site.

Several analogous RCRA concepts provide useful illustrations of different ways to establish cleanup levels or choose long-term management alternatives for wastes and/or sites. These include the processes for "clean closure" and alternate closure of surface impoundments (EPA, 1987A,B), and the petition process for delisting wastes to exempt them from RCRA Subtitle C management requirements where they can be demonstrated not to be hazardous on a site-specific basis (EPA, 1985N). These RCRA concepts might provide different models for establishing site-specific cleanup level procedures. Each has a different outcome in terms of the long-term management requirements for the site, but all are intended by statutory mandate to offer equivalent protection of public health and the environment. use of site-specific risk assessment varies but is limited in all cases; their relationship to this report will be discussed in more detail in Sections 3.3 and

## 3.2.1.4, respectively..

Many choices must be made up front by the risk assessor in order to set either generic or site-specific cleanup levels in this fashion, including the following:

- o Whether to use individual risk or population risk levels, that is, whether to assess the actual receptor population exposed or to assume a worst case maximum exposure scenario;
- o Which compounds to select as indicators upon which to base cleanup levels appropriate for all contaminants present, discussed further in Section 3.4.3;
- o Whether, or in what proportions, to use modeling versus actual sampling to make the exposure assessment;
- o What exposure scenario to assume (actual case, average, worst-case, "reasonable-worst-case", etc.); and
- o Whether or to what extent land-use, economic, or technology limitations should be factored into the definition of "acceptable" risk levels (Office of Technology Assessment, 1985; Rodricks, 1984).

Some of these concerns are shared with other approaches discussed in this chapter, since some components of risk assessment are used in the determination of generic national standards and/or of background levels as well. These concepts and choices, and their implications for setting cleanup levels, will be discussed in more detail in Chapters 4 and 6.

The principal advantage of this approach is that it provides maximum flexibility in determination of

cleanup levels by tailoring them to actual site wastes and physicochemical conditions more precisely than any other method discussed in this section. Further, cleanup levels so determined should be fully protective of public health and the environment by definition, and may satisfy the statutory mandate for permanence, depending upon the ultimate interpretation of that SARA requirement.

Thus, they may require removal or management of considerably smaller quantities of contaminated material than would cleanups to background or to generic national levels in many instances, resulting in lower overall costs and reduced dependence on limited commercial treatment and land disposal capacity (Office of Technology Assessment, 1985; Keystone Center, 1985). This would allow maximum flexibility in the use of limited Fund resources, since the resources expended at each site would be commensurate with the overall threat the site presents. As with cleanup levels based on national standards, depending upon the ground rules selected, cleanup levels using this approach may or may not explicitly consider technical feasibility or some other component of cost- effectiveness.

The weaknesses of the site-specific risk assessment approach for setting cleanup levels are closely tied to many of its strengths. This approach is

more data-intensive, and more demanding of human and analytical resources on a case-by case basis, than other cleanup level-setting approaches. The savings in cleanup costs may be somewhat offset by the increased sampling and analytical efforts and time required to minimize uncertainties. Both the accuracy and the precision of the cleanup level will depend heavily on the level of sophistication of the risk assessor's knowledge of the site, and/or the correctness and appropriateness of the assumptions made in the absence of data or in the selection and application of models used to simulate fate and transport processes (Office of Technology Assessment, 1985). As with cleanup levels based on background levels or national standards, in some instances cleanup levels determined by sitespecific risk assessments could be technically unachievable or economically infeasible, requiring the decision maker to consider other cleanup alternatives, even containment or management options.

Use of this approach is sensitive to public perceptions about the general appropriateness of risk-based approaches to set residual contamination levels, and to fears that differing residual cleanup levels yielded by this approach from one site to another could represent different residual risk levels and variable environmental protection. Note that this perception

factored significantly in the shift from risk-based to technology-based treatment standards in the RCRA land disposal restrictions program (EPA, 1986B). Careful attention must be paid to the standardization of methods and baseline risk values in order to minimize situations where this might occur (Office of Technology Assessment, 1985).

#### 3.2.1.4 Cleanup to RCRA Delisting Levels

The RCRA regulations at 40 CFR 260.20 and 260.22 allow owners and operators of hazardous waste facilities to petition EPA's Administrator to exclude their waste from the Subtitle C hazardous waste management requirements on a case-by-case basis, where the owner/ operator can demonstrate that a waste that would otherwise be subject to RCRA need not be so managed based on characteristics unique to that waste or to its management. The delisting process requires EPA to review detailed information on raw materials, production processes, and byproducts of the waste's manufacture; descriptions of quantities generated and methods of management of the waste; analytical data for all hazardous waste constituents given in 40 CFR 261 Appendix VIII; test results on representative waste samples for the characteristics of ignitability, reactivity, corrosivity, and toxicity as defined in 40

CFR 261; and additional information and analyses as necessary.

At some Superfund sites, the RCRA delisting procedures have been considered as a basis for determining cleanup levels, sometimes to determine safe residual contamination levels for excavation, but more recently to help determine a potential safe level for treatment residuals (for example, to set safe levels for incinerator ash when EPA's mobile incinerator was used to treat wastes and soils at the Denny Farm dioxin site near Times Beach, Missouri; EPA, 19850). The rationale is that the approach is sufficiently waste-specific to be appropriate for determining when CERCLA wastes to be taken off a site should be managed as RCRA hazardous wastes. However, it is not sufficiently site-specific to accurately establish appropriate residual concentrations to be left in place in site soils.

## 3.2.2 Technology-Based Approaches

Implicit in the second major category of cleanup level approaches is the assumption that risks should be reduced to the lowest level technically feasible through application of technology, by controlling the discharge of contaminants to the environment at levels near zero to the extent possible. Thus, near-background environmental concentrations of pollutants are achieved

indirectly by controlling their release, rather than by seeking to determine their "safe" numerical ambient concentration through the risk assessment process, and then directly clean up to that ambient level.

Technology-based approaches generally function in two different ways. They may either provide guidance for preventing exposure at any level, as for example RCRA's design and operating requirements for land treatment, storage, and disposal facilities; or they may regulate waste treatment/removal/ management activities to reduce the waste's hazard to "safe levels" allowable in residuals following contaminant treatment or removal by defining the technology to be used in order to reduce the waste's hazard to those levels, as for example RCRA's treatment levels under the Land Disposal Restriction regulations being promulgated under HSWA.

The background standard for ground water in 40 CFR Subpart F really represents a technology-based means of achieving a health-based endpoint. The attainment of safe levels from a public health and environmental perspective is assured by cleanup of any release from a facility to background or zero levels of contaminants without the expenditure of resources to determine actual, toxicologically-based safe levels above zero, although that option is also provided through the Alternate Concentration Limit demonstration process

(EPA, 1987D).

The design and operating requirements for RCRA facilities, on the other hand, are premised on the prevention of human or environmental exposures above zero through the proper design and operation of waste containment and treatment facilities. Containment remedies without treatment have been used at many Superfund sites historically in compliance with these standards, as was discussed in Chapter 2.

The same premise underlies the use of the Best

Demonstrated Available Technology (BDAT) to treat wastes

prior to discharge (Stewart and Krier, 1978; EPA, 1986B;

Brown, 1984; Office of Technology Assessment, 1985),

which is required by the RCRA land ban rules. These

require that a given waste stream always be treated to

the same level before it is allowed to be land disposed

in a regulated unit, regardless of the design or

location of that unit; in that sense, they represent

generic, national standards. However, land ban BDAT

treatment standards presently exist for only a few RCRA

waste streams. None have yet been promulgated for

contaminated soils (Hanson, 1988).

It might be technically infeasible or prohibitively costly to apply waste treatment standards to soils.

Then, the Superfund program probably would not meet its statutory requirements for technically feasible and

cost-effective remedies by applying the available land ban treatment standards to Superfund site soils without modification. This is discussed further in Section 3.3.2.

#### 3.2.3 Cost-benefit-based Approaches

A cost-benefit approach would require a sitespecific estimation of costs and benefits associated
with cleanup to different levels; thus, this approach
incorporates elements of one or more of the approaches
described previously. Selection of cleanup level would
be focused on attaining levels where the ratio of total
benefits to total costs was greater than or equal to
some set value, or where marginal benefits were greater
than or equal to marginal costs (Office of Technology
Assessment, 1985).

Superfund cleanups by statute are required to be costeffective. Currently, this is interpreted in the evaluation
of remedial alternatives by comparing several alternatives
which are all minimally capable of attaining the site
response objectives, i.e., which would be "effective"
remedies in terms of their cost, and selecting that
alternative providing the best balance of cost and
effectiveness, or the lowest-cost alternative among several
equally effective options (EPA, 1985A). This concept
likewise could be applied to soil cleanup levels.

One approach taken at several sites was to define the cleanup level or zone such that a substantial proportion of source strength is removed from the ecosystem, for example the removal of 90% or 95% of the contaminant by mass. This approach was taken at the Burnt Fly Bog site in New Jersey, and at the Fields Brook site in Ohio, among others (see Appendix I).

A common misconception held by EPA's critics is that cost benefit analysis or an explicit balancing of risks and costs is done to select Superfund remedies or to set appropriate cleanup levels. However, both are expressly forbidden by the Superfund statute, although allowed under other environmental statutes (EPA,1985A; Office of Technology Assessment, 1985; Stewart and Krier, 1978). Cost effectiveness of the remedy is required, however. This shifts the analytical and institutional debate to the question of how to best define effectiveness, and cost effectiveness in the Superfund context. In Section 2.3.1, one option that would comply with SARA was given, where long term effectiveness was described in terms of achieving "protectiveness" and "permanence."

Traditionally it has been politically difficult to obtain agreement among policy makers on an appropriate scale for quantifying environmental benefits. This problem plagues most state and national environmental

laws, as evidenced by the natural resource damage regulations promulgated pursuant to CERCLA (van Voris et al., 1985). Measurement of "effectiveness" and cost-effectiveness by some quantitative index of environmental improvement appears to be an unimplementable basis for Superfund site cleanup levels for the foreseeable future. This issue is addressed again in the context of utility functions in the discussion of decision analysis in Section 4.10.2.3.

A cost-benefit approach for cleanup levels likely would lead to inconsistent cleanup levels from site to site if implemented across the board. However, the Fund-balancing waiver in 40 CFR 300.68(i) provides for a kind of cost benefit balancing in exceptional circumstances where a remedy fully complying with all applicable or relevant and appropriate requirements would disproportionately drain the Fund's resources for the degree of environmental benefit obtained.

## 3.2.4 Site or Land-use Classification Systems

Under an approach recommended by the Office of Technology Assessment (1985), the extent of cleanup would be based largely on the present and expected future use of the site and its surroundings. Land-use classification would be the principal driver in selecting the type of remedial action and the extent of

cleanup, which clearly would combine implicitly both risk management and cost-benefit considerations in the assignment of land-use categories. This factor seldom has been paid explicit attention in past remedy selection decisions according to Office of Technology has been paid explicit attention in past remedy Assessment (1985), although implicitly it impacts many of EPA's past and ongoing remedy decisions.

This approach would require national agreement on a site-use or land-use classification scheme that might be similar in nature to the EPA Ground Water Protection Strategy (EPA, 1984B). The Strategy is based on the Agency's primary mission to protect public health and the environment, its inability to protect all ground water from contamination due to resource limitations, and the varying costs and difficulties associated with cleaning up contaminated aquifers.

To implement such a scheme, a policy decision would be required allowing the extent of cleanup to vary from site to site, and significant resources would be spent on classifying regions containing Superfund sites. It is questionable whether this approach would be an acceptable use of the Fund or in conformity with Congressional intent as expressed in SARA (Smith, 1988).

#### 3.2.5 Best Engineering Judgement

At many remedial sites handled in the early years of the Superfund program, and in many emergency response situations, cleanup levels were determined qualitatively on the basis of very limited site-specific information. Often best engineering judgement was used to determine a cleanup level by combining elements of some or all of the other approaches—use of health-based data and standards, technology-based levels, and elements of cost-benefit or cost-effectiveness—and using experience and judgement to supplement or substitute for knowledge gaps or uncertainties.

For example, contaminated soils at some sites were removed to the limits of visible contamination, especially where oily substances predominated in the solid contaminants (Heare, 1986; Haley, 1988; Haynos, 1988). Extent of excavation was modified according to compounds present, matrix, local soil conditions, and topography based on the judgement and experience of the site manager or on-scene coordinator and EPA's contractors. The principal negative outcome of this cleanup level approach is the inconsistencies it would create in cleanup decisions from site to site.

Obviously most everyday field decisions, such as exactly where and how to collect a particular sample,

how to adjust a model to account for certain unique site characteristics, or how to adjust certain construction and operating parameters of a system, use best engineering judgement to varying degrees. It will never be entirely removed from the remedial process, but it cannot provide the only basis for setting Superfund cleanup levels, since it cannot satisfy the need for program wide consistency as expressed in Section 1.3.3. As the depth and diversity of programmatic experience increases, the role of best engineering judgement in the determination of final cleanup levels can be gradually reduced as it is substituted by field data and prior experience.

# 3.3 <u>Institutional Issues Affecting the How Clean is</u> <u>Clean Decision</u>

As was discussed in Chapter 1, CERCLA was enacted in 1980 in part because of the perceived inability of existing federal environmental programs to address the problems of uncontrolled hazardous waste sites effectively. This mismatch occurred in three general ways: (1) the existing statutes did not provide jurisdiction over the releases, either because their jurisdictions tended to be limited to a single medium such as air or water, or because they lacked the power to force responsible parties to clean up the releases;

(2) the other regulatory programs did not have adequate human and/or fiscal resources to devote to a "new" class of problems; or (3) the other regulatory programs lacked the tools in terms of established procedures, policies, guidance, or experience to address complex, multimedia contamination problems.

Nonetheless, the Superfund program traditionally has looked to the requirements of other federal environmental statutes in seeking to ensure the adequacy of methods and approaches it uses to clean up sites and to determine appropriate cleanup levels in each medium contaminated by the site or where exposures might occur in the future (EPA, 1985A; Thomas, 1987). As mentioned in Chapter 1, however, the selection and application of other environmental laws and requirements to Superfund cleanups has traditionally presented the Agency with a "square peg/ round hole" problem that has proved difficult and controversial to address on a site-by-site basis (EPA, 1985A; Brown, 1984; Smith, 1988; Wolf and Warren, 1988).

The EPA has been criticized for providing in the National Contingency Plan neither a set of clear-cut remedy selection criteria, nor strict decision rules for selection of the appropriate alternative (Brown, 1984; Office of Technology Assessment, 1985; and preamble

discussion in EPA, 1985A). During the 1982 revisions to the National Contingency Plan, the EPA had considered setting national cleanup standards. However, this was rejected in favor of allowing cleanup standards to be set on a site-by-site basis (Smith, 1988). Note that EPA believed that setting new standards for the many hazardous substances found at Superfund sites would be too time-consuming and resource-intensive, and that many sites would have circumstances to which no existing standards clearly would apply, as stated in the 1982 National Contingency Plan (EPA, 1982A):

"For instance, acceptable levels of hazardous substances in soil are not established, and there are no generally accepted levels for many other hazardous substances in other media. Even when there are standards for a particular substance, they may not be applicable to the conditions surrounding the release. Therefore, if the Plan included a rigid requirement that standards be met, it would obscure the real issues in many cases of how to adequately protect public health." (National Contingency Plan, 47 Fed. Req. 31, page 31185).

Note that EPA's alternative was to provide the RI/FS process as

"(a) methodology which would provide structured and reasoned decision making while still allowing flexibility to deal with unique and unforeseen characteristics..." (EPA, 1982A).

The National Contingency Plan's remedy selection criteria will be modified within the next year to

conform to the additional requirements in SARA (see Section 1.1 herein). At most sites, it is difficult to establish that a single remedy is clearly superior to all others under consideration in terms of all the important cost and effectiveness factors listed in the National Contingency Plan. The decision maker generally is confronted with multiple tradeoffs and conflicting goals in the remedy selection process that are difficult to address comprehensively through the use of a specific set of national decision rules.

Likewise, no national weighting or scoring values for comparison of alternatives have been developed that adequately address the diversity in site conditions or that effectively capture the State's, community's, and enforcement considerations encountered at National Priorities List sites. As a result, the decision makers have operated without agreed-upon guidance. However, they benefited by retaining maximum flexibility to make tradeoffs between "lesser" criteria to enhance the appropriateness of a given remedy for specific site circumstances, community and responsible party concerns, and other needs and uses of the Trust Fund in that EPA Region.

One of the most significant shortcomings of the National Contingency Plan, and the primary focus of this study, has been its lack of explicit substantive

guidance on what degree of cleanup is to be achieved in either removal or remedial actions. The National Contingency Plan states currently in 40 CFR 300.68(i) that the appropriate extent of remedy is to be determined by selection of a cost- effective remedy that is technologically feasible and reliable and that provides adequate protection of public health and the environment. This has not provided sufficient or definitive guidance for many past decisions (Brown, 1984; Smith, 1988),

leading to assertions that past cleanup decisions have been ad hoc and inconsistent. As a result, the selection and use of cleanup technologies and the choice of cleanup levels have been difficult and contentious (Edelson, 1988; Wolf and Warren, 1988; Office of Technology Assessment, 1988).

## 3.3.1 Problems With the CERCLA Compliance Policy

The National Contingency Plan revisions promulgated in 1985 included the Agency's policy addressing how Superfund response actions should be consistent with other Federal or State environmental laws or public health standards. According to the policy, appended to the National Contingency Plan preamble (EPA, 1985A), protectiveness is achieved by the remedy's attainment of applicable or relevant and appropriate Federal and State

requirements (ARARs) that have been identified for the site and the response action in question, unless one of five specific circumstances described in 40 CFR 300.68 (i)(5) exists. EPA was required to document all analyses of such exceptional circumstances. As discussed in Section 1.2.2, the body of this policy was incorporated into the reauthorization of the statute in 1986.

However, this did not solve the problems identified by EPA in the 1982 National Contingency Plan. Available standards were still insufficient to address all Superfund soils problems. Many mismatches continued to occur as analysts attempted to sort out which standards were "applicable" to a given site, which meant that they must be complied with, and which could be considered only "relevant and appropriate," which was interpreted to give EPA greater flexibility in how strictly it applied such criteria or requirements to a site situation.

EPA's understanding of the application of existing requirements has been continuously evolving, as shown by the procedures in EPA's draft guidance manual for implementing its policy on compliance with other laws (EPA, 1985D). They have been hotly debated both inside and outside the Agency, largely due to misunderstandings about the fundamental differences in how various standards function (Smith, 1988).

These differences were illustrated by the five types of standards discussed in Section 3.2. They were highlighted by Smith (1988), who grouped ARARs into three broad categories:

- Chemical-specific ARARs-- standards that place a health- or risk- based limit on the quantity or concentration of a given contaminant that may be present in or discharged to the environment. These include ambient standards, effluent limits, emissions limits, discharge limits, or methodologies for establishing such limits, and encompass most of the health- based standards discussed in Section 3.2.1.
- Action-specific ARARs-- these are generally technology based requirements, as discussed in Section 3.2.2, that place restrictions on or direct one to undertake specific types of activities. Examples include the RCRA design, operating, closure, and post-closure care requirements for treatment, storage, and disposal facilities; and industrial wastewater pretreatment requirements promulgated under the Clean Water Act.
- <u>Location-specific ARARs</u>-- these are restrictions O against actions in certain locations, or prohibitions on contamination above certain levels in specified locations. Examples include Executive Orders 11988 and 11990 on floodplains and wetlands, respectively, which limit Federal activities in such areas; RCRA's prohibitions in 40 CFR 270 against locating hazardous waste facilities in floodplains or areas prone to landslides or seismic disturbances; and the regulations promulgated under the National Historic Preservation Act (36 CFR Part 800), which restrict federal activities at historic places or other protected sites. Several states also have facility siting requirements or prohibitions (Smith, 1988; Conservation Foundation, 1983).

Some existing standards are hybrids of several categories, for example, the RCRA land ban BDAT

requirements at 40 CFR Part 268, which are both actionspecific and chemical- specific. As mentioned in Section
2.3.5, they require pretreatment of hazardous waste to
specific concentrations prior to its disposal in the
land. Concentration levels are determined on a
compound specific basis, depending on the capability of
the Best Demonstrated Available Technology to achieve
those limits for each contaminant (EPA, 1986B).

Confusion arises partly because some applicable or relevant and appropriate requirements tend to be triggered by contaminants present at a Superfund site (generally the chemical specific ARARs), while others may be triggered by the specific remedy being contemplated to address the site. For example, if EPA were selecting remedial actions to address an abandoned surface impoundment filled with hazardous substances, they might choose to remove and/or treat the liquids and sludges, and contain the contaminated subsoils by closing the unit in place, as discussed in Section 2.3. Treatment and disposal of the liquids and sludges likely would trigger the land ban BDAT treatment requirements for those liquids and sludges that are listed or characteristic wastes regulated by RCRA. For the remaining contaminated soils, the Agency might seek to excavate soils to some health-based "safe level," as discussed in Section 3.2.1; treat the soils, as

discussed in Sections 2.3.5 and 2.3.6; or leave remaining soils in place under some containment system, in which case one must identify the appropriate requirements for "closing" such facilities under RCRA, as discussed in the following subsection.

# 3.3.2 <u>Use of RCRA Standards to Determine How Clean Is Clean</u>

Traditionally the CERCLA program has looked most closely to the hazardous waste management regulations developed under RCRA for guidance in fashioning remedies, especially the design and operating requirements for land disposal units. This is because ongoing management of hazardous waste at existing facilities which this body of regulations addresses most closely resembles the circumstances encountered when addressing uncontrolled, abandoned hazardous waste sites under Superfund.

At sites where wastes were left in place and contained under a cap, technology-based standards including the landfill design and operating standards at 40 CFR Part 270, and Part 264, Subpart G of the RCRA regulations governing landfill closure and post-closure care, have been used or modified to fit the site circumstances. Often RCRA's 40 CFR 264/265 Subpart F ground water protection standards, including the

"background" standard, were considered for management of contaminated ground water (in conjunction with Safe Drinking Water Act standards such as MCLs or Clean Water Act Water Quality Criteria).

The regulations most often consulted regarding cleanup levels for "uncapped" soils to be left in place have been the standards for "clean closure" of surface impoundments and landfill closure-in-place under 40 CFR 264.228 and 265.228. Note that until recently, clean closure was interpreted by the RCRA program as always requiring excavation to background. Cleanup levels were redefined by the final "clean closure" rule as cleanup to health-based levels in each potential exposure medium (EPA, 1987A).

The second RCRA regulation often considered for defining residual soil levels was the section defining the delisting requirements under 40 CFR 260.20 and 260.22 (EPA, 1985A). Use of delisting criteria was discussed in Section 3.2.1.4. As discussed in Section 3.2.2, a fourth set of "standards," the BDAT treatment levels for RCRA waste streams under the RCRA land ban rules have now also been considered for their appropriateness for soils as well.

The programmatic outcome of using technology-based cleanup standards, such as either background levels or BDAT- type treatment levels, is that resources are shifted

from the toxicological and environmental determination of "safe levels" to the actual cleanup. This is because excavation or treatment of wastes or soils to zero or background levels involves more material and energy due to the much larger volumes involved at most sites.

Treatment- or removal-based cleanups thus would be far more costly, but cleanup levels may be less publicly controversial. This is because the debate is shifted from toxicological considerations to engineering-related factors, such as sampling or analytical accuracy, or specific excavation/treatment methods used at a site; and to the cleanup costs.

## 3.4 Proposed Approach to the Problem

Many contaminated soils cleanups at Superfund sites involve leaving some quantities of residual contaminants in soils without imposing further management requirements for the soils, or without access and use restrictions on the land where the soils are located. For such soil cleanups, it is the belief of this author that of the many approaches to setting soils cleanup levels discussed in Section 3.2, the most effective use of Superfund program resources does not involve setting generic national soil standards, nor relying entirely on the inadequate set of existing standards.

The approach presented here involves setting

cleanup levels on a site-by-site basis, given the nature of the soils threat and the exposure pathways and receptors involved. These would be determined in a site specific risk assessment, as described in Section 3.2.1.3.

Cleanup levels for soils could be set by adapting them, or back calculating appropriate soil concentrations, from allowable ambient levels or standards for the contaminant in the medium affected by soils. For example, if the greatest threat or the most limiting exposure pathway involves volatilization of contaminants from soils to air, and a health based "safe level" for the contaminant in air at the nearest possible exposure point can be readily determined, the acceptable levels in soils would be set such that amounts released to air would never exceed the "safe level" at the nearest possible exposure point.

An effective response to the soil cleanup level problem requires an integrated approach that will address both the selection of the appropriate remedial action and selection of the appropriate extent of its application (i.e., the cleanup level). This concept has several main elements that track the principal stages of the Remedial Investigation/ Feasibility Study process, as described in Section 2.1.2:

- 1. Designing the <u>remedial response objectives</u> to mitigate current and future site soils threats when scoping the RI/FS, based on available (PA/SI) background information on the site problem. This may include initial assessments of the technical feasibility of performing cleanup to "walkaway" levels.
- 2. Collecting data in the RI for (1) an assessment of the site threat, defined in terms of the hazard presented by the soil source, and of the exposures and risks to public health and the environment; and (2) sufficient treatability evaluation of soils so that in the FS, remedial technologies can be identified that achieve the response objectives.
- 3. Performing the <u>exposure and risk assessments</u> in the public health evaluation. Using the RI data, EPA may use models and other techniques to determine baseline site risks for alternatives comparison with a "no action" alternative, and reevaluate walkaway cleanup level.
- 4. <u>Assembling</u>, <u>screening</u>, and performing a <u>detailed</u> evaluation of the remedial alternatives in the FS.
- 5. <u>Selecting the cleanup level</u> to be achieved by the selected remedy, based on the site-specific risk assessment.
- 6. Selecting and implementing the remedy in the ROD and subsequent design and construction phases. To address uncertainties in the remedy, the remedy should include verification of cleanup level and of any modeling approach, if one is used, through monitoring. This also may require maintenance of remedy, and access and land-use restrictions to prevent exposure during and possibly after verification period, and development of a "fallback" remedy.

Table 9 presents an outline of this approach.

General descriptions of the corresponding Remedial

Investigation/ Feasibility Study activities were

presented in Chapter 2. Each of these elements of the

# TABLE 9 GENERAL CONCEPTUAL APPROACH FOR SELECTING CONTAMINATED SOILS REMEDIAL ACTIONS

## 1. Design Remedial Response Objectives

- Initial estimates for purposes of developing RI/FS workplan, designing site investigation

 Initial estimates of requirements for "protective" remedy under CERCLA, SARA

- Initial assessment of feasibility of "walkaway" cleanup (see discussion of "walkaway" and SARA "permanent remedy")

 Based on limited available data (PA/SI, NPL listing)

- Could use order-of-magnitude-level modeling

# 2. Identify Site Threat (Perform Remedial Investigation)

- Site history, operations

- Wastes handled, management activities

Location, site setting

- Type/extent of contamination

- History of enforcement/mitigation activities

- Treatability data for candidate response technologies

 May be performed in phases as need for more data is successively evaluated (e.g., for more detailed risk evaluation, reduction of uncertainties, running more complex models)

# 3. <u>Perform Risk Assessment/ Public Health Evaluation</u> (Evaluate Findings of the RI)

- What contaminants are present

- In what media

- How indicator compounds selected

Actual/potential receptors

- Actual/potential exposure pathways (list/rank/eliminate for ea. contaminant of concern)
- Focus on soil contam./ground water pathway (or whichever other pathway is most limiting for ea. contaminant of concern)

- Results: magnitude of current/potential risks (baseline or "no action" site risks)

- Reevaluate "walkaway" cleanup levels

### TABLE 9 (Continued)

- May use progressively more complex models as site data base expands (reevaluate data needs/ costs)
- 4. <u>Analyze/Compare Remedial Alternatives</u> (Findings/Analyses of the FS)
  - General response objectives (desired reduction of risks) (all alternatives evaluated must be sufficiently protective; may have varying levels of "permanence" in terms of long-term management requirements)

 Assemble and screen alternatives (evaluate data needs, expand RI/perform pilot studies as needed)

- Analysis of alternatives (compare for relative risk reduction [in terms of selected cleanup/performance levels in targeted media, pathways]; "permanence;" effectiveness; cost-effectiveness, other SARA/NCP requirements)
- May use same or different models as RI progresses to compare effectiveness of alternatives

# 5. Select Remedy (The ROD)

- Document site threats, response objectives addressing them (summarize steps 1-4)
- Soil remedy may address only soils response objectives (one component of overall remedy); all source response objectives; or all site response objectives (includes any needed management of migration measures)
- Rationale for selecting that alternative (document how it "best" satisfies SARA and NCP criteria)
- Document numerical performance target/ cleanup level (reduction to a selected risk)
- Rationale for cleanup level--document as follows:
- a. <u>Select the Back-Calculation Approach</u> (if applicable AND if different from prior model[s])
- Verify what is known about contaminant properties, soils, aquifer(s)
- Identify which model(s) address these "knowns"
- Compare models in terms of waste/site "knowns"
- Approximate levels/types of uncertainties
- Identify more sophisticated/precise/better models

## TABLE 9 (Continued)

- Consider additional data requirements, obtain data if warranted
- b. Select the Cleanup Level for the ROD
- Select the point(s) of exposure
- Focus on soil contam./ground water pathway
- Verify indicator compounds
- Select target risk level/determine corresponding ground water concentrations of each indicator
- Back-calculate to determine corresponding soil levels
- Identify uncertainties/assumptions in data, calculation; how remedy addresses each

# 6. Design and Implement the Selected Remedy

- Waste and site considerations (may require maintenance of remedy, access and land-use restrictions, if not cleanup to "walkaway"--to prevent exposure during (and after) verification period
- Data considerations
   (may require verification of cleanup level and
   of modeling approach through monitoring)
- Types and levels of uncertainties
- Reducing uncertainties: verification monitoring vs. "better" model (more data) vs. more extensive cleanup
- May require "fallback" remedy if selected remedy (or cleanup level), or model used to determine it, is later found to be incorrect.

conceptual approach will be discussed in detail in the following sections of this chapter.

## 3.4.1 <u>Designing Overall Response Objectives</u>

Early in the scoping phase of the remedial action, a preliminary determination of likely response objectives for the site should be made. This should include an initial assessment of the type and nature of the responses that might possibly be undertaken at the site, i.e., general types of containment, excavation, and/or treatment actions, in order to develop data quality objectives for the Remedial Investigation. The extent of response may vary along a continuum ranging from no action to the complete removal and/or treatment of all materials with pollutant levels above detection limits or regional "background" levels.

The extent of remedy decision should consider, among other things, what level of long-term management is expected to be technically necessary at the site, and how this required level compares with the desired level. In other words, how much long-term management does the Agency or the State want or is it willing to accept? This decision involves a balancing among several tradeoffs involving different aspects of the overall quality of the remedy, as indicated by the following very general principles:

- o The greater the degree of cleanup, the more "protective" it is;
- The closer the cleanup level is to background or to "walkaway" health- and environment- based levels, the more "permanence" or long-term effectiveness it is likely to offer, depending on site and contaminant characteristics;
- o For purposes of this report, health- and environment- based cleanup levels will be assumed to be available for most compounds of concern at most sites, thus allowing consideration of cleanups above background at least on the basis of intrinsic chemical hazards;
- The closer the cleanup level is to background/
  "walkaway", the less the cleanup level depends on
  fate and transport assumptions or exposure
  assumptions, and the less it will be affected by
  uncertainties in the data, assumptions, and
  analyses. Therefore it would have a higher factor
  of safety;
- Whenever background/clean closure/"walkaway" levels are exceeded for residuals being left on site after conclusion of the remedial action, some form of long term management is necessary;
- o The mobility/ toxicity/volume (MTV) of the soil residuals might be measured in terms of concentrations of contaminants in their most mobile/toxic forms, if present, or of a surrogate/indicator parameter;
- Depending on the MTV of the residual soils, the type and extent of this long-term management may vary from verification monitoring and access/use restrictions only to active maintenance; e.g., from ground water or soil monitoring to active pumping/treatment, cap maintenance, etc.

Therefore, the closer the cleanup level is to background, the less long-term liability there is at the site, and the smaller the need for long-term O&M, monitoring, or land use, water use, or access restrictions.

Often there is substantial citizen support for complete removals, especially if wastes are taken elsewhere.

Thus the analyst may begin to consider as early as the scoping phase (1) the possibility of closing all or portions of the site such that EPA or the State can walk away at the completion of the remedial action with no further management or monitoring requirements of any kind-- a true "walkaway" cleanup level; and (2) whether such action is desirable and compatible with all other actions anticipated at the site. The size and nature of the site problem may make the walkaway goal unachievable for the entire site, or for certain portions thereof, necessitating some form of long term management regardless of the response action chosen.

where walkaway cleanups are possible, the attractiveness of cleanup levels approaching background is offset by the costs and technical limitations associated with achieving this level, especially at larger sites or where more complex soil/waste mixtures are present. These cost-effectiveness considerations include, for example (Ehrenfield and Bass, 1983):

- o Transport distance to off-site treatment and disposal facilities;
- o Quantities and types of wastes and soils;
- o Needs to implement other remedial actions independent of the excavation/treatment actions, e.g. ground water responses;
- o Nature of the site hazards;

- o Treatability of the wastes and soils; and
- o Costs of removal and/or treatment.

These initial determinations will guide the development of data quality objectives for the Remedial Investigation, and allow the analyst to begin the formulation of initial response objectives for the site. The site characterization data collected in the Remedial Investigation, when processed in the exposure and risk assessments, forms the basis for refining the remedial response objectives. These response objectives later will become the design targets and specifications of the remedy selected in the Record of Decision.

The level of detail in the exposure and risk assessments will depend upon the size and complexity of the site; the decision to develop site response objectives that consider cleanup levels other than background; and on consideration of environmental endpoints in between complete removal and total containment of the soils and wastes.

# 3.4.2 <u>Data Collection in the Remedial</u> Investigation

The site manager must assemble sufficient information in the Remedial Investigation to determine what remedial alternatives, including excavation and/or treatment to a walkaway cleanup level, are technically

achievable for the site or area. First, this requires a thorough understanding of what contaminants are present; how they are spatially distributed at the site; their physical and chemical states and concentrations; and their contaminant-occurrences with other compounds in each particular matrix that may be present--liquid and solid wastes, sludges, contaminated solids and soils, sediments, and surface and ground water. Second, the site manager must determine whether appropriate healthbased concentration levels exist for each contaminant of concern, by surveying the applicable or relevant and appropriate Federal and State health-based standards, criteria, advisories, limitations, or other values. Finally, this information on the types and degrees of hazard must be supplemented by knowledge of the environmental fates of the compounds, the distributions of human and environmental receptors, and pathways of actual or potential exposure. Chapter 4 includes a discussion of models and other methods to perform the exposure assessment and to set cleanup levels. It provides further discussion of how Remedial Investigation data collection may also need to be tailored to the data requirements of the models when used for these purposes.

Additionally, as discussed in Chapter 2 and Section 2.3, many potential remedial technologies may have

specific data requirements seldom addressed in current Remedial Investigation efforts. Some treatment technologies, while broadly applicable to the types of contaminants found at a given site, may be untested on the specific contaminant/ soil matrix present at that site. Field data and perhaps bench- or pilot-scale testing may be needed to verify the technology's ability to treat the soil contaminants, and to provide cost, effectiveness, and other data sufficient to conduct the Feasibility Study. Hazards and long-term management requirements of the treatment residuals must be determined to evaluate the remedy's "permanence," as well.

The Remedial Investigation can be designed to collect this information, with the level of detail increasing in a stepwise fashion through successive iterations as necessary, and with reasoned application of the data quality objectives process (Camp, Dresser and McKee, 1987A, B).

# 3.4.3 The Risk Assessment (Public Health Evaluation)

The concept of using site-specific risk assessments to set soil cleanup levels was introduced in Section 3.2.1.3 and is the primary focus of this report. The risk assessment concept was generally described by the

National Research Council (1983) as a process for characterizing the potential adverse health effects of human exposures to environmental hazards in four broad stages:

- "<u>Hazard Identification</u> -- the determination of whether a particular chemical is or is not causally linked to particular health effects.
- O <u>Dose-Response</u> <u>Assessment</u>— the determination of the relation between the magnitude of exposure and the probability of occurrence of the health effects in question.
- o <u>Exposure Assessment</u>— the determination of the extent of human exposure before or after application of regulatory controls.
- o <u>Risk Characterization</u>—the description of the nature and often the magnitude of human risk, including attendant uncertainty."

As described earlier, each Remedial Investigation/
Feasibility Study incorporates such an assessment,
called a Public Health Evaluation (EPA, 1986A; Schultz
et al., 1987). The public health evaluation includes
the baseline risk assessment and the development of
performance goals for remedial alternatives. The
baseline public health evaluation is required for all
Superfund remedial actions, as discussed under the "No
Action" alternative in Section 2.3.2. It provides the
remedial project manager with an assessment of the longterm threats presented by the site in the absence of
remedial action, and can also be used as the basis for

the Endangerment Assessment.

The Endangerment Assessment is an analysis of the extent to which the site poses an imminent and substantial endangerment to public health and the environment. This assessment, which is focused on but not limited to subchronic or short-term threats, is required by Section 106 of CERCLA to justify the initiation of any enforcement actions against potentially responsible parties.

The public health evaluation may contain some or all of the following major steps, most of which parallel the risk assessment process described by the National Research Council (1983):

- A. <u>Selection of indicator chemicals</u>— this step focuses the analysis on contaminants of greatest concern, generally the most mobile, toxic, persistent, and/or abundant at the site when many compounds are present (Table 10). At sites with only a few compounds, all chemicals present should be evaluated (EPA, 1986A);
- B. Estimation of exposure point concentrations and comparison to Applicable requirements— this step involves (1) identifying potential exposure pathways; (2) estimating exposure point concentrations of indicator compounds in each pathway using RI data and fate/transport models (these steps are discussed in detail in Section 3.1.3.4 and subsequent chapters); and (3) comparing these concentrations (the baseline exposure levels) to health— and environment—based applicable or relevant and appropriate requirements, or Agency—approved acceptable exposure levels;
- C. <u>Estimation of chemical intakes</u>— human exposures are evaluated in this step by converting exposure point concentrations into human intakes using

# TABLE 10 Selection of Indicator Compounds (Adapted from Research Triangle Institute, 1987)

#### 1. LIST ALL CHEMICALS OF CONCERN DETECTED AT SITE

- o Determine average and maximum concentrations
- o Identify media of occurrence
- o Identify carcinogens vs. systemic toxicants
- 2. OBTAIN TOXICITY VALUES/"SAFE DOSES" FOR EACH CHEMICAL
- 3. IDENTIFY KEY PHYSICAL/CHEMICAL PROPERTIES OF EACH CHEMICAL
- 4. <u>DEVELOP TOXICITY CONSTANTS FOR EACH CHEMICAL IN EACH MEDIUM</u>
  - o Based on media-specific standards where available
  - o Back-calculate "safe level" from dose using mediumspecific exposure/intake assumptions
- 5. LIST CHEMICALS BY (Toxicity Constant) \* (Concentration)
- 6. CANDIDATE SELECTION CRITERIA:
  - o Most mobile
  - o Most toxic
  - o Most persistent
  - o Highest concentrations
  - o Highest masses/volumes
  - o Most ubiquitous
  - o Most media of occurrence
  - o Toxic byproducts/daughters (from treatment or natural degradation)

standard Agency exposure assumptions for each pathway (e.g., for ground water exposure, ingestion of 2 /day by a 70 kg adult over 70 years; for soil ingestion of noncarcinogens, 1.0 g/day by a 17 kg child over 5 years). Intakes are expressed in mg/kg-day. Intakes for each contaminant are summed intakes across exposure routes, as appropriate. Note that exposure assumptions may be adjusted in some cases to account for site-specific conditions;

- D. <u>Toxicity assessment</u>— in this step, Agency-approved toxicity information, such as acceptable intakes for subchronic exposure, acceptable chronic intakes, and carcinogenic potency factors, is collected for contaminants of concern identified in the exposure assessment process; and
- E. Risk characterization -- in this step, exposure assessment results (Steps A-C) are combined with toxicity data from Step D to characterize actual or projected intakes and risks, and compared with target "acceptable" intakes and risks, for systemic toxicants and carcinogens, respectively.

These steps are described in more detail in EPA (1986A) and Schultz et al. (1987). Generally, the public health evaluation process follows EPA's guidelines for carcinogen risk assessment, exposure assessment, mutagenicity assessment, and assessment of health risks from chemical mixtures (EPA, 1986G,H,I,J), which include the following general principles:

- o Values for acceptable subchronic and chronic intakes are often derived from short-term and long-term animal studies. Where available and appropriate, values are based on human toxicity studies, and incorporate, at a minimum, uncertainty factors of 10 to extrapolate from animal to human effects and 10 for intraspecific variability in responses.
- Acceptable intakes are designed to protect sensitive populations and to account for teratogenic effects,

#### if known.

- o Compounds may exhibit carcinogenic or noncarcinogenic (i.e., systemic toxicant) effects, or both. Different effects may be expressed by a compound depending on exposure route, age of receptor, and other factors. Different compounds may affect different target organs. Both toxicities should be assessed for each contaminant through each exposure pathway. All toxicities for all (or all indicator) contaminants should be examined for the baseline risk estimate. Only the lower, or more limiting toxicities, and the most limiting exposure pathways, should be used to set cleanup levels or remedial response targets or performance goals.
- o Systemic toxicants are believed to have acceptable threshold levels based on the No Observed Adverse Effect Level (NOAEL). If possible, these levels are based on chronic toxicity studies. If unavailable, levels may be extrapolated from subchronic toxicity values using additional uncertainty factors (e.g., an additional factor of 10). These are used to calculate a Reference Dose (RfD) by EPA workgroups.
- Carcinogens are evaluated to determine a 0 Carcinogenic Potency Factor (CPF), expressed as lifetime cancer risk per mg contaminant per kg body weight per day. The CPF is an upper bound (95% confidence level) estimate, assuming a linearized multistage model of carcinogenesis. Thus, the method may overestimate actual carcinogenic risk of a given contaminant at a given site. The model assumes the response is in the linear portion of the compound's dose response curve, which may be valid only at relatively low environmental concentrations of the compound. At higher concentrations, other toxicity models (e.g., the "one-hit" dose response model) may better fit observed/expected responses.
- o Risks of exposure to multiple compounds (and by multiple exposure pathways) involve complex assessments. For multiple carcinogens, EPA assumes that:
  - (1) independent intakes are small;
  - (2) there are independent actions of all

contaminants (no synergistic/antagonistic
interactions);

- (3) all contaminants result in a cancer endpoint;
- (4) risks from different exposure routes are additive.
- o Prior to summation, each pathway must be separately calculated using pathway- and contaminant- specific potency factors. Risks should be estimated and reported separately for each contaminant and each exposure pathway along with the aggregate risk estimate.
- o For assessing risks of exposure to multiple noncarcinogens (systemic toxicants), EPA uses a hazard index approach (EPA, 1986-), expressed as the sum (for all toxicants) of the ratios of the exposure level (intake) of each toxicant to its reference level (acceptable intake). The approach assumes that potential risks exist when the hazard index exceeds unity, either for a single contaminant or for their sum. Therefore, it identifies potential risks but does not accurately quantify them. Note that mis- estimates could occur when summing toxicities involving:
  - (1) different target organs;
  - (2) different exposure pathways for the same compound or different compounds; or
  - (3) a mixture of subchronic and chronic toxicity values.
- o These should be re-calculated separately when possible, if the aggregate index exceeds unity.
- o Uncertainties, and assumptions or decisions made using best professional judgement to address uncertainties or interpret estimates, should be identified and reported.

Please note that a detailed discussion of the toxicological elements of the risk assessment process is a large and complex topic, and further expansion would

be outside the scope of this report. For more information, the reader should consult the references cited above.

Data collected to perform the baseline risk assessment should in most cases provide for development of performance goals for the remedial alternatives analyzed and compared in the Feasibility Study. Performance goals or performance targets may be set as acceptable ambient contaminant levels in a given medium at designated exposure points, for example, residual contaminant levels in soils following excavation or treatment, as discussed in Section 3.2. The focus of the following chapters is on use of exposure assessment models to make these risk-based determinations. Alternatively, performance goals or targets could be set as acceptable emissions levels from a given treatment train, i.e., technology-based performance goals, as discussed in Section 3.2.2, "using risk analysis concepts" (EPA, 1986A).

The risk assessment may range along a continuum of level of detail and complexity, from one that is largely qualitative and relatively straightforward, to a highly complex and highly quantitative evaluation, depending on several factors. Since no two sites are alike, flexibility in application of the process is required. For example, sites with a small number of contaminants,

where environmental standards or criteria are available for these contaminants, and where few exposure pathways exist or order-of-magnitude estimates are sufficient, may allow for simplified analysis. Many sites, however, may have many contaminants complexly distributed in various environmental media, having few Agency-approved risk numbers, complex transport and fate processes, and many exposure pathways present. Such sites clearly require complex analyses, especially if quantitative risk estimates with minimal uncertainty are desired.

Thus, analytical complexity depends on the number and type of contaminants present; media of their occurrence and distribution at the site; number and complexity of exposure pathways; quality and quantity of available data; availability of standards, toxicity data, or Agency approved health- and environment-based exposure levels; and the intended use of the risk assessment results, i.e., the need for precision and the acceptable level of uncertainty in the results (EPA, The level of detail and sophistication in 1986A). Superfund risk assessments has been increasing with time, as level of programmatic knowledge has increased, and as some level of standardization of the Superfund public health evaluation/ endangerment assessment process has begun to develop through the issuance of guidance (EPA, 1985L, 1986A; Boutwell et al., 1985;

Keely, 1987A; Schultz et al., 1987).

As discussed for Remedial Investigation data collection In Section 3.4.2, the concept of the analytical continuum applies to each individual step of the risk assessment process, particularly within the exposure assessment on which this report is focused, to maximize cost-effectiveness of the data collection and analysis efforts. For example, initial contaminant release analysis may be largely qualitative at the Remedial Investigation/ Feasibility Study Scoping stage to develop a general understanding of on site contaminant sources, so that general response objectives may be focused on their abatement. This preliminary screeninglevel assessment should help identify complete exposure pathways, target the analysis to key pathways, allow preliminary identification of potential applicable or relevant and appropriate requirements and candidate remedial technologies, and focus the data collection efforts toward a stepwise, phased effort to verify each pathway and fill in its details to the necessary extent.

The same approach is applied to other steps, such as contaminant fate and transport analysis and population exposure analysis. The relationship between analytical detail, sophistication of the available data base, and level of uncertainty in the analytical results, is further discussed in Sections 4.7 through

#### 4.9 and in Chapter 6.

#### 3.4.4 Use of Exposure Assessments

The exposure assessment forms an integral part (Step B) of the risk assessment/public health evaluation, and thus plays a critical role in both the Remedial Investigation and the Feasibility Study. Its goal is to provide an assessment of the types and magnitudes of actual and/or potential human exposures to contaminants present in or migrating from contaminated soils and waste sources at the site, such that this information can be fed into the public health evaluation for the assessment of risks to human health. While similar approaches could be used to assess threats to sensitive nonhuman environmental receptors, they have seldom been the primary focus of Superfund site risk assessments.

In the Remedial Investigation, the exposure assessment is used in the baseline public health evaluation in the assessment of the "No Action" alternative (EPA, 1985F,1986A; Schultz et al., 1987). In the Feasibility Study, it facilitates comparison of the public health and environmental impacts, or the risk reduction from baseline "no action" levels, afforded by the various remedial alternatives. The conceptual approach on which this report is premised is based on

it, in that the exposure assessment is especially critical to the choice of remedy and to its extent, by helping to define the appropriate cleanup level for the soils that will be left in place when the selected remedy has been completed (EPA, 1985B).

The general framework for Superfund's exposure assessment process involves the following steps (Schultz et al., 1987):

- contaminant release analysis—a chemical—and medium—specific analysis of on-site sources and actual or potential releases of contaminants from those source areas. Emissions rates or fluxes of each contaminant, including temporal and spatial patterns, are characterized each medium to the extent possible. Long-term and short-term estimates of contaminant mass loading to each pathway/medium (often expressed in units of grams contaminant/time) are made;
- Environmental fate analysis -- a chemical and 0 medium- specific assessment of transport and transformation of each contaminant of concern as it migrates from its source area through one or more media to human or environmental receptors via each identified exposure pathway at the site. Both actual RI data on environmental concentrations, and estimation methods including physical and/or mathematical models, are used. The result is a description of the spatial and temporal extent, distribution, and magnitude of environmental contamination in each medium of concern, and an estimate of contaminant concentrations in each medium, at times and exposure locations of interest;
- o <u>Exposed populations analysis</u>— this identifies, characterizes, and quantifies receptor population(s) likely to be exposed to each contaminant through each exposure pathway at each receptor location of concern; and

Integrated exposure analysis— integration of the findings of the preceding steps. Individual chemical specific exposure estimates are developed for each pathway (e.g., inhalation, dermal contact, water/food/ soil ingestion), generally using standardized Agency exposure assumptions (see EPA, 1986G,H). For each pathway, exposures of the receptor population to all contaminants are summed to the extent possible (EPA, 1986H,J). Results are fed back into the public health evaluation process for assessment of the site risks (Steps D and E in Section 3.4.3).

The exposure assessment must consider all important routes for exposure and contamination identified for the particular site, as discussed in 3.4.3. Human exposure assessments should consider the relative likelihood of uptake through all direct and indirect pathways for exposure and contamination identified for the site, such as inhalation of entrained particulates or gases, ingestion of drinking water, or food chain uptake of contaminated plants or animals. These direct and indirect pathways for exposure to contaminated soils were described in more detail in Section 3.1.

Exposure assessments are based on evaluations of the mobility, toxicity, quantity, and distribution of hazardous substance in the soil (called source and release analyses), to estimate their transport and transformation as they migrate from source soils to receptor locations (called fate analysis). Exposure point concentrations can then be estimated and converted into receptor doses using standardized Agency-approved

exposure assumptions (EPA, 1986A, H).

Note that exposure concentrations can be equated to receptor doses only when absorption of the contaminant by the target organ is 100 percent. This topic is controversial, and different absorption assumptions are used by different environmental programs for different exposure pathways, exposed populations, and exposure scenarios (EPA, 1985A,D; Sedman, 1987). In the absence of data, the conservative assumption of 100 percent absorption is often used, especially for a simplified, first-stage exposure analysis (Schultz et al., 1987). Other controversial issues include:

- <u>Apportionment</u>, i.e., how to accurately aggregate the risks from a given contaminant resulting from multiple exposure pathways;
- o Proper methods for accurately <u>aggregating risks</u>
  <u>from multiple contaminants</u> through a single
  pathway. This is especially crucial for Superfund
  soils since complex multi-contaminant mixtures are
  the norm;
- o Proper procedures to estimate <u>total risks from</u>
  <u>mixtures of carcinogens and systemic toxicants;</u>
- o How to compare site threats to "acceptable" levels when <u>few or no promulgated standards</u> are available for most contaminants in most environmental media, as discussed previously;
- o How and under what circumstances to assess "actual" current population risks, i.e., by quantifying actual, existing receptor population exposures, versus MEI (maximum exposed individual) risks, which can provide a basis for estimating future site threats by focusing on potential individual exposure; and

o How and under what circumstances to modify
"standard" exposure/intake assumptions to account
for site specific circumstances of actual and
future site uses and exposures.

Many of these issues constitute "risk management" decisions, although they significantly affect the outcome of the risk assessment (EPA, 1984C; National Research Council, 1983). The absorption and dose/response relationship issues, and others involving intakes, sensitive populations, extrapolation from animal data, and other primarily toxicological issues are fundamental to the risk assessment process, but a detailed discussion is beyond the scope of this study and will not be given here.

The focus here is on the exposure analysis and estimation of fate and transport to provide estimates of soil contaminants concentrations and distributions at receptor points, as discussed further when the soil/ground water conceptual system is discussed in Section 4.2 and succeeding portions of this report. Thus, the premises given in Section 3.1 will be used to support subsequent discussions of the role of exposure assessments in setting cleanup levels.

Following the calculation of receptor doses at the exposure points under "no action" conditions in the baseline risk assessment, remedial response objectives can be developed into design goals that mitigate or

prevent any exposures exceeding the threshold concentrations or doses. This requires several actions and decisions:

- Selection of exposure locations for each exposure pathway. These could vary depending on remedial alternatives being considered;
- o Development of acceptable exposure concentrations or levels at these locations for each compound of concern, i.e., performance goals or design target levels. They would be based on applicable or relevant and appropriate requirements and/or Agency- approved health-based levels, requiring selection of an "acceptable risk" level;
- o A decision to protect against actual population exposure (i.e., quantifiable risk) or potential (e.g., future, unquantifiable) exposure, i.e., MEI risks;
- o Estimation of "acceptable" levels of uncertainty. This dictates the level of detail and accuracy in the exposure assessment, intensity of data collection, and the level of conservatism of assumptions used; and
- o Determination of the most limiting or critical exposure pathways for each soil contaminant of concern.

Standards applicable to air or water, or chemical dosages for ingestion, dermal contact, or other limiting exposure pathways, can then be translated into appropriate threshold concentrations or acceptable doses at the receptor location. For example, to set targets for ground water cleanup for a ground water exposure/ contamination pathway, these acceptable values would be translated into acceptable chronic contaminant

concentrations at the nearest possible current/future drinking well location. If unlimited future site use is expected, this may dictate drinkable ground water directly beneath the site. If long-term containment with access restrictions may be the selected remedy, the nearest point of future ground water exposure likely would be at the downgradient fenceline of the site. Thus, models could back-calculate higher allowable residual levels in source soils because of the additional opportunities for lateral dilution or attenuation/ transformation of contaminants before they reach the receptor location.

The question then arises as to whether, and how accurately, each pathway can be identified and quantified. This must be examined in two ways: in terms of (1) the state of scientific understanding in describing and quantifying these various exposure pathways, and (2) for those that can be quantified successfully, the amounts and kinds of site data that must be collected during the Remedial Investigation to perform an adequate and accurate exposure assessment. As mentioned in Sections 3.3.2 and 3.3.3, this represents the tradeoff between the intensity and cost/time of the site investigation, and the level of precision in the resultant understanding of overall site risk. This issue of level of scientific uncertainties

about both the direct and indirect soils exposure pathways will be discussed further in Section 4.9, and the issue of data/ precision tradeoffs will be discussed in Chapters 4 and 6.

For most of the indirect soils exposure pathways listed in Section 3.1, there is disagreement among the scientific community as well as the agencies on the relative importance of contributions of each to the overall site risk; thus many pathways were ignored in the exposure assessments other than the ground water route and the surface water route at certain sites. At most Superfund sites, soil ingestion and exposure to contaminated ground water are considered the most critical pathways for direct and indirect exposure to contaminated soils, and past cleanup levels have generally focused almost exclusively on these pathways. Other exposure routes have been assumed to be less critical for soils at most sites, however this assumption generally has been based more on qualitative assessments or best engineering judgement than upon critical, quantitative analysis of other potential exposure routes.

To facilitate comparison in the Feasibility Study of the effectiveness of various remedial alternatives in achieving target levels of protection or "permanence" at the potential exposure points, exposure models could be

used either to calculate acceptable on-site residual concentrations, as described above, or to determine acceptable contaminant release rates under each remedial alternative. Then, either the release rates themselves, or the net reductions when subtracted from "no action" release rates, may be compared among alternatives (e.g., acceptable air emissions rates from an incinerator, or rates of surface runoff or leaching of soils to other media; EPA, 1986A; Schultz et al., 1987).

Estimation methods range in complexity from qualitative screening-level estimates to highly complex mathematical models. Qualitative screening-level estimates are prepared for simpler sites, or used in the early stages of analysis at complex sites. Simple numerical estimates may be based on limited data and conservative assumptions, for example, physical data such as generic leaching test results, or literature values for partition coefficients. Highly complex and data-intensive numerical fate and transport models can be used to predict exposure levels and concentrations, and to translate applicable or relevant and appropriate requirements into appropriate threshold concentrations or doses in a given medium. As discussed above, this capability is essential to developing soil cleanup levels due to the lack of accepted ambient soil concentration standards, to back-calculate acceptable

ambient soil concentrations at the source area in order to provide design goals usable by the engineer.

The scientific and regulatory communities lack consensus regarding the appropriate methods and assumptions to employ when assessing exposure. The latter issue is more complex for the indirect pathways described in Section 3.1.2 than for the direct pathways, because fate and transport mechanisms and multimedia transfers are involved in bringing contaminants from the soil source to the eventual receptor, as shown in Table 8. Controversy surrounds the appropriate analytical methods to use, since modeling is required in order to estimate future exposures.

Generally, no single model will be suitable for every situation, nor does any single transport equation account for all processes affecting all contaminants in all media, despite numerous attempts to solve this problem by creating new models. Some reviews have addressed model selection criteria for assessment purposes (Boutwell et al., 1985; Schultz et al., 1987), and several offices within EPA have initiated efforts to develop ground water model selection criteria and policies in particular (Bond and Hwang, 1988; Bierman et al., 1986; van der Heijde and Park, 1986).

However, no guidance has been developed that explicitly addresses the selection and use of models or

other estimation methods to help set risk-based soil cleanup levels at Superfund sites. The resultant problems in setting cleanup levels are discussed further in Section 3.5. Estimation methods and models for exposure assessment are discussed further in Sections 4.7 through 4.9, following a description of the fate and transport processes these methods are intended to simulate and predict. A process by which models might be selected and used to set soil cleanup levels more effectively and consistently is discussed in Chapters 4 through 6.

#### 3.5 Problems in Establishing Soil Cleanup Levels

The problems involved with determining appropriate cleanup levels are common to most sites subject to Superfund response actions and are the principal focus of this report. As indicated previously, these difficulties have resulted in the selection of a limited range of cleanup levels—usually removal or treatment to background levels or to the limits of visible contamination. The Office of Technology Assessment (1985, 1988) asserted that such cleanups "usually" have left significant quantities of residual contaminant in place, threatening ground water.

In a few cases, cleanup was performed to a level based on risk assessments as being a safe level for

human or environmental exposure. However, no systematic basis has been used for making these determinations in terms of the following factors:

- o Initial selection of compounds or contaminants considered most critical to the analysis (were the appropriate ones selected?);
- o Risk levels or standards used as the basis for setting acceptable exposure levels or concentrations (or what was done if none were appropriate/available?);
- Analyses of fate and transport used to translate risk levels for human or environmental exposure into acceptable ambient residual concentrations (were any used?);
- o Routes of fate and transport, receptor locations, and exposure times used in the exposure assessment, if any (were they accurate? all-inclusive?); and
- o Models used in the fate and exposure estimations (appropriate for site/ data/ end use?).

Different cleanup decisions have been made by different decision makers, as illustrated in previous sections of this report. Decisions were based on varying amounts of information, and made by different methods with different motivations and goals. As a result, the general appropriateness of establishing site-specific cleanup levels rather than allowing only generic, national levels has been a major focus of the "how clean is clean" debate. Another has been the question of what methods are appropriate for performing the risk assessment, especially the use of models in

site-specific estimation of exposure.

Which models are appropriate for making the sitespecific fate and transport assessments? Is one generic
model available for each medium of concern, or one model
encompassing all media, that applies effectively to all
site situations, or do different situations require
different models? If one must be selected, how? Can
decision rules be developed so that choices,
applications, and results can be consistent, given the
wide range of variability in site conditions, available
data, and end uses of the analysis?

The Superfund program needs guidance that will facilitate making these decisions flexibly yet consistently by performing the following tasks:

- Ensure that the appropriate type and quality of data on wastes, site hydrogeologic characteristics, and potential and actual exposure pathways is obtained in the Remedial Investigation;
- Relate the Remedial Investigation data to the environmental standards or health-based levels identified for the site;
- Provide a process for selecting and applying the appropriate physical and numerical models to analyze these relationships for the site soils; and
- 4. Provide a process for interpreting and using the results to make the soils cleanup decision in light of the limitations of available data and resources and the potential consequences of the decision.

An approach is proposed and discussed in Chapter 4, with particular emphasis on the ground water pathway of exposure to soil contaminants.

#### 4.0 MODELING THE SOIL-TO-GROUND-WATER PATHWAY

#### 4.1 Introduction

This study will now focus on approaches to evaluating the most prominent of the indirect soil exposure pathways, that is, the threats posed by contaminated soils to ground water, and on how these may be evaluated systematically to set soil cleanup levels when ground water is the critical exposure pathway of concern at a CERCLA site. Section 4.2 provides a systems overview of the soils/ ground water exposure linkage as a conceptual framework for the discussion of risk and exposure estimation methods later in this chapter. It will also indirectly illustrate some of the problems encountered when attempting to standardize assessment approaches for the other exposure pathways described in Section 3.1.

In this conceptual model, the site will be viewed at the conclusion of the remedial action. Highly contaminated wastes or source areas are assumed to have been removed from the site or treated in place, as has any plume of contamination in the ground water, or ground water has not yet been contaminated. What remains are residual levels of contaminants in the surface soils, which may represent a source of repeating or continuing contamination of the subsoils and the aquifer underlying or downgradient from the former

disposal site.

Section 4.3 then reviews the primary physical, geochemical, and biological mechanisms involved in transport and transformation of contaminants released from contaminated soils and migrating to ground water receptors. It should be noted that many naturally occurring attenuation mechanisms are used as the basis for many of the treatment technologies reviewed in Section 2.3.

Sections 4.4 through 4.6 discuss waste, leachate, and site characteristics affecting the fate and transport processes occurring at a given site. Section 4.6 describes human influences at the site that should be accounted for when estimating or simulating fate and transport of soil contaminants to ground water.

Sections 4.7 and 4.8 then discuss how models and other methods may be used to simulate and estimate fate and transport, and provide a cursory review of ground water models and their applications in this context.

Section 4.9 discusses the concepts of uncertainty and decision analysis as they may be applied to fate and transport modeling. Finally, Section 4.10 presents and discusses a decision-analysis- based approach for selecting and using ground water models to back-calculate soil residual cleanup levels.

# 4.2 Relationship of Soils to Ground Water Contamination

To be able to predict confidently the potential for contamination of ground water by residuals in soils, it is necessary to understand the physical (hydrogeologic), geochemical, and biological processes that generate, transport, and transform contaminants leached from these soils. A brief overview of these processes is provided in the following sections.

#### 4.2.1 General Conceptual System

As shown in Figure 6, the exposure pathway relating soils to ground water may be viewed as an interconnected physical/chemical/biological system of "compartments." Water, natural materials, and contaminants may move between the media "compartments," and between the soil/ground water system and other media compartments. This occurs through a series of transport and transformation mechanisms that are physical, chemical, and biological in nature. The conceptual system has four principal compartments:

- o The <u>soil source</u>, surface (or deeper) soils containing residual levels of contaminants;
- o The <u>unsaturated zone</u> or <u>vadose zone</u>, composed of soils located between the surface soil contaminant source and the ground water system;
- o One or more <u>saturated zones</u> through which ground water is moving beneath and away from the site; and

SURFICIAL AQUIFER SOIL SOURCE TIME SCALE DAYS
DIMENSIONS METERS UNSATURATED ZONE DIMENSIONS KILOMETERS TIME SCALE YEARS D WATER TABLE SATURATED ZONE

RIVER

GROUNDWÁTER

-SCREENED WELL

BEDROCK AQUIFER

FIGURE 6 The Conceptual Soil/Ground Water System

o The human, plant, or animal <u>receptor</u> exposed to the ground water at the nearest likely point of exposure, either beneath or (more commonly) downgradient of the site (e.g., at a private well).

Soil contaminants may be transported through each of these four compartments as solids, e.g., sorbed to soil or particulate matter, liquids, or gases. Fine sludges or solids may be transported with infiltrating solutions in rates and amounts that depend on factors including particle size, velocity of infiltration, surface area of waste or soil in contact with the solutions, and size and degree of interconnection of subsurface void spaces (Repa and Kufs, 1985). The liquids may include non-aqueous liquids of different densities, but at most sites, they are primarily aqueous.

The conceptual model is framed in hydrogeologic terms, and follows the path of water movement through each compartment from the contaminated soils source to the eventual ground water receptor. There are several reasons for this. First, it has been estimated that 60 percent of hazardous wastes are in liquid or sludge form (EPA, 1980). A frequently-occurring contamination/release mechanism to soils is that of direct spill or release of liquid wastes to soils (Schultz et al., 1987), and movement of the liquids through the soils.

Second, contamination of ground water by infiltration of contaminated leachate is considered the

most common contamination mechanism (Repa and Kufs, 1985; Barcelona et al., 1987). As rainfall or overland flow percolates through soils, some may evaporate through capillary action, taken up by plant root systems and transpired, or infiltrate to recharge ground water, comprising the principal subsurface elements of the hydrologic cycle (Freeze and Cherry, 1979). Contaminants may be leached and will move downwards with the infiltration due to capillarity and to gravitational forces until the ground water table is contacted, thence spreading horizontally and vertically, primarily in the direction of ground water flow. The migration rate of liquid contaminants is increased by the hydraulic head due to infiltration. Thus, the subsurface components of the hydrologic cycle provide a primary vector for contaminant migration in the subsurface.

Third, ground water hydrology provides a traditional, relatively well-understood framework for examining contaminant transport. Until recently, the research community focused primarily on physical processes of ground water transport because of historical interest in obtaining adequate water supplies (Keely et al., 1986; Keely, 1987A). As ground water quality considerations began to predominate, scientific research and regulatory interests have traditionally focused more on fate and transport of water, and movement

of solutes with water, through the soil compartments to ground water, than on other transport mechanisms and movement of solutes with water, through the soil (Office of Technology Assessment, 1982). The compartments are described briefly in the following sections.

## 4.2.2 Surface Soil Zone

The <u>surface soil zone</u>, described above as the soil contaminant source for purposes of this conceptual model, is the region most influenced by weathering of native geological material, climatic changes including temperature cycles and freeze-thaw conditions, human and animal disturbance, and nutrient cycling due to plant and microbial activity. This zone is continuous with and represents the topmost few meters of the vadose zone. For purposes of the conceptual model, it is for this source area of residual soil contamination that cleanup levels are to be determined. This zone is only partially saturated, and contains a distinct gas phase in which atmospheric air occupies most of the soil pore spaces.

Water movement in the upper vadose zone occurs primarily as unsaturated flow due to infiltration, percolation, evaporation and transpiration, and redistribution (Klute, 1965). Everett (1980) described the occurrence of shallow perched saturated zones within

this compartment under conditions of rapid infiltration over low-permeability soil horizons, as during improper application of liquid wastes during landspreading. horizons, as during improper application of liquid wastes.

#### 4.2.3 Vadose Zone

The weathered surface soils merge gradually at most sites with the relatively unweathered deeper soil materials of the second model compartment, called the intermediate unsaturated zone or vadose zone (Figure 6). This zone may be virtually absent at some sites, for example in the Rocky Mountains or in glacial till regions of the New England states, or in coastal plain areas with shallow aquifers; while in other areas such as arid Western desert basins the vadose zone may consist of hundreds of meters of alluvial deposits (Aller et al., 1987). Since most vadose zone materials result from depositional processes, they are seldom uniform in structure, containing interbedded lenses of sands, clays, silts, and gravels. Alluvial material deposited along former stream channels may form long, ribbonlike subsurface deposits (Barcelona et al., 1987).

As in the surface soil compartment, gases, mainly atmospheric air at subatmospheric pressure, occupy most of the pore spaces, and water may occur as soil moisture

and in perched zones which tend to spread infiltration laterally, sometimes at rates substantially greater than vertical upward or downward flow velocities (McWhorter and Brookman, 1972). Thus, water flow in this zone may have substantial lateral as well as vertical vectors, resulting in spreading of contamination substantial lateral as well as vertical vectors, resulting in and infiltration to underlying aquifers over a relatively large area in some cases. Where the unsaturated zone is relatively shallow, the path and duration of solute transport may be relatively short compared to that in the saturated zone—days or weeks compared to years (Kincaid et al., 1984).

At the base of the vadose zone is the <u>capillary</u> fringe, a transition zone between the partially-saturated vadose zone and the underlying fully-saturated zones of the principal water-bearing formations located beneath the ground water table. It is characterized by the presence of water at or near saturation conditions, and under approximately atmospheric pressure, rather than by changes in the nature of its geologic materials in most cases. However, its flux and hydraulic conductivity, and thus its thickness, are partly dictated by the coarseness of the material, as high values have been recorded for considerable vertical distances in some finer-grained formations (Kraijenhoff

van deLeur, 1962; Luthin and Day, 1955).

Research on flows and chemical transport and transformation processes in the capillary fringe has been limited until recently, although this zone may play a significant role in the transport of certain contaminants. Freeze and Cherry (1979) and others reported that petroleum hydrocarbons and other non-aqueous-phase organic liquids less dense than water, after leaking from surface spills, may tend to collect and move laterally along the capillary fringe, in effect "floating" at or near the surface of the ground water table and mixing only minimally with the ground water. These processes are discussed in more detail in section 4.3.

### 4.2.4 Saturated Zones

Below the phreatic surface occurs the third conceptual compartment, wherein porous materials are fully saturated with water except for entrapped gases. The water is under hydrostatic pressure. These formations are of interest in this study when capable of yielding sufficient quantities of water for economic use (aquifers). They may be:

o <u>Unconfined</u>-continuous with the phreatic surface, and thus with the atmosphere, such that water levels may fluctuate vertically due to atmospheric and discharge/ recharge conditions;

- o <u>Confined</u>--bounded above by overlying impervious strata and thus under pressure, such that water would rise above the base of overlying confining strata if the confined aquifer was perforated; or
- o <u>Perched</u>—as discussed in Section 4.2.3 above, in localized, limited areas of saturation within the vadose zone, where downward percolation of water is inhibited by relatively impervious beds of clay or silt.

Many sites are underlain by multiple systems of confined and unconfined aquifers having varying degrees of geographic occurrence and of vertical interconnection.

#### 4.2.5 Ground Water Receptor

The fourth compartment in the conceptual exposure model is the human, plant, or animal receptor exposed to contaminated ground water when it is withdrawn through wells or when it recharges surface waters (see Figure 6). Exposure may occur through one or more of the indirect exposure mechanisms for ground water exposure listed in Section 3.1.

As stated in Chapter 1, mechanisms of fate and transport of contaminants within the body to the receptor's target organs, compound-specific dose-response relationships, and other toxicological factors governing the response of the receptor to soil contaminants following the receptor's ingestion of ground water contaminated by soil residues, are beyond the scope of this report. They are discussed in further

detail in many sources, including EPA (1986A,G) and National Research Council (1983).

The conceptual system is described here in hydrogeologic terms to facilitate its simulation using primarily hydrologic estimation techniques in the risk However, a complex combination of physical, assessment. geochemical, and biological processes is involved in contaminant transport and complex combination of physical, geochemical, and biological transformation from the soil source through each compartment of the soil/ ground water system at a given site. These must be considered in the establishment of cleanup levels, and in the choice of estimation techniques to be used in setting levels. The relative contribution of each process to the environmental fate of the released contaminants depends on the physical and chemical characteristics of the wastes in the soils, and on hydrogeologic characteristics of the soilground water system, at that site. The processes and waste/site characteristics considered most significant by investigators in this field to date are reviewed in the following section.

# 4.3 <u>Fate and Transport Processes in the Soil-Ground</u> Water System

As mentioned previously in this chapter, movement and

fates of soil contaminants cannot be described solely in terms of movement of water through the soil/ground water system. Many natural processes affect contaminant transport and fate in the subsurface. They can be grouped into three general categories of processes—physical, geochemical, and biological (Table 11). Individual processes may occur in all zones; some are unique to a particular zone; and others control transfers of contaminants between the compartments (Boutwell et al. 1985).

Subsurface contaminant transport is due to a combination of these natural processes that is unique to each site. Repa and Kufs (1985) stressed that how the site's unique set of processes interact to produce the distribution and type of aquifer contamination found beneath it depends (1) on the types and intrinsic physical and chemical properties of contaminants producing leachate; and (2) on site and subsurface conditions such as soil type, aquifer geology and geometry, contact time of wastes/ contaminated soils with infiltration, age of the site, physical and chemical properties of the ground water itself. It will depend on anthropogenic activities and disturbances to site soils, for example pumping or diversion of ground water from the contaminated soils mass, or other changes in hydraulic gradients through the site. These factors

#### TABLE 11

# Fate and Transport Processes in the Soil-Ground Water System

## Physical Processes

Flow Processes in Porous Media

Flow Considerations in the Unsaturated Zone

Transport Processes in Porous Media: Advection, Dispersion, and Diffusion

Other Macroscale Transport Processes

Fractured Medium and Macropore Flow and Transport

### Geochemical Processes

Adsorption/Desorption
Precipitation/Dissolution
Aqueous Speciation
Kinetics
Electronic/Chemical
Alterations
Nuclear Alterations
Chemical Associations
Photolysis
Gas Generation

#### Biological Processes

Specific Microbial Processes

General Microbial Processes

are discussed in Sections 4.4 through 4.7 of this chapter.

Some of the major physical, geochemical, and biological processes identified by previous investigators are described in Sections 4.3.1, 4.3.2, and 4.3.3, respectively. A discussion of interactions and interferences is found in Section 4.6.

### 4.3.1 Physical Processes

Size, type, and configuration of leachate plumes in ground water originating from soil contamination are determined partly by hydrologic factors, including width and thickness of the aquifer, its flow characteristics, and physical properties of the contaminants themselves (Repa and Kufs, 1985). Ground water flow patterns tend to exert the greatest influence on plume path and size (Keely et al., 1986; Repa and Kufs, 1985).

In this discussion, physical processes are defined as those which determine the flow of water and the attendant transport of solutes in the subsurface (Kincaid et al., 1984), and only a brief discussion of the most important processes is given. These are listed in Table 11. More basic and comprehensive reviews of fundamental ground water flow theory are given in Freeze and Cherry (1979), Bear (1979), Hillel (1983), and Hanks and Ashcroft (1980). Additional surveys oriented toward modeling of these processes are given by Kincaid et al.

(1984), Repa and Kufs (1985), and Barcelona et al.(1987). Since the historical understanding of flow was developed first for saturated systems and later extended to the unsaturated zone, this review follows the same track (Kincaid et al., 1984). Flow processes in porous media will be described in Sections 4.3.1.1 and 4.3.1.2, and transport processes including advection, dispersion, and diffusion in Section 4.3.1.3. Finally other physical transport considerations such as heat transfer, fractured rock flow, non-aqueous phase transport, and inter-phase transfers will be described in Section 4.3.1.4.

# 4.3.1.1 Flow Processes in Porous Media

Ground water is generally thought to flow in aquifers from higher to lower energy levels, i.e., toward decreasing hydraulic head, along paths of least resistance among the interconnected fractures, joints, or pores that provide flowpaths. Energy levels are reflected by the potentiometric surface, which is the water table if the aquifer is unconfined, and which may be above the level of the upper aquifer/aquitard interface in a confined aquifer. Direction of decreasing energy level, and thus flow direction, often mimics surface topography in unconfined systems, while more direct measurements of flow direction are needed

for confined systems (Repa and Kufs, 1985; Freeze and Cherry, 1979).

Rates of flow are often calculated based on the following empirical relationship derived by Darcy (1856) to determine the quantity of water passing through a soil column per unit time:

$$Q = - KA (h_2 - h_1)/1$$
 (4-1)

where Q is the rate of discharge, K is a proportionality factor defined as the hydraulic conductivity, A is the cross-sectional area through which water flows, h<sub>1</sub> and h<sub>2</sub> are the water elevations above and below the column, A is the cross-sectional area through which water flows, h<sub>1</sub> respectively (the difference being hydraulic head), and 1 is the column length. This is often rearranged to give the average linear velocity of ground water:

$$V_{g} = \frac{KIA}{\eta} \tag{4-2}$$

where  $V_g$  is the average linear velocity, K is the hydraulic conductivity, I is the hydraulic gradient along the path of maximum rate of change in head,  $(h_2-h_1)/1$ , and  $\eta$  is the effective porosity, defined as the ratio of the volume of interconnected pore spaces to total volume of saturated medium, which equals the ratio

of volume of liquid the medium will yield under specific conditions after it is saturated (Freeze and Cherry, 1979).

This expression does not define the velocity of an individual fluid molecule, but rather an average velocity between two distant points along the same flowline. The validity of the Darcy equation is subject to the following assumptions and limitations (Longwell, 1966; Kincaid et al., 1984):

- o The fluid does not interact with the porous medium (e.g., no dissolution, precipitation, or swelling);
- o Fluid flow rates are in the viscous or laminar range (relatively low, such that inertial effects are negligible);
- o Fluid flow rates are in the viscous or laminar range;
- o The fluid is homogeneous and single phase (uniform in density and viscosity, no multiple phases);
- o For gases, the molecular mean free paths are much smaller than the pore diameters of the medium (deviations can occur at normal gas pressures when pore size is very small).

Within these constraints, Darcy's equation generally holds for most natural, uncontaminated saturated systems that are in a single phase and whose water is in chemical equilibrium with the porous medium (Kincaid et al., 1984), and becomes less applicable when ground water systems are chemically or thermally modified or where multiple immiscible fluid phases are present, as

will be discussed in Sections 4.4 and 4.6.

Hydraulic conductivity (K) in equation 4.2 is a key factor: the volume of water that will move through a unit area per unit time when measured orthogonally to the flow direction (Freeze and Cherry, 1979). K is interpreted physically as the rate at which fluid is conducted through a unit thickness of aquifer under the driving force of a unit gradient of fluid (Kincaid et al., 1984). It can be defined as follows (Jorgensen et al., 1982):

$$K = \underbrace{k \rho q}_{V} = \underbrace{k \mu}_{V} \tag{4-3}$$

where k is the intrinsic permeability (a measure of resistance to fluid flow through the medium—a unique property of each medium);  $\rho$  is the fluid density; g is gravitational acceleration;  $\mu$  is the fluid's specific weight; and v is its viscosity. Thus, while k is a property of the medium only, K depends on both the medium and the fluid (Table 12).

Both factors must be considered in using Darcy's equation to predict flow or velocity. First, the dependence of hydraulic conductivity on media characteristics is described in terms of homogeneity and isotropy of the aquifer. An aquifer is homogeneous when K is independent of spatial position, and isotropic if K

TABLE 12

Hydraulic Conductivity Ranges in Subsurface Materials
(Adapted from Repa and Kufs, 1985; and Freeze
and Cherry, 1979)

Geologic Material	Hydraulic Conductivity cm/sec
Gravel	10 <sup>-1</sup> - 10 <sup>2</sup>
Sand, well sorted	10 <sup>-4</sup> - 1
Silty sand	$10^{-5} - 10^{-1}$
Silt	$10^{-7} - 10^{-3}$
Clay, unweathered	$10^{-10} - 10^{-7}$
Glacial till	$10^{-10} - 10^{-4}$
Carbonate rocks	10 <sup>-7</sup> - 1
Sandstones	$10^{-8} - 10^{-4}$
Shales	$10^{-11} - 10^{-7}$
Crystalline rocks	•
Highly fractured	10 <sup>-6</sup> - 1
Relative unfractured	$10^{-12} - 10^{-8}$

is independent of direction of measurement, i.e., equal horizontally and vertically (Freeze and Cherry, 1979; Repa and Kufs, 1985; and others). Most aquifers are heterogeneous and anisotropic; zones of lower permeability and variable shape can exist within a limited geographic area of an aquifer, causing high spatial variability in potentiometric heads and ground water velocity, and plume migration along preferential flowpaths (Repa and Kufs, 1985). This can be handled in Darcy's equation by providing a spatially varying K, but can greatly affect arrival times of different contaminants and their distributions at a point of interest such as a downgradient receptor well (Kincaid et al., 1984). Many models lump these factors within the dispersion process, as will be discussed in Sections 4.3.1.2 and 4.5.

Second, the dependency of hydraulic conductivity, and pressure, on fluid properties, as illustrated in equation 4-3, may cause the hydraulic conductivity of a material to be lower than its pure water value if the fluid is highly viscous; or may cause pressure gradients between locations having zero head gradient because of density differences in the fluid (Repa and Kufs, 1985). This may be insignificant in many field situations (Freeze and Cherry, 1979), but in highly concentrated, dense or multiphase plumes, it may strongly affect

contaminant transport and distribution.

Changes in the effective stress and, consequently, in the storativity of an aquifer can also affect fate and transport of contaminants, especially when soils and/or ground water flows are disturbed through human activities transport of contaminants, especially when soils and/or such as pumping or reinjection of fluids, or installation of soil or synthetic covers (Kincaid et al., 1984; Repa and Kufs, 1985). Flow of ground water as expressed by Darcy's equation and release of water from storage are related through the continuity equation (given in Section 4.3.1.2), which expresses the conservation of mass in the ground water system. The derivation of the continuity equation is given by Freeze and Cherry (1979), Bear (1979), Walton (1970), and Kincaid et al. (1984), among others. This expression allows ground water flow to be calculated in terms of storativity, pressure, density, or piezometric head. See Bear (1979) and Kincaid et al. (1984) for a more detailed treatment of this topic.

The total load of overburden at a specific depth within the aquifer is supported by a combination of pore water pressure and intergranular or effective stress. Changes in pore water pressure produced by pumping or recharge of fluids can alter the effective stress by increasing the overburden load that must be supported by

the soil's effective stress (Kincaid et al., 1984).

Changes in stresses supporting the overburden load can cause expansion or compression of the fluids themselves. This compressibility is limited and is usually neglected in most mathematical simulations (Kincaid et al., 1984).

Changes in effective stress can cause deformation of the porous medium itself, usually causing rearrangement or consolidation of the soils rather than crushing the soil particles. If pore water pressure is reduced, effective stress increases and the soil grains rearrange and consolidate, which often decreases porosity. The pore water itself will expand at the same time, causing a release of water from storage. Specific storativity refers to the volume of water released from a unit aquifer volume in response to a unit reduction in pore water pressure. The process is not fully reversible; reinjection of fluids will not cause total recovery of original porosity of the soil matrix (Kincaid et al., 1984).

Storativity effects, which are time-dependent, become important to contaminant transport in confined aquifers when cyclical pump-and-treat injection/recovery systems are used to treat contaminated ground water, altering matrix characteristics, and thus flow and transport rates, in the process. They also can affect

unconfined aquifers when ground water is diverted or withdrawn rapidly, and are of interest when contaminated soils are consolidated and covered as part of a cleanup (Kincaid et al., 1984).

# 4.3.1.2 Flow Considerations in the Unsaturated Zone

The preceding discussion focused on the principal mechanisms of flow in saturated systems. These will also operate in saturated portions of the vadose zone, as described in Section 4.2.3, but in the unsaturated soils, a gas phase must also be considered that will affect flow of liquids and migration of contaminants. This soil air shares the void spaces with liquid water. The volume of voids, or pore volume, comprises 25 to 40% of the soil matrix of most soils (Kincaid et al., 1984).

As infiltration or leachate enters the soil column, it displaces pore water and may carry contaminants with it. Solutes may move with the infiltration, may transfer among the solid, liquid, or gas phases, or may be attenuated by the mechanisms to be discussed in Sections 4.3.2 and 4.3.3. If retained, the soil may act as a future contamination source to the ground water system.

Soil water content may vary from zero to 100% of the total pore volume. Liquid transport, and thus

contaminant transport as a solute, through this zone will vary according to the relative saturation (Kincaid et al., 1984). At low values, pendular rings of liquid form around soil grain contact points, with saddle-shaped air/ water interfaces determined by capillary forces and interfacial tension between liquid and gas phases. At equilibrium water saturation, a continuous water surface is present across the soil particles, allowing continuous liquid flow. Above this value, soil water content may be described as <u>funicular</u> when air and water phases are continuous, and transport in both phases may occur; or <u>insular</u>, when the air is suspended in individual, discontinuous droplets within the pore space, and air moves by solution into the liquid or by forcing of droplets under pressure.

water movement is determined by the total water potential, which is the sum of the gravitational potential and the soil water potential. The gravitational potential is the vertical difference between the point of interest and a reference point. The soil water potential was defined by Hanks and Ashcroft (1980) as the amount of work that a unit quantity of water in an equilibrium soil-water system can do when moved to a pool of water in the reference state at the same temperature. It is the sum of pressure potential, solute potential, and matric

potential. These terms are defined by Hillel (1983), Kincaid et al. (1984), and others. Water flows from areas of higher to lower total water potential under isothermal conditions.

Matric potential is one of the key components of total potential in the unsaturated soils. It is a measure of the tendency of the matrix to hold water against a negative pressure (suction), and is associated with the capillary pressure across the air/water interface within the soil pores (Kincaid et al., 1984). Greater negative values pressure across the air/water interface within the soil indicate drier soils having higher soil-water attractive forces.

In heterogeneous soils, a plot of matric potential versus depth gives a smooth curve, while soil moisture content plotted versus depth may have discontinuities at interfaces between different soil types (Kincaid et al., 1984). This may argue for use of matric potential rather than soil moisture content as a dependent variable when modeling flow in heterogeneous soil systems. For discussion see Kincaid et al. (1984).

Bear (1979) gave the general equation for motion of liquid water in unsaturated soils as

$$q = k_{ij} \underbrace{K_{rw}(\theta_{v})}_{\mu_{w}} *_{\delta x_{j}} *_{\rho_{w}} g (\psi_{m} - \psi_{p}) - g_{\delta} \rho_{w} z$$

$$[i=1,2,3...]$$

$$(4-4)$$

where  $k_{ij}$  is the permeability tensor at saturation,  $K_{TW}(\theta_V)$  is the relative permeability (given as a function of moisture content), and  $\psi_m$  and  $\psi_p$  are the soil matric and pressure potentials, respectively. At the free water surface as water content nears saturation, the matric potential becomes negligible and the relative permeability approaches 1. This is a unified statement of Darcy's equation, and can be applied to either saturated or unsaturated porous flow.

Bear (1979) gave the continuity equation for conservation of mass of liquid water in the soil medium as

$$\frac{\delta}{\delta t} \rho_W \theta_V + \operatorname{div}(\rho_W q) = 0 \tag{4-5}$$

where q is defined by equation 4-4 above,  $\rho_{\rm W}$  is the density of water, and  $\theta_{\rm V}$  is the pore water content (as a volume measure). This is analogous to the continuity equation for saturated systems presented in Section 4.3.1.1, except that soil water content rather than total porosity must be considered, and permeability is dependent on soil water content as given in equation 4-4.

Kincaid et al. (1984) derived variations of this expression in terms of specific water capacity of the medium, pressure, soil water content, and density, and

provide simplifications for cases of homogeneous fluids and isotropic soils. These two equations, 4-4 and 4-5, when taken together, can be used to describe the movement of fluids within the saturated and unsaturated zones.

# 4.3.1.3 <u>Transport Processes in Porous Media:</u> <u>Advection, Dispersion, and Diffusion</u>

The preceding sections described ground water flow as a basis for discussing physical transport mechanisms based on the movement of ground water in the subsurface. Contaminants are transported by three basic mechanisms: advection/ convection (movement coincident with the resident fluids), dispersion (spreading of contaminants in directions other than the average flow direction), and molecular diffusion (Kincaid et al., 1984).

Fluids and solutes are advected in the aquifer at a rate equal to the pore-water velocity (seepage velocity) or average linear velocity of the ground water (Freeze and Cherry, 1979). Since velocity varies considerably within the pore space, the flow path and velocity of individual fluid and solute particles varies from the average flow path or velocity, spreading the solute along the aquifer in the principal direction of flow.

Dispersion describes the mechanical mixing or spreading of solute in directions other than the

principal flow direction due to these variations in fluid velocity. It may be caused by microscopic factors such as flow path tortuosity (branching and interfingering channels); variability in pore space geometry, which creates drag on fluids contacting the grain surfaces, and velocity profiles within soil or aquifer pores (Freeze and Cherry, 1979; Repa and Kufs, 1985); and by macroscopic variations in fluid velocity due to natural heterogeneities in effective porosity and hydraulic conductivity of the matrix as fluids move through different geologic formations and soil materials (Kincaid et al., 1984; Boutwell et al., 1985).

Dispersion tends to be greatest in fractured bedrock and highly granular aquifers where turbulent flows are possible (Pettyjohn et al., 1982).

Dispersion occurs only when there is fluid movement, in contrast to molecular diffusion, which is the movement of contaminants due to their kinetic activity (Brownian motion) as driven by solute concentration gradients in the transporting fluid (Repa and Kufs, 1985; Kincaid et al., 1984). It occurs irrespective of macroscopic fluid flow, but tends to be slow, requiring long timeframes to exhibit significant effects over relatively short distances; thus it is often ignored in initial contaminant transport investigations (Repa and Kufs, 1985).

Transport of contaminants obeys mass conservation principles as does the transport of liquid through the porous media; thus the continuity equation (4-5) can be written to account for the physical transport of chemical species by subsurface fluids, as follows (Jennings et al., 1982; Rubin and James, 1973; Simpson, 1979:

$$\frac{\delta}{\delta t} \left( \theta_{\alpha} \rho_{\alpha} C \right) + \frac{\delta}{\delta t} \left( \theta_{o} \rho_{o} C_{o} \right) = -\nabla \cdot J + S \tag{4-6}$$

where

 $\theta_{\alpha}$  = volume of liquid per unit volume of the medium  $\rho_{\alpha}$  = mass of solution per unit volume of solution C = mass of solute per unit mass of solution

 $\theta_o$  = volume of solid phase per unit volume

of medium

 $\rho_o$  = mass of solid per unit volume of solid Co = mass of sorbed species per unit volume of solid

J = mass-flux vector of species in solution

S = mass of species per unit time per unit volume of medium (includes source terms and transformations such as root uptake, microbiological transformations, and radioactive decay)

This holds for the unsaturated zone when  $heta_lpha$  is interpreted as soil-water content,  $\theta_o$  is interpreted as soil volume per unit volume of medium that could, or does, react with the contaminant species, and when the mass-flux term accounts for the dependence of its media properties on soil water content. It holds for the saturated zone when  $\theta_{\alpha}$  is interpreted as porosity (  $\eta$  ) and  $\theta_o$  as its conjugate (1- $\eta$ ) (Kincaid et al.,

1984). Note that J, the mass-flux term, accounts for the three primary transport processes (advection, dispersion, and diffusion), as the sum of advective  $(J_a)$  and dispersive  $(J_d)$  fluxes, as follows (Simpson, 1979):

$$J = J_a + J_d = (\rho \alpha q_\alpha C) + (-\rho_\alpha \theta_\alpha D_h \nabla C)$$
(4-7)

where  $q_{\alpha}$  is the Darcy velocity and  $D_h$  is a second-rank tensor of hydrodynamic dispersion coefficients, according to Kincaid et al. (1984). Note that porewater velocity can be substituted for the Darcy velocity if pore volume  $(\theta_{\alpha})$  is considered constant. These massflux terms can be substituted into Equation 4-6 to derive a general form of the advective-dispersive transport equation. If (as in many modeling exercises) one assumes a constant liquid-filled pore space and no transformation reactions (discussed in Section 4.3.2), the generalized equation can be reduced to the following form (Kincaid et al., 1984):

$$\frac{\delta C}{\delta t} = \nabla * D_{h} \nabla C - \underline{q}_{\alpha} * \nabla C + \underline{S}$$

$$\underline{\theta}_{\alpha} \qquad \underline{\rho}_{\alpha} \underline{\theta}_{\alpha} \qquad (4-8)$$

It should be noted that the advective-dispersive equation has been criticized recently as inadequately describing solute transport, for two reasons. First, dispersivity has been classically described by extension

of the Fickian analogy from molecular diffusion, resulting in a mathematical expression showing solute moving upgradient against its concentration gradient more than is sometimes physically possible, irrespective of magnitude and direction of advection. For a complete discussion see Kincaid et al., (1984). Second, field values of both hydraulic gradient and dispersivity are not unique. They vary greatly depending on scale and method of measurement; dispersivity in particular exhibits marked dependence on scale (Keely et al., 1986; Kincaid et al., 1984), partly due to the fact that the foundational theories of solute transport do not provide a mathematically rigorous dispersivity definition that realistically describes the natural system (Sposito et al., 1978; Kincaid et al., 1984).

Investigators are currently reexamining the dispersion process to consider its dependence on solute paths and velocity variations (Gelhar et al., 1979; Barcelona et al., 1985), which may soon provide for improved models based on stochastic-convective concepts and/or kinematic pathline concepts. See Kincaid et al. (1984) for additional discussion of this topic. This also will require research on appropriate field methods for measuring hydraulic conductivities and dispersivities in both the saturated and unsaturated zones (Roberts, 1984; Keely et al., 1986; Repa and Kufs,

1985; Barcelona et al., 1985). The importance of collecting appropriate field data on site-specific transport processes to the soil cleanup level-setting process is discussed further in Sections 3.2 and 4.7.

# 4.3.1.4 Other Macroscale Transport Processes

The foregoing flow and transport discussions generally assume constant and uniform flow fields for ease of mathematical description. This is often not the case, especially in the surface and unsaturated zones, because of man-induced alterations in flow fields beneath a site due to ground water diversion, capping, pumping, or other actions (discussed in Section 4.6); and because of the transient nature of many flow phenomena comprising the hydrologic cycle, such as infiltration, runoff, erosion, drainage, evapotranspiration, and volatilization. These and other non-bulk-flow-related transport mechanisms, such as gas phase transport and facilitated transport, are discussed briefly below.

Rain droplets and wind can erode contaminated surfaces, detaching particulates for subsequent wind and water transport. Bulk water movement in the surface soil zone occurs as runoff or overland flow, which can entrain soil particles containing sorbed contaminants, or which can dissolve contaminants directly from soil or

waste surfaces, and transport them to surfaces and surface waters off-site, as described in Section 3.1.2. Methods of estimating rates and amounts of contaminant transfer from the site due to erosion and overland flow (e.g, by use of the Universal Soil Loss equation) are reviewed in Boutwell et al.(1985), Cowherd et al.(1985), and Schultz et al. (1987) among others.

Some precipitation, liquid wastes, or leachates may move downward through the unsaturated zone as infiltration, due to progressive wetting of underlying soils, gravity, and hydrostatic pressure, as described in Sections 4.2 and 4.3.1.2 (Boutwell et al., 1985). Infiltration depends on many factors including soil type, organic matter content, rate of water supply to the soil surface, antecedent soil moisture content, and vegetative cover which provides interception storage. It is high just after onset of a precipitation event and decreases as the soil profile becomes saturated (Boutwell et al., 1985), its minimum value being the saturated hydraulic conductivity of the soil. Infiltration rates may be estimated simply as an average value, as calculated by Linsley et al. (1982) and Holtan et al.(1975), or linked to precipitation as a step function in numerical models (see Boutwell et al., 1985; Schultz et al., 1987; Kincaid et al., 1984 for examples, and Section 4.8 for more discussion).

Fluids are transferred from the unsaturated zone to the saturated zones through drainage, the rate of which is affected by matric potential and degree of pore-water saturation, as described in Section 4.3.1.2.

Evapotranspiration and volatilization can be very important to physical transport of water and contaminants in the surface and unsaturated zones, where a gas phase is present in the soil pore spaces.

Evapotranspiration may include direct evaporation of water vapor from soil, water or ice surfaces and transpiration by plants. Rates depend on atmospheric water demand, moisture amounts available for evaporation and soil moisture content, soil type and permeability, type and amount of vegetative cover, soil and air temperatures, relative humidity, and other meteorological factors.

The quantitative basis for estimating rates is reviewed by Hillel (1983) and Kincaid et al. (1984). Methods based on pan evaporation data, energy budgets, the hydrologic cycle, the aerodynamic profile, and meteorological data are reviewed by Linsley et al. (1982), Hanks and Ashcroft (1980), and others. Root water-extraction models are reviewed by Molz (1981).

Under certain conditions, transport of contaminant through the subsurface in the gas phase may be substantial, especially of volatile organic compounds

moving through coarser, more porous media under favorable temperatures and pressures. Amounts, pathways, and extent of gas-phase transport is highly variable and dependent on both contaminant properties including density, viscosity, Henry's law constant, and on media properties including intrinsic porosity and permeability, organic carbon content, soil moisture content, pore size, and other factors. Diffusive mechanisms are generally thought to predominate over convective mechanisms (Barcelona et al., 1985). This phenomenon has been used to trace ground water plumes through analysis of soil gases with varying degrees of success.

Facilitated transport refers collectively to those mechanisms that may cause contaminant transport at faster rates than expected on the basis of solute transport coincident with Darcian flow, as modified by equilibrium sorption. The latter topic will be discussed in Section 4.3.2. Its effects are most evident in anomalous movement of large, complex molecules that are relatively insoluble in water, such as oils and other complex hydrophobic organics and may result in, for example, more distant transport or earlier arrival of contaminants at receptor wells than predicted by water movement alone. This phenomenon has been observed at several Superfund sites as well as in

bank filtration studies in the Netherlands (Piwoni, 1986).

Several hypothesized mechanisms include cosolvent effects (as regularly induced in agriculture to apply hydrophobic pesticides in aqueous mixtures; Keely et al., 1986); multiphase transport of micelles or microdroplets; and transport of fine particulates carrying hydrophobic compounds sorbed on their surfaces. Many of these effects are evidenced for contaminants having densities, temperatures, or viscosities differing significantly from those of the fluid (ground water) carrier. These effects will be discussed further in Section 4.4.

## 4.3.1.5 <u>Fractured Medium and Macropore</u> <u>Flow and Transport</u>

As mentioned in Section 4.3.1.1, subsurface materials are seldom homogeneous in terms of pore size and shape or hydraulic conductivity, and may change abruptly within short distances. Soils may contain cracks and channels (macropores) due to freeze-thaw effects, roots, burrowing animals, differential settling or expansion, and physical and chemical erosive processes. Rock materials often contain zones of secondary porosity such as bedding plane interfaces, fractures, faults, or solution cavities (Repa and Kufs,

macropores or rock fractures may produce much more rapid breakthrough downgradient of the source (Barcelona et al., 1985) than would be predicted by the mechanisms discussed in Sections 4.3.1.1 through 4.3.1.3. For example, flow rates in unfractured media have been measured between 0.3 and 4400 feet/year (Walker, 1973; Apgar and Langmuir, 1971; Jackson, 1980; Repa and Kufs, 1985), while Wedderburn (1977) measured tracer movements through limestone cavities at rates up to 1.47 million feet/year.

Generally, fractures will comprise a small fraction of a bedrock aquifer's total porosity, and most of the fluid is stored in the rock matrix. However, individual fractures may often have apertures many times the average matrix pore space, thus representing the primary flow paths. Hydraulic conductivity of the fracture system is dependent on fracture spacing, aperture distribution, and degree and frequency of interconnectedness of the fractures (Kincaid et al., 1984; Repa and Kufs, 1985); thus it varies greatly by rock type.

Alternatively, faults and bedding planes may act as flow barriers, if they trend across or obliquely to the direction of ground water flow, or if their voids are cemented by clay or silicate microparticulates brought

to the channels by facilitated transport mechanisms as mentioned in the preceding section. Faults and fractures likewise can provide facilitated transport mechanisms as mentioned in the conduits for interconnection of aquifers which otherwise appear to be isolated by impervious strata (Repa and Kufs, 1985, and others).

Jackson (1980) noted that transformation processes (discussed in Sections 4.3.2 and 4.3.3) can also affect contaminant migration in fracture zones in two general ways: (1) when large amounts of adsorptive or reactive substances coat the fracture surfaces (e.g., chlorite, illite, other clay minerals, carbonates, and various oxides), and (2) when slower flows and higher primary porosities allow significant levels of diffusion of contaminants directly into the rock matrix over which they are passing.

Currently, most mathematical estimates of fracture flow are made by determining porous-media equivalent parameters and using porous-media flow and transport equations (idealizing the aquifer as a homogeneous, isotropic system, or as an isotropic system of regular, interconnected fractures separated by impervious blocks of rock matrix; Kincaid et al., 1984; Barenblatt et al., 1960). Repa and Kufs (1985) and Kincaid et al.(1984) caution against use of mass transport approximations

based only on rock matrix properties. Neither flow nor transport is understood for fractured systems as well as for porous media systems at this time (Barcelona et al., 1985; Kincaid et al., 1984), though much research in this field is ongoing under the high-level nuclear waste disposal programs of the U.S. Nuclear Regulatory Commission and the governments of Canada, France, and Sweden (Kincaid et al., 1984). This phenomenon, and other site and hydrogeologic effects on fate and transport, are discussed further in Section 4.5.

### 4.3.2 Geochemical Processes

The preceding discussion focused on physical factors affecting concentration and distribution of contaminants presuming that they are ideal, nonreactive substances that, for the most part, are transported with the infiltration and ground water. However, few compounds will behave in this manner in the subsurface. As solute moves from the contaminated soils source through the subsurface matrix, its concentration will tend to change, and it may be subject to a variety of geochemical interactions that may enhance or retard its mobility within the transporting fluid, for example through the two primary mechanisms of sorption and precipitation, or transform its constituent chemical species to more or less toxic forms.

Different soil contaminants will tend to be attenuated or retarded by some processes more than others.

Cationic metals such as cadmium, zinc, copper, lead, chromium III, and mercury are attenuated by both sorption and precipitation at rates and extents affected by such factors as pH, free lime content, cation exchange capacity, soil particle surface area, and free iron oxide content (Repa and Kufs, 1985). Among anions commonly occurring in waste site leachates, phosphate is the least mobile, while nitrate and chloride tend to be highly mobile (Repa and Kufs, 1985). The minimal degree of attenuation of nitrate and chloride in most aquifers has led to their frequent use as indicators of plume migration (Kurtz and Melsted, 1973; Lindorff and Cartwright, 1977; Roberts et al., 1980).

Organic contaminants may be attenuated in one of three general ways in ground water: through rapid, complete degradation or precipitation; through partial sorption or precipitation, with sorption occurring at a slowly decreasing rate; through slow degradation, with degradation rate gradually increasing to some steady rate (Roberts et al., 1980). Repa and Kufs (1985) assembled the following list of generalizations concerning organic contaminant behavior in aquifers, based on the findings of Wilson et al. (1980), Roberts et al., (1980), and Lindorff and Cartwright (1977),

## among others:

- o Volatilization rates for low-molecular-weight contaminants are inhibited by the distance they must travel to reach a free water surface, and by the slow turnover rate for soil pore air within the unsaturated zone compartment;
- o Organics tend to be attenuated less than inorganics;
- o More attenuation occurs due to biochemical than to geochemical attenuation processes;
- o Some organic contaminants may be tightly sorbed to soil or aquifer particles;
- The degradation of simpler, less toxic compounds is more pronounced than that of more complex, generally more toxic contaminants;
- o Some organic pollutants may sorb from solution onto organics within the matrix;
- o Less soluble, more hydrophobic contaminants tend to have lower mobilities and slower migration rates than highly soluble, hydrophilic contaminants;
- o Tracing an organic plume's source may often be complicated by the degradation of the organic contaminants within the soils and ground water (Keely, 1987A; Barcelona et al., 1987);
- o The presence of some organic contaminants in the soils or leachate can influence the sorption and attenuation characteristics of others.

Keely et al. (1986) stated that while to some extent, the scientific understanding of these chemical interactions has been translated into predictive models, in certain areas the state of knowledge outpaces current modeling capabilities; while in others, many of the geochemical processes influencing contaminant mobility on a site-specific basis are not yet well defined.

Chemical interactions are introduced into the advection/ dispersion equation (Section 4.3.1) through a time derivative of the solid phase mass in terms of the time rate of change of storage of a given contaminant in the porous medium (often interpreted as a source/sink mechanism), as illustrated in the following equation describing this term for the j<sup>th</sup> compound (Kincaid et al., 1984):

$$\frac{\delta}{\delta t} C_{j}(q,t) = -\overline{V}*\nabla \cdot C_{j}(q,t) + D_{j}\nabla^{2}C_{j}(q,t) +$$

$$\omega_{j}(q,t) - \pi_{j}(q,t)$$
(4-9)

where  $C_j$  is the concentration of the j<sup>th</sup> compound;  $\overline{V}$  is the velocity vector;  $\nabla^2$  is the Laplacian operator;  $D_j$  is a "diffusion type coefficient constant;"  $w_j(q,t)$  is the rate of deposition of compound, by precipitation or adsorption, within the volume element; and  $\pi_j(q,t)$  is the corresponding rate of dissolution, ion exchange, or desorption within the volume element. Q represents an orthogonal coordinate system. The sum of  $(w_j + \pi_j)$  is defined as the source/sink term; at equilibrium, this term becomes zero.

As indicated above, two fundamental geochemical processes are believed to affect the sink/source term: adsorption/ desorption and precipitation/dissolution. Several additional processes indirectly control this

term, including aqueous speciation; kinetics and mass transfer; electrochemical alterations including oxidation/ reduction, ionic interactions, hydration and hydrolysis, and isomorphic substitutions; nuclear alterations including radionuclide decay; chemical associations including ion exchange, complexation, and cosolvation (and its reverse, partitioning into immiscible phases); degradation mechanisms such as photolysis; and gas generation (reviewed by Barcelona et al., 1987; Repa and Kufs, 1985; Boutwell et al., 1985; Kincaid et al., 1984; and others). These are discussed briefly in the following sections.

## 4.3.2.1 Adsorption/Desorption

Keely et al. (1986) stated that sorption processes are perhaps the most widely studied of the surface interactions affecting organic compounds in the subsurface. Adsorption and desorption of contaminants on active soil particles is an important process even at very low concentrations (Kincaid et al., 1984; Keely et al., 1986). Adsorption can be generally divided into two categories: specific adsorption and ion exchange.

Soils generally contain minerals that readily exchange cations or anions. In ion exchange, charged ions in the transporting fluid may exchange with ions on the matrix surface such that a metallic cation such as

Na+ or K+ in the aqueous fluid may exchange with H+ on the mineral surface, generally in weak bonds wherein most of the bond energy arises from electrostatic attractions of the exchanging ions to the charges associated with the mineral surface. This process may be highly selective for certain elements, and may shift the pH of the aquifer fluid (Kincaid et al., 1984).

Cation exchange is affected by other reactions in the subsurface including the weathering of clay minerals, redox reactions (discussed below), and decomposition of aquifer constituents, as well as the leachate and ground water cation composition (Repa and Kufs, 1985). Cations such as zinc and copper may become tightly sorbed, and then become unavailable for ion exchange due to secondary reactions. Nonionic contaminants may also exhibit strong sorption due to van der Waals forces, covalent bonds, polar attraction, weak hydrogen bonding, and other processes (Repa and Kufs, 1985).

Specific adsorption refers to strong ionic bonding or complexation of aqueous contaminant species with the matrix surfaces for example, when Cu<sup>2+</sup> ions form complexes by reacting with a surface hydroxy site. The distribution of a chemical element among its various ionic species will thus strongly affect the rate of sorption processes. Likewise, different models may be

needed to describe specific adsorption processes versus ion exchange processes (Kincaid et al., 1984).

Contaminant retardation, especially of organics, in the subsurface is frequently estimated using contaminant specific partition coefficients based on sorption isotherms, which relate the amount of contaminant in solution to the amount associated with the solid medium, usually through batch or column experiments. Linear isotherms indicate that the ratio at which the contaminant is partitioned between the two phases is independent of its equilibrium solution concentration. Nonlinear isotherms indicate that partitioning depends on the equilibrium solution concentration (Keely et al., 1986).

Modeling exercises are often based on linear sorption estimates for simplicity; however, this may cause mass balance errors whereby the contaminant mass in the fluid phase is underestimated and retardation is overestimated, thus overpredicting arrival times and concentrations at the downgradient receptor locations in many instances (Keely et al., 1986). Modelers may attempt to account for this discrepancy between predicted and observed results by adjusting other model parameters (e.g., dispersion) that may be likewise characterized inadequately, producing qualitatively and quantitatively erroneous model predictions.

This points to the need for improved mechanisms to describe and account for nonlinear sorption phenomena (Keely et al., 1986).

Likewise, researchers have begun to consider the importance of the time dependency of sorption.

Simplified models often contained assumptions of instantaneous, fully reversible sorption processes for the principal contaminant species of interest; however, recent research results suggest that the opposite may be the case, for smaller solvent molecules in low-carbon aquifer systems as well as for large hydrophobic organic molecules in subsurface environments having a relatively high total organic carbon (TOC) content (Keely et al., 1986). Kinetic effects are discussed further in Section 4.3.2.4.

As discussed in Section 4.3.1.4, even when contaminants are tightly sorbed to matrix surfaces, contaminant mobility may occur through facilitated transport mechanisms not accounted for through the sink/source term. Examples include Superfund sites underlain by glacial tills having a broad particle size distribution, where fine particulates (sometimes bearing sorbed contaminants) have accumulated in monitoring wells; and ferrous colloids found in wells at sites contaminated by domestic wastes (Keely et al., 1986). More research is required to evaluate the relative

importance of facilitated transport among the various mechanisms transforming and transporting contaminants at a given site.

## 4.3.2.2 Precipitation/Dissolution

Natural materials and contaminants alike may be precipitated when their solubility product, the product of activities of the combination of reacting aqueous species, exceeds a given value. This process is dependent on pH, temperature, and the physical and chemical properties of the fluid and the porous medium. For example, concentrated acids percolating after a spill into a highly carbonaceous soil or rock matrix with a high buffering capacity will dissolve minerals and simultaneously may be neutralized (Kincaid et al., 1984).

As neutralization occurs, solubility products of some compounds may be exceeded, leading to precipitation. The precipitates may differ by location and chemical composition based on microscale differences in equilibrium conditions. In some circumstances, these precipitation and dissolution processes could significantly alter flow paths through the porous medium as existing channels become plugged by precipitates and new flow paths are chemically eroded in the matrix (Kincaid et al., 1984; Repa and Kufs, 1985). In extreme

cases the flow models used to describe such sites might require modification to account for such chemical changes, for example by coupling the flow and chemical portions of the code (Kincaid et al., 1984; Boutwell et al., 1985). These effects, and some examples, are discussed further in Sections 4.4 and 4.5.

# 4.3.2.3 Aqueous Speciation

Aqueous phase chemical elements often form complex species or aqueous ion pairs. Typically these will tend to increase an element's fluid phase concentration, and thus the species of the major contaminants must be accounted for in order to accurately estimate sorption and precipitation, either by providing empirical activity coefficients or by including the major aqueous complexes directly (Kincaid et al., 1984). Failure to adequately account for these terms may lead to predictions of sorption or precipitation of a given compound at a lower fluid phase concentration than might actually be observed in the field, thus overpredicting retardation overall.

#### 4.3.2.4 Kinetics

As described previously, in some circumstances chemical kinetics may be much slower than predicted, thus invalidating the assumptions of chemical

equilibrium, reversibility, etc., and the predicted concentrations based on these assumptions. Kincaid et al. (1984) divided these cases into three broad categories:

- I. When rate of flow far exceeds the reaction rate for some compound j, the concentration of j exiting a unit volume would approximately equal its influent concentration.
- II. When flow rate is approximately equivalent to j's reaction rate, the effluent concentration will not equal the influent concentration, but will be determined by a combination of chemical equilibrium and reaction kinetics.
  - III. When the reaction rate is rapid relative to flow rate through the unit subsurface volume, effluent concentration can be expected to equal j's equilibrium concentration.

Temperature, leachate and ground water flow rates, and physical/ chemical composition of the matrix all influence the kinetic category for each contaminant of interest. Reaction rates increase with temperature, causing contaminants to shift from Category I to II and from II to III. Increasing flow rates cause the opposite to occur. Spatial changes in physical factors, such as surface area/ volume ratio of soil materials containing sorbed contaminants or precipitates, can also shift reactions to higher or lower categories (Kincaid et al., 1984).

As heterogeneity of the aquifer increases, the accuracy of sorption kinetic terms predicted by batch

sorption studies may decrease, especially for less mobile contaminants (Keely et al., 1986). In more complex systems, and at higher contaminant concentrations, observed sorption kinetics may deviate from batch sorption estimates due to increasing nonlinearity of the response.

Keely et al. (1986) suggested that a littleunderstood, subtle interplay between ground water flow
rates and sorption kinetics may be increasingly
important at higher flow rates such as may routinely be
expected in pump-and-treat actions to remediate
contaminated ground water. Laboratory soil column
studies have shown that metal attenuation rates
decreased with increasing flow rate (Alessi et al.,
1980), and site properties such as degree of soil
compaction and presence of low permeability layers
likewise affected metal attenuation rates (Repa and
Kufs, 1985). The effects of site conditions and of such
alterations of the physical and chemical subsurface
regimes on contaminant transport are discussed further
in Sections 4.5 and 4.6.

# 4.3.2.5 <u>Electronic/Chemical Alterations</u>

Keely et al. (1986) included oxidation/reduction, hydrolysis, substitution, and elimination reactions in this category. Redox reactions are especially important

for metals and other multivalent elements that can change valence states in aqueous media. Redox reactions may change a contaminant's solubility, sorptive behavior in the medium, or complexing capability, all of which may alter its mobility and/or toxicity (Keely et al., 1986; Kincaid et al., 1984). In addition, sorption of some anionic metals such as arsenic, selenium, and chromium VI+ increases with decreasing pH, and seems unaffected by ionic strength (Griffin and Shimp, 1978).

Therefore, the ability of a model to account for pH and oxidation state may significantly influence its accuracy in such situations. Likewise, kinetics must be for pH and oxidation state may significantly influence its considered, as such reactions are often slow and require substantial energy to break strong chemical bonds (Kincaid et al., 1984). While redox reactions are fundamentally well understood, they are more difficult to understand in the subsurface environment since the redox state of the soil or aquifer zone is difficult to determine, and the redox-active contaminants are not always readily identified or accurately measured in the Remedial Investigation (Keely et al., 1986).

Ions in aqueous solution tend to cluster as a result of their charges, modifying their equilibrium kinetics in various reactions. This is described thermodynamically in terms of the activity, defined as

the product of the concentration and the activity coefficient (Kincaid et al., 1984). The activity rather than the concentration must be used in thermodynamic calculations. Activity coefficients usually are derived semi-empirically using equations based on the Debye-Huckel theory of ion clustering, which calculates the extent of ion clustering based on charge density (as based on ionic strength; Kincaid et al., 1984). As ionic strength of leachate increases, the amount of cationic sorption decreases (Fuller, 1982). Various terms and coefficients for activity coefficients were summarized by Kincaid et al. (1984).

Elimination, substitution, and hydrolysis reactions are also part of this category. For example, some minerals such as alums, manganese oxides, amorphic iron, and zeolites allow relatively free substitution of ions within their matrices (Kincaid et al., 1984). While these processes have been well studied for many organic compounds in surface waters, their application to subsurface conditions is not as straightforward (Keely et al., 1986). Long residence times and other factors may lead to different results than those predicted on the basis of surface water kinetics. Current research efforts are underway to address these factors. Kincaid et al.(1984) suggested that the importance of some of these processes, such as isomorphic substitution, to

overall fate and transport at the majority of Superfund sites may be minor relative to other processes discussed in this chapter.

# 4.3.2.6 Nuclear Alterations

Radiodecay is the principal example in this category. This process may occur by several routes, but its rare is always directly proportional to the number of radioactive atoms present; thus processes involving each radionuclide can be readily characterized.

However, if in a transport model, the decay constant is applied to the contaminant's fluid concentration without regard to precipitation, sorption, or ion exchange events that may temporarily (or permanently, with respect to the timeframe of the analysis) remove the radionuclide from solution, errors in prediction of resultant concentrations may occur (Keely et al., 1986).

# 4.3.2.7 Chemical Associations

Keely et al. (1986) stated that processes leading to formation of new associations with other chemical species are not yet well understood for subsurface media, largely due to the nonspecific, nonstoichiometric nature of many reactions in complex subsurface environments. Such processes include ion exchange, complexation, contaminant-solvation, and phase

partitioning.

Complexation of organic compounds with natural humic and fulvic substances can significantly enhance the contaminants' apparent solubility and mobility, and is a subject of current research. If the chelating agent is a humic or fulvic acid, the chelated metals may be removed from solution (Repa and Kufs, 1985). Metalorganic complexes likewise may form under certain conditions (Keely et al., 1986). Some hydrolyzable metals (e.g., lead) may become chelated by certain organic compounds even when the lead was undissolved originally. When chelated, the metal may become highly mobile and remain in solution, remaining unavailable for precipitation or sorption (Griffin and Shimp, 1978).

Contaminant-solvation occurs when the water solubility of an otherwise relatively hydrophobic compound, such as a complex organic molecule with a high octanol-water partition coefficient, is enhanced by the presence of an organic solvent in the aqueous medium, as is done commonly for application of many organic pesticides. Keely et al. (1986) stated that current understanding of this phenomenon in the subsurface renders accurate site-specific predictions virtually impossible, although current research is underway using relatively simple solvent- contaminant mixtures.

As described in Section 4.2.3, the converse

situation in the extreme occurs, for example, in spills of petroleum hydrocarbons or other hydrophobic liquids in relatively large quantities and pure form, such as fuel oil spills or leaks from underground storage tanks (EPA, 1987E), in which a separate phase of relatively pure product may move through the subsurface, and partitioning of contaminant between aqueous and organic phases is likewise occurring. Keely et al. (1986) point out a wide range of possible effects, from enhancing to retarding the aqueous-phase mobility of the contaminant, interfering with chemical and biological transformation processes (by affecting the availability of the contaminant for other reactions), and increasing the volume of ground water affected by the release event through equilibrium partitioning.

#### 4.3.2.8 Photolysis

This process can significantly transform many complex organic compounds in surface waters (Zepp, 1988), but clearly will affect only the surface soil zone at terrestrial Superfund sites. Therefore, its relative contribution to overall distribution and transformation of contaminants is relatively minor at many sites, unless contaminants occur primarily distribution and transformation of contaminants is relatively within the upper few centimeters of this

zone. Some research is underway to better define the significance of this process at Superfund sites.

## 4.3.2.9 Gas Generation

Jackson (1980) reported that gas movement can occur through subsurface soils under unsaturated conditions in more porous soils, if gases are not dissolved in ground water. It favors aerobic breakdown of organic substances, and can lead to conditions where constituents that are more mobile under oxidized conditions can predominate, while substances such as iron or manganese may be more readily solubilized under anaerobic conditions.

reactions, which could create unsaturated areas within the saturated zone, complicating the flow (Kincaid et al., 1984). Carbon dioxide, oxygen, and ammonia are the gases most likely to be generated under such conditions. Note that they can also shift pH and redox state of the subsurface in localized areas. The relative importance of this phenomenon is highly site specific sand likely may be minimal at many sites.

#### 4.3.3 Biological Processes

Biological processes traditionally have been considered to affect the transformation of soil

contaminants more than their transport. This is the general case for most of the geochemical processes discussed previously in this chapter.

Certain macrobiological activities, however, are known to affect flow and transport of infiltration and soil contaminants in surface soils and in the unsaturated zone. These include the enhancement of surface weathering and erosion by plant roots; formation of soil channels by plant roots, burrowing mammals, and macroinvertebrates; and enhanced evapotranspiration of subsurface water and contaminants by plants. Further, it is now known that subsurface microbial activity may modify porosity and permeability of waste source areas and of underlying soils and aquifer matrices (Kincaid et al., 1984). However, the preponderance of biological effects to be considered here involve the microbial transformation of contaminants.

Until recently, it was also generally believed that subsoils and aquifers generally were sterile.

Biological transformation processes were thought to be largely confined to the topmost few meters of the surface soil zone, primarily as energy and nutrient cycling reactions and decomposition processes involving plants, terrestrial organisms, and soil macro- and microfauna (Walton and Edwards, 1986; and others).

These include, for example, nutrient and water uptake and exchange through the roots of growing plants; burrowing, food storage, and metabolic activity of terrestrial vertebrates on and beneath the soil surface; and nutrient cycling and other activities by invertebrates and microorganisms within the soil column. Bacterial decomposition processes in the surface soil zone are relatively well understood, and have been employed for many years for land treatment of municipal and industrial wastes and wastewater treatment sludges (Loehr, 1986; Huddleston et al., 1986; Ryan et al., 1986; and others).

Recent research has indicated that, in fact, the deeper subsurface zones often contain relatively dense microbial populations, sometimes reaching a million organisms per gram dry soil in uncontaminated aquifers (Barcelona et al., 1987). Rates of biodegradation of specific contaminants have been found to vary widely—by two to three orders of magnitude between aquifers. Similar variations have been recorded vertically, over a few meters distance within the same zone. However, natural biodegradation rates may be sufficiently rapid to protect ground water quality in many aquifers; natural biorestoration likely remediates many smaller-scale contamination events before they are ever detected (Barcelona et al., 1987).

Several factors are known to affect biodegradation rates and capacities in the subsurface, including temperature, pH, dissolved oxygen level, redox potential, salinity, soil moisture, the types and concentrations of contaminants present, microbial form and growth state of the community, types and extents of competetive interactions among resident microbial species, nutrient and mineral availabilities, and types and extents of competetive interactions among resident the nutritional quality of dissolved organic carbon in the ground water (Kincaid et al., 1984; Barcelona et al., 1987).

Typically, an initial lag period may follow the introduction of the contaminant front or slug, during which resident microbial populations become adapted to the changed nutrient and substrate conditions. This period may be greater for most anaerobes than for most aerobes due to slower metabolic processes (Wilson and Rees, 1985). Populations of "metabolically capable" microorganisms then increase, feeding on the contaminant substrate, until they are limited by a metabolic requirement for a substrate, specific mineral nutrients, or oxygen (in the case of aerobes). At this limiting point, biotransformation rates become controlled by the rate of transport processes supplying the limiting material (Barcelona et al., 1987).

Most microorganisms are attached to soil or aquifer

matrix particles. Keely et al. (1986) report that less than one percent of the microbial population is planktonic in most cases; thus population counts based only on ground water samples often are unrepresentative of the actual in situ populations. Advection and diffusion mechanisms, therefore, are important for supplying nutrients in the aqueous phase (by aqueous transport) or the soil gases (by gas transport through the unsaturated zone). In the saturated zone, aerobic biotransformation may be limited by the very low solubility of oxygen in water and by slow diffusion rates. Barcelona et al. (1987) listed the following general solubility of oxygen in water and by slow diffusion rates. determinants of biotransformation rate:

- o Stoichiometry of the particular metabolic process;
- o Microbial toxicity of the pollutant or of cooccurring substances;
- o Opportunities for colonization by metabolically capable organisms;
- o Concentrations of necessary nutrients in the fluid phase(s); and
- o Advective flow within the fluid phase (and/or magnitude of concentration gradients available to drive diffusion).

Much research is currently underway to better define the relative roles and effects of these environmental parameters.

The important processes of microbial transformation were grouped into two broad categories by Kincaid et al. (1984), as follows:

- Specific processes—these include transformation of organic contaminants to carbon dioxide, production of organometallic chelates, methylation of certain metals, biofouling, delivery of dissolved oxygen and nutrients, and protonation/ deprotonation; and
- o <u>General processes</u>--these include microbial colonization and growth, and responses to changes in substrates.

These are discussed briefly below.

## 4.3.3.1 Specific Microbial Processes

Microbial respiration processes can convert organic contaminants to carbon dioxide, either within a single organism, or by a mixed population transforming contaminants through a sequence of intermediate daughter products to carbon dioxide. For example, the chlorinated ethylenes undergo sequential reductive dehalogenation from tetrachloroethylene to trichloroethylene to (predominantly) cisdichloroethylene, and eventually to vinyl chloride, which may then be further catabolized under other subsurface conditions (Wood et al., 1985). Vinyl chloride is more toxic than its parent compounds; its environmental fate is not well understood (Wilson and Rees, 1985). Chloroalkanes follow similar reductive

dehalogenation sequences, which are similar to respirations in that the chlorinated compounds accept electrons and are reduced to their complementary hydrogenated forms, accompanied by the release of chloride ion. Electron donors for reductive dehalogenation of TCE have included landfill leachates and geologic materials such as flooded surface soils, and buried peats or coal seams (Barcelona et al., 1987).

rirst- or second-order rate equations were originally developed to describe these transformations in surface waters (Keely et al., 1986; Kincaid et al., 1984). First-order equations generally describe solid-substrate transformations, defined as the amount of contaminant transformed per unit time per unit weight of substrate. Second-order rates are given as the amount of contaminant transformed per unit time and per unit weight of active biomass.

As described in Section 4.3.2.7, hydrolyzable metals such as lead may become chelated by organic contaminants under certain conditions. Frequently these reactions, which may be microbially mediated, render the organometallic complexes available for biological uptake and increase the metals' mobility (Kincaid et al., 1984; Griffin and Shimp, 1978).

Organic contaminants may be transformed microbially, and subsequently may react with metals to

modify them directly (e.g., methylation). As contrasted with chelate formation, however, methylation is strictly anaerobic. Affected metals include arsenic, mercury, and selenium, among others. Methylation rates may be limited by either the metal substrate concentration or the organic agent concentration, depending on the specific reaction, and the relative abundances of each factor (Kincaid et al., 1984).

Biofouling is the reduction of ground water flow due to the constriction or plugging of matrix pore spaces, or due to increased frictional coefficient of the flowing ground water. This can occur due to extensive microbial growth on the surfaces of the soil or aquifer matrix particles in conditions where inorganic nutrient and metabolyzable organic carbon levels are not rate limiting (Kincaid et al., 1984), and may be similar to the effects of chemical precipitation on flow rates, as discussed in Section 4.3.2.2 (Repa and Kufs, 1985). The ability to interpret and predict such effects is currently under study.

As mentioned previously, physical and chemical properties of the substrate, such as temperature, pH dissolved oxygen content, or nutrient levels, can significantly affect types and extents of biotransformation reactions in a given subsurface setting, by affecting physiological states of

microorganisms and the size and composition of the microbial community present and actively catabolizing contaminant substrates. Protonation or deprotonation of a compound, for example, can change its bioavailability and thus, rates of its biotransformation.

For many of the compounds degraded aerobically, oxygen availability will generally be the limiting factor. For many of the solvents, approximately two moles of oxygen are required per mole of organic compound to achieve complete degradation to carbon dioxide. For example, well-oxygenated ground water containing 4 mg/l of oxygen can transform only about 2 mg/l of benzene, although the water solubility of Thus, only low concentrations of benzene is 1780 mg/l. benzene likely would be be completely degraded by biological mechanisms alone (i.e., within a few orders of magnitude of EPA's current MCL for benzene in drinking water of 0.005 mg/l); at higher levels, additional remedial measures are necessary (Barcelona et al., 1987).

At higher contaminant concentrations, available oxygen may be exhausted, and aerobic transformation will cease, but other bacteria, such as anaerobic methane-, sulfate-, or nitrate respiring species, can continue to degrade many contaminants, as illustrated in Table 13.

For example, until recently it was believed that benzene,

	CONTAMINA	CONTAMINANT BIOTRANSFORMATION IN SOILS AND GROUND WATER EXAMPLES FROM RECENT RESEARCH (Adapted from Barcelona et al., 1987)	IN SOILS AND GROENT RESEARCH ona et al., 1987	UND WATER: )	
Contaminant(s) Affected	Metabolic Requirement	Reaction Sequence/ Product(s)	Site/Waste Type	Cossents	Investigator
Acetone, isopropanol, methanol, ethanol, t-butanol, tolugne, benzene, xylenes, other alkylbenzenes	Aerobes	See original references	Gasoline, solvent spills		Novak et al. (1984) Lee & Ward (1984) Jhaveri and Mazzacca (1983) Wilson et al.
Fluorene, acenaphthene, naphthalene, methyl-naphthalenes, dibenzo-furans, other polyaromatic hydro-carbons	Aerobes	See original reference	Diesel fuel, heating oil spills		
Methylated phenols, heterocyclic organics	Aerobes	Not reported	Industrial wastewaters		Barcelona et al. (1987)
Dichlorobenzene, mono-, di-, trichloro- phenols, nitrilo- triacetic acid, methylene chloride	Aerobes	See original references			Kuhn et al. (1985) Suflita and Miller (1985) Ward (1985) Jhaveri and Mazzacca (1983)
PCE, TCE, cis-, trans- 1,2-dichloroethylene, 1,2-dichloroethane, 1,1,1-trichloroethane, 1,1,2-trichloroethane, chloroform, carbon	Methane, Propane, Other gaseous aliphatics (methanogens)	Not reported	Solvent- contaminated aquifers, underground storage tank leaks	Persistent compounds in oxygenated ground waters; cometabolized	Barcelona et al. (1987) Roberts et al. (1980)

TABLE 13 (Continued)

		TABLE 13 (Continued)	ontinued)		
Contaminant(s) Affected	Metabolic Requirement	Reaction Sequence/ Product(s)	Site/Waste Type	Comments	Investigator
Benzene, toluene, xylenes, other alkylbenzenes, methyl- and chlorophenols	Methanogens	See original references	Landfill- contaminated river sedi- ments; jet fuel- contaminated	At least half the carbon was fully metabolized to CO2 as shown by radioisotope tracers	Wilson and Rees (1985) Suflita and Miller (1985) Barcelona et al. (1987)
TCE, tetrachloro- ethylene, 1,1,1- dichloroethane, dichloroethylenes, chloroform, carbon tetrachloride, ethylene dibromide	Methanogens	Sequential reductive dehalogenation of chlorinated ethylenes to vinyl chloride, chloroalkanes to ethyl chloride	Contaminated methanogenic aquifers	Reaction products may be more toxic than parent compounds (e.g., vinyl chloride)	Parsons et al. (1984) Wood et al. (1985) Wilson and Rees (1985)
Phenols, cresols, xylenes, carbon tetrachloride, brominated methanes	Zitrate Trate	See original references	Contaminated river sediments	Not shown to degrade chloroform or chlorinated ethylenes,	Kuhn et al. (1985) Barcelona et al. (1987) Bouwer and McCarty (1983)
Tetrachloroethylene, TCE	Sulfate	Reductive dehalogenations	Contaminated river sediments	Chlorinated aromatics not degraded	Suflita and Gibson (1984) Suflita and

toluene, the xylenes, and other alkylbenzenes could only be degraded aerobically, since the one enzyme known to begin catabolism of this compound class requires oxygen as a contaminant substrate (Young, 1984). However, Wilson and Rees (1985) and Suflita and Miller (1985) reported extensive breakdown of these compounds in methanogenic river sediment materials contaminated with landfill leachate, such that at least half the carbon substrate added to samples spiked with radiolabeled toluene was degraded completely to carbon dioxide. Methanogens and nitrate- or sulfate-respiring bacteria may individually be able to degrade only a limited subset of the organic contaminants present at such a site, but they often participate in consortia with other microorganisms which can degrade other contaminants to forms available to the methanogens or sulfate-using species (Keely et al., 1986; Barcelona et al., 1987). Ability to model these processes accurately is still in the early stages of development, however.

#### 4.3.3.2 General Microbial Processes

The general processes most important to predictions of fate and transport at Superfund sites include growth and colonization processes occurring at a particular site, and the responses of its microbial community to alterations in substrate conditions (Kincaid et al.,

1984). Many of the site and contaminant factors believed to control rate and extent of colonization of a region initially lacking a significant microbial population have been mentioned earlier in this section, and will be reviewed in Sections 4.4 and 4.5. As substrate conditions change (e.g., concentrations of soluble salts, nutrient status, pH, Eh, etc.), the stability and composition of the microbial community may be affected markedly. Kincaid et al. (1984) asserted that predictive modeling of biotransformations should account for the following:

- Biotransformations are caused by simultanously occurring metabolic and cometabolic processes;
- o Some fraction of the resident microbial population is unaffected by the substrate changes;
- o Some substrate changes may be lethal to a sensitive subpopulation of microorganisms, and cause deleterious sublethal effects in others; and
- Metabolizing organisms may grow on both the introduced contaminant substrate source and the preexisting carbon source, while sensitive or contaminantmetabolizing organisms may be growing on the preexisting substrate carbon alone.

Field studies must collect the appropriate data to account for these factors; for example, microcosm studies of soil and aquifer samples, rather than ground water samples alone, may be needed to accurately determine first-order rate constants and fully represent the disappearance kinetics of a given soil or ground

water contaminant, especially if in situ remedies are being considered (Keely et al., 1986).

## 4.4 <u>Waste/Leachate Characteristics Affecting Fate</u> and <u>Transport</u>

Numerous examples have been presented throughout Section 4.3 to indicate the importance of the physical and chemical properties of the contaminant and leachate at a given site to the particular combination of transport and transformation processes acting to bring those contaminants and their products from source soils to ground water receptors. The types and concentrations of soil contaminants, and of the overlying wastes that may have been present originally to contribute to the existing soil and ground water contamination strongly influence the physical and chemical properties of leachate produced by this source. These in turn affect its flow and transformation characteristics, as described in Section 4.3.

The leachate rarely resembles the wastes from which it was produced, however (Repa and Kufs, 1985; and others). Thus, while the majority of wastes and contaminants of concern at Superfund sites are organic compounds, as discussed in Section 1.3, and while similarities in contaminant distributions (both organic and inorganic) might be inferred within each category of sites presented therein (Camp, Dresser and McKee, 1985A),

great variability in leachate composition and plume dynamics exists from site to site because of these modifying factors (Repa and Kufs, 1985). Physical and chemical properties of concern are summarized briefly below.

#### 4.4.1 Physical Properties

Repa and Kufs (1985) listed several physical parameters that they considered to be the most important when collecting field data or interpreting it to predict contaminant fate and transport. These include volume, viscosity, density, solubility (in water and in any predominating immiscible fluids or solvents), distribution or dispersion of the contaminants, and temperature or heat content.

Leachate quantity influences the overall volume and the flow rate of the ground water plume. Several site factors affect leachate quantity, including the type, amount, duration, and frequency of precipitation; evapotranspiration regimes including annual temperature fluctuation and amounts of insolation; site surface characteristics including slope steepness and length, vegetative cover types and abundances, and soil types and permeability; and subsurface factors including presence of water within the waste or contaminated soils mass, and rates and volumes of flow through the wastes

and soils (Repa and Kufs, 1985). These will be discussed further in Section 4.5.

Various water balance approaches have been used to estimate leachate production rates and quantities, most of which assume that source materials are not in direct contact with flowing ground water. These are discussed by Fenn et al. (1975) and Perrier and Gibson (1980). They form input distributions to several classes of models, as will be discussed further in Section 4.8.

Viscosity is another critical factor, as shown in derivations of the advection-dispersion equation and discussions of porous flow in Section 4.3.1. More viscous leachates would generally be expected to disperse less than less viscous ones, and to flow more slowly. Leachates more viscous than ground water would be expected to decrease the hydraulic conductivity of the system; however, field results indicate that leachate viscosity has relatively little influence on hydraulic conductivity (Jackson, 1980).

Leachate density will significantly affect its
transport and transformation characteristics, if the
density differs significantly from that of the ambient
ground water. Contaminants released to soil are
actively drawn into it by capillary action and gravity.
As the main contaminant slug migrates downward to
moister soil layers, the influence of gravity generally

becomes more important than capillary effects (Wilson and Conrad, 1984).

Low density wastes will tend to float at the top of the aquifer, and spread to form lenses of contaminants that have been measured up to tens of feet in thickness at some sites (Lindorff and Cartwright, 1977; EPA, 1987C; and others). Low density plumes often remain more concentrated than other leachates, especially since they often contain petroleum hydrocarbons or other relatively water-insoluble contaminants (Repa and Kufs, 1985; Barcelona et al., 1987). Higher density contaminants will continue to migrate downward once they enter the saturated zone, and can form concentrated layers near the base of the zone. This behavior was observed by Lindorff and Cartwright (1977) in chloride contaminants from oil production that entered a New Mexico aquifer, and in seawater intrusion interfaces in many coastal aquifers (Linsley et al., 1982).

High density contaminants may migrate downward in structurally controlled patterns (i.e., downdip or along faults or fracture planes) in directions opposite to the regional ground water flow (Repa and Kufs, 1985), although this behavior may be difficult to identify using conventional ground water monitoring schemes (Keely, 1987A; Barcelona et al., 1987; EPA, 1986D). Interactions between density and solubility will be

discussed further in Section 4.4.2.

Temperature and density may be closely correlated, as will other characteristics such as water solubility, reaction kinetics, and content of oxygen and other dissolved gases. Temperature of ground water generally changes relatively little within a subsurface zone due to its high specific heat capacity relative to matrix materials. It has been used as a tracer in some experimental settings, and has been used to track contaminant plume movement at some field sites, as well as vertical flows and aquifer recharge by rivers.

Leachate and contaminant temperatures could be elevated due to exothermic chemical transformations, aerobic decomposition, or other factors (such as geothermal influences or remedial actions). Warmer leachates will be more buoyant than surrounding waters, and will tend to rise within the aquifer zone. Temperature will affect pressure and viscosity as well, shifting flow directions and rates. It may increase the leachate's reaction rates with matrix and aquifer materials, and increase volatilization of some contaminant species.

Highly reactive contaminants could degrade interconnecting layers between isolated ground water zones. When hot furfural wastes (175 F) were injected into a confined, saline, carbonaceous aquifer in Florida,

they collected near the upper aquitard, dissolving portions of the confining layer (McKenzie, 1976).

Mathematical expressions addressing heat transport in the subsurface are reviewed in Kincaid et al. (1984).

## 4.4.2 Chemical Properties

Chemical properties of interest were discussed throughout Section 4.3.2, but a few are reviewed briefly here and summarized in Table 14. Repa and Kufs (1985) asserted that many processes are acting in concert at a given site, or in a specific subsurface microenvironment beneath the site, such that not all soil contaminants may reach, or be transported in, the ground water. Attenuation in soils and in ground water is a function of the interrelationship of these factors, including forms, quantities, and concentrations of each contaminant in the contaminant/soil mixture; physical and chemical properties of the contaminant mixture, the soils, and the leachate and ground water; flow rates and patterns; and surface areas, porosities, and types of geologic materials encountered by the contaminants as they move through the compartments of the soil- ground water system.

Water solubility is a key property having both physical and chemical influences on contaminant migration and fate. For example, some hydrocarbons or

# TABLE 14 Contaminant Behavior Observed in Landfills (Sources: Repa and Kufs, 1985; Jackson, 1980)

Chemical Waste	Behavior
Halogenated Organic Compounds	Evaporation (because of volatility) and sorption onto other solid wastes present may reduce the release of halo-solvents to groundwater.
Phenol s	Phenois are relatively soluble in groundwater, undergo biodegradation slowly, and are reversibly sorbed.
PCBs	Readily soluble in hydrocarbons, but not in water. Biodegradation inhibited by anaerobic conditions. Readily sorbed. PCBs are relatively inert within landfills and are not leached by water in high concentrations.
Mineral Oils	Sorption of oils onto solid fill material is an important attenuation process. Floats on groundwater because of low density relative to groundwater.
Organic Solvents	Some sorption on landfill materials and some biodegradation in sands and gravels have been observed.
Acids	Leaches sorbed contaminants and dissolves precipitates, thereby causing deterioration of groundwater quality. Inhibits microbiological activity. Releases harmful gases.
Cyanide (CN)	Most CN either volatilizes as HCN, or precipitates as cyanoferrate II compounds.
Heavy metals (e.g., Cr, Zn, Hg, Pb, Cd)	Heavy-metal cations (e.g., $Pb^{+2}$ , $Hg^{+2}$ , $Cd^{+2}$ ) controlled primarily by their insolubility as metal sulfides, carbonates, hydroxides or phosphates, and secondarily by sorption. Anionic forms (e.g., $Cr_2O_7^{-2}$ ) very mobile.

other relatively hydrophobic contaminants may be immobilized in the unsaturated zone until they are physically, chemically, or biologically removed (Barcelona et al., 1987). While liquid phase hydrocarbons are generally considered immiscible in both air and water, the individual constituents will volatilize into the air phase and dissolve into the aqueous phase such that a halo of dissolved hydrocarbons will precede the immiscible front in or atop the aquifer.

Some hydrocarbon is trapped in the pore spaces by processes known as by-passing and snap-off, remaining as pendular rings or isolated blobs in larger voids containing slower flows (Wilson and Conrad, 1984; Barcelona et al., 1987). These remnants may remain in the unsaturated zone at residual levels undetected in ground water samples, yet occupying 15 to 40 percent of the void volume. They will continue to contaminate ground water when, for example, recontacted by a fluctuating seasonal high ground water table, allowing small amounts of soluble components to be leached into the aqueous phase over long time periods (Barcelona et al., 1987; Cleary et al., 1985).

Residual hydrocarbon contaminants may be apparently remobilized through ground water pumping, but this may only redistribute the blobs within the matrix pore spaces

(Wilson and Conrad, 1984), and will often show rapid initial declines in ground water concentrations followed by a leveling off where ground water contains virtually undetectable hydrocarbon concentrations, while core samples contain substantial residual levels not accessible through physical remediation techniques. This phenomenon is the subject of intense research.

Mackay et al. (1985) pointed out that even in a relatively homogeneous subsurface matrix, the net effect of physical and chemical processes on a complex mixture of contaminants having different chemical characteristics may be such that a set of complex plumes may be created by a single, multi-contaminant, continuous source. In such a case, breakthrough of the most mobile contaminant at a downgradient receptor well may indicate the front of several overlapping plumes, each characterized by different contaminants migrating at different rates, which may continue to reach the well at levels potentially harmful to public health and the environment for many years following removal of the source.

#### 4.5 Site/Subsurface Factors Affecting Fate and Transport

Numerous examples were presented throughout Section
4.3 to indicate the importance of the physical
characteristics of a site to the particular combination

of transport and transformation processes acting to bring its contaminants, and their products, from source soils to ground water receptors. The location, climate, hydrogeological setting, and current and former land use patterns of the site and its immediate surroundings strongly influence the flow and transport regimes beneath it, and the transformation and fate of leachate produced by this source, as described in Section 4.3. Some of these factors are reviewed briefly in the following subsections.

#### 4.5.1 Site Factors

Attenuation rates and mechanisms of soil contaminants will be affected by site factors, including volumes and rates of infiltration percolating through the soil or waste source, density and solubility of contaminants, contact time between the contaminant source and the leaching medium, age of the site, initial moisture content of the source, rate of ground water flow receiving leachate, and various anthropogenic factors (Repa and Kufs, 1985).

Key climatic, topographic, and subsurface factors related to production of infiltration and its association with the contaminant soil source were discussed by Repa and Kufs (1985). Many of these are controlled by the hydrologic regime of the site.

National Priorities List sites are distributed throughout the continental United States and its territories in a wide variety of climatic and hydrogeologic settings. Climatic factors influence the volume of infiltration produced, and the amount reaching the ground water table, as well as the percent of time that contaminated soils will be moist or saturated.

These factors affect the types and amounts of contaminants that can desorb or become dissolved into the infiltrate, or volatilize to the soil gases and the atmosphere. They include precipitation types, amounts and durations (wet/dry cycles); mean annual temperature and thermal cycles; freeze-thaw cycles and amounts of snow cover; relative humidity and potential evapotranspiration; and amounts of surface run-on and runoff at the site (Linsley et al., 1982; Freeze and Cherry, 1979; and others).

Surface topography often influences the amount of run-on al., 1982; Freeze and Cherry, 1979; and others). and precipitation that can be expected to infiltrate to ground water, as well as the hydrology of many unconfined or water-table aquifers whose water table elevation may generally conform to the land surface contours (Freeze and Cherry, 1979), except at hydrologic divides or boundaries represented by recharge or discharge areas. Permeability and porosity of surface

soils and materials often will be greater at a hazardous waste site than in its immediate surroundings for two reasons: (1) the waste mass itself, such as a landfill or waste pile, is often highly permeable; and (2) soils near and beneath waste management units are often disturbed and may be composed of unconsolidated and/or uncompacted materials, as is the case surrounding buried piping in many instances (Cleary et al., 1985). The elevated permeability can lead to mounding of leachate or ground water beneath the site (Freeze and Cherry, 1979), and leachate penetrating the subsurface may move radially outward.

In a natural recharge area, the vertical gradient draws contaminants downward deeper into the saturated zone; while in discharge areas, the upward gradient exacerbates the mounding beneath the high-permeability area. Porous soils along buried structures, e.g, pipeline trenches or building foundations, can provide preferential contaminant migration pathways away from the site, as can movement along root channels, animal burrows, soil joints, or rock fractures as discussed in Section 4.3.1.5.

Transport of contaminants from Superfund sites

located near rivers, in floodplains, or in coastal zones
where the ground water table is directly affected by

flood waters, river stage, or tides, will likewise be

affected by changes in water table elevations and sometimes of flow directions and rates due to these influences (Repa and Kufs, 1985; Barcelona et al., 1987). The effects of cyclic water table fluctuations and surface water/aquifer interactions are discussed by Pettyjohn et al. (1982) and Hantush (1967), respectively. If the water body receives discharge from the contaminated aquifer(s), a smaller volume of aquifer is likely to be contaminated before the plume disperses into the surface water body and its sediments (Lindorff and Cartwright, 1977; Fenn et al., 1980).

Soil types and land use patterns also will strongly affect flow and transport processes at the site. Past land and soil use practices will affect the nutrient status and capacity of soils for biotransformation processes, as well as the background levels of various contaminants, for example, levels of pesticides in agricultural areas (Hern and Melancon, 1986), metals in industrial or mining areas, or organic compounds in urban or highly industrial settings (Carey and Gowen, 1976).

The site's age, and the time period over which the soils were in contact with wastes and contaminants, likewise will affect both the magnitude and nature of the source term, and add to the difficulties in simulating it using simplified expressions. First, the

soil/ contaminant interactions are transient over time and space. Different contaminants may have been disposed over time by intermittent intentional discharges to the soils, or by pulsed releases following floods, snowmelt, or rainfall events. Second, if the site was historically used for hazardous waste disposal and such practices caused the soil contaminant, strong acids and bases and nonpolar organic solvents may have been the primary leachates moving through soils at certain periods. Corrosives and solvents can change surface and subsurface soil characteristics in several important ways (Matrecon, 1983):

- o Alteration of natural aggregation properties (flocculation, dispersion);
- o Modification of sorption characteristics;
- Modifications in pore dimensions and configuration via precipitation, dissolution, or biofouling (see Sections 4.3.2, 4.3.3), changing flow paths/rates; and
- o Changes to natural shrink/swell properties.

Amount of vegetative cover will also affect wind erosion, volatilization, evapotranspiration (Kincaid et al., 1984), and runoff patterns (Mills et al., 1985; Boutwell et al., 1985). For a discussion of simplified estimation methods see Schwab et al. (1966); U.S. Department of Agriculture (1974); 1985). For a discussion of simplified estimation methods see Williams

(1975); Haith (1980); and Mills et al. (1982).

#### 4.5.2 Subsurface Factors

As emphasized throughout Section 4.3.1, the size and configuration of a leachate plume derived from contaminated soils are strongly influenced by subsurface geometry and geology, and by physical properties of both the matrix and the aquifer fluid. These properties include heterogeneity in aquifer geometry, porosity, and permeability; ground water flow rates; interconnection between conductive layers; and other factors which interact with leachate physical and chemical properties (described in Section 4.4).

Plume shape can be determined in a relatively straightforward manner in large, homogeneous, isotropic strata, as illustrated by the idealized plume of water-soluble contaminant in the upper (unconfined) saturated zone in Figure 6. However, many productive aquifers are not characterized by broad, tabular, sedimentary layers, but by elongated, sinuous lenses typified by buried former stream channels. These may be difficult to trace over distances when they occur as pods, sinuous or braided ribbons, or variable and complex belts (Pettyjohn, 1975), and difficult to model using many of the assumptions required by simplified codes (Boutwell et al., 1985; Kincaid et al., 1984).

Aquifer size can influence plume migration rates as well, since as size or thickness decreases (assuming the zone of interest is confined by aquitards), for example when a sandy aquifer pinches out in the direction of flow, ground water velocity and plume migration rates increase, since the same volume of ground water must flow through a smaller cross sectional area of aquifer. The opposite effect may be observed in conductive zones that broaden or expand in the downgradient direction (Repa and Kufs, 1985).

Flow rates and directions are likewise difficult to interpret or predict when a subsurface zone is highly heterogeneous with respect to hydraulic conductivity, for example in multilayered sedimentary deposits, and in formations with secondary porosity (e.g., uplifted or tilted strata offering flowpaths along joints, bedding planes, or fractures; shear zones along faults; and solution channels through carbonacous deposits), as illustrated in the lower formations shown in Figure 6. Such features may offer highly permeable conduits or highly impervious barriers, causing significant redirection of flows from predicted paths, as described in Section 4.3.1.5. Simplified calculations of fracture flow rates and distributions often use an average hydraulic conductivity intermediate between the primary and secondary porosities of the matrix, and use

adaptations of porous media flow and transport codes (reviewed by Kincaid et al., 1984; and others), which may not allow accurate porous media flow and transport codes (reviewed by Kincaid et estimation of fate and transport.

Some contaminant characteristics such as density and water solubility may be especially affected by geological factors such as porosity and structural continuity of the matrix, as described in Sections 4.3.2.7 and 4.4.1. Repa and Kufs (1985) and Freeze and Cherry (1979), among others, provide additional discussions of other effects of subsurface geology on contaminant flow and transport.

#### 4.6 Effects of Human Interactions

Repa and Kufs (1985) listed several human activities that can modify the flow of uncontaminated ground water, as well as the flow and transport properties of contaminants in the unsaturated and saturated zones, including changes in the ground water table; alterations of hydraulic gradients; changes in recharge and discharge areas; diverting overland and ground water flows; changing rates of leachate production; and containment or removal of leachate or of the contaminant plume. These changes could be caused by typical land use activities and surface and ground water

uses in the site vicinity, as well as by intentional site remediation activities, for example:

- o Manmade structures such as foundations, pipeline trenches, mines, and tunnels can provide porous conduits for preferential flow (discussed in Section 4.5.1);
- o Irrigation structures, lakes, ponds, surface impoundments, and drainage ditches can cause discharge or recharge of ground water;
- o Agricultural and industrial uses of surface and ground water near the site, such as various irrigation and cultivation practices, can change soil moisture and evapotranspiration regimes;
- o Construction or mine dewatering techniques, such as use of low-permeability subsurface barriers, drainage ditches, french drains, or extensive ground water pumping, can alter hydraulic gradients and flow regimes near or beneath the site; and
- O Use of extraction wells, injection wells, solution mining, infiltration galleries, or other remedial measures in or around the site itself, can alter ground water elevations, gradients, and flow paths (see Table 15).

As discussed in Section 4.3.2.4, extensive application of pump-and-treat methods to capture a ground water plume, for example via constant pumpage at rates several times greater than natural flow rates, may not allow contaminants sorbed to solids sufficient time to reach equilibrium concentrations in the dissolved phase before the ground water is extracted. Thus, ground water concentrations initially may decrease to undetectable levels, then a subsequent sample taken some time after pumping is stopped may again yield high

TABLE 15 Effects of Various Remedial Actions on Flow and Transport (Source: Repa and Kufs, 1985)

Remedial Action Measure		General Effects		Effects on Leachate Plume
Sealing of site surfaces, grading, revegetating and	1	Reduces the amount of water (from rain, snow or surface		Minimizes the volume of leachate generated.
diverting surface water from site		run-on) that infiltrates into the site and flows through the wastes.	2.	May result in a short-term increase in the concentra-
•	2.	Reduces groundwater recharge and mounding beneath the site.		plume because less dilution will occur.
			m	Concentrations of water soluble constituents from above the water table should be reduced in the leachate because solubilization is less likely.
			<b>~</b>	Radial spread of the plume beneath the landfill will be reduced.
Installing subsurface low permeability barriers upgradient from site	<b></b>	Initially diverts uncontaminated groundwater away from the site and the plume.	<b>=</b>	Initially reduces the like- hood of horizontal ground- water flow through the waste site bottom.
	۶.	Initially reduces the water table evaluation on the down-gradient (waste site) side.	2. exp	9

TABLE 15 (Continued)

Effects on Leachate Plume	3. Temporarily lessens the potential for leachate dilution	4. May temporarily reduce the severity of conditions within the lower parts of the waste site.	5. Should temporarily reduce amount of dissolution occurring (if waste was previously in contact with groundwater).	6. Reduces the flow rate of the plume.	7. Slightly reduces the degree of plume extent.	8. May result in a short-term increase in the concentration of contaminants in the plume because less dilution will occur.
	<b>(*)</b>	•	•			-
General Effects	. Initially reduces the flow rate on the downgradient side because the hydraulic gradient is reduced.					
	3.					
Remedial Action Measure	Installing of subsurface low permeability barriers upgradient from site (cont'd)		•			

Slower flow rates can allow additional attention and degradation to occur.

6

TABLE 15 (Continued)

Remedial Action Measure		General Effects		Effects on Leachate Plume
Installing subsurface,	-	1. Minimizes groundwater movement downgradient from barrier.	-	1. Prevents longitudinal migration of plume.
downgradient from the site	2.	<ol> <li>Causes rise in water table elevation upgradient from wall unless groundwater pumping or subsurface drains are used.</li> </ol>	<b>.</b>	Causes lateral migration of the plume along the sub- surface barrier unless groundwater pumping sub- surface drains are used.
Installing subsurface, low permeability barriers completely		1. Isolates groundwater in the site area from regional ground-	-	Prevents longitudinal migration of plume.
surrounding the site	2.	water. 2. Reduces groundwater velocity.	2.	Minimizes dilution of leachate

Allows dewatering of the

Reduces cost of treating

TABLE 15 (Continued)

Remedial Ac	Remedial Action Measure		General Effects		Effects on Leachate Plume
Permeable 9	Permeable Subsurface Treatment Beds	-	Modify groundwater chemistry by introducing sorptive or chemically active substances such as activated carbon or crushed limestone.	<b>-</b>	May reduce concentration of certain contaminants via sorption, precipitation or neutralization.
		.5	May cause local increases in flow velocity through the beds.	<b>.</b>	2. May change pH and solids content of leachate.
Groundwater Pumping	r Pumping	-	Upgradient pumping wells reduce the amount of groundwater flowing through the site and lower the	-	Upgradient wells can help stabilize the plume if operated carefully
		2.	water table elevations locally Downgradient pumping wells reduce the amount of groundwater		Downgradient wells can be used to extract the plume if pumped or divert the plume if used for injection
			the water table in localized areas downgradient of the site.	m	Wells may not affect all of plume if not properly sited.
Installing Subsu Drainage System	Installing Subsurface Drainage System	1:	1. Same as for groundwater pumping.	1:	Same as for groundwater pumping but with less of a change of allowing enhance-

TABLE 15 (Continued)

Remedial Action Measure	General Effects	Effects on Leachate Plume
Biorec lamation	1. Allows microbial degradation within contaminated aquifers.	1. Promotes microbial degrada- tion of plume constituents
		2. Can alter physical and chemical properties of the

contaminant levels from residual contaminants still sorbed to the matrix (Keely et al., 1986). This phenomenon is still under study. All these factors must be taken into account when planning a Remedial Investigation and when selecting the appropriate mathematical methods to simulate contaminant transport beneath the site.

### 4.7 Estimating Fate and Transport

To describe the processes of fate and transport occurring at a given site, and the key site and waste parameters influencing these processes, a variety of physical and mathematical simulation methods can be used, as will be described in Section 4.8. Chief among these for purposes of this report are mathematical models describing the process equations given in the preceding sections.

Development of a deterministic mathematical model to describe transport of contaminants through soils or ground water begins with construction of a conceptual model of system characteristics and processes. For example, initially one can describe physical relationships of soil-liquid and ground water flow, and flow directions and rates, in terms of general hydraulic gradients in/near a site.

Processes are then described by mathematical process

equations linking parameters (for example, hydraulic conductivity values or hydrolysis rates in the natural system) and variables (e.g., inputs such as temperature, precipitation/infiltration rates, or outputs such as storage, flow, chemical concentration; Donigan and Dean, 1985; Donigan and Rao, 1986A,B). For example, based on Darcy's law, many have developed governing equations for conservation of momentum as fluid flows through soils and the aquifer matrix (Mercer and Faust, 1980A), as discussed in Section 4.3. The roles of some of the key parameters within the equations describing some of the major processes were summarized by Jury and Valentine (1986).

Depending on the stage of the Remedial

Investigation and its level of detail, the amount of
data available to characterize the field values of key
parameters will vary greatly. As will be discussed in
Sections 4.8.3 and 4.8.4, the analyst's knowledge of the
actual values of key site and process parameters, and of
their spatial and temporal distribution at the site, is
critical to the choice of model or other estimation
technique.

As discussed by Jury and Valentine (1986), Boutwell et al. (1985), Repa and Kufs (1985), and others, the key parameters tend to be distributed in five broad categories. Some properties will show little variation

in the field, such as many of the static soil properties; thus, they can be characterized by relatively few samples. Others, such as many of the basic chemical properties, can be measured on the wastes or contaminants in the absence of the soil matrix, or even in some cases from laboratory bench studies or literature- derived values. Lyman et al. (1982) provided one of the most comprehensive published handbooks on initial estimation of contaminant properties.

A third category, including for example many water transport and retention properties, often have different characteristics, and/or higher coefficients of variation, when measured on extracted samples versus field conditions. Examples include soil moisture retention curves and hydraulic conductivity measurements, especially when K is estimated Examples include soil moisture retention curves and hydraulic from well pumping tests. See Keely (1987A), Matrecon (1983), Freeze and Cherry (1979), and Repa and Kufs (1985) for additional discussion of this topic.

A fourth group includes parameters which vary temporally; their range of variation will not be represented by a single "snapshot" sampling event. The fifth group, including many soil sorption parameters, must be measured in the laboratory, although translating

laboratory derived values to the field setting is often difficult. A variation of the last group is characterized by tortuosity functions for soil, which cannot be thoroughly characterized in laboratory tests and are more reliably represented by models, such as the Millington and Quirk model describing the effect of soil water content on liquid and vapor diffusion in the soil matrix (Jury and Valentine, 1986). These five parameter categories are summarized in Table 16.

Therefore, one of the key decisions to be made iteratively throughout the site characterization process will be determining when and what kinds of additional data is necessary to obtain a sufficient level of confidence in the conceptual model of the site or in the prediction of the soil cleanup target. This problem has been discussed by many authors, for example by Jury (1986A,B), who discussed the spatial variability of key soil properties affecting fate and transport, and their effects on the statistical representativeness yielded by various soil sampling strategies. Sampling schemes are further discussed and reviewed by Mason (1983); Barth and Mason (1984); EPA (1986K); and Camp, Dresser and McKee (1987A).

## 4.8 <u>Using Models in Exposure Assessments</u>

In Sections 4.2 and 4.3, the soil-ground water

TABLE 16

Categories of Key Soil Properties/Model Parameters
(Adapted from Jury, 1986A)

P	ARAMETER	WHERE DETERMINED
1.	STATIC SOIL PROPERTIES	
+•	Porosity	Lab
	Bulk density	Lab
	Particle size	Lab
	Percent composition	Lab
	Specific surface area	Lab
	pH	Lab
	Cation exchange capacity	Lab
	Organic carbon content	Lab
	Organic Carbon Concent	Dab
2.	WATER TRANSPORT/RETENTION P	PROPERTIES
	Matric potential/water cont	
	function	Field, Lab
	Saturated hydraulic	·
	conductivity	Lab, Field
	Unsaturated hydraulic	·
	conductivity	Lab, Field
	Water flux	Field
	Volatilization flux	Field
	Solute velocities	Lab
	Solute dispersion	
	coefficient	Lab
3.	BASIC CHEMICAL PROPERTIES	_
	Vapor pressure	Lab
	Henry's law constant	Calculated
	Octanol-water partition	
	coefficient	Lab
	Vapor diffusion coefficient	: Literature
	Liquid diffusion	
	coefficient	Literature
4.	TIME DEPENDENT PARAMETERS	
4.	Water content	Field to Lab
	Potential evaporation	Field to Laz
	Solute concentration	Field
	Volatilization boundary	1 1014
		Calculated
	layer thickness	Calculaceu

# TABLE 16 (Continued)

P	ARAMETER	WHERE DETERMINED
5.	SOIL ADSORPTION PARAMETERS Freundlich Isotherm Distribution coefficient Organic carbon partition coefficient	Lab Lab Calculated
6.	TORTUOSITY FUNCTIONS Liquid diffusion tortuosity Vapor diffusion tortuosity	Lab Lab

conceptual system was introduced, and the primary natural processes affecting transport and transformation of contaminants migrating from a soil source to ground water receptors were described. Sections 4.4 through 4.6 listed site and waste characteristics, and anthropogenic influences, that could affect the naturally occurring transport/ transformation processes at a given Superfund site. In the preceding section, simple techniques for estimating some of these parameters and effects were introduced. This section focuses on describing how these fate and transport processes can be modeled; compilations of available models; and some principles that are currently employed to varying degrees to assist in the selection and use of models to simulate soil and ground water systems and to describe Superfund ground water contamination problems.

Models as discussed herein are representations or approximations of natural terrestrial soil- ground water systems, or of one or more of their constituent components, which in most cases are constructed and operated to simulate and analyze system behavior under past, current, or future conditions (Donigan and Rao, 1986). Models can be conceptual, physical, or mathematical in form. They can be used to simulate physical flow and transport processes, as well as geochemical and biological transformation processes, for

many purposes including the following (Mercer and Faust, 1980A; Office of Technology Assessment, 1982; van der Heijde et al., 1985; Bachmat et al., 1978; Barcelona et al., 1987; Keely, 1987A):

- o Assessing quantity, and providing for management of ground water aquifers or basins (i.e., water resource planning, allocation, and management);
- Assessing physical and environmental impacts of withdrawal or injection schemes, e.g., mine dewatering, land subsidence, coastal aquifer seawater intrusion, oil and gas production and waste management, etc.;
- o Assessing ground water chemical and biological quality, and impacts of land uses thereon, at the regional level;
- o Predicting and analyzing outcomes of various source control or aquifer remedial actions, at the site specific level; and
- o Estimating exposure levels and contaminant concentrations at a receptor location at different times under different scenarios.

Possibly their most frequent use is for history matching. This means calibrating the model to the field situation it is to simulate. Models are also used for site-specific prediction of aquifer and/or soil system behavior under a variety of "what if" situations (Mercer and Faust, 1980A; Donigan and Rao, 1986; and others).

A tremendous number and variety of models have been published in recent years. They vary greatly in characteristics, complexity, and level of detail. Some represent fluid flows only, in one, two, or three

spatial dimensions; while others are (or can be combined with) algorithms representing contaminant transport or transformation. Some are for continuous, steady-state conditions while others can represent transient episodes; some codes are proprietary and can be used only through purchase of a license agreement, while a great many others are in the public domain.

Section 4.8.1 provides an overview of the categories of soil and ground water models used to simulate migration and transformation of water and contaminants in soils and ground water, from the interdisciplinary model user's perspective rather than that of the hydrogeologist or modeler. It is not intended to be comprehensive description of the types and uses of models, nor a comprehensive derivation of the mathematical bases of the various methods. For more detailed discussion of general principles, many fundamental texts can be consulted including Freeze and Cherry (1979) and Bear (1979), among others. For more information on specific model categories, the reader is referred to the specific references in each subsection.

Many reviews and compilations of models have been published in recent years. The main features of some of the more prominent reviews are summarized in Table 17. Because this field is expanding so rapidly, many model compilations become outdated soon after their

TABLE 17. Recent Model Reviews and Compilations

Author of compilation	Year of publication	No. of sodele	Describes model features and parameters	Considera level of available documentation	Cites published reference for models considered	Considers andel per formance	Includes code	Includes earple problem	Critques models	Provides model postre or primary contact
Appel & Bredehoeft	9/61	23	<b>*</b>		ĸ	×				×
Ault & van der Heijde	1984	₹	ĸ							×
Rachmut et al.	1980	250	ĸ	ĸ		×				×
Boutwell et al.	1985	92	ĸ					×	ĸ	×
Cirhowicz & Ficke	1986	91	ĸ	×	×	ĸ			ĸ	ĸ
Codell et al.	1982	•	×	Ħ	×	×	×	ĸ	×	*
Coben & Miller	1983	¥	ĸ							×
EPA	1982F	103	<b>K</b>		*					×
GCA Corp.	1985	01	×	×					ĸ	
Javandel et al.	1986	31	×	×			×	*		×
Kincaid et al.	1984	11	×	*	ĸ	×		×	×	×
Mock	1985	=	×			×			×	ĸ
Hoiser et al	1980	102	ĸ		×		•			×
Onter	1987	\$\$/10	×	sk	×	×			ĸ	ĸ
Swedish Muclear	1984	22	×		¥	×		×		×
Thomas et al.	1982	111/181	ĸ	×	×	×	ĸ		ĸ	×
0.80%	1984	13								×
115GS	1985	<u>\$</u>								×
van Genuchten	1978	20	×		×					*
van der Heidje	1484	39	×							×
Van der Heidje 6 Brinivasen	9961	797	ĸ							*

publication, as existing codes are constantly being refined and updated, and new ones are constantly being developed. Therefore, a compilation of models was not included in this report. Several authors have argued that the fluid nature of this field dictated that the most valuable model compilation would be a regularly updated database such as that maintained by the International Ground Water Modeling Research Center (IGWMC) of the Holcomb Research Institute of Butler University (Keely, 1987A; van der Heijde and Beljin, 1986; Rice, 1986; van der Heijde and Williams, 1987).

The IGWMC was founded in 1978, largely through funding from EPA, to carry out research and training in ground water modeling. It organizes many seminars and short courses, and operates a clearinghouse for dissemination of information on (primarily) mathematical ground water modeling. The IGWMC also distributes public domain software for many of these codes, program documentation, and support systems including graphical outputs and statistical programs to manipulate and analyze model results. Current listings can be obtained from the IGWMC of the many models they have available.

A tremendous variety and diversity of model capabilities and features is currently available to address Superfund ground water flow and contaminant transport problems. As will be discussed in this

section, a subset of these methods may be used to address Superfund soil contamination problems, especially to perform exposure assessments and set preliminary soil cleanup levels.

#### 4.8.1 Types of Models

The proliferation of models describing contaminant fate and transport in recent years has been accompanied by a broad array of descriptive terms such as deterministic, analytical, numerical, mechanistic, equilibrium, continuum, stochastic, kinetic, etc. This nomenclature has not been applied consistently by the many model authors and reviewers (Donigan and Rao, 1986A). This may be due partly to the variety of disciplinary interests and backgrounds of the model developers, and to the diversity of purposes for which they developed the models. As a result, the many model users and developers have grouped soil and ground water models into many different and overlapping categories in the review literature.

For example, in a given site problem, the investigator could choose a model having a deterministic approach to represent the site processes, but the model solves the governing transport procedure by numerical methods, assumes equilibrium conditions for certain transformation processes such as sorption, and uses

first-order kinetics to describe biodegradation processes (Donigan and Rao, 1986A). This is illustrated in the model categorization schemes described in the following paragraphs.

Models have been categorized in a variety of ways: in terms of their physical nature (conceptual vs. physical vs. electric analog vs. mathematical); processes simulated (fluid flow, physical solute transport, heat transport, deformation, geochemical transport/ transformation, biological transport/ transformation); analytical use (parameter identification, prediction, resource management, data manipulation); spatial or temporal dimensionality; areal representativeness (regional vs. local vs. site specific); zone modeled (unsaturated, surface soil, saturated); or <u>nature of media modeled</u> (porous matrix vs. fractured matrix); among others, depending on the interests of the reviewer. Mathematical models can be further subdivided in several ways (deterministic vs. stochastic; deterministic by analytical, semianalytical, numerical); numerical by solution techniques), as will be discussed subsequently.

The <u>conceptual model</u> describes the conceptual understanding of subsurface geometry, physical and chemical characteristics, and transport/transformation processes that is developed by the investigator and

modeler for each site (Mercer and Faust, 1980A; Boutwell et al., 1985; Keely, 1987A; and others), as was developed generically in Section 4.2. This model is simple initially, and becomes progressively more sophisticated, and presumably more accurate, as the site investigation and exposure assessment progresses. As more data is collected, it is used to help guide the choice(s) of model techniques at each stage. It is fundamental to the conceptual approach to risk assessment and site (and soil) cleanup described in Section 3.1, and it is basic to the selection and use of models.

The conceptual model is universally recognized among modelers, and is an integral part of most of the various categorization approaches of the model reviewers summarized below. The role of the conceptual model of the site will be discussed further in the context of model selection and use approaches in Sections 4.8.3 and 4.8.4.

Keely (1987A) and Mercer and Faust (1980A) categorized models according to their <u>physical nature</u>:

Physical models include laboratory sandbox "aquifers" (Bear, 1979); soil columns (Darcy, 1856; Schwartzenbach and Westall, 1981; Weber et al., 1965); soil or aquifer microcosms used for biodegradation estimation (Wilson et al., 1986A; Barcelona et al., 1987); and batch leaching apparatus, for example EPA's Extraction Procedure (EP) toxicity test or Toxicity Characteristic Leaching Procedure (TCLP) (40 CFR 261 Appendix II

and 40 CFR 268 Appendix I), or California's Waste Extraction Test. Physical models generally are highly time- and resource-intensive. Their similarity to in situ conditions is limited by the spatial representativeness of the individual sample (which, in turn, is limited by the difficulty in extracting an undisturbed subsurface sample, and installing and testing it successfully in the laboratory apparatus), and the representativeness of the total sample population.

- o Analog models are also physically based, but are intended to simulate rather than sample actual conditions (Keely, 1987A). Examples include electric analog models which replicate the effects of changes of aquifer storage using electric circuits. Disadvantages include the limited transferability of model data to the field, timeand resource-intensiveness of data generation, and relative inflexibility of a given model to changes in experimental conditions due to the "hard wiring" of the model circuitry.
- Mathematical models are non-physical representations of field conditions and processes through mathematical equations describing the relationships among the process variables, as discussed throughout this chapter. Advantages include ability to generate large amounts of data with relatively little expenditure of time and resources (once initial design, construction, and calibration of the model have been performed). Therefore, effects of changes in many conditions and parameters can be predicted and analyzed, allowing the implications of various outcomes to be evaluated with a given level of effort.

  Mathematical models will be discussed in detail in subsequent portions of this section.

Many reviewers have subdivided mathematical soil and ground water models in terms of <u>processes simulated</u>. Kincaid et al. (1984) distinguished methods for simulating physical, geochemical, and biological processes in their code compilations. Mercer and Faust (1980A) described mathematical models for simulating

fluid flow, heat or solute transport, or physical deformation processes in terms of variables and variations based on differing applications. Water supply or flow often can be described in terms of one equation, which is typically solved for hydraulic heads, pressures, or changes in unit volume fluid storage or flows at one or more which is typically solved for hydraulic heads, pressures, or locations. Flow models are used to solve this equation. Solute transport models are then used to describe migration of contaminants through the subsurface in relationship to soil or ground water flow fields. Heat transport models have been used to describe heat movement, like the solute transport equation(s) describe contaminant migration, in geothermal energy, radioactive waste disposal, and aquifer heat storage applications (Mercer and Faust, 1980A; Kincaid et al., 1984). Deformation models have been used to describe physical compaction/expansion of subsurface zones and land subsidence due to fluid withdrawal or injection in water withdrawal, geothermal energy, waste disposal, and oil/gas production applications (van Poollen et al., 1969).

Other reviewers have divided models into categories based on analytical application (Mercer and Faust, 1980A; Keely, 1987A; Bachmat et al., 1978; van der

Heijde et al., 1985), as follows:

- parameter identification models are used to estimate particular subsurface physical or chemical characteristics, or rate or process coefficients governing fate and transport, as described in Section 4.7. Examples include estimation of dispersivity (Strecker and Chu, 1986; Guven et al., 1984), annual recharge amounts (Puri, 1984), and storage and permeability coefficients (Khan, 1986A, B; Shelton, 1982).
- o <u>Prediction models</u> are the most frequently used and most abundant methods for hypothesis testing and problem solving in all applications described previously (Mercer and Faust, 1980A,B; Krabbenhoft and Anderson, 1986; Anderson et al., 1984; Donigan and Rao, 1986A), especially for risk and exposure assessment purposes at Superfund sites.
- Resource management models combine some or all of the types of models discussed herein to provide decision making tools for managers, e.g., by using predictive flow models and linear programs or other optimization routines for setting pumping rates or drawdowns in one well or a field to optimize yields, minimize costs, etc. (Keely, 1987A; Mercer and Faust, 1980A). These methods are in relatively early stages of development, and efforts toward further evolution are limited (Office of Technology Assessment, 1982; van der Heijde, 1984A, B).
- Data manipulation codes include pre-, co-, and postprocessors, soft code linkages, and shell programs used to link models together (for example, fluid flow and solute transport codes), simplify data loading, and manipulate results for statistical analyses, graphical displays, etc. (Srinivasan, 1984; van der Heijde and Srinivasan, 1983; Moses and Herman, 1986; Keely, 1986; Mercer and Faust, 1980A; Brown, 1986).

<u>Areal representativeness</u> is another basis for model classification. Generally, different sets of models are used for regional studies, for example to enhance watersupply management of a ground water basin, than are used

for localized site investigations (Keely, 1987A).

Although the large scale regional models are applicable at smaller scales in concept, site-specific modeling at the scale of tens to hundreds of feet demands higher complexity in representation of hydrologic parameters and fate and transport processes than is possible or appropriate in large-scale modeling efforts (Mercer and Faust, 1980A; Keely, 1987A; Barcelona et al., 1987).

The modeler must be aware of a model's limitations in representing the actual system, and consider its applicability to the site problem, the soundness of the conceptual understanding of the site to be modeled, and the spatial and temporal representativeness of the data available to, characterize the site. Data representativeness relates not only to the physical scale, then, but to the appropriateness of the conceptual model invoked (Keely, 1987A), as will be discussed further below.

Keely (1987B) has also distinguished models on the basis of <u>dimensionality</u>. The differentiation may be spatial (1-, 2-, or 3-dimension), temporal (steady-state vs. transient conditions), or models may be non-dimensional.

Kincaid et al. (1984) distinguished models on the basis of the <u>media</u> being simulated. Media differences relate to system homogeneity in terms of

fluid flow, transmissivity, or hydraulic conductivity, i.e. porous medium vs. fractured bedrock models, as discussed in Section 4.3.1.5. Fractured flow can be grossly estimated by using an equivalent average velocity in a simpler model to represent combined flow through both matrix pore spaces and secondary pores. This might be done early in the RI/FS process, as discussed in Section 3.1.3. However, it could cause serious differences between estimated and actual contaminant transport in fractured systems (Kincaid et al., 1984) when one attempts to use simplified methods to perform a more detailed exposure assessment. Therefore, the media distinction is a function of the complexity of the model being used, and of the data base supporting it, as will be discussed further in Section 4.8.4.

some reviewers have also differentiated models in terms of the zone modeled, primarily classifying them for the <u>unsaturated</u> vs. <u>saturated</u> zone (Kincaid et al., 1984; Boutwell et al., 1985; Schultz et al., 1987, among others). While the fundamental processes of fluid flow are similar in the two zones, and can be described by the same fundamental conservation equations for mass and momentum (Mercer and Faust, 1980A, B; Kincaid et al., 1984; and others), complexity increases in the unsaturated zone due to unsaturated conditions and the

requirement to consider the gas phase. The complexity likewise increases when non aqueous phase liquids are present whose densities differ significantly from 1.0, as discussed in Section 4.3 and subsequently in this section.

Additional categorizations of models are given by Thomas (1973); Karplus (1976); Bachmat et al. (1978); and Appel and Bredehoeft (1976), among others.

#### 4.8.1.1 Mathematical Models

Mathematical models are the primary focus of this part of the discussion. They, too, can be subdivided according to several general schemes, the broadest being deterministic versus stochastic models (Addiscott and Wagenet, 1985):

- Deterministic models are the most common, and are based on cause-and-effect relationships of the system being modeled, i.e., the premise that a system or process will always yield the same outcome given the same set of events as input, or the same set of values assigned to the process variables. These can be subdivided into mechanistic and functional models, described below.
- o <u>Stochastic models</u>, by contrast, are structured to account for uncertain outcomes in terms of probabilities and statistical confidence levels for the input parameters as well as the output values (Addiscott and Wagenet, 1985; Donigan and Rao, 1986A). They often contain deterministic elements, however. These may be subdivided into mechanistic vs. non-mechanistic models, described below.

Stochastic models have been used less frequently than

deterministic models, and are in far earlier stages of development. Their principal use has been for parameter estimation, and they could help in assignment of levels of certainty to parameter values, as will be discussed further in Section 4.9. The two major subcategories of stochastic models according to Donigan and Rao (1986A) and Addiscott and Wagenet (1985) are:

- Mechanistic models, which are partly based on deterministic representations of soils and ground water processes, but which use stochastic arrays of input values to represent variation in subsurface characteristics or processes (e.g., Dagan and Bresler, 1979; Amoozegar-Fard et al., 1982); and
- o <u>Non-mechanistic</u> models, which are purely statistical in nature. They are based on transfer functions (Jury, 1982; Jury et al., 1982; Addiscott and Wagenet, 1985) and on some level of calibration of model parameters.

Further discussion of stochastic modeling aside from Section 4.9 is beyond the scope of this report.

Deterministic models were divided by Addiscott and Wagenet (1985) into two broad subcategories: mechanistic and functional. Mechanistic models, based on rate parameters, incorporate fundamental concepts of soil processes such as Richard's equation for soil/water movement (for a discussion see Donigan and Rao, 1986A,B). They can be further subdivided by solution method (into analytical versus numerical), as will be discussed subsequently. Functional models are generally based on capacity parameters, e.g., using field capacity

as a simplified representation of soil moisture retention. Solutions may be partially analytical (De Smedt and Wierenga, 1978; Rose et al., 1982A,B) or may use layered or other methods. See Bresler (1967), Burns (1974), and Addiscott (1977) for examples and description.

## 4.8.1.2 Development of Mathematical Models

The general mathematical model for ground water flow, as was presented in Section 4.3.1, describes the flow or velocity field in terms of the rate of propagation of a pressure or head change in the aquifer. It consists of a partial differential equation expressing conservation of mass of the fluid, combined with the momentum conservation equation, to describe certain continuous variables (such as hydraulic head, for example) in the area of interest, under certain specified initial and boundary conditions, using certain assumptions, for example that flow is one— or two—dimensional, or that the aquifer being simulated is leaky, or artesian, etc.) (Mercer and Faust, 1980A, B).

Once the flow model is developed, solute transport can be described with additional partial differential equations for conservation of mass and energy for each contaminant species of interest, as described in Section 4.3.1.3. The resultant advective/dispersive equation of solute transport (equation 4-8, 4-9) is based on a mass

balance of the contaminant and on momentum conservation. It includes a source/sink term, a dispersion term, a convection term, and a rate change term for contaminant concentration (Mercer and Faust, 1980B). A separate expression must be developed for each contaminant species of interest.

## 4.8.1.3 Analytical Models

Mathematical models have two basic components: the process equation(s), described in Section 4.3, and the solution technique used to solve the process equation. The two general categories of solution techniques most commonly described by reviewers are <u>analytical</u> and <u>numerical</u> methods. Numerical models can be further subdivided in terms of specific methods used to solve the algebraic equations they generate. They will be described in Section 4.8.1.4.

Analytical models are simpler to use and to solve than numerical models. They are based on simplifications of the general process equation, using many assumptions, to obtain an exact solution to the equation (Mercer and Faust, 1980A; Keely, 1987A).

Depending on the complexity of the method, an exact solution to the equation (Mercer and Faust, 1980A; they may be solved by hand calculation, graphical estimation techniques, or by using a calculator or a computer.

Advantages of analytical models are their availability, relative simplicity, ease of use, and relatively small requirements of time, input data, and resources in most cases as compared to numerical methods. For cleanup level estimation, another advantage may relate to their having exact solutions, as will be discussed in subsequent sections.

Boutwell et al. (1985) divided the more common analytical methods into eight categories which included a combination of processes simulated - both those processes naturally occurring and those associated with remedial actions - and solution techniques for the equations, as follows:

- o Well hydraulics;
- o Drain hydraulics;
- o Ground water mounding;
- o Seepage and infiltration;
- o Superposition (discussed below);
- o Transformation methods;
- o Contaminant transport; and
- o Conformal mapping.

Conformal mapping is an analytical solution method for transforming problems from one geometrical domain into another in which the solution can be calculated (Harr, 1962; Boutwell et al., 1985). It is used for complex flow problems such as seepage under partially penetrating barriers. For additional discussion of conformal mapping see Boutwell et al. (1985).

The more commonly used analytical methods have been compiled in several review documents, as described previously. Walton (1984), for example, compiled a relatively complete listing of well hydraulics solutions, including graphs and tables of well functions. Cohen and Miller (1983) assembled and described many drain hydraulic solutions. Contaminant transport solutions have been compiled by many reviewers, including Kincaid et al. (1984); Cleary and Ungs (1978); Boutwell et al. (1985); Walton (1984), who described several one-dimensional models and radial-flow solutions; Javandel et al. (1984); Bear (1979); and van Genuchten and Alves (1982), who derived and described a broad set of one-dimensional solutions.

Microcomputer or hand calculator programs have been written for the more commonly used methods. Many are available in the public domain from a variety of sources, including the model clearinghouse operated by the IGWMC at Butler University (Keely, 1987A; van der Heijde and Beljin, 1986; Rice, 1986; van der Heijde and Williams, 1987).

Despite the advantages of their simplicity of application, the burden with analytical models is on the user to test and justify the assumptions and simplifications used in a given setting, in terms of their appropriateness to the field situations and the

sensitivity of the result to a given assumed input parameter (Javandel et al., 1984; Keely, 1987A).

Boutwell et al. (1985) observed the following:

- o Many analytical and semi-analytical flow and transport models were developed for specific aquifer types or conditions (for example, confined, unconfined, or leaky) or for specific configurations of wells or drains (typically assumed to be fully penetrating, to neglect vertical components of flow). Wells of "non-negligible" diameters, or partially penetrating designs, must be modeled using corrections or models designed specifically for the configuration present.
- Aquifer conditions in most models are highly idealized for purposes of simplifying elements of the equation to a solvable form, e.g., horizontal, infinite in extent, constant thickness, homogeneous, and isotropic. Deviations from these conditions in the field situation (which occur typically, if not universally) are compensated for using transformation methods (e.g., equivalent sections, incremental solution methods) and corrections for anisotropy.
- Many analytical methods were derived for very 0 idealized flow regimes, for example radial flow, or a uniform one- or two-dimensional horizontal flow field. More complex flow patterns can be analyzed by using superposition principles to combine several simple, idealized patterns (McWhorter and Sunada, 1977; Bear, 1979). Superposition is valid for linear, homogeneous, partial differential equations. It is appropriate in water table aquifers only when head changes are relatively insignificant compared to total saturated Thus, analytical methods generally thickness. should not be used for analysis of remedial actions involving large elevation changes in water table aquifers, nor for analyzing flows near or around the ends of impermeable barriers.
- o Most analytical solutions for contaminant transport consider several major processes at a site (e.g., advection, dispersion, retardation, degradation). Semi-analytical solutions typically consider only

advection and (sometimes) retardation, but offer greater capability to analyze more complex flow regimes.

- o Since most analytical solutions apply only to radial or one dimensional flow patterns, their use to predict effects of remedial actions on contaminant transport or concentrations generally is limited to sites where contaminant sources or sinks can be estimated as points.
- o Most analytical models assume that subsurface characteristics affecting contaminant transport and transformation, like those affecting fluid flow discussed in Section 4.3 and 4.5, are homogeneous and isotropic in their subsurface distributions. Therefore, they will not predict changes in spatial distributions of these properties in response to certain remedial actions.

Thus, the applicability of analytical methods to field conditions is often quite limited. The Theis equation, for example, is an analytical expression used to predict changes in piezometric head in confined aquifers under different injection or extraction scenarios. This equation was reported by Keely (1987A); Freeze and Cherry (1979); Boutwell et al. (1985); and Todd (1980), among others, and it relies on several major assumptions including a homogeneous, isotropic aquifer of infinite areal extent; an insignificantly small volume of water in storage in the well casing relative to aquifer volume; instantaneous volume changes from pumping; and a well screened over the full saturated thickness of the aquifer (Lohman, 1972).

The Theis equation can be solved either by

graphical analysis using type curves (Lohman, 1972; Walton, 1984) or by further simplification to obtain a direct solution. Applicability of the direct solution is restricted (by the simplification) to limited distances from the pumping well, except over long pumping intervals approaching steady-state conditions (Keely, 1987A).

Several two-dimensional analytical transport models were considered for use in setting target soil cleanup levels at the McKin site, as will be discussed in Section 5.7. The pros and cons of this approach will be discussed in subsequent parts of this chapter and in Chapters 5 and 6.

#### 4.8.1.4 Numerical Models

Numerical models are often suitable for application to aquifers with irregular boundaries, heterogeneous subsurface conditions, or highly variable rates of aquifer pumping and/ or recharge with space or time (Mercer and Faust, 1980A). Unlike the analytical solutions, numerical solutions involve representing the area to be modeled by a grid in which each grid block defines a subarea assumed to have identical properties. Then one approximates the partial differential equations by replacing the continuous variables in the flow and/or transport equation(s) with discrete variables defined at

grid blocks or at nodes, depending on the solution technique being employed. For example, the continuous differential equation defining hydraulic head throughout an aquifer would be replaced with a set of algebraic equations defining the head at specific grid points, with certain specified initial and boundary conditions, as discussed in Section 4.8.3. The set of equations is then solved using a variety of methods, most often matrix techniques (Mercer and Faust, 1980A).

several general discussions and reviews of theory and application of numerical models have been prepared, including Freeze and Cherry (1979); Mercer and Faust (1980B); Faust and Mercer (1980); Orlob (1971); Bachmat et al. (1978); Donigan (1981); and Javandel et al. (1984); among others. Boutwell et al. (1985) made the following generalizations and observations about numerical models:

- o Although the complexity (and thus the computational efficiency) of the solution technique depends on the assumptions made, generally far fewer simplifying assumptions are used compared with analytical methods.
- Numerical methods allow several independent variables (e.g., temperature, ground water velocity, and contaminant concentration), and interactions among them, to be simulated simultaneously.
- o Key parameters such as contaminant concentration, velocity, or heads, are calculated at discrete space and time steps that can be adjusted by the modeler to suit the problem requirements, e.g.

desired level of accuracy, specificity, computational ease, etc.

- o The increased ability of numerical methods to represent heterogeneities in site conditions requires much higher resolution in the types and quantities of field data required to represent these heterogeneities accurately, but at greater data collection costs.
- o Because approximate solutions to the partial differential process equation(s) are obtained by numerical methods, level and type of error depends on choice of solution method, specifics of the computation method such as round-off and truncation errors, numerical dispersion, etc.
- o Additional resources are required to implement numerical models compared to those needed for many analytical techniques, perhaps by a factor of 2 to 10, in the areas of quantity/quality of field data; computer hardware, data capacity, and run time requirements; model user knowledge and expertise; and other human resources.

partial differential equations, provide the primary bases for differentiating types of numerical models. The two major categories are finite difference and finite element methods. Emerging methods such as the upwind and moving-front techniques (Newman, 1983 and others) are still being developed and are not yet ready for widespread application to Superfund soil and ground water problems. They will not be discussed herein.

Finite difference models (FDM) are based on use of a grid to represent the area of interest, generally in map view for two-dimensional applications, by dividing it into small subregions or blocks with a series of node

points representing the positions at which the solutions of the equations are to be obtained. Two grid designs are commonly used, depending on the boundary conditions involved (Faust and Mercer, 1980; Kincaid et al., 1984; Freeze and Cherry, 1979):

- o <u>Mesh-centered</u> grids, where the nodes form the intersections of the grid lines. This design is favored, for example, in flow problems where head values are specified at the boundaries; and
- o <u>Block-centered</u> grids, where the nodes are centered within each block, between grid lines. This design is preferred, for example, in flow problems where fluxes across the boundaries are specified.

FDM grids often are rectangular in shape and equilateral in block size, but may be irregularly sized. For example, closer grid spacing might be used near well points where drawdowns are being carefully examined. In some cases the blocks may not be rectangular.

Frequently, it is assumed that water levels are equal across a block and identical to the level at the node point (in the block centered system), and that all fluid withdrawals and recharges occur only at node points (Faust and Mercer, 1980). An example of grid design and application at the McKin Superfund site is illustrated in Section 5.3.

Difference approximations are developed to approximate the space and time derivatives for the process equation or equations. Frequently, Taylor

series are used to approximate the derivatives; typically they are truncated after the first derivative (Faust and Mercer, 1980). Alternatively, Prickett and Lonnquist (1971) used a more intuitive approach that considered the fluxes into and out of a finite difference block.

The end result is an algebraic equation for each node in the grid, where the variable for each node (for example, hydraulic head in a flow equation) receives contributions from the four nodes surrounding it, which are evaluated at each new time step and related to a known quantity calculated from the previous time step. If a uniform grid is used, the difference formulas for neighboring nodes are unchanged and only physical parameters are updated at each succeeding time step.

Nonuniform grids become more complex to solve (Kincaid et al., 1984), especially near the system boundaries.

A system of N equations with N unknown values of the variable to be solved for is written for the region being modeled, where N is the total number of nodes in the grid. This system of equations is often solved using matrix methods, as will be discussed briefly in Section 4.8.1.4.

Freeze and Cherry (1979) provide an explicit development of the FDM equations using truncated Taylor series and a block centered design. A brief overview is

given by Faust and Mercer (1980). Pinder and Bredehoeft (1968) and Remson et al. (1971) provide historical descriptions of use of the finite difference method to solve the ground water flow equation. Applications to petroleum recovery problems are discussed by Peaceman (1977) and Crichlow (1977), among others.

A variant of finite difference methods is the integrated finite difference method (IFDM), originally termed the polygonal model when first applied to ground water flow problems by Tyson and Weber (1964). Narasimhan and Witherspoon (1976) described its current structure, which forms the basis for several flow and transport models developed by the Lawrence Berkeley Laboratories (Mangold et al., 1980; Pruess and Schroeder, 1980; Reisenauer et al., 1982). This method uses an arbitrary grid composed of polygonal subregions or blocks with nodes at their centers. The nodes are connected to each other by a series of lines arranging the nodes in a repeating triangular or rectangular pattern (Mercer and Faust, 1980A, B). The sides of each subregion or block are formed by the perpendicular bisectors of the lines connecting the nodes. Polygonal blocks are created when nodes are triangularly arranged, and rectangles when nodes are in rectangular patterns.

The assumptions of equivalent head averaged across each block, and of restricting head changes to the

nodes, are generally made for IFDMs as for other FDMs (Kincaid et al., 1984; Faust and Mercer, 1980).

Likewise, similar approaches to Prickett and Lonnquist's (1971) intuitive derivations are used to develop the nodal equations (Faust and Mercer, 1980). Further discussion of IFDMs is found in Kincaid et al. (1984).

Finite element methods (FEMs) are based on the use of integration, rather than differentiation, to solve the partial differential process equations. The analytical technique was introduced by Galerkin (1915), and was used for structural analysis before first being applied to ground water problems by Zienkiewicz and Cheung (1965).

In FEMs, the continuum of the dependent variable(s), e.g., contaminant concentration, pressure, etc., is approximated with a set of well-defined surfaces (Kincaid et al., 1984; Faust and Mercer, 1980), which in turn are described by a set of interpolation functions. This is done by dividing the region to be modeled into a grid of subregions called elements using lines connecting the node points, much like the mesh centered FDM design. However, node arrangement and spacing is flexible, thus FEMs can more accurately accommodate highly complex and irregular site geometry than can many FDM grid designs. Nodes may be located at alternate points in an element, such as along edges or

within the element, in some cases depending on the degree of the basis functions (Kincaid et al., 1984).

Element shapes depend on the dimensionality of the site problem. For 1-D problems, the elements are lines, while for 2-D models they are typically triangles or quadrilaterals, and for 3-D scenarios they are prisms or tetrahedrons, respectively. Time may also be approximated by finite elements, but typically, finite difference approximations are used for the time derivatives in transient problems (Faust and Mercer, 1980, and others).

The FEM involves (1) deriving an integral representation of the partial differential process equation(s) (i.e., the elements of the grid); (2) approximating the dependent variables, using interpolation functions called basis functions; (3) expressing the integral relationship for each grid element as a function of the coordinates of all nodes circumscribing the element; (4) calculating the values for the integrals for each element; (5) combining the integral values across all elements (together with boundary conditions) to give a set of first order linear differential equations in time. Finite elements (together with boundary conditions) to give a set of difference approximations are then used to generate a set of algebraic equations which, as with FDMs, are

usually solved using matrix techniques (Faust and Mercer, 1980).

Derivation of integrals representing the partial differential equation is done by several different methods including the method of weighted residuals (described by Finlayson, 1972, and Faust and Mercer, 1980 C) and the variational method (described by Zienkiewicz, 1971, and others). Basis functions used to approximate the dependent variables can be nearly any system of independent functions, but low-order polynomials are often used for computational simplicity (Faust and Mercer, 1980; Zienkiewicz, 1971; Desai and Abel, 1972; and others). Additional discussion of the FEM computational steps can be found in Remson et al. (1971) and Pinder and Gray (1977), as well as in many of the general references cited previously.

#### 4.8.1.5 Numerical Solution Techniques

The numerical methods discussed in the previous section result in a series of N algebraic equations with N unknowns, where N represents the number of nodes in the grid. Each dependent variable at each node is represented by an equation, commonly written in matrix form as (Faust and Mercer, 1980; Kincaid et al., 1984):

$$\mathbf{A} \ \overline{\mathbf{h}} = \overline{\mathbf{D}} \tag{4-10}$$

where A is the matrix of coefficients related to problem geometry (e.g., transmissivity, etc.) and grid spacing; h represents the solution vector, consisting of the values of the dependent variable to be determined at each node; and D describes the boundary conditions, stresses, and other information (such as pumpage rates, etc.) to completely specify the system. Solutions typically are obtained by one of two general methods (or a combination):

- o <u>Direct methods</u>, in which the solution sequence is performed once for the entire matrix A. The solution is exact, except for round-off and other such errors; and
- o <u>Iterative</u> methods, in which subsets of equations are formed and solved to successively approximate the solution. The process is repeated until an acceptable level of convergence is obtained in the solution. Thus, ability of the solution to converge and rate of convergence are important considerations.

Faust and Mercer (1980) compared the two methods. For certain problems, the direct method becomes more practicable and convenient, since the matrix solution is generally considered the most expensive component of the modeling effort in terms of computer run time and costs. For more complex matrices, say, with more than 1000 unknowns, iterative methods often are favored.

Direct methods may be further subdivided into several categories: solution by determinants, solution

by matrix inversion, and solution by successive elimination of unknowns (defined and reviewed by Faust and Mercer, 1980). The latter approach, using successive elimination and back substitution methods such as Gaussian elimination and Cholesky decomposition, is most widely used (defined and discussed by Scarborough, 1966; Weaver, 1967; Narasimhan and Witherspoon, 1976). The primary disadvantages of direct methods lie in round-off errors, and in the excessive storage capacities and computation times required for solving large problems. These requirements may be limiting for 3-D simulations (Faust and Mercer, 1980). Price and Coats (1974), among others, have developed schemes for numbering the nodes (e.g., in alternating directions) to increase computational efficiency.

Many iterative techniques have been developed.

Commonly used iterative methods cited by Faust and

Mercer (1980) include alternating direction implicit

procedures (described by Douglas and Ratchford, 1956);

iterative alternating direction implicit procedures

(described by Wachpress and Habetler, 1960); the

strongly implicit procedure (described by Stone, 1968);

and successive over-relaxation methods (see Varga,

1962). A complete description of these methods is

beyond the scope of this report, and is contained in the

references cited.

Iterative methods offer an advantage in eliminating the requirement to store large matrices. Disadvantages include the following: (1) since the rapidity of convergence is partially dependent on the accuracy of the initial solution estimate, the method is not favored for steady-state problems (Narasimhan and Witherspoon, 1977); (2) an error criterion (i.e., some confidence band around the actual solution value) must be defined to provide the stopping point for the iteration procedure, which is very site- and problem-specific; (3) the definition of relaxation and acceleration factors is also site- and problem-specific; and (4) the matrix must be well-conditioned. That is, the main diagonal terms should not be significantly smaller than other terms in the matrix. Narasimhan and Witherspoon (1977) considered this last requirement crucial, since the lack of conditioning can affect the rate of convergence or prevent it altogether (Faust and Mercer, 1980).

In addition to direct and iterative solution categories, special techniques exist. Special circumstances, and some problems commonly encountered with these two methods, have led to the development of several special solution techniques (including the method of characteristics approach and some nonlinear methods), as well as several alternative numerical modeling approaches, such as the discrete parcel random

walk and other particle tracking methods. These will be reviewed briefly below.

The first method, method of characteristics (MOC), was developed in response to the concern that since advection dominates the advection/dispersion transport equation, two types of numerical problems occurred when applying conventional FEM and FDM solutions to transport problems with convection alone: either numerical dispersion (solutions that are "smeared out"), or oscillatory solutions (e.g., large negative concentrations of solutes) (Faust and Mercer, 1980).

Typically, finite difference approximations are used for the ground water flow equation, and the finite difference grid is used for the transport equation.

However, with MOC, the the ground water flow equation, and the finite difference grid is transport equation is not solved directly; rather, three ordinary differential equations are solved (in the case of 2-D transport problems). The first two describe the movement of fluid particles which advect with the flowing ground water and arrive conservatively at their new locations (concentrations are unchanged), i.e., equations for velocity in the x and y directions; while the third describes the total time rate of change of concentration due to such effects as sources and sinks, hydrodynamic dispersion, and changes in aquifer saturated thickness

(Kincaid et al., 1984). The solutions are described by characteristic curves (hence, MOC).

The concentrations and gradients of the contaminant of interest are changed by the dominant advection process during the time step. This is simulated numerically by introducing a set of reference particles whose movement can be traced along the stationary finite difference grid. As particles move within each block (distance of movement is proportional to the time step and to the velocity fields in each block), they simulate advective movement as concentrations at each node change due to movement of reference particles into and out of a given block (Konikow and Bredehoeft, 1978; Faust and Mercer, 1980).

This ability to handle the advection-dominated calculation is the principal advantage of the MOC approach. It has been applied to many ground water solute transport problems, mainly through its development for the U.S. Geological Survey by Konikow and Bredehoeft (1978), and subsequently for other agencies including the Nuclear Regulatory Commission and EPA (Kincaid et al., 1984). Several applications are described by Bredehoeft and Pinder (1973); Konikow and Bredehoeft (1974); and Konikow (1977). Additional discussion of the theoretical underpinnings of the MOC approach is found in Konikow and Bredehoeft (1978);

Reddell and Sunada (1970); Pinder and Cooper (1970); and Bredehoeft and Pinder (1973); among others.

Nonlinear methods are necessary when the system of differential equations describing flow and/or transport are nonlinear, i.e., when they include products and/or derivatives of dependent variables. Typically, confined aquifers are linear. Nonlinear flow problems arise, for example in very thin unconfined aquifers because transmissivity is a function of saturated thickness, and thus, of head. Nonlinear flow problems arise in unsaturated flow models because of the effect of soilwater content on most of the other critical physical parameters affecting flow. Nonlinear transport problems occur when changes in contaminant concentration, pressure, and temperature affect density, porosity, or viscosity, or heat transport (Faust and Mercer, 1980; Kincaid et al., 1984). Nonlinearities are often seen also in solving the geochemistry equations, since the process equations typically assume attainment of equilibrium, and absence of temporal and spatial dependence of the geochemical transformation (Kincaid et al., 1984).

The effect of nonlinearity is that equation parameters (e.g., density) change during each time step due to changes in dependent variable values (e.g., concentration, pressure) with time, producing mass

balance errors, and producing a coefficient matrix A whose entries depend on the solution vector h (Mercer and Faust, 1980C; Kincaid et al., 1984).

Nonlinear solution methods are typically varations of the iterative processes discussed previously, including the Newton/ Raphson method, Brinkley's and NASA's methods, the component reduction and sliding target methods, and methods of successive reaction adjustments such as nested iterative schemes (reviewed and discussed in Kincaid et al., 1984, among others). These may not be effective for highly nonlinear problems where convergence does not occur. Other methods include extrapolation and quasilinearization methods, which were described by Peaceman (1977).

The discrete parcel random walk method is somewhat of an alternative to the FDM and FEM, rather than a special solution technique. The random walk approaches are similar to MOC in that they model advection by a particle tracking approach; but they model dispersion as a random process, typically assigning it a Gaussian distribution in a porous medium. This avoids many of the characteristic difficulties of the traditional FDM and FEM processes (Kincaid et al., 1984). Another advantage is that these methods are linear. Disadvantages include the requirement to use a relatively large number of particles to adequately

describe the solute distribution as it moves and changes in the subsurface. This may be a limiting requirement for complex site problems. Insufficient particle populations have led to discontinuous concentration fields, and to cells with concentrations exceeding the initial model conditions (Kincaid et al., 1984). The most widely known and best-developed example of this approach is the Illinois State Water Survey code developed by Prickett, Naymik, and Lonnquist (1981).

#### 4.8.1.6 Coupling of Codes

Some of the codes in each of these categories are compartmental codes, developed specifically to describe phenomena in one compartment: surface soils, unsaturated zone, confined and unconfined aquifers. Others may be termed continuum codes (Donigan and Rao, 1986A, B; Mercer and Faust, 1980B; Kincaid et al., 1984). No single flow and transport code has yet been developed that reliably simulates all relevant fate and transport processes taking soil contaminants through all compartments from abandoned hazardous waste disposal sites to ground water receptors (Kincaid et al., 1984).

A comprehensive theoretical framework has not yet been developed that addresses all important phenomena with sufficient accuracy and thoroughness to eliminate the need for collecting detailed site characterization data (Keely, 1987A). Thus, many model reviewers have placed strong for collecting detailed site characterization data (Keely, emphasis on codes that can be effectively linked to provide a complete simulation of the soil/ground water pathway (Kincaid et al., 1984; Boutwell et al., 1985).

### 4.8.2 Model Selection and Application Process

The preceding section provided an overview of model types, illustrating several of the ways in which they have been categorized. In this section, the procedure by which mathematical soil and ground water models are applied to a subsurface contamination problem is outlined. Many model developers and reviewers have described various parts of this procedure. Most expert modelers and hydrogeologists follow many of these principles implicitly when choosing and using models for various purposes.

In this discussion, the modeling process is described with particular emphasis on the use of models to assess exposures to soil contaminants via the ground water ingestion pathway, for the purpose of establishing acceptable soil residual cleanup levels. In this context, the model would be used ultimately to back calculate residual soil concentration levels of a contaminant based on some maximum allowable receptor

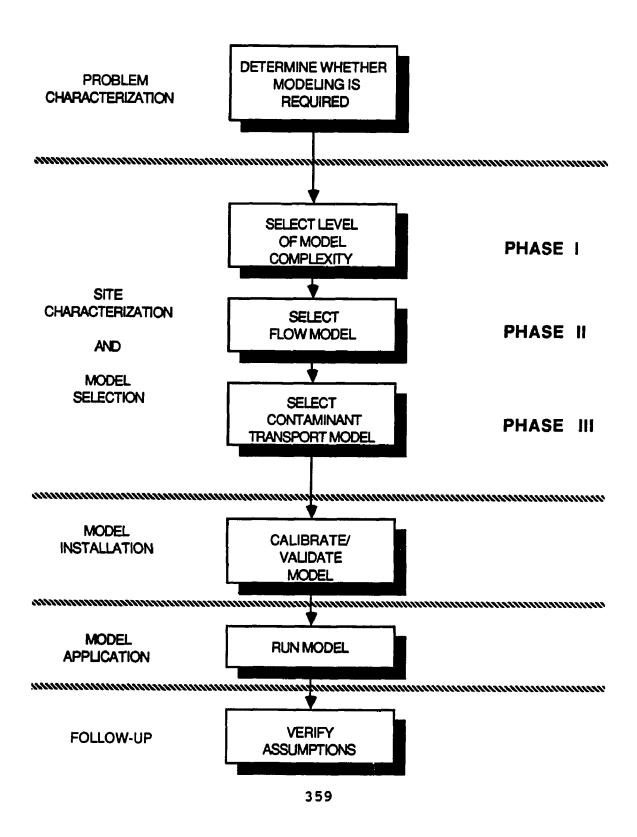
point concentration defined by the analyst. This initially requires "forward calculation" of ground water exposure levels as the soil contaminants migrate to the ground water as described in Sections 4.2 through 4.6 of this chapter.

The following description was adapted and compiled from the existing model reviews and model use literature for this particular application. For more detailed discussion of individual aspects of model use or variations of this approach, the reader is referred to Mercer and Faust (1980A,B); Walton (1984); Kincaid et al. (1984); Boutwell et al. (1985); Donigan and Rao (1986A), and other model review literature summarized in Table 17.

Many authors have identified the following typical stages in the model selection and application process, as shown in Figure 7:

- o <u>Problem characterization</u>—the analyst must identify the objectives and constraints of the analysis, to the extent possible. This may be initiated during the Remedial Investigation/Feasibility study scoping stages when site response objectives are framed (see Section 3.5.1). The primary focus is to begin to develop a clear conceptual model of the site problem, and of likely fate/transport processes and subsurface behavior, to determine whether modeling is necessary and/or appropriate.
- o <u>Site Characterization</u>--available site data is reviewed, and more data is collected, to refine the conceptual model to incorporate all contaminant fate and transport processes of interest that occur at the site. Screening-level analyses, using

FIGURE 7
Overall Model Selection/Use Process



simplified models, may be used to define data needs and uncertainties; determine which processes are important to the receptor point exposure and to overall site risk, given the study objectives; and to produce the specifications for the model(s) to be used to simulate/ predict all the important processes.

- o <u>Model Selection</u>—various selection criteria (see Section 4.3) are used to compare available models. The model(s) providing the best fit to all criteria are selected. In this process, the analyst may iteratively reevaluate the weight of each selection criterion in light of the model's intended use, the are selected. In this process, the analyst may value of collecting more/better data to allow a given model to be used, and the analyst's resource constraints.
- o <u>Model Installation</u>—if the model is a computer code, the code is installed and tested to verify its proper operation on the analyst's computer system and its ability to reproduce solutions to certain "standard" example problems, as appropriate. The code and/ or operating system may be adjusted if necessary.
- o <u>Model Application</u>—the verified model is run using site data as input to simulate exposures or predict possible consequences of different remedial action scenarios. For each application, repeated calibration, validation, and operation sequences may be performed, depending on the modeling objectives. All the assumptions and sources of uncertainty in the modeling effort should be identified and quantified to the extent possible.

Two important points must be kept in mind when examining these general process steps. First, they seldom follow a single linear process flow. Rather, the sequence of activities within any single step, e.g., within the problem characterization step, may be performed repeatedly before the investigator moves to the next step in a trial-and-error fashion. Likewise

the entire sequence of steps, or some of the steps, may be performed iteratively (Mercer and Faust, 1980A,B; Boutwell et al., 1985; Donigan and Rao, 1986A). The modeler's understanding of the site problem is evolving continuously as new information about site processes and parameters is brought to light. This causes continual refinements and adjustments in the goals and objectives of the modeling exercise, and in the assumptions and input parameters used, at any point in the site investigation in a series of feedback loops. Therefore, these steps may not exactly correspond to given stages in either the RI/FS process or the contaminated soil conceptual approach presented in Table 9.

Second, this general process is discussed in the context of applying existing, well-developed mathematical models to this class of problems, not developing new models to address the problem. The sequence of steps undertaken to develop a new model, or to perform a research grade field validation study of a model for, say, predicting ground water impacts of pesticide application or ground water basin management, are somewhat different than those discussed here in several respects, for example in terms of site selection and use of controls, and, in some cases, the intensiveness of the field data collection effort. For a more detailed discussion see Hern et al. (1986);

Donigan and Rao (1986B); and Hedden (1986). Ideally, similar levels of quality assurance should be practiced in Superfund soil and ground water contaminant assessment problems, but this seldom occurs for many reasons. These will be discussed further in Chapter 6.

# 4.8.2.1 <u>Problem Characterization: Is Modeling Necessary/ Appropriate?</u>

Two important events occur in this phase. First, the conceptual model of the site is formulated. At this stage, it helps shape the objectives of the assessment and the analyst's general expectations about the type of assessment and the general level of accuracy or confidence. These objectives and expectations are constrained by project schedule, budget, and available resources, as discussed in Section 4.8.3.

Second, the analyst makes the decision to use, or not to use, a mathematical model for parts or all of the exposure assessment, or to assist decisionmaking for some other part of the remedial process at the site. The critical question to be asked iteratively throughout the process is, "will the resources expended and the results obtained be worth the modeling effort?"

(Boutwell et al., 1985). This decision is a function of the modeling objectives, the extent of contamination, the complexity of the geohydrologic setting, the range

of remedial actions being considered, and other factors (Boutwell et al., 1985). A typical sequence of questions the analyst answers to make this decision was discussed by Boutwell et al. (1985):

- 1. Can assumptions in the conceptual model be confirmed with existing data?
- 2. Will additional data improve understanding?
- 3. Do you need quantitative estimates of future conditions?

Three key features of this sequence should be noted. First, it is based on the adequacy of the conceptual model (Keely, 1987A; Mercer and Faust, 1980A,B). Second, the decision pathway related to the question, "Will additional data improve understanding?" should not be misconstrued to imply that modeling should substitute for gathering more data. Rather, the question embodies several assumptions, including:

- A "no" response could be obtained when the site has homogeneous conditions, e.g., a single soil type or a single, simple aquifer, and exposure pathways are few and well characterized, or nonexistent. Few sites that have been placed on the NPL fit this category.
- A "no" response could indicate that assumptions in the conceptual model can be confirmed with existing data. This implies that fluxes of contaminants via all exposure pathways are at equilibrium, allowing risks at each receptor point to be measured directly in terms of existing ambient concentrations, rather than predicted. This seldom if ever occurs at NPL sites. Contaminants are continuously migrating from the

site, and environmental concentrations may be changing continuously or intermittently.

Third, Boutwell et al. (1985) indicated that modeling is necessary whenever the study objectives include the need for quantitative estimates of future conditions, for example, when performing a quantitative risk/exposure assessment for the "no action" alternative, when comparing the relative effectiveness of remedial alternatives, or when backcalculating to estimate cleanup levels.

# 4.8.2.2 <u>Site Characterization (RI Data Collection)</u> and Model Selection

A key event in these stages is the selection of the model(s) to be used. The selection process requires the modeler to consider a complex set of selection criteria based on the objectives of the analysis, technical site and hardware constraints, resource requirements, and other factors (Boutwell et al., 1985; Mercer and Faust, 1980A,B). This process, and criteria that have been used for selecting models, will be discussed in Section 4.8.3.

Ideally, both the choice of model and the process by which it is selected will help determine data requirements, and thus identify when and what kinds of additional site characterization activities are needed.

However, the concept of Remedial Investigation data collection primarily to support a particular model is still new to the Remedial Investigation scoping process (Keely, 1987A). The traditional focus of the Remedial Investigation data collection effort has been to characterize sources, types, and extents of contamination, and contaminant migration pathways and receptors, so that the exposure assessment and the public health evaluation can be completed (EPA, 1982A; 1985A,B,F; 1986A), as described in Section 3.5. Data collection solely to fulfill input data requirements for a specific model has only in rare instances been a primary goal of the Remedial Investigation (Keely, 1987A).

The modeler and the remedial project manager are faced with two opposing pressures: the Congressional mandate given in SARA to streamline and accelerate the remedial process, which dictates a more rapid and less detailed RI; and Agency pressures to collect high quality data to support a more complex remedial decision making process. A phased, "state-of-the-art" data collection process could meet both goals in the long run. This is discussed further in Chapter 6.

Selection of an analytical model requires less data but, usually, more assumptions than a numerical method. As discussed in Section 4.7, many input parameters may be estimated initially using literature values, results of simplified screening-level analyses, or best professional judgement. These parameters may be progressively refined, or replaced by site data, if data is collected in a phased manner as needed. This process is discussed further by Mercer and Faust (1980B), Hern et al. (1986), and others. Boutwell et al. (1985), Lyman et al. (1982), Repa and Kufs (1985), and Jury (1986A), among others, provide guidance on input parameter estimation for remedial action modeling.

Selection and use of a particular numerical procedure involves (1) determination of the boundaries of the area to be modeled; (2) discretization of the area, i.e., subdividing it into a grid composed of blocks or subareas known, or assumed for purposes of solution, to have similar physical and/or chemical properties (Mercer and Faust, 1980A); and (3) specifying initial conditions to obtain a unique solution to the partial differential process equation(s) when solving unsteady-state problems (Mercer and Faust, 1980B).

Boundaries may be arbitrarily established for modeling convenience, or based on actual physical conditions (e.g., impermeable barriers, no flow areas, constant head, recharge or specified flux zones).

Initial conditions may be a combination of field values and literature estimates for certain parameters (Mercer and Faust, 1980B; Faust and Mercer, 1980).

#### 4.8.2.3 Model Installation and Application

When a computer code, especially for a complex numerical model, is installed on an operating system, the user must verify that it is operating properly on the system. This is often done by running a set of well-defined example problems, and validating the model's mathematics by comparing outputs to known analytical solutions; verifying the model framework by successful simulation of a subset of the observed field data; and benchmarking the model's ability to solve the site problem compared with other models (Huyakorn et al., 1984).

Keely (1987A) noted that the validation step is inherently deceptive and self-limiting in that the assumptions required for the analytical solutions limit their ability to test many of the capabilities of the numerical method, especially for more complex hydrogeologic settings and contaminant distributions. Huyakorn et al. (1984) and Ross et al. (1982) discuss the growing capabilities of benchmarking routines for cross-comparisons of model effectiveness.

Keely (1987A,B) defined two additional levels of quality control he considered necessary to address the soundness of the selected model's application to the specific site problem: (1) a critical review of how well

the selected model meets the requirements suggested by the conceptual model, as discussed above, and (2) evaluation of the appropriateness of specifics of the model application, such as grid design, time steps, and boundary conditions, to the physical problem.

Keely (1987A) defined field verification in conventional research-level terms, i.e., first calibrating the model using one set of historical records as input data, and then attempting to predict current conditions. Mismatches indicate either incorrect problem conceptualization, improper model formulation, or erroneously chosen input parameters, either measured or asssumed. Usually this results in the need for additional data collection, otherwise Keely indicated that the model's applicability could be limited to the conditions of calibration only, i.e., a "black box" solution due to nonunique input parameters. However, it has been pointed out that such rigorous verification is not typically seen in model efforts that are part of Superfund site investigations. highlights the importance of verification monitoring over the entire time period of model predictions, as will be discussed in Section 4.9 and subsequently in this report.

#### 4.8.3 Model Selection Criteria

Once the decision to model has been made, the analyst must choose the mathematical model or models to be used. This decision affects the types and amounts of data collected to characterize the site, and vice versa (see Section 4.8.2.2). As described previously, the model selection decision could be revisited repeatedly throughout the site characterization and feasibility study, as analytical objectives and needs are revised, and conceptual understanding of the site continues and feasibility study, as analytical objectives and needs are to evolve.

Some EPA programs and other government agencies have developed specific policies regarding the selection and use of models. Some of these specify using only models having prior approval, while others provide criteria a candidate model must satisfy (Bachmat et al., 1978; Office of Technology Assessment, 1982; van der Heijde and Park, 1986). As of this writing, the Superfund program has not specified the use of particular models, nor has it established guidelines or specifications for selection and application of fate and transport models.

Several efforts have been targeted at alleviating this problem. The American Society for Testing and

Materials (1984) has developed a standard protocol for evaluating environmental fate and transport models, and EPA's Environmental Monitoring and Systems Laboratory in Las Vegas is conducting a similar effort with specific focus on standardizing modeling practices for hazardous waste site applications (D'Lugosz, 1988).

Once a clear conceptual understanding of the site has been developed, based on available data, the modeler must decide the level of complexity required in the model, based on the goals and objectives of modeling and the expected quantity and quality of field data to be obtained in the Remedial Investigation. The output of an overly simple model may be too conservative and have unacceptably large uncertainties associated with it, but the use of an overly sophisticated, complex model likewise may distort the results (Boutwell et al., 1985; Javandel et al., 1984; Keely, 1987A).

Before a given model is chosen, the analyst must ensure that the available site data are sufficient for its input requirements; otherwise, either the goals must be reassessed and a simpler model must be selected, or more data must be collected. It should not be assumed, however, that an analytical model will always be easier or less resourceintensive to use in a given setting than a numerical model. The opposite can occur in some situations.

Many modelers have applied some or all of the following criteria to select and use models for contaminant transport predictions. These selection criteria can be grouped generally into the broad categories of objectives criteria, technical criteria, and implementation criteria. These categories are described in the following subsections.

## 4.8.3.1 Objectives Criteria

As discussed in the previous section, the modeling process is iterative by nature. The analyst must continuously reevaluate the appropriateness of the model to the site conditions as new data becomes available. The reevaluation can lead to a modification of study objectives, and thence to a change in the level of complexity of the model selected. Objectives criteria often lead modelers to divide models into two broad classes, depending on whether the objective is to perform a screening-level or a detailed assessment (Boutwell et al., 1985).

As discussed previously, limited detail in site understanding could lead to selection of simplified models in initial stages of a study to make a screening-level assessment, and to guide decisions to collect additional data. The objectives of the study can be modified to allow selection of more complex models to

set cleanup levels at such time as data is sufficient to support their use (Boutwell et al., 1985; Schultz et al., 1987).

#### 4.8.3.2 <u>Technical Criteria</u>

Technical criteria are used to evaluate a model's ability to simulate successfully the specific parameters of interest at a given site. The technical criteria should include all physical, geochemical, and biological processes that significantly affect site conditions and pathways, as well as those physical and chemical characteristics of the contaminants of interest that significantly affect their migration at the site.

Various investigators have classified technical criteria into broad classes as follows:

o <u>Domain configuration</u> <u>criteria</u>— these could apply to either flow models or transport models. They describe the model's representativeness of the spatial (geometric) and temporal domains of interest in the study (Mercer and Faust, 1980A; Boutwell et al., 1985; Keely, 1987A).

Geometric domains refer to description of the physical arrangement of the flow system, i.e., whether a water-table or confined aquifer; single- or multiple-phase flow; single- or multiple- layer aquifer system; constant-thickness or variable-thickness aquifer; porous medium or fracture zone; constant-flux or no-flow boundaries; and one, two, or three dimensional simulation of the physical system. They also describe the configuration of the contaminant source as either a point, line, or area source. Both the flow field and source may have different temporal domains as well; i.e., steady

- state or transient flow conditions; continuous, pulsed, variable, or intermittent source.
- o Fluid and/or media properties criteria—selection criteria in this category are often related to whether the site can be represented as homogeneous in terms of certain physical parameters such as hydraulic conductivity, specific storage, porosity, and recharge. If so, simpler analytical models may yield acceptable levels of accuracy; otherwise a numerical method might be necessary for development of a cleanup target.
- Transport/transformation process criteria— the model selected must be able to represent with an acceptable degree of accuracy and reproducibility all physical, geochemical, and biological processes significantly affecting the migration and fate of contaminants through soils and ground water at a given site. Development of these criteria is dependent on the accuracy and sufficiency of the analyst's conceptual model of the site, and the analyst's ability to develop an acceptance criterion in terms of level of accuracy or detail.

Several fundamental differences must be kept in mind that affect the selection criteria for physical (flow, transport) process codes versus geochemical or microbial codes. As discussed in Sections 4.3 and 4.8.1, flow and transport codes include, and are based on, spatially and temporally varying process models and parameters. Geochemical and, to a lesser extent, some microbial codes generally are founded on either equilibrium or batch-reactor process conditions (Mercer and Faust, 1980A,B; Kincaid et al., 1984). Therefore, for flow and transport codes, their ability to simulate the variety of boundary conditions, the spatial

domain(s) at the site, and the variability of the physical parameters describing the matrix as well as those for the liquids, solids, and/or gases being transported, are critical selection criteria.

Geochemical and microbial codes, on the other hand, seldom if ever consider spatial dependence, and the completeness of the geochemical data base for the site will be more critical to selection of a specific code (Kincaid et al., 1984; Mercer and Faust, 1980A,B).

In summary, model selection begins with use of objectives criteria to direct initial selection of a screening-level or detail-level model. Technical and implementation criteria then guide the choice of specific model (Boutwell et al., 1985).

## 4.8.3.3 Implementation Criteria

Implementation criteria are the practical considerations attendant to model selection and application, such as ease of acquisition of the desired model, i.e., whether it is in the public domain or a proprietary code; compatibility with the analyst's hardware and software; computer time needed to make model runs, e.g., to obtain acceptable convergence of a numerical solution to a complicated finite element code; availability and ease of use of model documentation and manuals; user support provided by the model vendor;

extent to which a given model has been validated on computer systems like the analyst's; availability of validation/benchmarking data sets; availability of appropriate data for the code selected; schedule and budget limitations of the model study; staff resources and expertise; staff familiarity with the selected model; and other similar factors (Boutwell et al., 1985; Mercer and Faust, 1980A,B; Kincaid et al., 1984; Donigan and Rao, 1986A; Keely, 1987A).

Staff resources and user experience/ familiarity can significantly impact the model choice, and the interpretation of the results. The analyst must be able to determine the fit of the selected model to the conceptual understanding of the physical system in order to determine necessary or acceptable adjustments to a given model. Several authors have argued that neither equipment constraints nor user familiarity should lead to selection of a model that does not meet the technical criteria of the study.

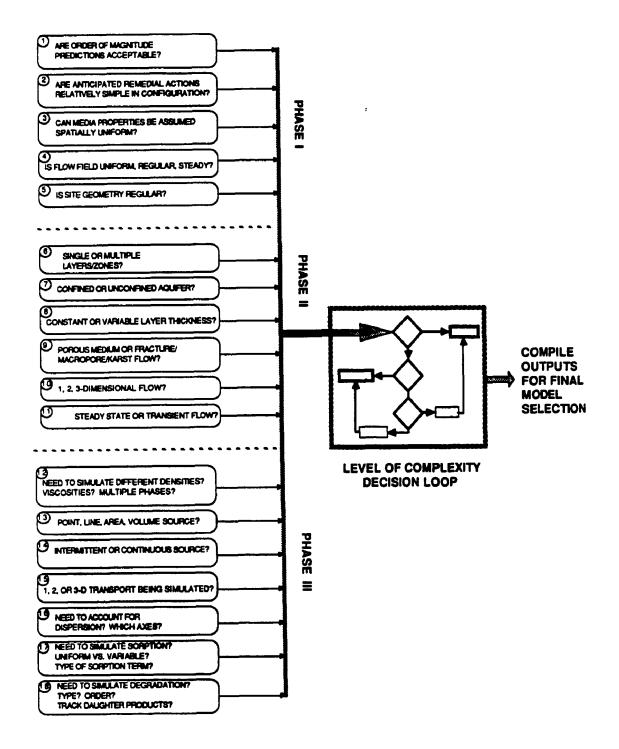
Others have pointed out that in many cases, the largest discrepancies in model predictions have resulted not from the choice of model, but rather its application and interpretation (Ornstein, 1988). Different models, if appropriate to the site study, should give similar results using the same input data set. However, different modelers applying the same model to a given

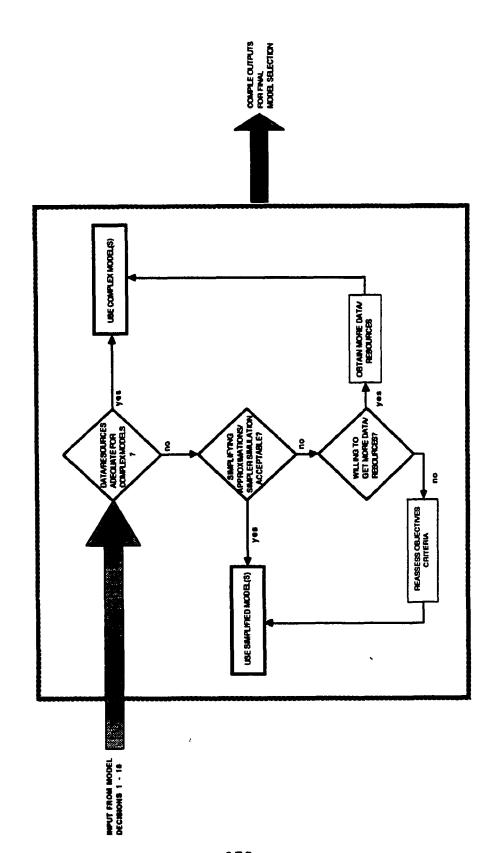
site may get varying results based on individual choices of grid layout, time step, convergence criteria, choices of initial and boundary conditions, and other factors dependent on subjective judgement and individual experience (Keely, 1987A), as occurred in the case study presented in Chapters 5 and 6. This problem has led some analysts to use models only for comparing different scenarios or remedial alternatives, rather than for predicting an absolute value, for example a cleanup level (Mercer and Faust, 1980A,B; Boutwell et al., 1985; and others).

# 4.8.4 A Model Selection Decision Framework

The analyst must make a sequence of decisions, based on the specific technical and implementation criteria appropriate to a given site problem, to select a model for exposure assessment or cleanup level-setting. This section presents a decision framework for model selection, as shown in Figure 8. It was compiled from the selection criteria discussed by several reviewers, including Mercer and Faust (1980A), Boutwell et al. (1985), and Bond and Hwang (1988). This framework is by no means intended to be comprehensive, but rather to illustrate some of the main decisions common to most contaminant transport modeling exercises, especially in the earlier stages of model selection. Individual sites

FIGURE 8
Model Selection Decision Framework for SOCEM





and analytical applications likely will have many unique complexities which cannot be accounted for in such a simplified scheme.

This decision framework would operate during the three site characterization/ model selection phases presented in Figure 7: determining the level of model required (Phase I); selecting the model or models for simulating the unsaturated and/or saturated flow fields (Phase II); and selecting the model or models for simulating transport and transformation processes affecting the contaminant(s) of interest (Phase III). In each phase, one uses technical criteria to obtain an initial set of candidate models, then further screens them against a set of implementation criteria.

By using this framework, the analyst would continuously reevaluate the type and/or level of complexity of the desired model against the level of data available to support its use. This means considering whether to collect additional data to support the more complex model, or reassess whether the reduced uncertainty or increased precision expected to result is worth the added effort and expense. Any single decision could direct the analyst to reevaluate the study objectives and modify the choice or application of the model, or the level of confidence expected in the result. This is depicted in Figure 8 by

taking each key decision through the Level of Complexity Decision Loop.

The analyst must then combine the outcomes of the individual decisions, each of which should yield a "short list" of acceptable models. The model or models common to all individual "short lists" that best achieves all technical, implementation, and objectives criteria is/are selected. The analyst then installs, calibrates, and runs the model(s) to back-calculate a cleanup level, as described in Section 4.8.2.

The individual decisions are described in the following subsections. A brief discussion of the potential consequences associated with an incorrect choice at each major decision step is given as well.

#### Phase I. Selecting the Level of Model

As discussed in Section 4.8.2.1, once the decision has been made to model, the analyst makes an initial selection between screening-level and detail-level assessment tools. Boutwell et al. (1985) and Mercer and Faust (1980A) equated this to the choice between using analytical and numerical models, as shown by questions 1-5 in Figure 8. "Yes" answers to all of these questions imply that one or more analytical models will adequately satisfy the analytical objectives at this stage. "No" answers to any of these questions, as

discussed in Sections 4.8.4.1 through 4.8.4.5, would drive the user to select, or strongly consider, a numerical model.

## 4.8.4.1 Order-of-Magnitude Predictive Accuracy

Several authors, including Keely (1987A) and Boutwell et al. (1985), consider analytical models incapable of yielding predictions with accuracy greater than Boutwell et al. (1985), consider analytical models one (in some cases several) order of magnitude. In the initial RI/FS stages, such as designing the Remedial Investigation data collection efforts or developing a list of technologies or remedial alternatives for initial screening, such accuracy may be acceptable.

However, for detailed comparisons of the effectiveness of several alternatives in achieving a given source strength reduction later in the FS, for example, or when developing a more quantitative risk estimate or cleanup level estimate, greater accuracy likely is required. Boutwell et al. (1985) and others would argue that such analytical objectives demand the use of numerical methods; this will be discussed further in Chapter 6.

# 4.8.4.2 Complexity of Anticipated Remedial Actions

Many authors consider models more applicable when

comparing the effectiveness of various remedial alternatives than when estimating an absolute cleanup level (Boutwell et al., 1985; Mercer and Faust, 1980A; Randall, 1985). This is because, presumably, the same model will be used for comparing several remedies, using the same input data set; therefore, uncertainties and errors in the results should be the same between model runs even if their absolute value cannot be determined. However, many remedial actions, such the same between model runs even if their absolute value as partiallypenetrating wells, permeable treatment beds, or some types of subsurface drains, cannot be simulated accurately using analytical methods because of their effects on the flow field or because they must be represented using variable media properties (Boutwell et al., 1985). Therefore, it may be difficult to make meaningful cross comparisons of all remedial alternatives being considered for a site cleanup by using a single model or set of models, although the model(s) could still provide useful insights in the initial screening phases of the Feasibility Study.

While this report focuses on back-calculation of cleanup levels, recall that earlier in Chapters 3 and 4 the concept of consistency in model application was highlighted. In other words, even early in the scoping stages, the analyst should look ahead to both selecting

a remedy and selecting a cleanup level, to optimize the design of the Remedial Investigation. Therefore, if the same model or model set can be applied throughout the analysis to achieve both purposes effectively, the consistency of the exposure assessments from site to site is maximized, while uncertainties are minimized to the extent possible.

## 4.8.4.3 <u>Homogeneity of Media Properties</u>

The next several decisions consider the domain configuration. Question 3 asks whether, or to what extent, media properties important to definition of the flow field can be assumed to be uniform in the x,y, or z directions over the area of interest. As discussed repeatedly throughout this chapter, homogeneity and isotropy seldom exists over the distances of interest at a Superfund site; however, depending on the immediate objectives of the analysis and the scale of the site problem, such assumptions have often been employed to simplify the analysis.

As discussed in Section 4.8.1.3, many analytical models and some simpler numerical codes can only simulate a single value for certain hydraulic properties of the medium over the entire model region, for example hydraulic conductivity or recharge. Numerical models using finite element or finite difference grids allow

for representation of the spatial variability of such parameters, but the increase in simulation accuracy thus gained will be highly dependent on how accurately and how precisely the grid represents the variations in the physical system over the area being modeled, i.e., on the level of detail available at a given stage in the site characterization. At many hazardous waste sites, the spatial distribution of recharge, porosity, storage, and other physical parameters is seldom well known, and the analyst may be tempted to use averaged or equivalent values for many parameters, especially if known variations are limited (e.g., hydraulic conductivities vary by less than a factor of 10). The magnitude of errors thus generated can only be assessed on a sitespecific basis (Mercer and Faust, 1980B; Camp, Dresser and McKee, 1987B; Keely, 1987A).

However, early in the site investigation, the analyst might assume uniformity of media properties such as hydraulic conductivity, and estimate their values from the literature for input to a simplified model to obtain gross estimates of ground water velocities. This can help direct further field investigations to focus on measurement of those media properties to which the flow estimates are shown to be the most sensitive using the simplified model's calculations (Bachmat et al., 1978; Keely, 1987A; Camp, Dresser and McKee, 1987B).

## 4.8.4.4 Uniformity of the Flow Field

Question 4 asks whether it is reasonable to assume the flow field is uniform and steady (Boutwell et al., 1985). Most analytical models assume steady, uniform flow conditions, i.e., invariant over time or over the width of the flow field, as discussed in Section 4.8.1.3. This is seldom the case in the unsaturated zone (Donigan and Rao, 1986A; Jury, 1986A; Kincaid et al., 1984) except under relatively constant recharge situations, such as beneath recharge basins (Boutwell et al., 1985). A simplifying assumption often made at the screening stage is to neglect the unsaturated zone in order to simulate saturated flow and/ or transport using an analytical technique (Boutwell et al., 1985).

#### 4.8.4.5 Regular Site Geometry

Many analytical models assume regular site geometries (e.g., circular, conical, or rectangular in shape, constant aquifer thickness, etc.). Boutwell et al. (1985) point out that while these conditions are rarely observed in the field, they may provide acceptable first-order approximations in many cases, for example when the contaminant source is a rectangular surface impoundment or when single-or double-layer shallow aquifers are being simulated.

Once an initial decision has been made either that an analytical model is adequate on technical grounds, or that the study objectives and site complexity warrant use of a numerical model, the analyst revisits the implementation criteria to ensure that data, resources, and other factors support the level of model being considered.

## Phase II. Selecting the Flow Model

contaminant transport may be simulated using a separate code, or simultaneously with the flow using a single model; but in either case, fluid flows are simulated first. Therefore, selecting the fluid flow model (or the fluid flow portion of a combined code) represents Phase II of the decision process in Figures 7 and 8. In both succeeding phases, certain decision points clearly revisit parameters or factors previously addressed, but at a greater level of detail.

## 4.8.4.6 Single or Multiple Layer/Zone

The analyst must account for all fluid conducting layers or zones of interest in the saturated zone, or multiple saturated zones if contaminant transport therein is known or suspected. Additionally, simulation of unsaturated zone flow may be necessary. Many simpler models (especially many analytical methods) simulate

single-layer flows only. This may provide an acceptable first approximation if the majority of flow in a multi-layered system is conducted through one zone, or where hydraulic conductivity and other properties are virtually equal in all zones such that they can be simulated as a single equivalent layer (e.g., porosities and hydraulic gradients within approximately 25 percent of each other; hydraulic conductivities within an order of magnitude).

# 4.8.4.7 Unconfined versus Confined Aquifer

The model must simulate the physical system at the site, which may involve either water table aquifers or confined systems, or both. Additionally, simulation of unsaturated zone flows may be desired. The majority of flow models have been written to simulate confined flow conditions, since the solution is simpler and thus more rapidly solved than the water table condition.

Some modelers have elected to solve mixed-condition or water table problems with a confined flow model due to computational efficiencies and/or familiarity with a given code. However, this approach can cause errors because the transmissivity value is held constant in confined systems, whereas it varies with head in an unconfined aquifer. These errors are often manageable, or neglected, if it can be assumed that water table

fluctuations are minor (say, less than 10 percent) compared to the total saturated thickness of the unconfined zone. In several scenarios this assumption will likely be violated, e.g., where the unconfined aquifer is thin (say, less than 25 feet in thickness, depending on matrix properties and flow rates), or under various remedial action scenarios involving significant pumping or recharge rates.

# 4.8.4.8 Spatial Variability of Layer Thickness

Many simpler models, especially analytical methods, are limited to use for essentially constant thickness layers. One general rule is that simulation of flow in a layer varying in thickness by more than about 10 percent of its average value over the area of interest will require discretization into elements and use of a numerical method. As with the unconfined aquifer condition described in Section 4.8.4.7, failure to account for varying thickness results in an inaccurate transmissivity distribution, which in turn will skew the calculated fluid velocities and any subsequent prediction of contaminant travel times.

# 4.8.4.9 <u>Porous Media versus Fracture/Macropore/Karstic Flow</u>

As discussed in Section 4.3.1.5, flows beneath

sites with fractured subsurface media are difficult to simulate. The majority of available flow codes are designed for porous media, and currently many analysts continue to apply porous media models to fractured systems by using some average of the matrix pore velocity and fracture/channel velocity, or by using a numerical method and applying dual porosity estimates (Kincaid et al., 1984). For example, some analysts have simulated flow near fault systems using a linear series of finite elements having hydraulic properties of the materials in the shear zone, as contrasted with those of the surrounding matrix.

The applicability of such assumptions is dependent on degree of fracturing and scale of the analysis. The more highly fractured the soil or rock medium, and the smaller the ratio of the pore sizes, the less accuracy will be sacrificed by using an equivalent porosity. Likewise, the smaller the average fracture spacing relative to the size of area being simulated, the smaller the error likely to be introduced by an equivalent porosity assumption. In time this problem will be alleviated somewhat as fractured rock models enter mainstream use. However, the magnitude of analytical errors from this source will continue to be attributable primarily to the adequacy of the site investigation effort; i.e., whether any fracture system

present at a site is successfully detected and adequately studied.

#### 4.8.4.10 Dimensionality Required in the Flow Model

Different schools of thought exist regarding the complexity of the flow field to be simulated. The more spatial dimensions the model is simulating, the more complex it tends to be, resulting in both more intensive and detailed input data requirements, and greater resource requirements including computer storage capacity, computational time, data coding effort/ time, etc.

Kincaid et al. (1984), Boutwell et al. (1985), and others have pointed out that the dimensionality of the flow simulation may be limited by the requirements of the transport model. The model used to simulate a given aquifer layer or site zone (e.g., surface soils) likewise may affect the dimensionality of models used to simulate other zones. Conversely, in the case where the analyst is considering combining a multidimensional transport code with a geochemical code, the state-of-theart in available codes, combined with data and computer resource limitations, may limit the user to, say, one-dimensional transport with a relatively limited or "compact" equilibrium geochemical code. However, two- or three-dimensional flow and transport codes would

be needed up front to properly characterize the onedimensional transport pathway, and a more complete geochemical code and data base would be used up front to feed the compact code used in the coupled model (Kincaid et al., 1984).

Some modelers have suggested selecting a three-dimensional model as the default unless it can be demonstrated satisfactorily that fewer dimensions are sufficiently accurate, based on the level of homogeneity and isotropy in important media properties. However, data is seldom collected in sufficient detail to run a three-dimensional model at Superfund sites. In many cases, a one- or two-dimensional model was selected based on data availability, where not enough was known about spatial heterogeneity even to determine whether a three-dimensional simulation was necessary (Mercer and Faust, 1980A, B; Keely, 1987A; Kincaid et al., 1984).

In many such cases, however, a number of one- or two-dimensional model runs might be performed within a project's resource constraints, and still greatly enhance conceptual understanding of the site. Lower-dimensional modeling for screening purposes may also help guide decisions on whether collection of additional data to run the three-dimensional simulation is worthwhile.

# 4.8.4.11 <u>Temporal Flow Domain (Steady-state vs. Transient)</u>

The analyst must consider whether flows are steady, or can be acceptably simulated as steady-state conditions, or whether the model must simulate transient flow conditions in the area of interest. Freeze and Cherry (1979) defined steady-state flow as the condition where the magnitude and direction of the velocity vector defining the flow field at any point throughout the area of interest (as given in terms of the gradient and hydraulic conductivity at that point) is constant with time. Strictly speaking, a steady-state model would be applicable only if the ground water table maintained its elevations over the area of interest throughout the period being simulated by the model. This seldom occurs in actuality due to transient head fluctuations caused by natural and anthropogenic events of recharge and discharge.

However, as with other factors discussed in this section, typically the analytical models and some simpler numerical techniques use steady state assumptions. Transient flow simulations generally require far more data and computational resources than steady-state codes, and require use of the more complex codes. Time-series data on recharge, discharge, and heads is seldom available in sufficient detail at

Superfund sites to support runs of highly complex transient-flow codes, and the analyst is forced to use steady-state approximations.

Errors associated with erroneous application of the steady- state assumption can be quantified only on a site- specific basis. For example, the magnitude of error would be expected to be greater at a site whose actual hydrologic regime was highly erratic, e.g., sporadic pumping schedules in the area, and where hydraulic gradients and flow directions are highly sensitive to pumping events, than in an agricultural area where cycles of pumping and recharge are consistent from year to year and readily traceable to precipitation and planting patterns.

As with other factors, the steady-state approximation may be acceptable, depending on the modeling objectives, if transient head fluctuations tend to be small relative to the total saturated thickness (say, less than ten percent of the total aquifer or flow system thickness), and if the topographic configuration of the water table remains relatively constant despite the transient events (i.e., high and low points retain their relative differences in elevation). In such cases, many modelers have applied a steady-state analysis assuming a fixed head at its mean value at a given point or points. A second approach is to solve a

series of steady- state solutions for each time period where the system experiences significant hydrologic stresses (e.g., known, significant pumping or recharge events).

## Phase III. Selecting the Contaminant Transport Model

The preceding decisions should result in compilation of a "short list" of flow models meeting the study criteria by the end of Phase II. The analyst can select a flow model and then choose a separate, compatible transport model, or seek a single model that combines simulation of flow and transport. Frequently modelers have used a more sophisticated model for flow than for transport, in part because transport phenomena are generally less well understood at a given site.

#### 4.8.4.12 Contaminant Density, Solubility, Viscosity

The next two questions concern waste or contaminant characteristics. Contaminants with approximately the density of the advecting fluid will tend to be transported with it, and their transport can be represented adequately with the flow model or with simplified transport models. Denser or lighter contaminants may migrate in separate phases, as discussed in Section 4.4. Such behavior can only be simulated adequately by specialized numerical models.

Likewise, water-insoluble contaminants may be highly retarded, or may migrate ahead of the dissolved contaminant front in the ground water.

Most simplified saturated-zone transport models assume water solubility of the contaminants and single-phase flow. For small gradients in fluid density, viscosity, concentration, and/or temperature, if the analyst can show or assume safely that they have negligible effects on the fluid velocity distribution, such methods will be adequate. In most natural settings, such effects are negligible, unless the system being simulated includes geothermal fluids or a coastal area affected by seawater intrusion.

However, anthropogenically-altered systems may have flow fields affected by heat, e.g., near geologic repositories for high level radioactive wastes (UCLA, 1981, 1982; Simmons and Cole, 1985; Kincaid et al., 1984), or reinjection zones for geothermal fluids (UCLA, 1981). Likewise, there may be significant density and/or viscosity effects near releases of very buoyant or dense concentrated contaminants such as hydrocarbons from underground storage tanks, pipelines, production facilities, and hazardous waste disposal areas (see Sections 4.4, 4.6). Some more complex saturated zone models, and some unsaturated zone models, account for multiphase transport, often including a gas phase in the

vadose zone.

Again, for screening-level investigations, the assumption of miscible flow may provide a useful first approximation, given careful choices of boundary conditions (e.g., assuming a continuous-release area source (see next subsection) in situations where relatively large releases would cause a large, coherent blob of contaminant to float atop the ground water or sink to the lower confining layer). The importance of simulating these factors depends greatly on their importance in the conceptual model, which is completely site-specific (Barcelona et al., 1987). Truly coupled models account for changes in flow due to density and viscosity of the fluid (Kincaid et al., 1984; Mercer and Faust, 1980A,B).

# 4.8.4.13 Source Spatial Configuration

The contaminant may enter soils and/or ground water at a point (e.g., a pipe outfall, a pinhole leak in an impoundment liner, or an injection well), along a line (e.g., an infiltration trench or relatively conductive backfill material surrounding a leaking pipeline), or from an areal or nonpoint source (e.g., beneath an unlined landfill or surface impoundment; soils surrounding leaking, scattered drums; or subsoils beneath fields sprayed with pesticides or liquified

wastes). The source type can affect the dimensionality and thus the complexity of the transport model.

Point sources may be simulated with one-, two-, or three- dimensional models. Line sources or areal sources generally require two- or three- dimensional models, while a volume source, such as a block of contaminated soils within the saturated zone, would require a three-dimensional source simulation. As with the dimensionality of the flow model (discussed in Section 4.8.4.10), for screening-level analyses (and sometimes for more complex analyses if data is limited), it is sometimes possible to "collapse" the dimensionality of the model in one direction to simplify the analysis, if homogeneity can be assumed in the "collapsed" dimension (Mercer and Faust, 1980B). Line or area sources can be simulated with one-dimensional models if contaminant concentration is assumed uniform except in the dimension simulated, for example, by using averaged concentration and velocity values (Donigan and Rao, 1986A; Mercer and Faust, 1980B; Faust and Mercer, 1980).

The analyst must be prepared to account for the potential effects of such simplifying assumptions on the accuracy of the model output, especially if the results are expected to be used in setting numerical cleanup targets or in quantitatively assessing risks. Use of a

one-dimensional transport model to simulate an areal source or a line source typically causes overestimation of concentration and underestimation of plume width. This effect is very scale dependent, diminishing with increased downgradient distance of the receptor from the source (Domenico and Palciauskas, 1982; van Genuchten and Alves, 1982; Javendel et al., 1984; Molz et al., 1983).

Likewise, the analyst may use maximum concentrations rather than means as initial inputs, especially in screening-stage analyses, to give conservative "reasonable worst case" receptor concentrations. These effects should be considered together when model outputs are being used to make decisions on collecting more data or setting final cleanup targets.

## 4.8.4.14 Source Temporal Configuration

The contaminant release configuration in the model should be matched to the source pattern of release in the system, to the extent possible. Contaminants can enter soils, or move from surface soils into ground water, as intermittent pulses or as relatively continuous flows or seeps. Intermittent release patterns may be related to many factors, including intermittent application of contaminants to the surface

or subsurface (through dumping, land application, etc.); natural variations in infiltration carrying the contaminants, for example, variations in precipitation, snowmelt, or surface runoff; or source strength decay with time (Donigan and Rao, 1986A).

As with other factors discussed in this section, most simpler models are limited to simulation either of slug sources or continuous sources, while more complex models provide for complex, intermittent or time-varying contaminant release distributions through variable time steps and other approaches. Again, simplified methods may provide useful insight at the screening stages provided the consequences of their use are considered by the analyst. The errors due to inappropriate representation of the temporal release pattern are difficult to quantify and are site-specific.

Typically, the effect of using a continuous source model to predict an intermittent source varies according to the source strength used as input. Use of average source strength or contaminant flux leads to underprediction of discrete concentration fronts at the receptor location. These effects tend to decrease with increasing receptor distance from the source.

Conversely, use of the maximum contaminant concentration for conservative predictions will over-predict receptor point concentrations if a continuous-source model is

used to simulate an intermittent-release system.

# 4.8.4.15 <u>Dimensionality Required in the Transport Model</u>

A widely-applied guideline is that the dimensionality of the transport model should always be less than or equal to that of the flow model (Mercer and Faust, 1980A,B; Kincaid et al., 1984; and others). Some modelers have suggested selecting a three-dimensional model as the default unless it can be demonstrated satisfactorily that fewer dimensions are sufficiently accurate, based on the level of homogeneity and isotropy in important media properties affecting transport. However, data is seldom collected in sufficient detail to run a three- or, often, even a twodimensional transport model at Superfund sites.

In many cases, a one-dimensional model was selected based on data availability, where not enough spatial detail on transport properties and characteristics was available to support use of the more complex models. Until recently, analysts were limited by the lack of available, sufficiently documented 2-D and 3-D models as well. However, one-dimensional models have significant limitations, including inability to simulate transverse dispersion (normal to the flow path of the model) or multiple sources, and limited validity if the areal

source is not large or the concentration is not homogeneous in the plane normal to the flow path of the model.

This results in overprediction of receptor point concentrations, the magnitude of which is site-specific and difficult to quantify. As with other factors, this does not preclude the use of such methods at the screening stages, but their applicability and limitations must be carefully considered.

## 4.8.4.16 Simulation of Dispersion

As with most other factors discussed in this section, the importance of dispersion to the migration and distribution of a given contaminant varies on a site-specific basis. Most models have some ability to account for either longitudinal or transverse dispersion, or both. Simplified models in which dispersion is not considered, or for either longitudinal or transverse dispersion, or both. model runs in which dispersion effects are "turned off," will result in a worst-case prediction of maximum contaminant concentration at the downgradient receptor point. This also causes travel time for breakthrough of the contaminant to be over-predicted in some instances.

As discussed in Section 4.3.1, many researchers have expressed dissatisfaction with the adequacy of the

advection-dispersion equation in estimating dispersive effects measured in the field, and its apparent relationship to the scale of measurement or simulation of contaminant transport (Keely, 1987A; Simmons and Cole, 1985; Kincaid et al., 1984; Jury, 1982; Gelhar et al., 1979; and others). Likewise, coefficients of dispersion are very difficult to measure in the field, and such measurements are not routinely made in Superfund site investigations. Typically, dispersion values are adjusted in modeling studies during the calibration process, but accurate and reasonable estimates are time- and data-intensive to obtain.

# 4.8.4.17 Simulation of Sorption

Question 17 concerns whether the transport model is capable of simulating sorption. Since most sites are highly heterogeneous in terms of (a) temporal and spatial distributions of soil properties affecting sorption and (b) contaminant concentrations, it may be important to simulate temporally and/or spatially varying sorption characteristics (Donigan and Rao, 1986A, B; Jury 1986A; Jury and Valentine, 1986). Sorption, as discussed in Sections 4.3.2 and 4.7, is often represented by partition or distribution coefficients to approximate retardation effects in the transport equation.

Partitioning of contaminants in a given medium are expressed in terms of equilibrium solution concentrations of the contaminant in each phase, as discussed in Section 4.7. In dilute solutions, sorption relationships can generally be expressed as a linear isotherm, while as contaminant concentrations increase, sorption effects become nonlinear (Kincaid et al., 1984; Jury and Valentine, 1986). For many hydrophobic contaminants, nonlinearity becomes significant when contaminant concentrations exceed approximately 50 percent of their water solubility (Neely and Blau, 1985); while for hydrophilic contaminants, this threshold must be determined on a site-specific basis.

Simpler models often may not assume any sorption (or other mechanisms collectively comprising retardation), and thus generate conservative estimates of worst-case contaminant receptor concentrations and/or travel times. These still may be useful as screening-level estimates, but one often-used criterion suggests that if the retardation factor is greater than 5, models that account for sorption and/or other retardation mechanisms should be selected (Bond and Hwang, 1988). Many modelers have asserted that more complex or detailed analyses, such as those used to generate final targets or risks, always should consider sorption effects for all contaminants affected by retardation.

While a nonlinear isotherm model would be more accurate for most transport analyses, especially for mixtures of relatively hydrophobic contaminants, the majority of the for most transport analyses, especially for mixtures of transport models currently in widespread use that simulate sorption use a linear isotherm (Kincaid et al., 1984). In simpler models, a single retardation term often represents the combined effects of a variety of subsurface sorption mechanisms, while some geochemical codes explicitly consider the individual contributions of the most significant mechanisms (Kincaid et al., 1984).

Use of a single, lumped sorption/retardation term based on a linear isotherm can lead to mass balance errors at very low contaminant concentrations. These produce conservative over-predictions of contaminant transport by overestimating the solution phase concentration and under-representing the sorbed phase concentration, which indicates higher-than-observed contaminant receptor point concentrations and shorter travel times in many instances.

#### 4.8.4.18 <u>Simulation of Degradation</u>

Chemical and biological degradation processes, and radionuclide decay, can be significant factors at many sites, as discussed in Sections 4.3.2 and 4.3.3.

Simplified analytical models seldom account for these processes, and generate conservative receptor concentrations useful for screening-level estimation. More sophisticated analyses require using models capable of accounting for the most significant transformation processes active at the site of interest, and on the analyst's ability to identify these processes and incorporate them into the conceptual model.

Many transport models simulate first-order decay, while relatively few simulate higher-order decay processes. Fewer still can effectively track migration of daughter products and byproducts through the subsurface. The extensive data base of geochemical and site geohydrologic properties required to employ such models is seldom assembled in Superfund investigations.

Some analysts have attempted to simulate transformation by simulating conservative transport of the parent compound and then apportioning receptor concentrations on the basis of estimated or assumed transformation rates, which does not account for differences in sorption properties and chemical or biological decay rates often seen in the daughter products (Barcelona et al., 1987). Many models capable of simulating radionuclide decay are available and others are under development (Kincaid et al., 1984; Office of Technology Assessment, 1982; Simmons and Cole,

1985; van der Heijde and Beljin, 1986; and others). As with many factors discussed in this section, errors due to failure to account for these mechanisms in individual transport simulations are difficult to quantify confidently, and their magnitude depends greatly on conditions at the site in question.

#### 4.9 Assumptions and Uncertainties

When modeling contaminant transport and transformation to assess risks or set cleanup levels, it is seldom if ever possible to simulate mathematically all processes and interactions at a given site. causes problems when site risks or cleanup levels are estimated on the basis of models or other extrapolations of fate and transport, since significant errors may result from the difference between actual and estimated distributions and concentrations of contaminants (Barcelona et al., 1987; and others). Most theoretical expressions discussed in this chapter contain assumptions and simplifications in order to solve practical problems such as incompleteness of data, or to obtain mathematically tractable solutions (Barcelona et 1987: Keely, 1987A). al.

Much attention has been given to the importance of uncertainty analysis in risk assessments, and in the application of fate and transport models within the risk

Institute, 1987). Uncertainties may be related to the model selection criteria, the specific decision steps followed in selecting the appropriate model, and to the choice of input parameters used in its application.

These uncertainties must be identified and characterized to the extent possible, so that the decision maker is aware of the consequences of alternative decisions when risk assessments are used to set cleanup levels on a site specific basis.

Therefore, it is essential to analyze and track the magnitude of errors introduced by each simplifying assumption or expression. Even rough approximations of contaminant levels can be difficult to make because of the number and variety of processes involved, and the resultant difficulties in obtaining sufficient site data to adequately characterize each important fate and transport process (Keely, 1987A). The user must be able to assess what effect such assumptions will have on the outcome. An erroneous assumption of homogeneous hydraulic conductivity, for example, could lead to overor under-predictions of contaminant time of travel to a receptor by one to several orders of magnitude (Keely, 1987A,B; Barcelona et al., 1987), and to other predictive errors.

This section provides a brief overview of the

sources of uncertainty typically being encountered in setting cleanup levels; analytical methods to assess uncertainty; and some approaches for presenting this analysis and its results to the decision maker.

#### 4.9.1 Sources of Uncertainty

Many sources of uncertainty may be present in the exposure assessment, and in other components of the risk assessment, as have been mentioned throughout Chapters 3 and 4. These may be grouped into the following categories:

- 1. Chemical-specific unknowns--uncertainties related to the toxicological properties of the chemical contaminants at the site, including mode of action, target organs and individuals, and accuracy of the dose-response models used to characterize their toxicity to human and environmental receptors (National Research Council, 1983; Cox and Baybutt, 1981);
- 2. Unknowns of contaminant distribution—knowledge of specific concentrations, spatial distributions at the site, exact chemical species and their mixtures is often very limited and/or absent for many areas at a given Superfund site. The length of time they have been present, and their temporal patterns of disposal or release, are often poorly understood also, making it difficult to characterize transformation/degradation phenomena in site soils, as well as site-specific transport and toxicity characteristics of the mixture of compounds at any particular location;
- 3. Problems with selecting appropriate indicators— In some instances, Superfund analysts will model a subset of the most mobile and/or most toxic compounds as indicators of the behavior of the contaminant mixture. A subset of indicators is regularly monitored to detect releases to ground

water at operating RCRA facilities, as a sort of "early warning" system (40 CFR Parts 264 and 265, Subpart F; EPA,1986D). The unknowns of site data and contaminant distributions exacerbate the difficulties associated with trying to model the behavior of all contaminants present, and make it similarly difficult to select a representative subset that is feasible to model, in order to simplify the analysis (EPA, 1986A). Using a subset of indicators introduces its own set of uncertainties into the risk assessment, as will be discussed further in Chapter 6;

Uncertainties in site characterization -- This 4. includes imperfect knowledge of contaminant distributions in surface and subsurface soils (both temporal and spatial), and of the spatial variability of soil types and physical/chemical properties, and of hydrogeologic characteristics (site heterogeneity). Some physical and chemical parameters are distributed spatially as random variables, while others clearly follow more ordered patterns related to geologic layering, etc. (e.g., horizontal vs. vertical distributions of transmissivity and hydraulic conductivity; Kincaid et al., 1984; Barcelona et al., 1987). Accuracy of exposure estimates that are calculated based on these parameter estimates often decreases as receptor distance increases from the source (Bolten et al., 1983; and others).

Likewise, uncertainties are introduced by using statistical methods to collect random samples to characterize these parameters, and errors may be caused by inappropriate sample sizes, stratifications, or individual sample measurement errors. These errors are difficult to quantify and can be characterized only on a site-specific basis (Cox and Baybutt, 1981; EPA, 1986K; Camp, Dresser and McKee, 1987A; Mason, 1983; Barth and Mason, 1984);

5. Uncertainties in the components of the exposure assessment— This includes uncertainties regarding correct values for physical and chemical parameters, as mentioned previously (Cox and Baybutt, 1981); in time rates of contaminant emissions or release from source areas (Bolten et al., 1983); in the appropriate choice of models and their application, as discussed previously; and in characterization of current and/or potential future

- receptors in the model runs (Bolten et al., 1983; Schultz et al., 1987);
- 6. Uncertainties regarding choice of model, including for example the lack of completeness of any single model in characterizing site processes (Cox and Baybutt, 1981; and others), as discussed throughout this chapter; and
- 7. <u>Uncertainties of model application to the site problem</u>, as discussed throughout this chapter.

#### 4.9.2 Methods for Uncertainty Analysis

Uncertainty analyses are useful in situations such as model-based quantitative exposure assessments where the exact functional relationships relating the output variable (e.g., target dose, or contaminant concentration at the receptor location) to the various input variables are not known with certainty, and are being estimated imperfectly by simplified mathematical expressions (the analytical or numerical model). Their purpose is to estimate (to the extent possible) the magnitude of error or uncertainty in the output variable, and the extent to which each input variable contributes to the uncertainty in the value of this output.

This section provides a synopsis of nine categories of methods used for quantitative uncertainty analyses of dose-response modeling or exposure assessments. It is compiled largely from reviews by Cox and Baybutt (1981) and Bolten et al. (1983), among others. Section 4.9.3

presents several examples illustrating general applications of such methods to analyses similar to Superfund soil cleanup problems, showing how uncertainties might be presented to a decision maker.

The nine categories are presented roughly in order of increasing complexity of application. This corresponds somewhat to an increasing level of knowledge of the actual system being simulated (i.e., accuracy and detail of the conceptual model), as well as to the level of detail in the site characterization data available to the analyst. They are as follows:

- 1. Sensitivity analysis is a simple, widely used method for determining which input variables have the greatest influence on the value of the output variable by calculating the output value while varying each input parameter over its range of values. Variations of this method using subsets of the input parameters or other measures describing the distributions of their values are given below.
- 2. The extreme value approach can be used when it is not possible to estimate probability distributions of the input variables or summary statistics describing them. The analyst selects maximum, minimum, and "best" values for each input variable, and calculates the corresponding combinations of maximum, minimum, and "best" values for the output. Neither the relative contributions of each input variable to the uncertainty nor the probabilities of various output values are calculated in this approach.
- 3. The confidence interval method produces confidence interval bounds for various estimates of the output variable due to statistical variability in the input parameters, but does not rank or calculate the relative contributions of each input variable to the bounds of the output confidence intervals, nor does it calculate an overall uncertainty. It

requires that the functional relationship between the inputs and the output variable(s) be fairly well known.

- Linear propagation of errors is a modularized method applicable to components or all of a multisystem assessment. It involves calculating a first order Taylor series expansion of the output function, expressed as a function of random input variables. From the Taylor series coefficients, the variance of the output variable can be calculated based on the covariances of the inputs.
- 5. The analytic approach can be used when the functional relationship between the input and output variables is known, is relatively simple, and can be expressed as an explicit formula (e.g., when it can be well described by one of the simpler analytical solutions). Thus, either the probability distributions must be known for the input and output variables, or they must be characterized by certain summary statistics. It is sometimes possible to approximate the values for the summary statistics using Taylor series expansions, however, this produces only approximations of the probability distributions of the input and output variables. This approach is sometimes used to apportion the output's estimated uncertainty among the input parameters.
- Monte Carlo simulation is another frequently used method which requires that the probability distributions be known, or adequately estimated, for all the input variables. Input variables must be independent of each other, or in the case of dependence (as evidenced among many of the flow and transformation parameters), joint probability distributions are estimated for sets of dependent variables. A large number of model runs then are made, using many independent samples of each input variable to yield a probability distribution of the output variable. Confidence intervals or summary statistics can be computed for the output variable, but the relative contributions of each input parameter to the output's uncertainty is not calculated or estimated.
- 7. The response surface approach does not require that the true relationship between input and output variables be known. Their relationship is estimated by a response surface defined by a

combination of simpler (usually linear) functions, which are obtained by fitting observed data using least squares methods. Using the response surface and the probability distributions of the input parameters, the probability distribution of the output can be estimated using either the Monte Carlo or the analytic approaches. However, the analyst has no measure of the uncertainty concerning how accurately the response surface represents the actual relationship between inputs and outputs at the site when this approach is used.

- 8. The differential sensitivity method requires estimates of the uncertainty associated with the value of each input parameter, as well as a specific (analytical) relationship between inputs and outputs. The derivatives of this equation with respect to each input variable can then be used, together with uncertainty estimates for the inputs, to form a series of equations describing the relative contributions of each input to the uncertainty in the output variable(s).
- 9. <u>Decision analysis methods</u> can be used to provide semiquantitative estimates of uncertainties associated with each input value, based on combinations of site data and expert judgements, and calculating expected values of various outcomes using probabilistic concepts derived from decision theory. These approaches are beginning to be applied to hazardous waste management decisionmaking, and will be discussed further in Section 4.10.

Inman and Helton (1988) recently compared two additional uncertainty analysis techniques, Latin hypercube sampling (with and without regression analysis) and differential analysis, with the response surface approach described previously. They were applied to three well-documented, complex computer models used for predicting environmental fate and transport of radionuclides, movement of aerosols, and

dissolution of salts in bedded salt formations, respectively. Each model had complex, large sets of input and output variables and large uncertainties, and has been broadly used for risk assessments, chiefly by the Nuclear Regulatory Commission. The Latin hypercube method gave the best overall performance for complex model applications. See Inman and Helton (1988) for a description and discussion of these methods.

#### 4.9.3 Presentation of Results

The usefulness of uncertainty analyses is that they provide the planner and decisionmaker with some measure of the reliability of the predictive information gained from the exposure modeling. Without such a measure, the decision maker has no assessment of the value of this information, and no basis for weighing model results against other available data when making site cleanup decisions (Reckhow et al., 1980).

The results of the uncertainty analysis can be presented to the decision maker in a variety of ways. Several examples will be described in the following paragraphs.

The Midwest Research Institute (MRI, 1984) used a three step uncertainty analysis in a study comparing risks and costs of alternative strategies for managing hazardous wastes. First, sources of uncertainty were

identified and their magnitudes were estimated and discussed qualitatively. Second, sensitivity analyses were performed on selected key parameters to determine the changes in aggregate risk estimates produced by changes in the key variables. Finally, uncertainties were aggregated across each scenario using a form of the propagation of errors method, by assuming that the overall output risk is the product of a series of factors having individual uncertainties. Upper-bound, lower-bound, and "best" risk estimates were presented to the decision maker in a table giving a 68 percent confidence interval for the estimated risks. Broad ranges surrounded the best-estimate values, perhaps since expert judgements had been used to define uncertainty ranges for many of the input parameters; the authors believed the experts wished to err on the safe side in providing conservative estimates.

Bolten et al. (1983) performed extensive
sensitivity analyses in their comparison of four doseresponse models for toxicity. First, input parameters
were screened in terms of two criteria: (1) parameters
whose values were variable and uncertain, and (2)
parameters for which a change in value contributed
significantly to changing the output value. Second,
optimistic, pessimistic, and nominal values were
selected for each of the screened input variables; and

finally, output risks were calculated using each of the four dose-response models for the various combinations of inputs. Results were provided in graphic form showing the upper and lower bounds of the risk estimates, but probabilities of Results were provided in graphic form showing the upper and observing the optimistic, pessimistic, or nominal input conditions were not given. This gave some information to the decision maker on the potential effects on the output uncertainties of collecting more data to better define the input uncertainties, without requiring that the key input parameters (in terms of their contributing significantly to output variability) have continuous distributions.

Mauskopf (1985) used a Monte Carlo approach to generate expected values of health risks in a study on the regulation of various levels of organic toxicants as hazardous wastes by EPA. Like sensitivity analysis or the decision-analysis-based approach, Monte Carlo simulations do not require that output risks be calculated as the product of other factors, nor must the input variables have continuous probability distributions. Mauskopf assumed probability distributions for each input parameter, and calculated a probability distribution for the output health risk estimates using the study model. The mean of the distribution was reported as an estimate of the expected

output risks, and an upper bound confidence limit for the expected risks was also reported based on the estimated probability distribution of the outputs.

Nichols and Zeckhauser (1985) used an approach incorporating some decision analysis concepts in their risk assessment for carcinogenicity of selected indoor air pollutants. In their approach, several concepts in their risk assessment for carcinogenicity of plausible risk estimates were calculated from combinations of input parameter estimates. The probability of occurrence of each of these input parameter combinations was estimated, and then an expected value of output health risks was calculated for each combination based on the probabilities and risks of each. In most cases, such an approach will require applying expert judgement to estimate the probability of accuracy of each set of assumptions surrounding the input variables, although in rare circumstances, sufficient data may be collected to support more rigorous statistical analyses of the inputs.

The Research Triangle Institute (1987) summarized general techniques that could be applied to report uncertainty at various levels of analytical complexity in both a qualitative and a quantitative fashion.

#### 4.9.4 Limitations

Even at sites where it is possible to estimate the

uncertainty in the estimated exposure or the predicted cleanup level, the decision maker needs to remain aware of the limitations of the uncertainty analysis techniques used for a given site problem. Likewise the analyst still must observe caution when selecting appropriate values or estimates of input parameters and coefficients, one of the principal uses of the analysis (Reckhow et al., 1980). The importance of these uncertainties related to several specific processes and parameters, and examples of errors and biases that could these uncertainties related to several specific processes or resulting from certain soil or ground water modeling applications, were presented in Section 4.8.4.

The results of the uncertainty analysis are a critical component of any effort to set quantitative cleanup targets for contaminated soils on a site-specific basis, if model results are to be the basis for such levels. They will provide insight to the decision maker on the consequences of, say, choosing between a more stringent and a less stringent (higher) cleanup level in terms of the maximum individual risk from the new higher level, the probability of observing such a risk in reality, and the average additional risk to be expected under the alternative cleanup level (Research Triangle Institute, 1987).

Likewise, they can help to illustrate the value of

collecting additional information to allow for a nominal or "likely case" cleanup. This is especially important to the Superfund cost-effectiveness mandate when the tradeoff involves cleanup to a more stringent, more conservative level due to use of "worst-case" scenarios necessitated by uncertainties or lack of site data. example, if cleanup targets at a site do not vary significantly using worst-case input values from those due to using estimated or predicted nominal-case inputs, the decision maker is confident that additional data would not alter the expected value of the outcome. If the estimates differ substantially, the decision maker may want to consider the value of obtaining additional data compared with costs of the more extensive cleanup, weighed against the uncertainties in the output risk estimates.

Use of uncertainty analyses could have important consequences in determining priorities for cleanup among sites, as in the National Priorities List ranking process described in Chapter 2, or among operable units at a site, for example in determining whether to perform source control actions before cleaning up an extensive ground water plume. Consider two sites, A and B. The mean health risks are higher at A, but the range of uncertainty in the risk value is much broader for B. If worst-case rather than nominal or best-case risk

estimates are used, they may be based on the upper bound of a confidence range rather than, say, the mean or some other measure of central tendency.

Thus, based on worst-case assumptions, the most sensitive and/or most exposed individuals may be better off on a national level, since B would be addressed before A; however, the total number of affected receptors (and thus the total expected value of adverse effects on public health and the environment) might be higher, because cleanup is delayed at A although its average risk is greater than at site B (Research Triangle Institute, 1987).

Finally, uncertainty analysis may be useful in comparing cleanup alternatives and/or cleanup level alternatives in the feasibility study, to determine whether the selected alternative might change under worst-case parameter estimates compared with nominal or best-case conditions. If best-case estimates indicate that no other alternative would be found cost-effective, but if worst-case estimates would lead to selection of a different alternative or a different cleanup level, the best-case estimates may be preferable when performing the cost-effectiveness analysis. Site-specific level, the best-case estimates may be preferable when circumstances ultimately dictate the choice of parameters used for protectiveness versus cost-

effectiveness determinations, however.

The rationale for the cost-effectiveness analysis is that the effectiveness estimates, measured in terms of achieving protection of public health and the environment by mitigating or preventing site risks, should be initially considered in the same fashion as in the NPL example cited above. That is, average as well as upper- bound risks, and considered in the same fashion as in the NPL example cited the uncertainties in defining the distribution of output risks, should be considered in the protectiveness analysis. However, cost estimates are equivalent under either analysis. In any event, the decision maker must justify the selected alternative in light of all the selection factors in the Superfund statute and its implementing regulations, as discussed in Chapters 1 and 2.

#### 4.10 New Approaches

The previous discussions in this chapter have described the many unknowns and uncertainties involved in understanding and characterizing accurately the transport and transformation processes operating at a given Superfund site to carry contaminants from the soil source to ground water receptors. Use of models simulating these processes to set site-specific cleanup levels depends on accurate, adequate knowledge of these

processes and their attendant uncertainties, and on the ability of the decision maker to evaluate the consequences of choosing among different alternatives having different uncertainties.

As mentioned in Section 4.8.3, the Superfund remedial program has not mandated the use of specific models or set modeling requirements. Nor has it developed specific criteria for selecting or using models in any of their potential remedial action applications, including, for example, site characterization; exposure and risk assessment; prediction of a remedial technology's effectiveness; comparing predicted performance among several alternatives; estimating cleanup levels; predicting outcomes of various cleanup scenarios; etc.

As described previously in this chapter, only limited guidance has been provided by EPA on methods by which models would be applied for these purposes, either in terms of estimating or measuring appropriate input parameters, or of characterizing and presenting the uncertainty associated with the results of such assessments (Boutwell et al., 1985; Repa and Kufs, 1985; EPA, 1986A; Schultz et al., 1987). Therefore, a new approach is needed that will tie together the decision framework for selecting and applying models with methods by which the uncertainties associated with each decision

step, and with their outputs (the ground water receptor point concentrations of key contaminants used to back-calculate residual soil cleanup targets).

Such an approach is presented in this section, tentatively titled Soil Contaminant Evaluation Methodology (SOCEM). The prototype presented herein uses the model selection decision framework presented in Section 4.8.4, which provides a general structure applicable to the broad modeling issues likely to be encountered at the majority of Superfund sites. concept is not new (Randall, 1985), nor are the decision steps given in this framework. Rather, the intent is to use "state of the science" soil and ground water transport models effectively in a new application (i.e., assisting in soil cleanup level decisionmaking) by applying heuristic knowledge in the new context to shift the modeling procedure from a "product oriented" to a "process oriented" one (Newell and Bedient, 1987).

product-oriented modeling may be the status quo in many applications, wherein the model experts are given a few very specific technical questions to address. They use models to answer them in relative isolation from other aspects of the site problem, then provide the results to a decisionmaker, who often may misunderstand or mistrust the results (Loucks et al., 1985), because they may consider them in a different context, and apply

a different conceptual model to the site problem, than did the modeler. A more process-oriented approach would encourage a more iterative and interactive relationship between the decision maker, the model, and the analysis itself in the technical modeling process. This will be facilitated by a more explicit analysis and presentation of uncertainty to the analyst and/or the decision maker throughout the model selection and application procedure.

Uncertainties may be characterized by many methods, as discussed in Section 4.9, but in this approach the use of decision analysis methods is proposed to provide a semiquantitative means of assessing the uncertainties and signaling to the decision maker the expected values of model results and of additional information. The decision analysis component is described in more detail in Section 4.10.2.

clearly, not all site-specific circumstances are expected to be addressed in the prototype framework, nor would the same decision made at any given decision step necessarily apply to all sites. SOCEM can assist primarily in earlier stages of the site characterization when site information is limited, although it can be used to help refine the conceptual site model at later stages of the analysis, by helping the decisionmaker to assess the value of collecting additional data to help refine or verify a tentative model decision or output

cleanup level.

#### 4.10.1 Expert Systems

The decision framework described in Section 4.8.4 could lend itself readily to incorporation within an expert system. Expert systems are a class of decisionmaking tools which combine the knowledge and experience of acknowledged subject matter experts in a given discipline into a set of inferences and decision rules. These can be applied by relatively untrained users to address site problems, or other situations requiring assistance from experts, to achieve decisions consistent with those expected to be made by the human experts facing similar decision situations.

These systems constitute an emerging category of artificial intelligence systems that are readily amenable to computer applications, which capture and program the heuristic knowledge of the human expert within relatively limited problem domains (Feigenbaum, 1977; Hayes-Roth, 1983). Commercially produced expert system software, especially "shells" to support decisionmaking systems addressing a wide variety of scientific and business/ commercial applications, are being newly developed on a continuing basis (for reviews see Southerland and Spooner, 1985; Ludvigsen et al., 1986; Stephanopoulos, 1987).

Similar applications of expert systems to related environmental decision making situations are under development by EPA, universities, and other institutions. EPA's Office of Water has developed a personal computer-based expert system package to assist permit writers in preparing permits under the National Pollutant Discharge Elimination System requirements mandated by the Clean Water Act (Eng. 1988). Office of Research and Development is preparing a prototype expert system designed to assist users in selecting surface models for simulating contaminant fate and transport in surface water systems (Segna, 1988). The IGWMC is considering development of an expert system "shell" to assist users in selecting appropriate flow and transport models to address ground water problems, to interact with their Model Annotation and Retrieval System (MARS) database of ground water models (van der Heijde and Park, 1986; van der Heijde and Williams, 1987).

The Hazardous Materials Control Research Institute is developing an interactive, modularized system for assisting decision makers in making a variety of site cleanup and hazardous waste management decisions (Shih and Bernard, 1988 A,B). The system, called the Hazardous Wastes and Management Expert System (HAWAMAX), organizes data into files according to predefined

site/environmental characteristics. It then makes inferences and decision rules, and develops alternative plans to address the hazardous waste management problem in question. The expanding set of inferences is stored and compiled. Another module provides information to enhance the user's conceptual understanding of physical, geochemical, and biological processes involved in the site problem, as well as long- and short-term risks and pertinent institutional considerations and regulatory requirements. problem, as well as long- and short-term risks and pertinent This is accomplished by compiling functional data and logical relationships describing the specific site problem. These are acted upon by two other components:

- o The Knowledge Base of Facts and Rules Module contains the sets of standards and rules, engineering and regulatory data, and functional relationships between processes and parameters assembled from expert knowledge in the form of multiple, interconnected data hierarchies; and
- The Risk/Decision Analysis Module (RIDAM), which can interact with several other modules simultaneously and is the final driver for the overall analysis. RIDAM identifies and quantifies the risks associated with various aspects of the decision problem; evaluates the acceptability of different risks or risk levels; generates various risk management alternatives; and performs a multiattribute decision analysis, providing the expected values of the various outcomes associated with each risk managment alternative.

A detailed description of each component of HAWAMAX, and

a sample application involving risk management alternatives for dioxin cleanup, is given by Shih and Bernard (1988A,B).

Section 4.10.3 provides a brief discussion on how expert systems can interact with decision analysis techniques for decision support systems of this type, a prototype of which is illustrated by RIDAM. The decision framework discussed in this report (see Section 4.8.4) was not developed into a computer-based expert system as a part of the investigation described in this report. Such efforts may be undertaken in future research, as outlined in Chapter 7. However, research is currently underway at Rice University, supported by EPA's Robert S. Kerr Environmental Research Laboratory, to develop a prototype of a similar system (Newell and Bedient, 1987).

#### 4.10.2 Use of Decision Analysis

The methodology of decision analysis provides a semiquantitative structure in which to formulate and analyze decisions having complex and uncertain outcomes by combining the scientific logic and fact base of known physical-chemical relationships with expert judgement (North, 1968; Raiffa, 1968). General reviews of the fundamental theory and principles of decision analysis can be found in Raiffa (1968); North (1968); Keeney and Raiffa (1976); Stokey and Zeckhauser (1978); and

Holloway (1979). A detailed review of this topic is beyond the scope of this report. Only brief comments outlining its potential application to the subject problem will be presented here.

Decision analysis principles have been used to address a broad range of environmental and socioeconomic problems such as analyzing impacts of acid deposition control strategies (North and Balson, 1985); risk-cost balancing in chemical product regulation under the 1976 Toxic Substances Control Act (North, 1983); corporate decision making on liability insurance (Tani, 1978); electric utility industry decision making about coal combustion byproduct disposal (North et al,., 1986), and utility management of polychlorinated biphenyls (PCBs) (Boyd et al., 1984).

Several applications targeted specifically to aid in making site-specific cleanup decisions at hazardous waste sites are currently being developed by Decision Focus, Incorporated for the Electric Power Research Institute (North et al., 1986; Cohan, 1986; Niemeyer, 1986), focusing on coal combustion byproduct contamination (North et al., 1986) and polychlorinated biphenyl capacitor decommissioning and spill cleanups (Boyd et al., 1984). Also using decision analysis methods is the RIDAM component of the HAWAMAX expert system being developed by the Hazardous Materials

Control Research Institute (Shih and Bernard, 1988A,B).

Decision analysis can provide a structured means by which to approach complex issues and develop solutions based on a combination of objective analysis and subjective judgement that identifies the relative contributions of each (Shih and Bernard, 1988B). analyst can compare outcomes of various alternative decisions, given the available data and estimates of the uncertainty associated with each alternative, in this case, for example, the selection of a particular model or a particular cleanup level based on model results. The value of implementing a given decision can be weighed against those of its alternatives, or compared with the value of obtaining supplemental data to reduce the uncertainties associated with that decision (termed "the value of perfect information" by Raiffa, 1968, and Shih, 1980).

## 4.10.2.1 <u>Elements of a Decision Analysis</u>

The main elements of a comprehensive decision analysis include the following (Raiffa, 1968; Shih and Bernard, 1988B):

- Constructing a decision tree to represent the problem structure, using a framework similar to an event tree or a fault tree (Vesely et al., 1981; Rowe, 1977);
- o Stating numerical preferences (i.e., quantifying

utilities) for the various consequences or outcomes (adjusted to establish what are termed risk referents, as defined in Shih and Bernard, 1988A);

- o Assigning probabilities to each branch point of the decision tree where chance may act, and determining the risks of each branch;
- o Performing a detailed risk analysis which compares the objective risks of each branch point with the risk referents. Based on the comparison, decision branches may be modified or eliminated from further consideration;
- o Performing a sensitivity/uncertainty analysis of the risk comparisons to determine whether any remaining alternatives are only marginally acceptable;
- o Determining the optimal strategy on the basis of the maximum utility values; and
- o Performing a sensitivity/uncertainty analysis of the decisions.

Not all elements of this process will necessarily be applied in the SOCEM framework. For example, calculation of utilities in monetary terms for human health effects and environmental damage historically has been controversial, and EPA lacks a single, consistent set of techniques for this purpose. Similarly, translation into risk referents embodies concepts of risk management, in that it assigns values to population preferences for various risk outcomes. For additional discussion of these concepts see Keeney and Raiffa (1976); Shih and Bernard (1988A); Rowe (1977); and Parkhurst (1982). Such a process is outside the scope of this effort, and may exceed Superfund statutory

authority (see Brown, 1984; Office of Technology Assessment, 1985). These considerations will be discussed further in Chapter 6.

Additionally, insufficient data may be available to calculate many of the risk components, especially at earlier stages. However, in such cases this process will be especially useful, in that best-available expert judgements are substituted to estimate parameters, risk elements, and confidence ranges surrounding each estimated parameter and risk element. The decision analysis framework allows the decision maker to identify and track these estimates in order to evaluate the confidence to be placed in decisions based on the analysis. However, obtaining these "best estimates" often is the most difficult effort of a decision analysis (Parkhurst, 1982).

#### 4.10.2.2 Construction of the Decision Tree

The decision tree represents the foundation of the process. In this application, the prototype decision framework presented in Section 4.8.4 would serve as the starting point for making model selections at a site about which little is known initially. This should begin at the scoping/ response objectives stage, as shown on Table 9, which corresponds to the problem characterization phase of modeling studies, as discussed

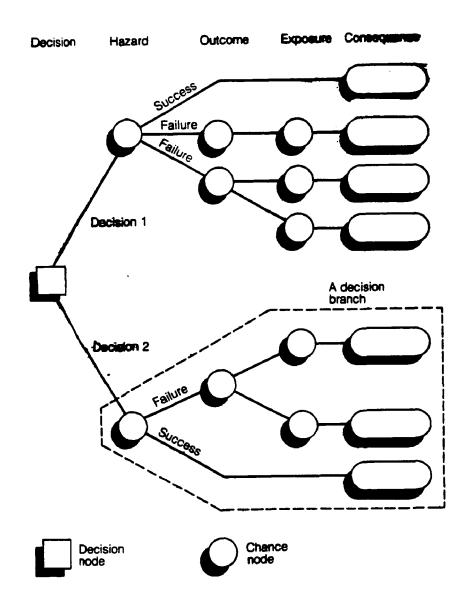
in Section 4.8.2.1. In further stages of site characterization, or at a site where much is already known, the specific questions asked at any given decision point could be modified to take site conditions and questions explicitly into account.

To generate the decision tree, this starting point must be modified to form an objective hierarchy terminating in the final decisions, identifying the values (utilities) and risks assigned to the consequences of each decision. This is described in the following paragraphs.

First, "viable courses of action," defined by Shih and Bernard (1988B) as those remaining after the full array of possible alternatives has been screened using some predetermined, relatively unambiguous feasibility criteria, are identified. Chance events or probable decision outcomes related to each are determined. The alternatives and resulting chance events are arranged in a chronological causeand-effect sequence to form the tree. Figure 9 shows the relationship of these elements in a generalized decision tree structure for a risk assessment/ management problem, as given by Shih and Bernard (1988B).

Specific probabilities of occurrence of each chance event are then calculated or estimated, and values are assigned to the attributes or consequences of the outcomes of each decision point.

FIGURE 9
Typical Decision Tree for Decision Analyses



#### 4.10.2.3 Utility Functions

Use of this approach with a multiattribute utility function could maintain flexibility, but also provide a welldeveloped capability for addressing the uncertainties and multiple objectives involved in site cleanups. Such a function was incorporated into RIDAM by Shih and Bernard (1988B). The determination of an attribute's utility (a simplified example of which is calculating the expected value of the consequences of selecting a given cleanup level) is traditionally done by questioning the characteristics of the decision maker's (or the affected population's) preferences. These quantitative and qualitative characteristics are transformed into a numerical measurement called utility, defined such that the most desirable alternative has the highest utility, with others having lesser utilities in decreasing order of their preference (Shih and Bernard, 1988B).

A multiattribute utility function is developed by assessing the types and extents of independence among the various attributes, then combining the individual functions describing each attribute's utility into a single function. Details of this procedure and of the underlying theory are found in Keeney and Raiffa (1976), and are outside the scope of this report. Its purpose in this application is to allow a means for calculating the expected utilities of the various

alternative outcomes of each decision point in the tree, which is done by "averaging out and folding back" (Shih and Bernard, 1988B). This involves calculating the product of the utility of each decision path and the joint probabilities defining the overall probability of occurrence of that particular decision path.

Clearly, the development of utility functions is complex, political, highly subjective, and laden with uncertainties. One goal of this study is to provide a preliminary evaluation of the feasibility and effectiveness associated with attempting to perform utility evaluations of the cleanup level decision elements at Superfund sites. It may not be desirable on a program-wide basis, given the resource and institutional constraints faced by the Superfund program. Further discussion of the issues surrounding multiattribute utility theory is given in Keeney and Raiffa (1976), and Rowe (1977).

#### 4.10.2.4 <u>Use of Sensitivity Analysis</u>

The primary purpose for using decision analysis in the SOCEM approach would be to provide a formalized, semiquantitative mechanism for identifying and evaluating the uncertainties associated with each decision step in the model selection/cleanup level-setting process. Shih and Bernard (1988B) used sensitivity analysis at two points within their decision analysis procedure: after the risk analysis, and at

the end of the decision analysis. They did not specify use of any particular method (see uncertainty analysis discussion in Section 4.9), but highlighted the value of a retrospective assessment of the uncertainty associated with individual risk and decision steps, and with the outcome of the decision process, in the decision maker's ability to place confidence in the decision.

#### 4.10.2.5 Example Application

A brief example of decision analysis applied to site cleanup decisions was given by Shih and Bernard (1988B), concerning the cleanup of dioxins at the Denny Farm Superfund site in Missouri. The problem was simplified for purposes of illustration, so that four site cleanup alternatives were being considered solely on the basis of human health risks to voluntarily exposed cleanup workers and involuntarily-exposed nearby residents. Health risks were simplified to two broad categories, morbidity and mortality, defined arbitrarily by Environmental and socioeconomic damages and the authors. consequences were not considered. The four alternatives were (1) leave wastes amd soils buried in place; (2) monitor and (if necessary) treat ground water; (3) excavate soils and wastes and store on-site; and (4) remove liquid and solid wastes (and some soils) for offsite treatment and disposal.

Utilities and joint probabilities of each decision path resulting from the four alternatives, given as both long-term

and short-term consequences, were calculated by Buchanan et al. (1980). Costs of the remedial alternatives, fatalities and morbidities (as a measure of the utility of human health risks), and lead times required to implement each alternative were the three principal decision criteria.

Objective risks were assessed and risk referents estimated using assumptions about workers' and public's perceptions about direct and indirect costs and benefits, and about the controllability of each alternative. No direct information was available for a sensitivity analysis, therefore the authors made judgements about the variance distributions of the decision tree parameters, which helped focus the analysis on "realistically acceptable" options, Alternatives 3 and 4. The utility functions for these alternatives indicated that 3 was the preferred alternative, based on addition of utilities for the individual decision paths. See Shih and Bernard (1988A,B) for a complete discussion of this problem.

### 4.10.3 Soil Contaminant Evaluation Methodology

The Soil Contaminant Evaluation Methodology (SOCEM) is proposed here as an approach for providing a basic, generalized decision structure for analysis of the site soils problem and for selection of appropriate analytical methods. The intent is to provide a framework, incorporating some problem and for selection of appropriate analytical methods.

principles and methods of decision analysis, that allows different problems at different sites to be approached in a consistent manner. This enhances the likelihood of selecting similar cleanup levels in similar site circumstances. Yet it must maintain sufficient flexibility to address the range of soils problems encountered at Superfund sites by not specifying a single universal model. The utility of this concept has been discussed by several reviewers, including Boutwell et al. (1985).

SOCEM is intended to guide the selection and use of existing exposure assessment models, focusing in this study primarily on the assessment of fate and transport of soil contaminant to ground water. Randall (1985) presented several fundamental principles that underlie the approach, as discussed below.

#### 4.10.3.1 Matching the Model to the Available Data

The sophistication of the prediction technique should be matched to the quantity and quality of the input data. Use of a sophisticated model with an inadequate data base will not yield more accurate results than a simple technique, and may instead give the user an unjustified level of confidence in the results, as discussed in Section 4.8.

#### 4.10.3.2 Maintaining a Flexible Approach

The SOCEM framework is independent of the actual models

used. Thus, it can be applied at different stages of the RI/FS process for different purposes, for example, to select a simple, conservative transport equation at the scoping stage when little data is available. The simple equation can then yield an order-of-magnitude estimate of source strength reduction required to attain a given cleanup level and indicate uncertainties in the estimate, to help the user determine data requirements of the Remedial Investigation. Later, with more data, more sophisticated models might be used to refine target cleanup levels or to compare the effectiveness of various remedial alternatives.

# 4.10.3.3 <u>Matching the Conservatism of the Results</u> to the Precision of the Analytical Technique

Remedial Investigations do not often result in sufficient data to characterize completely the complex physical, geochemical, and biological processes affecting contaminant fate and transport at a given site. Assumptions used in simpler models in the absence of complete data, together with the uncertainties in the Remedial Investigation data and inherent in ground water co fate and transport predictions, necessarily result in conservative predictions of ground water quality at a potential receptor. As discussed in Section 4.9.4, SOCEM will indicate to the decision maker the level of conservatism in the selected cleanup level, thus allowing an analysis of the tradeoffs

between implementing the cleanup action at the conservative level, collecting more data to reduce the uncertainty (thus allowing a less conservative cleanup level), or implementing a less extensive cleanup that depends on more long-term management.

This approach can aid the Superfund program over the long term by highlighting areas in which future Remedial Investigation data bases need to be more comprehensive in general. It can also suggest ways in which Superfund's data acquisition and management can better facilitate the use of more accurate and precise prediction techniques that account for more of the physical, chemical, and biological factors affecting contaminant migration and transformation. This would simultaneously reduce both the uncertainty and the required conservatism in the cleanup levels selected.

# 4.10.3.4 <u>Identifying the Use of "Best Engineering</u> Judgement"

No model accounts completely for all factors and processes affecting fate and transport in a particular soil/ ground water system. Therefore, the expertise, experience, and subjective judgement of the user must be relied upon in any modeling process, from selecting the appropriate model to interpreting the results. Decision analysis provides for the labeling of each uncertainty, and "semi-quantification" through the assignment of expert-derived probability

estimates for each uncertain value. SOCEM will identify when and where this occurs, and track the attendant uncertainties and uses of expert judgment for the decision maker, to the extent possible.

# 4.10.3.5 <u>Identifying the Need for Verification</u> Monitoring

Use of this methodology will require monitoring of a site subsequent to cleanup to verify the accuracy of estimates and assumptions used in the models and the actual effectiveness of the implemented remedy. However, it will also provide the decision maker with estimates of the expected value related to the risks of various cleanup levels, and the probability of their occurrence.

This information can be used to make decisions regarding the length and type of verification monitoring, and of the tradeoffs between more stringent cleanup levels (that might require less intensive or shorter monitoring programs) and less conservative cleanup levels that might dictate longer monitoring programs or other long-term management of the site using the SOCEM framework to evaluate its applicability to Superfund soil cleanup decisions of this type. following cleanup, in order to incorporate these factors into the cleanup level decision up front wherever possible.

### 4.11 Summary

In this chapter, the complexities associated with understanding and predicting the transport and transformation of soil contaminant to ground water receptors were presented. This provided an introduction to the use of fate and transport models in helping the Superfund decison maker to set soil cleanup levels at sites where the ground water exposure pathway is of primary concern. In preceding chapters the contention was established that these levels are most appropriately set on a site-specific basis. chapter, it was proposed that the uncertainties associated most appropriately set on a site-specific basis. In this with contaminant transport through soils and ground water necessitate the use of a variety of models to predict cleanup levels, since no one model will be capable of simulating the variety of processes and conditions encountered at Superfund sites.

In Chapter 5, a case study will be presented illustrating the selection of a ground water fate and transport model to back calculate a soil cleanup level at the McKin Superfund site, using the concepts discussed in Sections 4.8 through 4.10. While the approach presented herein as SOCEM was not followed explicitly, the general concepts and principles presented in this chapter were considered in selection and use of the model. The SOCEM

prototype decision framework presented in Section 4.8.4 was developed and refined as a result of that effort.

In Chapter 6, the McKin site decisions will be reexamined using the SOCEM framework to evaluate its applicability to Superfund cleanup decisions of this type.

### 5.0 CASE STUDY--MCKIN, MAINE

In Chapters 3 and 4, problems of soil contamination at Superfund sites and the difficulties in selecting appropriate cleanup levels were discussed. In Sections 4.8 through 4.10, a conceptual framework for approaching the cleanup level and model selection problem, entitled SOCEM, was presented. In this chapter, one of the earliest Superfund site cleanup decisions is described wherein numerical cleanup targets were established for soils, and ground water, by applying some of the concepts presented in Chapters 3 and 4.

This example is taken from events surrounding the development of the Record of Decision (ROD) for the McKin Company site in Gray, Maine, signed by EPA in July, 1985 (EPA, 1985J). It is not intended to represent a "typical" Superfund site, nor a typical Superfund soil contamination problem, nor an exemplary cleanup level decision. However, as will be discussed here and in ensuing chapters, this site decision was somewhat prototypical, since it ushered in a new phase of specificity in ROD cleanup decisions made by EPA.

Nonetheless, the reader should keep in mind that not all aspects of the SOCEM methodology were employed in the McKin ROD as previously presented. This occurred partly for managerial or institutional reasons, in that

EPA managers were facing constant pressures to make a decision and expedite cleanup actions despite the many uncertainties and gaps in the site knowledge base, a universal problem in Superfund as in other environmental regulatory programs. Another reason was the still—undeveloped nature of the SOCEM methodology at the time of its application to the McKin site. Many lessons were learned that can be used to refine the concepts so that they may be employed in a more sophisticated fashion in future cleanup level decisions at other contaminated sites.

Sections 5.1 through 5.6 describe the McKin site, the nature of the threat, and the studies and other actions that led to the ROD decisions. Sections 5.7 through 5.12 discuss the use of SOCEM concepts in selecting and using models to back-calculate numerical cleanup targets for the ROD, as well as initial outcomes of the analysis, and refinements made during the Remedial Design and implementation stages at McKin. Further refinements, limitations, and constraints in implementing the SOCEM approach at other Superfund sites, and recommendations for future development efforts will be discussed in Chapters 6 and 7.

### 5.1 Background

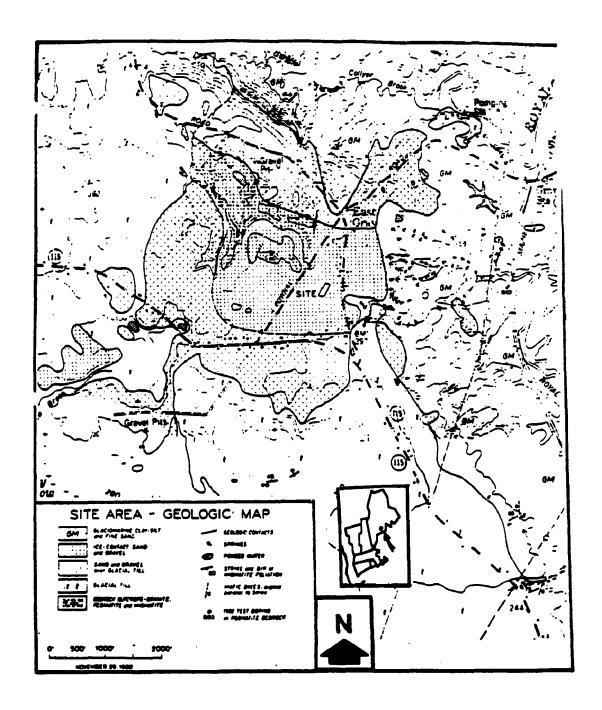
The McKin Company site is located in Gray, Maine,

approximately fifteen miles north and west of Portland. Prior to 1963, the site was used intermittently as a sand and gravel pit. From 1963 to 1978, it was used by the McKin Company for storage, treatment, and disposal of both petroleum wastes and industrial chemical wastes collected by their tank cleaning and waste management business.

Approximately 100,00 to 200,000 gallons of waste were received per year between 1972 and 1977. On-site operations included storage in 22 above-ground tanks and an asphalt-lined lagoon; waste discharge to the ground; burial of residuals; collection of wastes for transport off-site; and incineration of oily wastes, including cleanup wastes from a major offshore oil spill. The incinerator was permitted by the Maine Department of Environmental Protection during the 1970's, and ceased operation in approximately 1973. Site operations ended in approximately 1978.

The McKin site is located on a relatively permeable glacial outwash plain consisting of stratified sand, gravel, and boulders overlying heavily weathered and fractured granitic bedrock (Figure 10). The site is approximately seven acres in size. Approximately 4.5 acres have been cleared and partially excavated. It is surrounded by residential areas, wooded lands, and rural farmlands which slope steeply upwards to the north,

FIGURE 10
Geologic Map of the McKin Site Area, Gray,
Maine (Adapted from EPA, 1985J)



south, and west, and downwards to the east of the site toward the Royal River, located approximately 3/4 mile east of the McKin site.

Most nearby residences are located at least 1500 feet north and west of the site, but one is located within 200 feet of the site. No surface runoff has been observed from McKin, and incident precipitation or runon is believed feet of the site. No surface runoff has been observed from either to be contained on-site, to percolate into the underlying soils, or to be lost by evapotranspiration. Ground water occurs beneath and in the vicinity of the site in at least two water-bearing zones, a surficial zone and a fractured bedrock zone. Evidently they are interconnected to some extent. Until it became contaminated, the bedrock aquifer was the private water supply for the homes located to the north of the site.

Both zones eventually discharge downgradient to the Royal River system through a series of springs and seeps. The Royal River is designated by the state of Maine as acceptable for recreational fishing and boating, but not for direct contact water sports nor for use as drinking water without prior treatment.

### 5.2 Events Preceding EPA's Remedial Actions

Nearby residents of East Gray reported discolored

laundry and odors in well water beginning in 1973. Residential well samples contained organic contaminants, and the Town of Gray issued an Emergency Health Ordinance placing a moratorium on any new construction within two miles of the McKin site. An EPA-funded hydrogeologic assessment (Fred C. Hart Associates, 1977) found organic contaminants in many local private wells, and in December 1977, sixteen of the wells were capped. Residents were provided bottled water until August 1978, when they were connected to a public water supply. state-funded hydrogeologic study (Gerber, 1982) concluded, based on flow modeling, that the surficial and bedrock aguifer contamination in the vicinity of McKin had originated from the improper waste management operations at the site. This study is described in Section 5.3.

In December 1977 the Town of Gray issued an

Emergency Cleanup Order to the McKin Company, and in

1978 the state Attorney General filed a still-unresolved

suit. A Gray citizens' group likewise filed a class

action suit, since settled out of court. During 1979

and 1980, the state supervised the removal of some

35,000 gallons of oil and liquid chemical wastes from

the above-ground tanks and drums, as well as the

relocation of empty drums, installation of monitoring

wells, and the collection of soil and ground water samples

and magnetometer data. EPA monitored air quality at the site in 1982, and the state analyzed residuals in the above-ground tanks in 1983.

In an Initial Remedial Measure (EPA, 1983C), state contractors rinsed and crushed many drums and containers in April 1983, and cleaned and removed all remaining aboveground tanks in September 1983. They also partially cleared, excavated, and fenced the site. Subsequently, EPA initiated its remedial process, which led to the Record of Decision and to the major on-site cleanup.

### 5.3 Data Available Prior to Remedial Investigation

The two major sources of written information available to EPA and its contractor, Camp, Dresser and McKee, at the time of model selection were (1) the Remedial Investigation and Feasibility Study reports (Camp, Dresser and McKee, 1985C,D) and (2) the hydrogeologic study prepared earlier for the state by Gerber (1982). Gerber's investigation included borings, surficial geologic mapping, aerial photo interpretation and lineament analysis, seismic refraction transects, surveys of nearby private wter supply wells, and analyses of state-conducted chemical sampling of several existing monitoring wells. In addition, Gerber performed regional flow and transport modeling of both

the surficial and bedrock aquifers.

The Gerber study provided a <u>regional-level</u> picture of geology and of the apparent flow and contaminant transport regimes. The area investigated corresponded to the surface and ground water drainage area within approximately a 1- to 2- mile radius of the McKin site. The Remedial Investigation provided supplementary data to refine the conceptual model of the region, but also focused on the site itself to enhance EPA's understanding of the source and its threats.

### 5.3.1 Domain Configuration/Flow System

exit the site in the ground water. No surface runoff from the site has ever been observed, and Camp, Dresser and McKee (1985C) stated that all precipitation reaching the site either percolates into the soils or is lost through evapotranspiration. Camp, Dresser and McKee postulated that percolation rates through contaminated site soils were likely to be twice the typical regional rates, contributing further to the unlikelihood of surface runoff. Average annual precipitation is approximately 42 inches, with average regional runoff of approximately 30 inches. Monthly precipitation records for several years immediately following site abandonment, reflecting the period most likely corresponding to

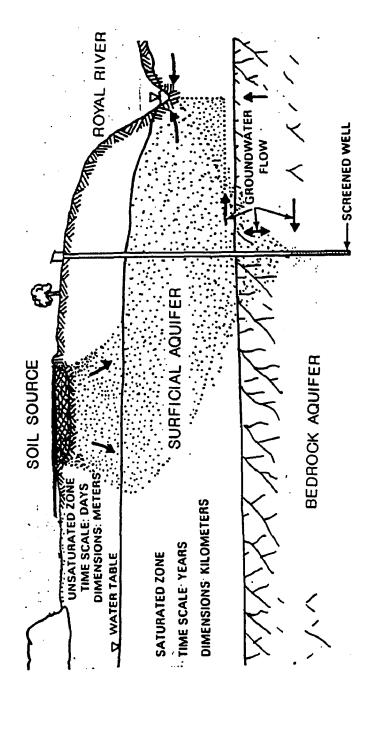
infiltration and movement of site contaminants from soils to ground water, were presented by Gerber (1982).

Ground water flows beneath the site in two saturated zones: a surficial zone and a bedrock zone which is heavily weathered and fractured. Ground water elevations in both zones slope downward toward the river (Figure 11). Virtually all ground water originating beneath the site in either aquifer appeared to discharge to the surface (and thence to the river) through the Boiling Springs, or directly to the Royal River in their vicinity, approximately 4000 feet east- northeast of the site. The upgradient area available for recharge (and dilution of any leachate entering the aquifers beneath the site) was found by Gerber (1982) to be small.

### 5.3.1.1 Soils and Surficial Aquifer

Camp, Dresser and McKee noted in the Remedial
Investigation that the dominant surficial soil
association of the area is Colton-Adams, and that soils
in the site vicinity belong to the Foxton-WoodbridgeHollis association, with the majority in the Hinkley
series. They are characterized by "deep, well- to
moderately well-drained, moderately coarse-textured soils
and shallow, somewhat excessively drained, moderately
coarse-textured soils" (Camp, Dresser and McKee, 1985C),
typical of glacial outwash deposits on terraces and

FIGURE 11 Conceptual Model of McKin Contamination



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eskers. According to Camp, Dresser and McKee, representative Hinkley soils near the McKin site have a four-inch organic litter layer covering approximately seven inches of dark, gray-brown sandy loam. The following three inches of subsoil are typically composed of very friable, yellowish-brown sandy loam, over approximately 14 inches of yellowish-brown, highly friable to loose gravelly loamy sand to very gravelly sand. Substratum at the 24-inch depth is composed of loose, gravelly loamy sand which is olive brown in color. Camp, Dresser and McKee stated that such soils typically are highly permeable and have low available water capacities.

Gerber identified three major soil units comprising the surficial aquifer in most of the site vicinity: (1) stratified sands and gravels, predominating north and west of the site. These are most heterogeneous along a buried glacial meltwater stream bed, consisting of coarse cobbles and gravels, which runs west-east from beyond the intersection of Pownal and Mayall Roads to Boiling Springs; (2) low-permeability glacial till underlying the sands in most areas near the site, exposed upland to the west and south; and (3) glaciomarine sands, silts, and clays which overlie the sand and till in some areas east of the site, especially along the west bank of the river near Boiling Springs

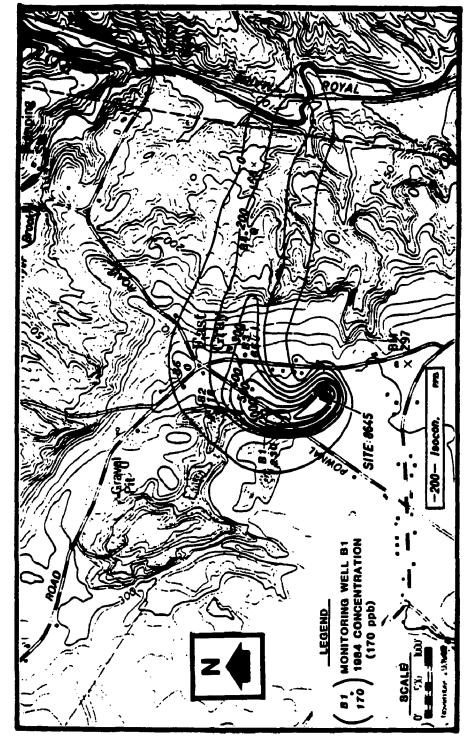
(see geologic map in Figure 10). The clayey glaciomarine deposits provide a barrier to ground water flow, especially along the west bank of the river where they form a delta to the buried meltwater channel, and act as a leaky dam through which the ground water surfaces in the seeps and springs known as Boiling Springs. Gerber did not prepare a soil thickness map, nor a saturated-thickness map of the surficial aquifer.

Gerber found that ground water leaving the site in the surficial aquifer moves initially in a northwesterly direction. Then it turns abruptly eastward under Mayall and Pownal Roads to flow along the coarse gravels of a buried glacial meltwater channel and discharges to Boiling Springs, and to the bed of the river, as shown in Figure 12. Gerber found no evidence that surficial flows originating from the site move south or east beyond the river. Till and bedrock ridges to the far north, south, and west of the site, and the river to the east, provide lateral boundaries to the surficial flows in the site vicinity.

### 5.3.1.2 Bedrock Aquifer

Ground water in the bedrock aquifer flows primarily through openings created by steeply-dipping joints, fractures, dikes, and micaceous partings, whose strikes are oriented primarily along two horizontal axes as

FIGURE 12 Ground Water and Contaminant Flows in the Surficial Aquifer (Source: EPA, 1985J)



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shown in the rose diagram on Figure 14. The bedrock surface generally slopes downward to the north and east of the site, rising to the south of the site. Ridges were inferred by Gerber (1982) to exist beneath and north of the site, and a trough was mapped to the northwest.

Although he did not core to bedrock beneath the site, Gerber believed that the bedrock surface played a key role in controlling the flow system in both zones. Ground water leaving the site in the bedrock zone flows northward initially, then it begins to spread laterally as it too turns eastward, then southeast, generally following the flow directions in the surficial zone. It discharges diffusely north and east of Mayall Road, with a concentration of discharge of site ground water to the surficial aquifer at Boiling Springs.

### 5.3.2 Source Characterization

Gerber (1982) did not know the time history of contaminant leakage into the aquifer beneath the site, nor did available data allow calculation of source strength remaining in site soils. No borings or other samples were taken by Gerber beneath the site to measure actual concentrations or amounts of residual contaminants in the unsaturated or saturated soils. Further, at the time of the Gerber investigation, storage

tanks were still present on-site that may or may not have been leaking. However, it was known that the site was constructed in an abandoned sand and gravel pit in 1972, and that 100,000 to 200,000 gallons of wastes were accepted annually until operations ceased in 1977 (Camp, Dresser and McKee, 1985C,D). It was also known that the McKin Chemical Company was in operation for several years preceding 1972, and it has been alleged that wastes and byproducts of septic tank cleaning may have been stored and/or disposed in the gravel pit for several years prior to construction of the site in 1972 (Gerber, 1982; Camp, Dresser and McKee, 1985D).

Since relatively constant concentrations of 1,1,1trichloroethane (TCA) of around 200 ppb were measured at
Boiling Springs and the river for several years, Gerber
(1982) inferred that the source term probably remained
relatively constant over a period of years. However,
recent decreases in TCA concentrations at Boiling
Springs, combined with modeling results, also led Gerber
to speculate that contaminants could have entered the
ground water as a large slug initially, but decreased
subsequently to some that contaminants could have
entered the ground water as a steady-state influx rate.
Gerber concluded that the contaminants at the source

"...are settling slowly through about 40' of unsaturated soil under the site. Whenever it rains,

a little of the contaminant is transported downward to the water table. Over time this can result in a fairly steady application rate of the contaminant to the aquifer."

For transport modeling, Gerber inferred leachate influx rates into ground water beneath the site by using an arbitrary percentage input and back-calculating source concentrations that would result in roughly a 200 ppb TCA receptor concentration in ground water at Boiling Springs. This resulted in a back-calculated average influx of 26 gallons of TCA per year, although other data indicated that TCA inputs to ground water beneath the site could have ranged as high as 125 gallons per year.

### 5.3.3 Regional Modeling

Gerber (1982) did not model the unsaturated zone, citing insufficient data. Two saturated-zone numerical models were used to simulate the hydrologic system in the vicinity of the McKin site, in order to develop and refine conceptual understanding of the contaminant transport regime:

o The Aquifer Finite Element Model (AQUIFEM) was used to simulate the regional flow system in the surficial and bedrock aquifers. AQUIFEM is a 2-dimensional, single layer, saturated-flow numerical model based on the Galerkin-type finite-element method, as described in Section 4.8.1.3 (Townley and Wilson, 1980). The model is capable of simulating phreatic or confined, anisotropic, heterogeneous, leaky or non-leaky aquifers.

Boundary conditions may vary with time (e.g., using specified Section 4.8.1.3 (Townley and Wilson, 1980). The model heads, or point, lineal, or areal discharge or recharge rates), and changes of aquifer status (e.g., from confined to phreatic) are possible.

The <u>USGS 2-D model</u> (also known as "MOC") was used to simulate site-specific contaminant transport in the surficial and bedrock aquifers, respectively. This numerical model, developed by Konikow and Bredehoeft (1978), uses a 2-dimensional block-centered finite difference grid design to approximate ground water flow, which is solved using an alternating-direction implicit procedure. It couples the flow equation with the solute transport equation, and uses MOC (the method of characteristics) to solve the transport equation. This involves a particle tracking approach and a two-step explicit solution procedure for the finite difference equation, as described in Section 4.8.1.4.

The grids established for each aquifer are shown in Figures 13 and 14 for each of the models. Note that the FEM grid for the bedrock aquifer was oriented with the two major inferred axes of bedrock openings, as shown in Figure 14. Choices of boundary conditions and parameter values, simulation of leakage and contaminant transfer between zones, and the calibration and application steps, were described in detail by Gerber (1982). These are summarized in Table 18.

### 5.3.4 Contaminant Transport Regime (Model Results)

Gerber's (1982) surficial flow model results suggested that more glacial till likely underlies the site than had been hypothesized; and that virtually all

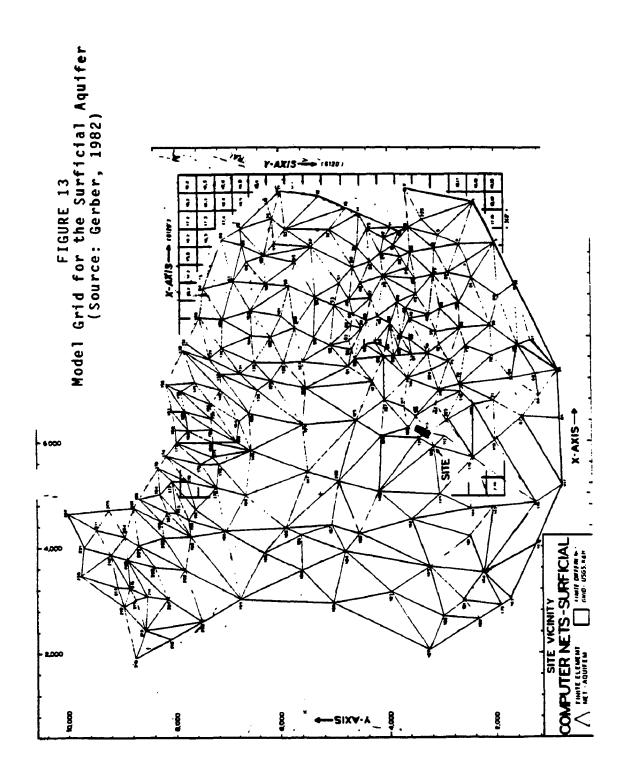
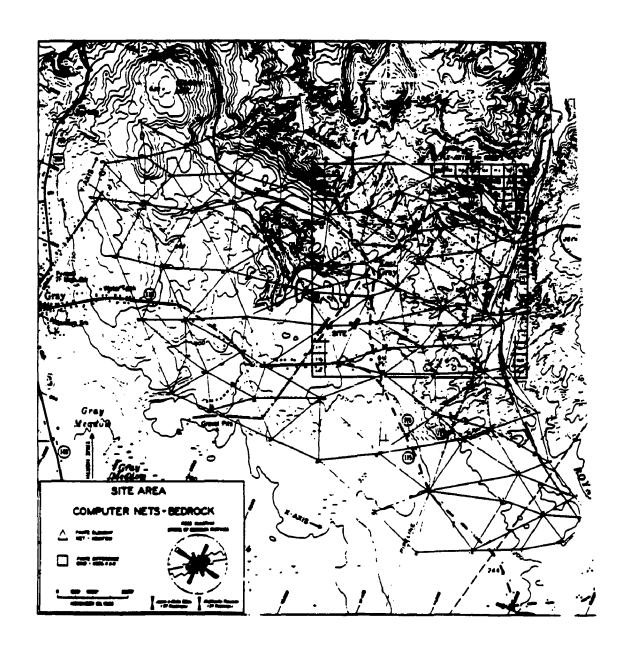


FIGURE 14 Model Grid for the Bedrock Aquifer (Source: Gerber, 1982)



and Boundary Conditions Flow and Transport Modeling	Rationale	Inflows estimated from recharge areas and "typical recharge per unit area values;" adjusted for till transmissivities, intermittent springs/streams, recharge areas, etc.		Based on 43 in/yr avg. precip.(given monthly variation); USGS records; regional studies. Coefficients calibrated w/models.	TCA concentrations represent vertically-averaged values over entire element
Assumptions, for Regional	Assigned Value	Constant-flux W and S; No-flow N and E along river, Collyer Brook	No-flow assumed	Assumed 60% (sand/gravel); 25% (till); 5% (glaciomarine). Leakage coefficients developed for bedrock	340'x 340' elements
Input Parameters, Used by Gerber (1982)	Parameter/Factor	Surficial Zone Boundary Conditions (AQUIFEM)	Bedrock Zone Boundary Conditions	Recharge	Grid Element Configuration (MOC)

# TABLE 18 (Continued)

Assigned Value

Fluxes estimated as a function of leakage coefficients, surficial vs. bedrock heads, vertical permeabilities	No direct measure- ments; estimated from perm. vs grain size tables, bore- hole estimates at B102, B103 (surficial) and private well yields (bedrock)
Developed leakage coefficients	Assumed isotropic in surficial; treated as iso-tropic in bedrock, supported by modeling.  Model-inferred permeabilities of 10-100'/day (coarse ice contact deposits); 0.01'/day (till); inferred bedrock transmiss-ivities of 100 ft2/
Interaquifer Water/ Contaminant Transfer	Permeability/ Transmissivity

TABLE 18 (Continued)

Rationale	Simulations were steady-state, long term (10 yrs).	Literature-based values "for regional models involving several thousand feet of flow in stratified sand/gravel aquifers" (Fried, 1975; Gerber, 1982)	No field data, lack of scientific under- standing of dispersion in bedrock cited.	USGS model does not account for evaporation, soil sorption; no field data (Note: Gerber suggested TCE more strongly retarded in gw than TCA, based on field observations).
Assigned Value	Not determined	Surficial: used 50'(longitudinal), 15'(transverse)	Bedrock: none (assumed convective flow)	None assumed
Parameter/Factor	Specific yield	Dispersivity		Retardation

ground water from the site discharges to the springs and seeps, with virtually none discharging directly to the river bed. Bedrock flow modeling implied that average transmissivities were among the highest measured in Maine sites.

### 5.3.4.1 Surficial Aquifer Transport

because of the limited data. Surficial transport modeling suggested that, based on an assumed source influx of 26 gallons of TCA to the surficial zone annually, breakthrough of TCA at Boiling Springs probably occurred 5 years after contaminant introduction to the aquifer, and an additional 4 years for a steady-state concentration of approximately 200 ppb to be reached at the discharge area.

It appeared that the contaminants migrated northward to the permeable outwash channel deposits, then traveled eastward along this conduit to the river in a relatively narrow, well-defined plume (Figure 12). There was no evidence that contaminants migrated south past this bend in the river. Discrepancies between observed and measured TCA concentrations were attributed to density effects not accounted for in the model, i.e., that the contaminants tended to move along the bedrock surface at the bottom of the surficial aquifer.

### 5.3.4.2 Bedrock Aquifer Transport

Bedrock model results suggested that, even without accounting for dispersion, the bedrock plume tended to be more dispersed laterally than the surficial TCA plume. Gerber (1982) suggested that its distribution was controlled principally by the bedrock flow and by distribution of TCA in the surficial aquifer, as well as by anthropogenic factors. The higher-than-expected bedrock TCA levels were believed to be due to pumping of private bedrock wells during the late 1970s, which may have drawn more contaminants into the bedrock zone than would have otherwise occurred. Gerber inferred that breakthrough of TCA at Boiling Springs in the bedrock zone may have taken as little as 2 years, but that the time rate of increase in concentration appears to be slower, and seemed unlikely to have achieved a steady state even following 10 years of simulation.

However, Gerber's 10-year "forward" modeling results predicted that, while trichloroethylene (TCE) levels were still increasing in some wells in 1982, the apparent declines in TCA levels observed in the early 1980s were likely to continue in the surficial aquifer, and eventually in the bedrock zone as well. Therefore, if the source were removed or contained, Gerber predicted that after 10 years TCA levels in most portions

of the surficial plume would decline below 30 ppb, and below 15 ppb in much of the bedrock zone, due to natural flushing and attenuation mechanisms (as discussed in Section 4.3).

## 5.4 Characterization of the Site Problem: the Remedial Investigation

The remedial process leading to the Record of Decision began with a state-funded Remedial Investigation and Feasibility Study (RI/FS) conducted by EPA's contractor, Camp, Dresser and McKee, Inc. (1985C,D). These studies were initiated in January 1984 and completed in March 1985.

The Remedial Investigation identified two major contamination problems at the McKin site: contaminated ground water in the surficial and bedrock aquifers downgradient of the site, and contaminated site soils. Some of the structures, such as the tanks, had been cleared as part of the removal actions, so that at the time of the Remedial Investigation, the site was a fenced enclosure containing the incinerator, the lagoon, a concrete building, a buried fuel tank, and miscellaneous debris.

### 5.4.1 Ground Water Contamination

Ground water was sampled at various depths in both the

surficial and bedrock aquifers during the Remedial Investigation. Prior investigations had found a range of contaminants including TCE, TCA, chloroform, 1,1-dichloroethane, 1,2-dichloroethane, tetrachloroethylene and less common pollutants such as dimethyl sulfide and Freon (Camp, Dresser and McKee, 1985C,D); however, of the series of contaminants analyzed for during the Remedial Investigation, only TCE and TCA were detected at significant concentrations in both water-bearing zones.

Levels of TCE and TCA ranged as high as 16,000 ppb and 170 ppb, respectively, in Well B-3 screened in the surficial aquifer approximately 600 feet north of the site. As described in Section 5.3, the surficial aquifer plume is inferred to extend approximately 1000 feet north of the site, whereupon it trends eastward towards the Royal River.

Prior to 1977, the bedrock aquifer provided the primary drinking water supply for several nearby residences. Ground water evidently is conducted through the many fractures and cracks in this zone, as discussed in Section 5.3. Levels of TCE and TCA ranged up to 29,000 ppb and 500 ppb, respectively, in Well B-1, which is screened in the bedrock some 800 feet north of the site. The bedrock aquifer plume is believed generally to track the directions and configuration of the surficial

aquifer plume, although it is more broadly dispersed by the bedrock fractures.

Surface water samples from Boiling Springs, the discharge points of both aquifers to surface waters, contained up to 44 ppb TCE and up to 30 ppb TCA. Trace levels of volatile organic compounds had been found in Collyer Brook, a tributary to the river, in earlier investigations. However, no detectable concentrations of TCE or TCA were found in Collyer Brook or the Royal River during the Remedial Investigation.

### 5.4.2 Soil Contamination

contained polycyclic aromatic hydrocarbons, phenols, phthalates, and other pollutants. Remedial Investigation soil samples were collected by drilling, hand auger borings, and test pits. Sample locations were selected on the basis of historical disposal data, visual evidence of contamination, and magnetometer survey results. Soil contaminants occurred mainly in six areas of the site, as shown in Figure 15. Area 1 was divided further into three subareas as shown, based on chemical and physical properties of the contaminated soils. Estimated volumes of contaminated soils in each area are shown in Table 19. Three areas (1A, 1C, and 2) were tentatively identified as former oil disposal

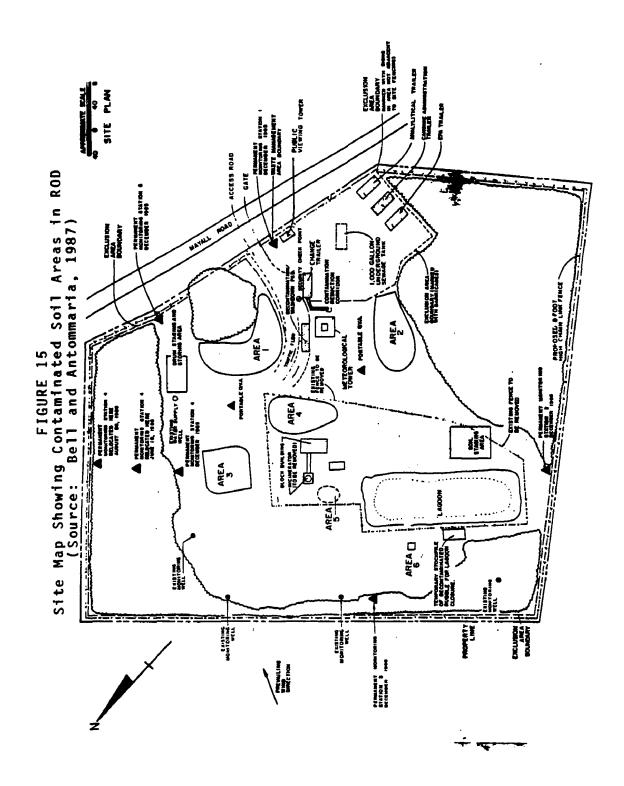


TABLE 19
Soil Volumes Estimated in the Record of Decision (Source: Camp, Dresser and McKee, 1985D)

	Approximate Surface Area	Estimated Depth	Estimated Volume*				
Area #1 A	4864 Sq.Ft.	Average 3 Feet	540 Cubic Yards				
В	1152 Sa.Ft.	Average 5 Feet	213 Cubic Yards				
B C	2816 Sq.Ft.	Average 5 Feet	521 Cubic Yards				
Sub-Total	8832 Sq.Ft.	_	1274 Cubic Yards				
Area #2	4032 Sq.Ft.	Average 5 Feet	747 Cubic Yards				
Area #3	1500 Sq.Ft. Saturated Soils	Average 40 Feet	2222 Cubic Yards				
	1400 Sq.ft. No Discoloration	Average 40 Feet	2074 Cupic Yards				
Sub-Total	2900 Sq.Ft.		4296 Cubic Yards				
Area #4	3200 Sq.Ft.	Average 3 Feet	356 Cubic Yards				
Area #5	150 Sq.Ft.	Average 3 Feet	17 Cubic Yards				

<sup>\*</sup> up to 3 feet of clean soil has been placed on top of contaminated soils and these clean soils have been calculated into total volumes.

locations, containing oil-soaked debris covered by fill.

Remedial Investigation analyses were targeted to the

remaining areas, especially Areas 3, 4, and 5, where

soils were visibly discolored.

Soils on-site were found to contain at least 17 hazardous compounds (Table 20), mainly volatile organic compounds such as TCE and TCA. Low levels (generally 15 ppm or less) of metals such as arsenic, chromium, and lead were found in some samples. Note that of the soil contaminants identified, only TCE and TCA occurred also in a majority of ground water samples. No significant levels of metals or petroleum hydrocarbons were found in ground water.

concentrations of TCE in soils ranged to 1400 mg/kg in Area 3, which also contained up to 49 mg/kg methylene chloride, 4.5 mg/kg TCA, and other compounds. TCE levels ranged to to 1500 mg/kg in Area 4, which also contained up to 21 mg/kg xylenes, 9.2 mg/kg dichlorobenzene, and other compounds. Depth of soil contamination was six feet or less in most of these areas, except in Area 3, where it reached 12 feet in some locations, extending approximately 40 feet to the water table in others. Some soils around the 16 buried drums still on-site also were contaminated. The Feasibility Study focused partly on source control actions for these areas, as will be described in Section

### TABLE 20 Contaminants Found In McKin Site Soils (Source: EPA, 1985J)

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<sup>\*</sup> Approximately
\*\* Sample taken July 10, 1984, analyzed September 4, 1984
due to delay specific concentrations are unknown
a \* Tylene not analyzed for in this sample.

\*\*RD = Selow Detection Limits.\*\*
b = Field Blank

# 5.4.3 <u>Current/Potential Risks Posed by the Unremediated Site</u>

The Remedial Investigation data was combined with prior information about the site to refine the conceptual model of the contamination problem in the site risk assessment, which was performed in this instance as part of the Feasibility Study. Current and future risks posed by the McKin site were evaluated, especially the possible pathways and likelihoods of exposure to contaminated soils and ground water both on-and off-site should the "no action" alternative be selected. Most of the potential direct and indirect pathways presented in Section 3.1 exist at the McKin site to varying degrees. However, the most critical exposure pathway affecting longterm implementation of the selected remedy was considered to be the leaching of contaminants to ground water.

On-site air concentrations of contaminants were found not to exceed available state guidelines (Camp, Dresser and McKee, 1985D); thus inhalation risks were deemed insignificant so long as site soils were left undisturbed. Off-site transport of contaminants in surface runoff has not been observed and was judged unlikely at the McKin site. The probability that soil

contaminants will be taken up by plants on-site, bioaccumulated, and subsequently ingested by humans or animals likewise was considered negligible. Based on surface concentrations, likelihood of occurrence, and the volatile nature of the principal contaminants, it was estimated that exposure via either acute or chronic dermal contact would have negligible human health impacts.

Risks due to ingesting site soils were evaluated by EPA's contractors using worst-case assumptions of soil ingestion by children entering the site and contacting the most highly contaminated soils found during the Remedial Investigation (1500 mg/kg TCE). estimated that ingestion of a 10-gram dose of the most highly contaminated soils would not result in acute toxicity effects due to TCE, based on the toxicity range of 50-7000 mg/kg TCE dosage recorded by the National Institute for Occupational Safety and Health (Camp, Dresser and McKee, 1985d). Risks from chronic ingestion of recorded by the National Institute for Occupational Safety contaminated soils on-site were considered insignificant based on ambient soil concentrations of TCE and TCA, and on the limited probability of site access.

Risks from dermal exposure were calculated to be insignificant (Camp, Dresser and McKee, 1985D).

Inhalation risks related to excavation or disturbance of

volatiles- containing soils were estimated by EPA's contractors not to be likely to exceed 1/50 of the ambient levels published as guidelines by the New York Department of Environmental Conservation. These guidelines, which are calculated as 1/300 of the Threshold Limit Values established for 8 hour worker exposure by the American Council of Governmental and Industrial Hygienists, represented the ARARs, or the the most nearly relevant and appropriate criteria, identified for inhalation risks in this study (Camp, Dresser and McKee, 1985D). Therefore, all contaminated soils exposure pathways other than leaching to ground water were eliminated from further consideration.

Soil contaminants have leached to ground water at McKin, creating a plume of contaminated ground water in both the surficial and bedrock aquifers that continues to contaminate private wells downgradient. It provides for potential exposures through ingestion of contaminated ground water by humans, animals, and plants, and through inhalation of contaminants that volatilize during showering, cooking, and other activities. As stated previously, all private wells downgradient that are known to be affected have been closed, and their users were provided an alternative water supply; thus, ground water is a potential, rather than current, exposure pathway. However, future use of

the ground water resource is precluded so long as TCE and TCA contamination exceeds levels that may be safe for public health and the environment. The applicable or relevant Federal "safe levels" for human health for the primary contaminants in the McKin site situation were identified as 200 ppb for TCA (the proposed Recommended Maximum Contaminant Level) and 28 ppb for TCE (the 10-5 risk level for a 70 kg adult drinking 2 liters of contaminated ground water daily; EPA, 1985P). The TCA "safe level" was exceeded in the B-1 bedrock well, while the TCE threshold was exceeded at most wells, during both the Remedial Investigation and prior sampling. "Safe levels" for terrestrial environmental receptors were not established during this study.

In addition, the plume(s) have reached nearby surface waters including the Royal River. Based on comparisons with applicable or relevant and appropriate EPA criteria, TCE and TCA levels measured in the Royal River during the Remedial Investigation and prior studies pose insignificant public health risks through ingestion of river water or dermal contact during swimming (Camp, Dresser and McKee, 1985D), and were estimated in the Feasibility Study not to threaten aquatic life. The possible effects of future changes in surface water contaminant concentrations (for example, due to later discharge of a pulse of more highly

contaminated ground water to surface waters) was not evaluated during the RI/FS.

# 5.5. <u>Analysis of Remedial Alternatives: the Feasibility Study</u>

## 5.5.1 General Response Objectives

Based on the findings of the Remedial Investigation and the site risk assessment, the following response objectives were identified for the McKin site and used to evaluate and compare remedial alternatives during the Feasibility Study. They focused on reducing the risks posed by the unmitigated site:

- o Maintenance of adequate safe drinking water for the potential ground water receptor population;
- o Prevention of human exposure to inhalation of harmful levels of airborne contaminants;
- o Prevention of release of contaminated ground water to aquifers off-site;
- o Restoration of the contaminated aquifer(s) offsite to levels protective of public health (i.e., restore useability as a drinking water supply) and the environment "within a reasonable time and practical limits" (EPA, 1985J);
- o Protection of state-designated uses of surface water, and aquatic life, in the Royal River; and
- o Prevention of ingestion of, or dermal contact with, contaminated soils by the public.

#### 5.5.2 Initial Screening

A series of technologies were assembled and combined into

alternatives for the initial screen. All alternatives shared several common activities, such as removal and disposal of all metallic structures, above-ground debris, and buried drums, as well as the buried tank and the block building; draining and backfilling the asphaltlined lagoon; removing and disposing of all wastes and decontamination rinsates generated during remedial actions; and loaming, revegetating, fencing, and posting signs around the entire cleared site.

Several of these alternatives, or elements thereof, did not attain the response objectives. They were rejected from more detailed analysis (Camp, Dresser and McKee, 1985D) using the National Contingency Plan criteria in 40 CFR 300.68 (h), as follows:

- o No action. This option did not mitigate the public health or environmental threats.
- o <u>Capping the entire cleared site area</u>. This option did not provide substantially greater benefits than less costly alternatives.
- o <u>Installing a containment wall around the</u>
  contaminated areas. This option did not provide
  substantially greater benefits.
- o <u>On-site soil encapsulation</u>. This option did not provide substantially greater benefits.
- o Systematically recovering contaminated ground water from the fractured bedrock aquifer to comprehensively decontaminate this zone. This was determined to be technically infeasible.

#### 5.5.3 <u>Detailed Evaluation of Alternatives</u>

The remaining alternatives were evaluated in detail according to the National Contingency Plan criteria set forth in 40 CFR 300.68(h) including protectiveness of the environment and public health, short-term impacts, technical feasibility, reliability, implementability, long-term effectiveness including operations and maintenance requirements and other factors, and costs and cost-effectiveness, as described in the initial chapters of this report. The alternatives evaluated in detail included five general "source control" alternatives and three general "management of migration" alternatives (off-site remedial actions), as described briefly below (EPA, 1985J):

- No Action With Monitoring-Monitoring wells would be installed around the site and ground water contamination would be monitored periodically.
- 2. <u>Capping</u>— Contaminated areas 1B, 3, 4, and 5 shown in Figure 15 would be covered with a single impervious cap. Area 6 would be capped independently, or excavated and either consolidated under the main cap or disposed off-site.
- 3. Excavation and Off-Site Disposal -- Contaminated soils would be excavated and transported off-site for disposal by either landfilling or incineration.
- 4. On-Site Incineration -- Contaminated soils would be excavated and incinerated on-site. Residues would be disposed on-site.
- 5. <u>Aeration--</u> Contaminated soils would be tilled and exposed to the air to enhance volatilization of the organic contaminants. Three options were considered:

- (A) onsite aeration, (B) excavation and aeration off-site, and (C) partial excavation and aeration off-site (Area 3 would be left in place and capped).
- 6. No Action With Off-Site Monitoring-- Off-site wells would be monitored periodically.
- 7. Ground Water Extraction/Treatment— Contaminated ground water would be removed by extraction wells, and contaminants removed by air stripping and adsorbed onto activated carbon. Three alternatives, using one, two, and three series of extraction wells respectively, were considered in the Feasibility Study. Treated ground water would be recirculated to the ground water beneath the site. An additional alternative was developed that used an unspecified number of wells screened primarily in the surficial aquifer. Extracted ground water would be discharged to surface water following treatment, rather than being recycled to the aquifer.
- 8. Land Use/Development Restrictions— Future development would be restricted in all areas affected by the ground water plume. New wells would not be allowed in presently undeveloped areas in this zone, and additional water supplies would not have to be imported to the area.

## 5.5.4 <u>Selected Remedy: The Record of Decision</u>

Following public comment on the completed studies,
EPA selected a combination of source control and
management of migration actions, combining elements of
Alternatives 5 and 7, to satisfy the site response
objectives comprehensively and to attain the National
Contingency Plan decision criteria at 40 CFR 300.68(i).
The McKin ROD (EPA, 1985J) documented EPA's selection of
the following remedial actions:

- o Aeration of contaminated soils in several discrete areas on-site to reduce their hazardous substance levels (primarily TCE and TCA) such that residual concentrations are safe for public health and the environment by all routes of exposure;
- o Disposal of sixteen remaining drums off-site;
- o Characterization of contamination in petroleumcontaminated soil areas;
- o Construction and operation of a ground water extraction/ treatment system involving a series of extraction wells located mainly in the surficial aquifer and the uppermost portion of the bedrock zone, with discharge of extracted ground water to surface waters following treatment by air stripping and activated carbon adsorption; and
- o Other demolition, removal, disposal, and backfill/ revegetation activities as described in Section 5.5.2.

soils would be aerated in Areas 1B, 3, 4, 5, and 6 at a rate dependent on the final system design. Selection of an open versus closed system would depend on whether rates of volatiles release could be assured not to adversely impact offsite air quality. Design of the soil aeration system would be based partly on an onsite pilot study, which would determine the effectiveness of this technology to remove volatile organic contaminants from the McKin site soils, and verify specific engineering controls required to prevent public health and environmental impacts during construction and operation of the treatment system.

The remedy was to feature continuous air monitoring during operation, and soil verification monitoring to

evaluate the attainment of the soil target standards, and/or any need for their subsequent modification.

The ground water system would be operated for a minimum of five years, with target performance standards of 92 ppb TCA and 28 ppb TCE to be achieved in the aquifers. Both source control and ground water remedial actions would be monitored regularly during the active life of the remedial actions. The effectiveness of the remediation (i.e., the performance standards and system design/operation) will be reevaluated after five years, or earlier if warranted by system performance or events at the site.

EPA's analysts estimated that, assuming the source were removed or controlled, total volatile organics levels in the aquifers would fall below 50 ppb within ten years through natural flushing and attenuation mechanisms. However, an active ground water restoration alternative was selected for the following reasons: uncertainty in the cleanup time estimate; the possibility for other, less mobile contaminants to be present, undetected, at dangerous levels; the uncertain effectiveness of institutional controls on aquifer use over the long term; and the desire to assure environmental as well as public health protection, through active removal of contaminants to the greatest extent practicable, to assure consistency with the intent

of CERCLA, RCRA, and EPA's Ground Water Protection Strategy (EPA, 1984B).

Many uncertainties regarding ground water flows, modeling assumptions, likely yields, treatability of the pumped liquids, appropriate well locations and designs were not resolvable at the time of the ROD based on the data then available. These uncertainties were to be addressed (1) by retaining flexibility in the number, location, and design of wells in the Record of Decision; (2) by gathering additional data during the design stage to refine EPA's understanding of the ground water flow system and plume distribution, hydraulic conductivities, likely drawdowns, saturated thicknesses, and optimal number and placement of the extraction wells; and (3) by continuously monitoring and evaluating the performance of the system in improving ground water quality, and maintaining surface water quality. If after five years the performance standards have not been met, the system will be reevaluated. Its operation will be terminated or modified, or the performance targets themselves reexamined if necessary. Changes may be made earlier, if warranted by monitoring results.

## 5.6 Selecting the Cleanup Level for the ROD

The McKin ROD represented one of EPA's first remedial decision documents to specify numerical

performance targets. These are target cleanup levels to be achieved in the site soils by the source control actions, and in the ground water (both on- and off-site) by the management of migration actions.

#### 5.6.1 Ground Water Performance Targets

Ground water cleanup targets provided the basis for the performance targets for both soils and ground water at the McKin site, because (1) they represent the desired "safe level" endpoints for cleanup of the current aquifer contamination, and (2) soil cleanup targets were then set such that residual soil contaminants would never recontaminate the aquifers above these "safe levels" after both soils and aquifer restoration had been completed. EPA's intent was to set "safe levels" for unrestricted use of the ground water that would protect both human and environmental receptors, considering the likelihoods and types of exposures, and the possible synergistic effects of the specific contaminant mixture to which a receptor might be exposed.

Ground water targets are to be met at all points in the aquifers downgradient of the closest potential receptor location. For the contaminated ground water exposure pathway, this point was taken to be the site boundary, the nearest possible location of any future

receptor well at the McKin site.

Targets were set for the indicator compounds TCE and TCA in the McKin ground water based on the Remedial Investigation results. As described in Section 5.4, the Remedial Investigation indicated that only TCE and TCA were present in the ground water at levels of concern, despite the slightly more complex mixture of organic and metal contaminants present in site soils for a number of years.

For TCE, a suspected human carcinogen, the "safe level" of 28 ppb was selected as the target, which represents a 10<sup>-5</sup> lifetime cancer risk for a 70 kg adult drinking 2 liters of TCE-contaminated ground water daily over 70 years (EPA, 1985P). EPA's choice of the 10<sup>-5</sup> cancer risk for this compound in ground water was based on several factors:

- o The extremely low likelihood of ground water consumption within the plume area during the expected remediation period. The affected property is already relatively developed, and all residents use municipal water supplies rather than wells;
- o EPA's expectation that, given the mobility of TCE in ground water, the permeability of surficial aquifer materials, the fractured nature of the bedrock, and other hydrogeologic factors, natural dispersion and attenuation mechanisms will continue to reduce residual TCE levels in ground water relatively rapidly following cessation of active restoration measures. Thus, chronic risk levels will continue to decline from this estimated level;
- o EPA's expectation that the uncertainties in EPA's knowledge of contaminant distribution and composition,

and of the effectiveness of the proposed aquifer restoration system, will be reduced during design and implementation of the system; and

o The conservatism inherent in the toxicological analyses on which the TCE risk levels were established (EPA, 1986G,J).

These adjustments, based on site-specific considerations of exposure, contaminant properties, etc., are in conformance with EPA's risk assessment policy (EPA, 1984C; 1985G,J), which provides for the establishment of target levels for known or suspected human carcinogens within an acceptable risk range of 10<sup>-4</sup> to 10<sup>-7</sup>.

For TCA, a non-carcinogenic toxicant, 92 ppb was set as the target, which is significantly below the 200 ppb RMCL proposed by EPA based on the threshold level for expected adverse human health effects (EPA, 1985P). This adjustment to 92 ppb was based on EPA's consideration of the following factors:

- o Possible synergistic or additive effects with TCE, considering a 52 ppb adjusted Acceptable Daily Intake for TCE in drinking water and assuming similar systemic effects and direct additivity;
- o The 28 ppb target set for TCE at this site; and
- o The 200 ppb RMCL proposed for TCA.

## 5.6.2 Soil Performance Targets

Soil performance targets constituted both the levels judged as safe to leave untreated at the

conclusion of remedial actions, and the expected residual levels following soil treatment. They were derived based on the following findings and assumptions of the Remedial Investigation's risk assessment, as described in Section 5.4:

- o Many potential exposure pathways that may exist following soil cleanup, including inhalation of volatilized soil contaminants; ingestion of soils, dusts, or contaminants bioaccumulated in plants; dermal contact; and exposure to soils transported by surface runoff. However, leaching of soil contaminants to ground water is the primary exposure pathway of concern for the McKin contaminated soils, and the limiting pathway for purposes of setting soil cleanup levels;
- o TCE was judged to be the appropriate soil indicator compound, based on its presence in both soils and ground water, its toxicity relative to other McKin soil contaminants, and other factors;
- o Detailed fate and transport analysis was required to describe the linkage of the two media and the movement of TCE and other compounds from soils to ground water, in order to set appropriate soil performance targets;
- o Metals generally were present in scattered locations at relatively low concentrations (Table 20). Although aeration may not remove metals from the soils effectively, the mixing afforded through the aeration process was expected to dilute the metals to safe levels without subsequent treatment; and
- o Uncertainties related to these assumptions would be reduced through more extensive monitoring, sampling, and modeling as necessary during the design phase and the pilot study, as described in Section 5.5.

Different modeling approaches were employed to set soil targets based on these findings and assumptions, for the two classes of indicator compounds used (metals

and TCE). For the low-level metals present, target residual levels were set by physical modeling of leachate using the RCRA Extraction Procedure (EP) toxicity test given in 40 CFR 261.24. Numerical EP targets were not set in the ROD, for the above-mentioned reasons; rather, residuals would be measured using the EP test to verify attainment of cleanup targets at the conclusion of cleanup. Cleanup targets for metals would be attained when soil concentrations following treatment would no longer produce RCRA-toxic-characteristic leachates, i.e., those with concentrations passing the EP test.

TCE soil targets were established using a threestage numerical modeling approach. First, a fate and
transport model was selected that provided the most
reasonable and accurate prediction of movement of TCE
from soils to ground water possible at the time of the
Record of Decision, based on the level of understanding
of the site at that time. The model simulated the rates
and amounts of migration of leachate from the zone of
leachate generation within the contaminated soil areas
to the surficial and bedrock aquifers. Using the
previously-derived ground water performance targets as
input values (28 ppb TCE and 92 ppb TCA), acceptable
maximum leachate values for the soils were then backcalculated with the same model.

Finally, acceptable residual soil targets were back-calculated from these approximate leachate targets using numerical estimates of soil leaching. Based on this three-stage modeling process, the preliminary soil performance target for TCE was set in the Record of Decision at a residual concentration of 0.1 ppm, averaged over a treatment volume.

Selection and use of the models for this purpose depended on several factors, including the type and nature of the assumptions used regarding fate and transport; the uncertainties inherent in these assumptions and estimates; the degree of conservatism desired in the output cleanup target; and the choice of such critical inputs as the inferred nearest ground water receptor location, or point of exposure to contaminated ground water. These factors and their effects on the McKin soil level decisions are discussed further in the following sections of this chapter.

#### 5.7 <u>Selecting the Back-Calculation Approach</u>

Model selection efforts for setting soil TCE levels focused on several relatively simple analytical solute transport models for back-calculating acceptable leachate concentrations entering ground water at the downgradient site boundary. Candidates had to yield realistic results based on the conservative assumptions

required by the limitations in site knowledge at the time of ROD signature. The following initial assumptions were used:

- o Residual soils will be a continuous source (and are the only source) of TCE loading to the aquifers;
- o No dilution occurs as unsaturated zone leachate enters and mixes with the ground water beneath the site:
- o No dilution occurs from precipitation recharge entering the aquifers between the downgradient edge of the site and the receptor:
- o No sorption occurs in the saturated zone; and
- o No chemical or biological transformations occur in the aquifers.

## 5.7.1 Candidate Models Considered

Five models were considered: a pulse-source equation (Freeze and Cherry, 1979), and four continuous-source equations (Kent et. al., 1985; EPA, 1986L; Wilson and Miller, 1978; and Domenico and Palciauskas, 1982). The first three were rapidly rejected. The pulse-source model did not simulate a continuous source, assuming instead an instantaneous influx of the entire contaminant mass from surface soils to the upper aquifer zone. This conflicted with field results. The second model, based on Kent et al.'s equation, yielded an undefined mathematical term based on the input parameters.

The third model, EPA's Organic Leaching Model,

solves a two dimensional solute transport equation using dimensionless numbers, as described by EPA (1986L) and Camp, Dresser and McKee (1985E). This method was rejected because downgradient contaminant concentrations calculated using the model did not approximate field values and were unrealistic. Further, the model's infiltration term I, in units of 1/time, did not convert acceptably from actual infiltration values, expressed in in/yr or cm/yr. The remaining two models were considered in more detail.

#### 5.7.2 The Wilson-Miller Model

This model, published in 1978 by Wilson and Miller, was used for the McKin analysis as modified by Wilson according to the following equation:

$$C_{r} = \frac{C_{0}Q \exp (x/\beta)}{4\pi\beta\eta_{e} \sqrt{D_{x}D_{y}}} * W(\mu, r/\beta)$$
 (5-1)

where C<sub>r</sub> = concentration at the receptor well at distance r directly downgradient from the source)

Co = leachate input concentration "injected"
 into the aquifer at the waste source

Q = volumetric injection rate

β = uniform saturated thickness

 $W(\mu, r/\beta)$  = the Hantush-Jacob Leaky Well Function (Hantush and Jacob, 1955) Other terms are derived as follows:

$$r = 1 + (2\beta\lambda R_d)/V = \sqrt{X^2 + (D_{XX}Y^2)/D_{yy}}$$

= a weighted radial distance downgradient from the source, based on relative dispersion  $(\alpha_L/\alpha_T)$  and radioactive decay (  $\lambda$  ).

 $\alpha_{T}$ = lateral dispersivity

 $\alpha_T$ = transverse dispersivity

$$\mu = r^2/(4\gamma D_{XX}t)$$

The expression can be simplified to yield the steady-state concentration (at t+ $\infty$  and  $\mu$ +0), where equilibrium has been reached between the injection rate and and the dispersion rate, for circumstances where  $(r/\beta) > 1$ . At the centerline of the plume, under a worst-case scenario, y=0 and r=x (using r as defined in equation 5.1). When  $\beta$  is thus substituted to back-calculate source concentrations of leachate from maximum acceptable downgradient concentrations, this equation must be rewritten to solve for  $C_0$  as follows:

$$C_{O} = \frac{C_{\Gamma} 2\pi \beta \eta_{e}}{Q} * \sqrt{(D_{X}D_{Y}X)/(\pi \alpha_{L})}$$
(5-2)

Equation 5-2 was then tested using McKin site data obtained during the Remedial Investigation and from Gerber (1982) to obtain a  $C_0 = 7.2 \times 10^6$  mg/l. This represents a TCE concentration in leachate entering the aquifer at the downgradient boundary of the site of

7,200,000 ppm. Since the maximum solubility of TCE in pure water is 1100 ppm, the model was rejected as not representing field conditions.

## 5.7.3 The Vertical and Horizontal Spread (VHS) Model

The VHS model was erroneously titled SOCEM in the attachment to the McKin Record of Decision. It was published by Domenico and Palciauskas in 1982, and has since been modified and adopted by EPA for use in evaluating potential ground water threats from delisted wastes in delisting petitions filed pursuant to the RCRA regulations at 40 CFR 261. The model solves a partial differential equation describing advection and dispersion of a contaminated ground water parcel in the horizontal and vertical directions as the parcel moves downgradient from a continuous source in a steady one-dimensional flow field. When simplified by applying the boundary condition that the centerline of the plume is the principal area of concern, the equation may be written in the following form:

$$C_{O} = \frac{C_{X}}{\text{erf}[Z/(2/\alpha_{T}X) * \text{erf}[Y/(4/\alpha_{T}X)]}$$
(5-3)

 Y = Lateral extent of leachate zone entering aquifer at site boundary

erf = Error function

 $\alpha_T$  = Transverse dispersivity

Using site data ( $C_X$ =15 ppm TCE, X=800', Y=200', Z=15',  $\alpha$  =3.3'), the model gave a  $C_O$  (the resultant source concentration entering ground water) of 117 ppm. This was considered reasonable by EPA's contractors, given field observations. For example, Gerber (1982) reported TCE at 130 ppm in an on-site well.

Note also that the maximum solubility of TCE in water, 1100 ppm, is approximately 10 times this calculated value. Mackay et al.(1985) supported the EPA contractor's conclusions, in that they found many organic compounds occurring only infrequently in ground water at concentrations greater than ten percent of their maximum water solubility, and only rarely at concentrations approaching their solubility limits. On these grounds, the VHS model was selected for estimating ground water source strength entering the aquifer at the McKin site boundary.

#### 5.8 Running and Interpreting the Model

The model was then applied to back-calculate the source concentration  $(C_0)$  at the downgradient edge of the contaminated soil area that would assure ground water concentrations not exceeding the selected ground

water target of 28 ppb TCE at the downgradient site boundary, considered to be the nearest potential ground water receptor for purposes of EPA's Record of Decision. The VHS model was used as before, substituting 28 ppb for C<sub>X</sub> and setting x=200 feet. C<sub>O</sub>=96 ppb was calculated as the maximum TCE level allowable in leachate entering ground water beneath the McKin contaminated soils mass. The next step was to back-calculate acceptable maximum soil TCE levels that may be left as residual concentrations following aeration, or that may be left untreated, that would not leach TCE into ground water in excess of the 0.096 ppm value.

## 5.8.1 <u>Leachate Estimation Method</u>

As indicated in EPA (1985N), the Agency does not currently have available physical models such as the EP, TCLP, or other leaching test procedures, capable of accurately and reliably estimating the expected leachate production of organic pollutants from a contaminated soils mass in a natural environment. Given the paucity of data available at the time of the Record of Decision, and the uncertainty present in other estimations made for this decision, a mathematical method was selected for this analysis.

Soil TCE concentrations were estimated by assuming that the concentration of TCE in leachate was dependent

on the establishment of an equilibrium between two phases: the TCE sorbed to soil particles and the TCE in the leaching medium (assumed to be "pure" rain water). A soil partition coefficient  $K_d$ , defined as the ratio of the soil concentration ( $C_S$ ) to the water concentration ( $C_W$ ), was used to calculate the soil concentration as follows:

$$C_{s} = C_{w} * K_{d}$$
 (5-4)

K<sub>d</sub> values were estimated from literature values for K<sub>OC</sub>, the organic carbon partition coefficient (see Lyman et al. (1982) for definition and discussion). This estimation process assumes (1) that total organic carbon content, rather than surface area, cation exchange capacity, clay content, or other parameters, is the most significant soil parameter affecting sorption of TCE to the soil particles; and (2) that K<sub>OC</sub> tends to be relatively constant for a given organic compound, and relatively independent of soil type (Lyman et al., 1982). The K<sub>OC</sub> for TCE was estimated to be 38 mL/g by A.D. Little (1981). This value was corrected to account for soil organic matter not contributing to sorption according to the following equation (Lyman et al., 1982):

$$K_{OC} \simeq 1.724 K_{Om}$$
 (5-5)

where  $K_{\text{om}}$  is the soil organic matter partition

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coefficient.  $K_d$  was then estimated using the  $K_{om}$  value and the fractional organic matter content in McKin soils  $(f_{om})$ , which was approximated using a literature value of 5% (EPA, 1982D).  $K_d$  was calculated as follows:

$$K_d = K_{Om} * f_{Om} = (0.05)(22) = 1.1 \text{ ml/g}$$
 (5-6)

#### 5.8.2 Calculation of the Soil Performance Target

Using Equation 5-4, the soil TCE concentration,

C<sub>S</sub>, was then calculated to be 0.11 ppm TCE. Thus,

EPA's contractor estimated that a soil cleanup target of

0.1 ppm TCE in the Record of Decision would provide a

residual concentration in soils that would not leach TCE

to ground water beneath the site in excess of 96 ppb,

which in turn was estimated to yield ground water

concentrations at the site boundary that would not

exceed 28 ppb TCE, the ground water performance target.

The Record of Decision provided several caveats related to derivation and use of these cleanup targets, including the following (EPA, 1985J):

- o The analysis described above was described as only an initial analysis, based on best engineering judgement and limited by the availability of detailed site data;
- o Uncertainty in the accuracy of the VHS model results was attributed to the anisotropic nature of the aquifers. This conflicts with the model's underlying assumption of isotropy (Domenico and Palciauskas, 1982); and

o Heterogeneity in McKin soils was found by Gerber (1982) in the horizontal and vertical directions, which compounded the modeling difficulties introduced by the large differences in aquifer characteristics between the surficial and fractured-bedrock saturated zones.

#### 5.9 Uncertainties and Their Reduction

No formal numerical estimate of uncertainty in either the soil or ground water performance targets was made in the Record of Decision. Rather, the uncertainties were broadly discussed, and the conservatism associated with the estimation methods was offered as the major compensatory mechanism. Further, as noted in section 5.5.4 above, some of these uncertainties were expected to be reduced through verification monitoring and through the collection of additional data during design and implementation of the remedy at the McKin site (EPA, 1985J).

EPA further stated in the McKin Record of Decision that the remedy would be modified or refined as necessary based on these subsequent findings, and that part of any such refinement may be based on more sophisticated modeling during the design phase, if possible (and if judged worthwhile) based on such additional data.

## 5.10 Events Following the Record of Decision

A series of events followed the Record of Decision that significantly affected the cleanup level decision that had been made therein. These events will be examined in the following sections in terms of how the additional information gathered during design and implementation of the selected remedy, as well as the various reexaminations of the modeling effort that took place during this period, enhanced the Agency's and the responsible parties' understanding of the contaminant transport regime at the site. The correspondence between these events and the SOCEM framework presented in Sections 4.8 and 4.10 will be discussed in Section 6.2.

These events occurred over a two-year period extending from the McKin Record of Decision in July, 1985, through the Remedial Design and the pilot study, to completion of the soil aeration and site closure activities in July, 1987. They can be traced through an ongoing exchange of correspondence between EPA (and its contractor, Camp, Dresser and McKee) and the Responsible Parties (and their contractors, E.C. Jordan Company and Canonie Engineers) which on occasion involved the state, local citizen groups, other regulatory agencies, and other interested parties. Several general observations

may be made about this "paper trail:"

- The primary interest of the responsible parties was to perform a soil cleanup which fully achieved the response objectives of the ROD, but which at the same time minimized their expenditure of time and resources.
- Therefore, the responsible parties repeatedly challenged EPA's selection of the 0.1 ppm TCE soil cleanup level in the Record of Decision, arguing that higher (less stringent) levels would be fully protective of public health and the environment. Virtually no strong challenges were made to the ground water performance target on which the soil cleanup level was based.
- o Challenges initially were directed at EPA's choice of the VHS model, but the majority of issues shifted to the use of the model, choice of input parameters, and interpretation of the results.
- o Initial challenges were made using the available literature to support positions and contentions. Later, as the Remedial Design progressed and more data was obtained, this additional site data was used to support or to question various choices of parameters or results. Eventually EPA and the state accepted a higher cleanup level of 1.0 ppm for residual TCE in site soils.

#### 5.10.1 Initial Challenges to VHS Model

A consultant to the McKin responsible parties, E.C. Jordan Company, challenged the cleanup level and the use of the VHS model in a memorandum to EPA in August, 1985. E.C. Jordan charged that Camp, Dresser and McKee used a form of the model inappropriate for the site conditions, and contested their definitions of Z (vertical mixing zone), X (receptor distance), dispersivity, porosity, and carbon content. They developed a mixing length

interpretation, and estimated a recharge value and a new set of dilution factors. From these E.C. Jordan calculated a new TCE leachate concentration ( $C_0$ ) of 0.35 ppm, and a TCE soil cleanup level of 0.6 ppm, using a different form of the VHS equation presented by Domenico and Palciauskas (1982) than the one used by Camp, Dresser and McKee (1985E) for the Record of Decision.

Duchesneau (1985A), writing on behalf of EPA's consultant, Camp, Dresser and McKee, defended their version of the VHS, and their choices of Z, X, and dispersivity, as well as their assumptions neglecting retardation, degradation, and recharge dilution. He and Christian and Adams (1986) provided additional evidence to support Camp, Dresser and McKee's selection of TCE as indicator compound, and their estimate of soil organic carbon content. Discussions with EPA Headquarters staff, including this author, supported many of these positions (Duchesneau, 1985B; Hooper, 1985).

## 5.10.2 Soil Aeration Pilot Study

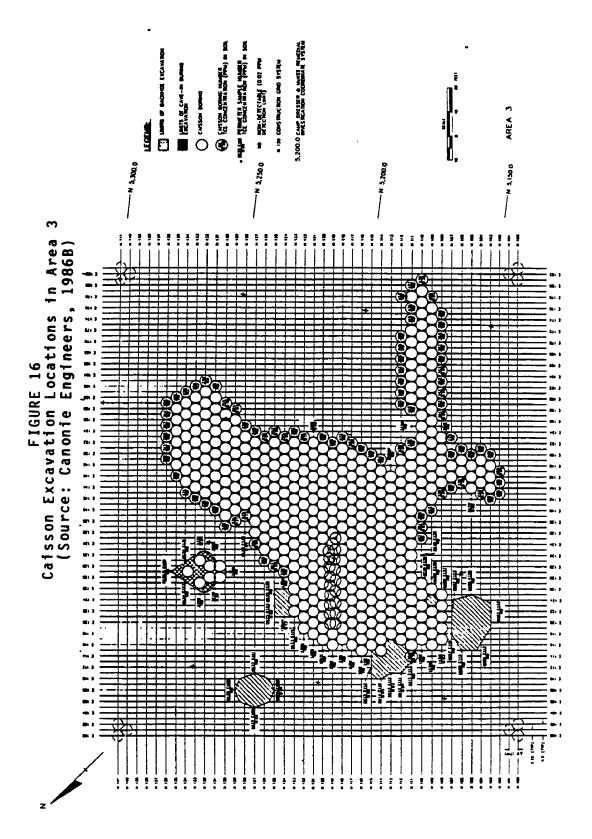
Pursuant to a consent order signed by the EPA and several of the Potentially Responsible Parties in August 1985, Canonie Engineers, consultants to the responsible parties, designed and conducted a pilot study of the soil aeration process on-site (Webster, 1986; Canonie

1986A). As part of the study, they performed substantial additional characterization of the contaminated soils source areas, and built and pilot tested a "low-temperature" aeration system as discussed in Section 2.3.5.2.

The chosen design combines several conventional construction and pollution control technologies, some of which are components of a portable asphalt batch plant. It is an innovative way to excavate and treat the contaminated soils in an enclosed system which minimizes the loss of the volatile contaminants to the atmosphere at each stage of the excavation, treatment, and redeposition process (Webster, 1986).

## 5.10.2.1 Excavation by Caisson Digging Bucket

Vertical columns of soil were excavated from most areas using a kelly bar caisson unit suspended from a 100-foot crane and fitted with a 5-foot by 4-foot cylindrical digging bucket. To prevent volatilization losses, soils were discharged to a covered front-end loader, and deeper excavations were cased with cylindrical steel caissons. The caissons also prevented collapse of the sandy sidewalls following soil removal. Circular excavation holes were sited throughout each area to be excavated in overlapping honeycomb patterns. Area 3's pattern is shown in Figure 16 as an example.



In the pilot study, approximately 640 square feet of source areas were excavated to depths up to 17 feet using this method (Webster, 1986).

Their extensive additional characterization of contaminant locations in the soils during the design phase had allowed Canonie (1986A,B) to develop a detailed three-dimensional map of the contaminated zones, which were found to be intermittently distributed both vertically and horizontally throughout the subsurface soils. This helped confirm the conceptual model of intermittent, pulsed releases of contaminants to ground water, either through periodic disposal of contaminated liquids in the lagoon and other source areas during the facility's operating life, or subsequent leaching of soil contaminants following precipitation events, or both. It also provided a basis for Canonie to propose that uncontaminated soils found vertically between "hot spot" zones be set aside and used for backfill, thus lowering treatment volumes and minimizing the overall cost of the remedy.

#### 5.10.2.2 Soil Treatment System

Excavated soils were aerated in a materials dryer consisting of an inclined, rotating drum approximately 7 feet in diameter and 28 feet long which was fed forced hot air (7,500-15,000 cfm at 150-380 F). Soils made

multiple passes through the drum on a belt or, later, enclosed bucket conveyors. Approximately 3 cubic yards were treated in each batch, which made 3-8 passes through the treatment system prior to discharge to a cement mixer truck. Retention times of 6-8 minutes per pass were typical.

Exhaust air containing extracted contaminants was treated in several stages. These included a baghouse for particulate removal; a packed-tower air scrubber containing plastic packing media washed by water, to remove water-soluble contaminants and residual particulates and condition the exhaust stream; and a vapor-phase carbon adsorption unit for removal of remaining contaminants (Webster, 1986; Canonie, 1986A).

## 5.10.2.3 <u>Solidification and Redeposition of Treated</u> <u>Soils</u>

Treated soils were mixed with a Portland cementwater slurry for physical stabilization of the soils (and of any residual contaminants retained thereon), and redeposited into the caisson holes. Mixtures of 9 cubic yards of soil with about 1200 pounds of cement and 600 gallons of water were typical (Webster, 1986).

## 5.10.3 Excavation Plan (Proposal to Relax Cleanup Level)

The pilot study had included a considerable amount of

additional sampling, which was used as a basis for developing the soil excavation plan (Canonie, 1986B). For example, Area 3 had been identified in the Remedial Investigation as the area with the highest TCE levels. The additional sampling revealed a much more extensive contaminated soil mass than found in the Remedial Investigation, totalling approximately 7600 cubic yards of contaminated soils containing approximately 790 pounds of TCE. Migration of contaminants to the ground water table was also discovered in this area.

In their excavation plan, Canonie proposed to treat soils in Areas 3, 4, 6, and 8 that contained more than 1.0 ppm TCE. According to this proposal, Areas 1B and 5 would not require aeration, since sampling results indicated that soil concentrations were less than 1.0 ppm in those areas. Note that Canonie (1986C) proposed to excavate and treat some soils in Area 1B even assuming the cleanup level was raised to 1 ppm TCE, due to the presence of benzene found during the additional soil characterization). Excluding treatment of "clean" soils at intervening depths (between two hot spots, found only in Area 3), Canonie estimated that a total of 5,025 cubic yards of soil would be processed on the site, leaving an averatge residual concentration between 0.14 and 0.24 ppm TCE.

However, EPA and the state asked Canonie to compare the

volumes of soil treated, pounds of TCE removed, and soil residual TCE levels that would be expected following treatment of all areas with soils contaminated above 1.0 ppm, 0.5 ppm, and 0.1 ppm, respectively, as summarized in Table 21 (Canonie 1986A,B). Canonie also compared the costs associated with each of these cleanup levels, using an estimate of \$246/cubic yard. For example, in Area 3, treatment to the 1.0 ppm contour would affect 2,824 cubic yards. 785.3 pounds of TCE would be removed, leaving an average residual concentration of 0.28 ppm. "Over-excavation" due to use of the bucket auger would increase the volume processed to approximately 3,200 cubic yards of soil, removing an additional 0.7 pounds of TCE and resulting in a residual soil concentration of 0.23 ppm.

Excavation and treatment to the 0.5 ppm TCE contour would involve processing 4,289 cubic yards of contaminated soils, removing some 788 pounds of TCE from this soil and leaving a residual soil TCE concentration of approximately 0.15 ppm. Use of the bucket auger would extend the treated zone beyond the 0.5 ppm contour, increasing the total volume processed in Area 3 to 4,930 cubic yards, and removing another 0.5 pound TCE. The residual concentration then would be 0.10 ppm TCE. Treatment to the 0.1 ppm TCE contour would involve excavation and treatment of 7,593 cubic yards of

TABLE 21
Volumes and Costs of Excavation to
Different Cleanup Levels
(Source: Gerken, 1986A)

	Volume, in c.y. of Affected Soils with TCE Concentrations			Mass of TCE	Cost of	Average Cost
Area	>.1 ppm	>.5 ppm	>1.0 ppm	Removed (1bs)	Removal (\$246/cy)	Per Pound of TCE Removed
18	1,064	25	0	0.407 0.032 -0-	\$ 261,744 6,150 -0-	\$ 643,110 192,200 -0-
3	8,700	4,930	3,200	789.3 788.3 786.0	2,140,200 1,212,780 787,200	2,710 1,540 1,000
4	555	305	205	4.20 4.08 3.91	136,530 75,030 50,430	32,500 18,400 12,900
5	31	-0-	-0-	0.01 -0- -0-	7,380 -0- -0-	738,000 -0- -0-
6 -	2,690	1,625	1,115	581.3 580.91 580.25	661,740 399,750 274,290	1,140 690 470
8	1,175	746	<u>505</u>	31.57 31.31 30.90	289,050 183,516 124,230	9,160 5,860 <u>4,020</u>
TOTALS						
(0.1 ppm) 14,215 (0.5 ppm) (1.0 ppm)		7,631	5,025	1,406.79 1,404.63 1,401.06	\$3,496.600 \$1,877,200 \$1,236,200	\$2,480 \$1,340 \$880

contaminated soils, removing some 789 pounds of TCE and leaving a residual level of about 0.05 ppm in the Area 3 soils. Again, the bucket auger would increase the total yardage excavated by about 15 percent, to about 8,700 cubic yards.

Canonie had also found that contamination was not continuously distributed vertically beneath Area 3.
"Hot spots" or pulses of contamination were found between layers of relatively "clean" soil, possibly indicating an intermittent pattern of dumping and/or leaching into the site soils. For example, if the 1.0 ppm cleanup level were selected, treatment of the intervening "clean" soils would cause an additional 540 cubic yards to be processed, lowering the average residual concentration following treatment to 0.21 ppm. Canonie (1986A,B) hoped to identify and set aside these relatively uncontaminated soils during the excavation process for later use as backfill.

Canonie (1986B) proposed to excavate areas 1B, 4, and 8 with a conventional backhoe, rather than the bucket auger used elsewhere, due to the limited contaminant depth (12 feet) and relatively low maximum TCE levels in those areas (below 20 ppm). Continuous air monitoring during excavation would permit the rate of excavation to be controlled to avoid excessive volatiles releases to air.

In their excavation plan, Canonie (1986B) not only proposed excavation/ treatment to a less stringent level than that selected in the Record of Decision, but they also proposed to limit the extent of excavation to the same 1 ppm TCE contour both horizontally and vertically. EPA and the state specified a five-foot vertical buffer, i.e., that each boring would extend five feet below the cleanup level concentration contour to provide an additional factor of safety for the uncertainties in the initial ROD modeling and in the measurements of the extent of contamination (Canonie 1986A, B; Aho, 1986A). Where the cleanup level would be attained within a given 5-foot auger lift, Canonie proposed to stop and verify attainment of the cleanup level rather than automatically excavating the additional lift of soil for the buffer (Canonie, 1986B,C).

In the horizontal plane, Canonie planned to remove contaminated soils borehole-by-borehole up to the concentration contour approved by EPA and the state. Samples would be analyzed from each borehole overlapping the chosen isopleth corresponding to the proposed outermost excavation limit. Where borehole concentrations exceeded the cleanup level, one or more additional boreholes would be excavated and treated outwards from the center in the horizontal plane, and concentrations verified. The process would be repeated

as necessary until the required cleanup level was reached, again, with the intent of omitting the additional buffer zone (Canonie, 1986B,C).

EPA, the state, and other agencies reviewed the additional documentation supporting the Responsible Parties proposal to elevate the soil cleanup level. Agency for Toxic Substances and Disease Registry commented that the 1 ppm soil TCE level appeared "more than adequate" to protect the health of humans exposed by inhalation, ingestion, or dermal contact, but would not estimate the potential ground water threat without leachability data (DiSirio, 1986). The U.S. Geological Survey supported the 1 ppm TCE soil level proposal, believing that the expected post-treatment average soil concentration of 0.14 - 0.24 ppm would not cause unacceptable TCE levels in ground water, given their knowledge of local geology and of the many uncertainties in EPA's modeling (Olimpio, 1986). However, the state held to the original 0.1 ppm TCE cleanup level, stating that additional data would be required to support relaxation of the cleanup level (Aho, 1986B).

#### 5.10.4 Subsequent Challenges to VHS Model

Canonie re-ran the VHS model using the additional data they had collected during the Remedial Design phase (Gerken, 1986A). First, Canonie postulated that Areas 3

and 6 seemed to be the principal sources of the ground water contamination, not the lagoon as believed by EPA and Camp, Dresser and McKee at the time of the Record of Decision. Gerken, writing for Canonie, asserted that apportioning the amounts of contaminants migrating to Well B-1 was unneccesary, since the two areas were aligned with each other approximately perpendicularly to the ground water flow direction. However, he suggested that each area should be modeled independently.

Substituting newly measured or estimated values for X, Y, Z, and dispersivity, Gerken calculated acceptable leachate concentrations of 0.23 ppm and 0.083 ppm beneath Areas 3 and 6, respectively. Using a K<sub>d</sub> of 9.0 obtained from other sites (McCarty et al., 1986), Gerken then calculated the acceptable residual soil TCE levels to be 2.1 ppm and 0.75 ppm for Areas 3 and 6, respectively. Based on his earlier "over-excavation" arguments and on Canonie's calculations of residual levels expected after excavation/treatment, Gerken (1986A) claimed that excavation to Canonie's proposed 1 ppm contour would meet the new soil limits in both source areas.

Following a series of meetings with EPA and Camp,
Dresser and McKee, Gerken (1986B) submitted more
evidence to justify his choices of input parameters for
the VHS model recalculation, especially the derivation

of the transverse dispersivity value. More data from the McCarty et al. (1986) study was provided to support Gerken's use of their  $K_d$  and its applicability to partially saturated or unsaturated conditions. Other soil characteristics from the California samples were given to support the appropriateness of their  $K_d$  to describe sorption in the McKin soils, as discussed in Section 6.2.1.4.

### 5.11 Approval of Higher Cleanup Level

EPA and the state gave conditional approval to the excavation plan in October 1986, allowing Canonie to excavate to the 1 ppm TCE contour in the site soils (Aho, 1986B). However, conditions were placed on the excavation, including the requirement for verification sampling at the vertical and horizontal limits of excavation, and excavation vertically to include a 5-foot "buffer zone" below the deepest measured value of TCE greater than 1 ppm. While Canonie had agreed to the horizontal perimeter sampling in their July, 1986 proposed excavation plan, they objected to the need for a 5-foot vertical buffer depth (Christian, 1986A,B).

Canonie had proposed to excavate to a depth halfway between the last 5-foot section known to contain more than 1 ppm TCE and the first "clean" 5-foot soil interval (i.e., providing a maximum 2.5-foot buffer)

without additional verification (Canonie, 1986B), as they felt that the additional samples would overload the capacity of their on-site laboratory. Canonie also believed their revisions to the modeling supported their position that sufficient conservatism was incorporated into their excavation proposal without the additional buffer (Gerken 1986A,B). As the remedy was implemented, it was found that approximately 90 percent of the perimeter samples analyzed after excavation and before treatment, in fact, contained TCE concentrations in soils less than 0.1 ppm (Serian, 1986).

#### 5.12 Completion of Remedy

Full-scale aeration of the site soils began in July, 1986, using the pilot study equipment with certain modifications to the material handling and air pollution control systems, and to the air quality monitoring network on and off the site, in accordance with conditions established by EPA (Bell and Antommaria, 1987). Aeration was completed for all on-site areas in April, 1987. Demobilization and final closure was completed in June, 1987 (Bell and Antommaria, 1987), which included regrading and revegetating the backfilled, treated areas, and decontaminating and removing all remaining equipment and structures.

#### 6.0 DISCUSSION

In this chapter, the events surrounding the choice of soil cleanup levels at the McKin site will be examined in more detail, both before and after EPA issued the Record of Decision described in Chapter 5. The purpose of this analysis is to discuss the relationship between these events and the many technical and institutional factors associated with Superfund soil cleanups, as introduced in Chapters 1 through 4. discussion will focus on the following topics: first, the extent to which SOCEM-type model selection decisions played a role in the process; second, the ways in which the outcome at McKin might or might not have changed, had a formal SOCEM type decision framework been available to EPA at that time; third, the pros and cons to the Superfund program of adopting such a soil cleanup decision process on a broad scale; and finally, what additional research areas suggest themselves based on the McKin experience.

McKin was not a "traditional" case study in several respects, as mentioned in the introduction to Chapter 5. First, it does not represent a classical test of the hypotheses presented herein, in that the decision framework in Chapter 4 was assembled after the site investigation and cleanup level selection had occurred,

rather than being tested at McKin per se. As will be discussed subsequently, many of the decision steps were followed, both in initial selection of the model (informally), and later evidenced in the challenges to the modeling that were made by Responsible Parties and others during the design and implementation of the selected remedy, as will be discussed in Section 6.1. The McKin decisions will be analyzed retrospectively in this chapter.

Second, the model selection and cleanup-levelsetting decisions at McKin did not illustrate all
aspects of SOCEM presented in Section 4.10. Recall that
SOCEM has two main elements: the set of model selection
decisions generally representing currently accepted
hydrogeologic practice, and methods for estimating and
tracking the uncertainties associated with each decision
in the model selection and cleanup level-setting
processes. Decision analysis is the candidate method
here. At McKin one sees the following:

- o The model selection framework given in Section 4.8.4 was not followed explicitly, although many steps were followed in some form by the modeler, and the fundamental literature from which it was derived was all available and familiar to the EPA project managers and their contractors;
- No quantitative, or even semiquantitative, uncertainty analyses, including decision analysis, were provided in the Record of Decision. What was given was a general discussion of some of the sources of uncertainty (see Section 4.9), and

qualitative statements citing these uncertainties as the basis for the conservative cleanup choices, choice of model, and assumptions made in its application; and

The choice of back-calculation model (VHS), and the choices of input parameters and assumptions, appear on first inspection to have been made without considering the full range of site data available to EPA at that time. While this suggests an unwarranted incompleteness of the conceptual model of the situation, EPA's and Camp, Dresser and McKee's rationale supports many, but not necessarily all, of these decisions.

However, closer examination indicates a more reasonable fit of many (but not all) of the SOCEM components to the case study than suggested above. This will be demonstrated further in this chapter.

Third, McKin is not necessarily prototypical of all Superfund sites or Superfund soils problems. As discussed in Chapters 3 and 4, Superfund sites vary widely, in terms of hydrogeologic setting; volumes, types, and distributions of contaminants in soils; and institutional factors associated with individual sites. Variability in site settings stems from their range of sizes, geologies, climates and hydrologic regimes; levels of subsurface heterogeneity ranging from highly heterogeneous sites to homogeneity/isotropy; the range of soil types (sands vs. high-clay-content soils); diversity of nearby land uses/ receptors; varieties of other media contaminated and relative extents; and the varying degrees to which problems in other media are

interrelated with the soil problem.

Some sites have far more complex "soups" of contaminants in site soils than the combination of chlorinated hydrocarbons and oily waste constituents predominating at McKin. Soil release patterns may vary across the spectrum from pulses to discrete units/profiles, to randomly scattered hot spots, to evenly sprayed wastes, to flows of contaminants from pulses to discrete units/profiles, to randomly scattered or contaminated soil particles along channels or fractures. Concentrations may vary from high levels, for example pure contaminants or percent concentration levels, to trace or background levels at the same site, and from one site to another. All these factors contributed to the rationale for selecting both models and final cleanup levels on a site-specific basis.

However, McKin remains a useful example, because it represented one of the first sites where the numerical cleanup level issue, and its attendant problems and consequences, came to a head within the Superfund program. Ideas were tried that led to the prototype decision framework. This postmortem look will consider whether it would have made a difference to the model choice or cleanup level decision had the SOCEM concepts been used as given here, explicitly or formally, at various points in the overall site

investigation and cleanup process.

# 6.1 <u>Fit of ROD Model Selection Decisions to SOCEM</u> Framework

Camp, Dresser and McKee's (1985E) criteria for comparing various models for back-calculation at the McKin site, made in consultation with EPA, were based on several principles and assumptions, as specified in the attachment to the Record of Decision:

- The ground water contamination source is entirely represented by residual contamination in unsaturated zone soils;
- o No dilution of leachate occurs as it mixes with ground water while entering the saturated zone beneath the site (i.e., leachate or pore water contaminant concentrations are at equilibrium with ground water concentrations directly beneath the site);
- o No chemical or biological degradation occurs;
- Contaminant sorption in the saturated zone is neglected; and
- o Dilution from recharge infiltration is neglected.

As described in Section 5.7, the models considered were mainly analytical solutions simulating (with one exception) a continuous source input, and yielding steady-state contaminant concentrations in ground water at a downgradient receptor point. Consideration was limited to models giving conservative predictions that reflected observed concentrations in the field, and

giving workable results. For example, when field values were used as input parameters, Kent et al.'s (1985) method gave an undefined term, a negative square root, as output, while the Organic Leaching model (EPA, 1986L) gave unrealistically low downgradient concentrations. The modified Wilson-Miller model gave unrealistically high source concentrations (Wilson, 1980).

EPA's consultants also pointed out in the technical attachment to the McKin Record of Decision that their use of the VHS model for the back-calculation effort represented

"...an initial attempt to evaluate permissible levels of contamination for a remedial action. Prior to proceeding with additional work, it is necessary to establish that the methodology used in this analysis is conceptually correct (reflects the real world situation); have been properly formulated (mathematically); have utilized the most appropriate input data; have been properly computed (no arithmetic errors); and have been tempered to reflect many of the assumptions inherent in their development." (Camp, Dresser and McKee, 1985E).

They also pointed out that their analysis was

"...based upon the data available to describe site conditions at McKin and the application of acceptable engineering analysis."

# 6.2 <u>Comparison of McKin Modeling Reinterpretations with</u> SOCEM Framework

Many of the discussions and reevaluations of the VHS modeling mentioned in Section 6.3 correspond closely to

individual decision elements of the SOCEM framework described in Section 4.8.4, providing an illustration of how use of such a framework early (and throughout) the Remedial Investigation/Feasibility Study process might have affected its outcome. As stated in the introduction to this chapter, comparing the reinterpretations of the McKin model-based analyses done by the Responsible Parties and by EPA's contractors, as described below and in Section 5.10, with the modeling decision framework proposed in Section 4.8.4, necessarily was done retrospectively in this study.

This comparison of the SOCEM framework to the McKin events has inherent limitations. First, the SOCEM framework suggested in Section 4.8 is oriented more toward selection of the model than toward the model's application. Many of its decision outcomes direct the user to choose a different model. However, at McKin, most discussions focused on different choices of parameters, or different interpretations of model results obtained using VHS. No change of model was made, although the mixing length discussions outlined in Sections 5.10.1 and 6.2.2.1 were used initially by the Responsible Parties to argue for switching to a different form of Domenico and Palciauskas'(1982) transport equation.

Second, uncertainties were not quantified as part of the

McKin modeling study in any rigorous fashion. The concepts of decision analysis were not used at McKin, nor were any of the other uncertainty analysis approaches described in Section 4.9 explicitly presented. Limited, semi-quantitative discussions of uncertainties in various parameters and assumptions were referenced at various points in the Remedial Design discussions between the agencies and the Responsible Parties, as will be described further in Section 6.3. These played into the agencies' eventual decision to relax the soil cleanup target, as discussed in Sections 5.10 and 6.2.4.

The McKin events will be compared to the proposed decision framework in the following sections. They focus on four general areas: (1) the basis for the soil cleanup level (Section 6.2.1); (2) the choice and application of the model parameters (Section 6.2.2); (3) other assumptions used by EPA and its contractors in selecting and applying the VHS model (Section 6.2.3); and (4) possible impacts of the McKin reevaluations on the final remedy, had the SOCEM framework been used in the initial model selection process (Section 6.2.4).

#### 6.2.1 Basis for Cleanup Level

Use of the SOCEM decision framework presented in Sections 4.8.4 and 4.10 to set soil cleanup levels

presupposes that the following determinations have been made:

- 1. The cleanup level for a given site must be calculated on a site-specific basis. This was discussed in Chapters 3 and 4.
- 2. Exposure to soil contaminants that have leached to and been transported in ground water is the limiting exposure pathway of concern for soil contaminants at that site, i.e., it would drive the cleanup levels lower than had they been based on direct contact, surface or airborne runoff of soil particles, bioaccumulation, or any of the other pathways identified in Section 3.1.1. This was determined at McKin during the Remedial Investigation/ Feasibility Study (Camp, Dresser and McKee, 1985 C,D), as described in Chapter 5.
- 3. Ground water performance levels, and acceptable exposure points laterally downgradient of the source soils can be identified. This was described in the McKin Record of Decision and in Camp, Dresser and McKee (1985 C,E).
- 4. Fate and transport processes occurring between the contaminated soils source and the ground water receptor have been characterized, and sources of uncertainty identified, to a sufficient extent that appropriate fate and transport models can be selected. This was discussed in Camp, Dresser and McKee (1985 C,D,E).
- 5. Sufficient data, resources, and expertise are available to use the selected models and interpret their results. This was a factor in choosing a simplified method such as the VHS (Camp, Dresser and McKee, 1985E).

The written record for McKin did not indicate that the Responsible Parties or other parties disagreed with EPA's concept of basing the soil cleanup level at McKin on the achievement of a health-based performance target level in the ground water. Nor was there any evidence

of disagreement with the general design of back-calculating the soil cleanup level from the ground water concentration by modeling. Only a few comments were made on the choice of the ground water cleanup targets themselves. Most disagreements focused on the following:

- o Initially, but only briefly, they centered on the choice of ground water transport model;
- o Choices of model simplifying assumptions and/or input parameters, e.g., distance to the potential ground water receptor, as discussed in Section 6.2.2;
- o Choice of partition coefficients used to back-calculate soil concentrations from maximum leachate concentrations entering ground water beneath the source. Note that no objections were raised to the partition coefficient approach. The use of alternate methods, such as physical leaching tests or mathematical unsaturated-zone models, was never suggested by either side; and
- o Methods of assuring acceptable margins of safety in the implementation of the remedy (e.g., treating additional "buffer zones" of less-contaminated soils, performing more rigorous verification sampling, or adhering to a stringent cleanup level) to compensate for uncertainties in the data and/or analyses.

#### 6.2.1.1 Establishment of Ground Water Targets

Selection of human health-based levels for TCE and TCA in ground water at the site was documented by EPA (1985J) in the McKin Record of Decision, and discussed in both the Feasibility Study and the Attachment to the Record of Decision (Camp, Dresser and McKee, 1985 D,E).

As described in Sections 5.4 and 5.6, the decision was made to set ground water performance targets based on a  $10^{-5}$  human cancer risk due to ingestion of contaminated ground water.

It was also recognized, however, that TCE entering surface waters from ground water in the vicinity of the Boiling Springs could pose potential threats to aquatic life in the Royal River. EPA postulated that ground water cleanup to meet the 10<sup>-5</sup> risk levels, combined with dilution and attenuation in ground water and volatilization at the point of discharge to surface waters, would be protective for these environmental receptors, although quantitative justification for this position was not provided (EPA, 1985J; Camp, Dresser and McKee, 1985 D,E).

Therefore, this target level was used as a basis for the soil cleanup level, based on the presumption that ground water would be cleaned up to meet these levels at all locations on and off the site by the completion of the remedial actions. Residual soil levels had to be sufficiently low to assure that continued leaching would not transport organic contaminants into the ground water above these safe levels in the future. The choice of target levels was reexamined by both EPA's contractor, Camp, Dresser and McKee, and contractors for the Responsible Parties, as

described in Section 6.2.1.3. However, they concluded that the additional data obtained by Canonie during the Remedial Design did not support changing the indicators or the ground water target levels.

#### 6.2.1.2 Choice of Transport Model

An initial review of the decision framework in Section 4.8.4 seems to indicate that many of its decision steps could have led EPA to choose another model at various stages in the McKin cleanup:

- 1. Order-of-magnitude predictions would be unacceptable for a final cleanup level in the strictest sense, since this translates directly to a 1-3 orders of magnitude risk range for exposure to carcinogens (i.e., actual risks varying between 10<sup>-4</sup> and 10<sup>-6</sup> if the ground water target gives a 10<sup>-5</sup> cancer risk). Seemingly this would argue for selection of a numerical model to increase the precision in the resulting cleanup level.
- 2. Media properties were deliberately assumed spatially uniform to facilitate use of simplified models, although heterogeneities were well known within each aquifer (Gerber, 1982; Camp, Dresser and McKee, 1985 D.E). Additionally, the discussions in Section 6.2.2 indicate that Camp, Dresser and McKee intended the VHS to estimate fate and transport in both surficial and bedrock (upper portion) zones, although that clearly was not envisioned by the VHS model authors (Domenico and Palciauskas, 1982).
- 3. Steady flow field and regular site geometry likewise were assumed despite contradicting site evidence, because Camp, Dresser and McKee and EPA intended to set the initial cleanup target without collecting additional data to support a more complex model that would more accurately represent spatial and flow domains at McKin.

- 4. The VHS considers only a limited set of transport mechanisms operating at steady-state in a continuous flow field. Many of the Phase II decisions (questions 6-11 in the SOCEM framework) could ideally have led to multiple layer simulations, or a more thoroughly developed "equivalent single layer" approximation; or a different treatment of aquifer thickness, as discussed in Section 6.2.2.3. Additional data collection at the time of the Record of Decision, or subsequently, might have allowed for an explicit treatment of the fractured flow system in the bedrock, as Gerber did in the regional modeling, described in Section 5.3. Possibly, EPA might have used a 3-D flow model, and/or a model explicitly treating the seasonally-transient flow field (see Sections 5.3, 6.2.3.1, and 6.2.3.2).
- 5. The Phase III decisions (questions 12-18 in the framework) might have led EPA to models simulating dense multiple phase transport, as mentioned in Sections 5.3 and 6.2.2.3 (Gerber, 1982; Duchesneau, 1986); three-dimensional, volumetric source; intermittent and finite source, rather than continuous and infinite source as assumed in the VHS (see Section 6.2.3); three-dimensional transport, rather than a 1-D transport affected by 2-D dispersion mechanisms, as assumed by the VHS; and appropriate retardation mechanisms such as sorption, volatilization, etc. (see Section 6.2.3).

However, the agencies recognized that the uncertainty in both toxicological risk data and in fate and transport likely spanned a broader range than the order-of-magnitude level implied by question 1, as will be discussed in Section 6.3. EPA and Camp, Dresser and McKee deliberately selected an analytical model that made simplified, "reasonable-worstcase" assumptions for many of these variables and that ignored several attenuation mechanisms likely present at the McKin site, in the interest of obtaining an expedient site cleanup

decision. It was felt that the conservatism of these assumptions would compensate sufficiently for EPA's inexact knowledge of these modifying factors at the time of the Record of Decision.

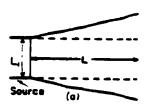
It must also be noted that many alternative models could have been suggested to address various individual decision outcomes in the SOCEM framework, had it been applied rigorously at McKin. It is beyond the scope of this study to identify a likely subset of alternates, especially since these likely would have varied at each step in the framework if applied at any single point in time, for instance, when the McKin Record of Decision was signed. They might vary even more at different times in the cleanup process, for example later during the design phase after additional soil sampling had been completed. Thus, different model outcomes cannot be predicted on the basis of present information, nor is it possible to predict which alternative model might have been used at a given stage.

It is interesting to note that the written record of discussions and rebuttals following the selection of remedy and cleanup level does not indicate that any explicit proposals were made by the Responsible Parties or others to use a different transport equation than the VHS model or modifications thereof. The review of assumptions and parameters that resulted from this

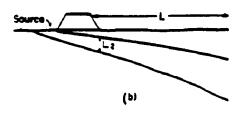
exchange did lead to changes in some aspects of the use of the model and the interpretation of the results, and most disagreements were centered around these differing interpretations.

The Responsible Parties' consultants, in a letter to EPA, claimed that EPA and its consultants had used the wrong form of the VHS model as published by Domenico and Palciauskas (E.C. Jordan, 1985). Based on their arguments concerning an effective "mixing length" downgradient of the site, as described further in Section 6.2.2.1, E.C. Jordan proposed using a different form of the equation published in the same paper by Domenico and Palciauskas--their equation 20, rather than equation 19 as used by Camp, Dresser and McKee. Jordan contended that at a distance of approximately 50 feet downgradient of the boundary of the contaminated soils area (i.e., at X= 50'), the contaminant had spread vertically throughout the entire saturated thickness of the surficial aguifer (i.e., Z=H). Further downgradient, any additional contaminant dilution by dispersion was due solely to continued lateral spreading (Figure 17). This constituted the contaminant "mixing length" in the X direction, defined as L' according to Domenico and Palciauskas (1982); beyond this point, E.C. Jordan asserted, transport should be defined according to the following equation:

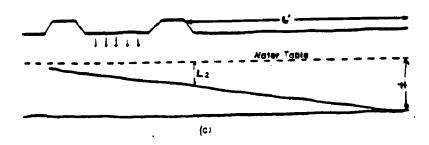
# FIGURE 17 Mixing Length Concepts in the VHS Model (Adapted from Domenico and Palciauskas, 1982)



## (a) Map view of plume



## (b) Cross section of plume



(c) Cross section at mixing length (plume occupies full saturated thickness) E.C. Jordan contended that this form of the VHS equation should be used at McKin. Using values of  $\alpha_{\rm T}=3.3$  feet, L'= 50 feet, and Z = 2 feet, E.C. Jordan calculated that  $C_{\rm X}$  would be diluted to about 8.76% of  $C_{\rm O}$  at X=L', resulting in  $C_{\rm O}$ =182 ppm TCE at X=150 feet, where  $C_{\rm X}$ =16 ppm TCE. This was then used to develop a series of dilution factors (where the dilution factor is the ratio of  $C_{\rm O}/C_{\rm X}$ ) at various distances X downgradient of the site.

However, E.C. Jordan did not document the basis for the  $C_X$  value, and used a somewhat circular derivation for their L' value. Further, Duchesneau (1985A), writing in response to E.C. Jordan's comments on behalf of EPA's contractor, Camp, Dresser and McKee, pointed out the following:

- O Domenico and Palciauskas had originally limited the applicability of their equation 19 (reported herein as equation 6-1) to situations where a low-permeability unit such as clay, etc. forms the lower confining layer of the aquifer. However, no such layer was found in field sampling. Rather, a substantial body of direct measurements and indirect evidence supports the interconnection of the surficial zone and the underlying fractured bedrock zone throughout the site vicinity.
- o Camp, Dresser and McKee asserted that their use of Domenico and Palciauskas's equation 19, given herein as equation 5.8, calibrated with a Co of 117 ppm,

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conformed well with reported field values. They measured 130 ppm TCE in on-site well DEP-7, which also supported the possibility for additional vertical dilution of contaminants into the bedrock.

In addition, it should be noted that Domenico and Palciauskas (1982) further limited the use of equation 6-1 to situations where H is "abnormally thin... (perhaps two times Z)," although insufficient data was available at the time of the McKin Record of Decision to allow a determination as to whether the saturated thickness of the surficial zone would in fact be a limiting constraint to use of their equation 19. E.C. Jordan raised neither of these points in recommending equation 6-1.

It seems that if the mixing length concept applies within the X distance of concern at McKin, both E.C.

Jordan's and Duchesneau's arguments suggest that a different model should have been considered altogether. For example, the on-site well (DEP-7) was inferred by Duchesneau to penetrate the bedrock zone slightly, although this could not be confirmed in the file data reviewed. Therefore, Duchesneau seems to have implied that the VHS would acceptably simulate vertical dilution in both the surficial zone and the upper portion of the bedrock zone. Additionally, E.C. Jordan's mixing length arguments could just as effectively have supported use of a more complex, multple layer simulation for the two

zones. However, the site files contained no suggestions that either party considered alternative models during the Remedial Design phase, beyond one Canonie proposal to develop an alternate model, which was never implemented.

As mentioned earlier, the remaining disagreements involved differing interpretations of the input parameters and of the model results. These will be discussed in Section 6.2.2.

#### 6.2.1.3 TCE As the Indicator Compound

selection of TCE as the indicator compound for establishing the soil cleanup level was documented by Camp, Dresser and McKee (1985E) in the attachment to the Record of Decision, as described in Sections 5.4 and 5.6. E.C. Jordan (1985) challenged this decision, stating that other volatiles present at the site are not carcinogens and have higher "safe levels" in ground water than the 28 ppb TCE ground water target used at McKin. Evidently this argument was intended to support adoption of a higher, i.e., less conservative, calculated soil level.

Note that this would seem to argue in favor of a more explicit calculation of total ground water risks due to the cumulative effects of all contaminants present. However, such a calculation in fact was done

by EPA in the Record of Decision (1985J) for the only two contaminants found in any significant concentrations in either aquifer during the Remedial Investigation, TCE and TCA, as discussed in Section 5.6. The 10<sup>-5</sup> total risk level and 50 ppm total Volatile Organic Compound (VOC) targets resulted from this analysis.

Alternatively, EPA might have arbitrarily added a safety factor to the ground water target to account for synergism,

in the absence of complete toxicological data.

Christian and Adams (1986) reexamined the indicator compound decision based on additional soil and ground water sampling done on behalf of EPA in mid-1985.

Camp, Dresser and McKee found some 27 compounds in ground water samples collected from approximately 20 wells. Occurrence was assessed in terms of number and percent of contaminated samples, and geometric mean concentration. Means and maxima then were divided by an informal EPAcalculated health-based threshold called the Preliminary Protective Concentration Limit (PPCL, as defined and discussed in Salee, 1984) to yield an index, as was done to select indicators in Attachment A to the Record of Decision (Camp, Dresser and McKee, 1985E).

TCE was found to be the most commonly found contaminant, present in 50 percent of the samples, with a mean of 764 ppb and a maximum of 17,000 ppb in the bedrock at off-site well B-1. The mean was 415 times

times the PPCL. The only other contaminant considered by Christian and Adams to have a very high (mean:PPCL) ratio was pyrene, which was found in one sample at 31,000 times its PPCL. Since this was much lower than the pyrene (mean:PPCL) ratio calculated for the Record of Decision (Camp, Dresser and McKee, 1985E), and since pyrene was detected in only one sample and was considered highly biodegradable, Camp, Dresser and McKee concluded that pyrene did not meet their criteria as a useable indicator compound for ground water contamination.

It should be noted that in Attachment A to the McKin Record of Decision (Camp, Dresser and McKee, 1985E), only two of the compounds considered as indicators had (mean:PPCL) ratios less than 1.0. The majority had ratios of at least several hundred, while several compounds were in the hundreds of thousands — the two highest being TCE at about 815,000 and 1,2—dichloroethylene at 365,500. Camp, Dresser and McKee did not present their rationale for restricting the indicator set to those with such high ratios compared to their health-based concentrations. This raises the question of whether the differences in acceptable soil concentrations based on other pathways (e.g., ingestion of soil contaminants) might have driven the indicator selection process to include different or additional

contaminants based on exposure pathways other than ground water. However, such an analysis is beyond the scope of the present study. Methods for making this comparison quantitatively should be developed in future investigations.

Christian and Adams also examined soils from eight locations and identified 24 organic compounds on-site. While bis (2-ethylhexyl) phthalate was most widely distributed, occurring in 4 of the 8 samples, it was not considered a good indicator because of its high PPCL relative to other contaminants present in the soils. Conversely, the three contaminants with the highest (mean:PPCL) ratios, 4,4'-DDT, 2-methylnaphthalene, and N-nitrosodiphenylamine, were found in only one or two samples each. TCE was found at much lower concentrations in only two samples, and thus had a much lower (mean:PPCL) ratio among the contaminants found in this sampling event, but Christian and Adams considered the overall evidence insufficient to support selecting an alternate soil indicator.

Christian and Adams (1986) also analyzed soil data obtained by Canonie, the contractor for the Responsible Parties, which showed high (mean:PPCL) ratios in soil for benzene, 2-methylnaphthalene, anthracene, phenanthrene, and naphthalene. However, they rejected these contaminants as alternate indicators because they

were either (1) present in only a few of Camp, Dresser and McKee's or Canonie's soil samples, e.g., benzene, 2-methyl naphthalene; (2) absent from ground water, e.g., naphthalene; or (3) believed to be very rapidly biodegraded, e.g., naphthalene, anthracene, and phenanthrene.

In the site remediation, Canonie excavated and treated on-site areas of both volatile-organic-contaminated soils (mainly with TCE) and petroleum-contaminated soils (Bell and Antommaria, 1987). As soils were excavated prior to treatment, boreholes were sampled to assure that all soils containing more than 1 ppm TCE were removed and treated, as described in Section 5.10. Treated soils were tested to ensure that TCE had been removed such that residuals contained no more than 0.1 mg/kg, based on the mean residual levels in daily treatment batches (Bell and Antommaria, 1987). Only one day's batch showed levels exceeding this treatment target, when transfer chutes for the baghouse became plugged.

In addition to TCE, Canonie routinely analyzed treated soil batches for several volatile organic constituents, including benzene, 1,2-dichlorobenzene, 1,3-dichlorobenzene, 1,4dichlorobenzene, ethylbenzene, trans-1,2-dichloroethane, tetrachloroethylene, toluene, 1,1,1-trichloroethane (TCA), and xylenes. Petroleum-

contaminated areas were similarly analyzed, with additional sampling for polycyclic aromatic hydrocarbons (PAHs) and total extractable hydrocarbons. Posttreatment soil analyses showed nondetectable (below 1 ppm) levels of aromatic constituents, and not more than 1 ppm of each PAH constituent nor more than 10 ppm total PAHs, in all batches sampled.

Bell and Antommaria (1987) noted that volatile organics other than TCE had been completely removed by aeration except for a few samples that still contained a few volatiles such as dichlorobenzene or tetrachloroethylene at concentrations barely above their detection limits. It was noted, however, that a few perimeter boreholes contained detectable levels of ethylbenzene and/or xylene (approaching 1 mg/kg) that were left untreated. However, they asserted that these levels would not affect ground water based on analyses similar to those done for TCE. Details of these analyses were not given.

Therefore, based on available records, TCE was an adequate indicator for purposes of the soil remediation itself. However, data will need to be obtained through long-term ground water monitoring to verify its appropriateness as an indicator of the contaminated soils' impact to site ground water.

#### 6.2.1.4 Use of Partition Coefficient for Soil Level

The SOCEM concept presented in Section 4.10 does not specify an approach for back-calculating the allowable soil concentration from the leachate concentration entering the aquifer. The model selection decisions given in Section 4.8.4 are focused primarily on simulation of fate and transport in the saturated zone for two reasons:

- o Saturated-zone modeling is generally better understood and historically has been more widely used than unsaturated-zone modeling. Selection decisions specific to the vadose zone are not yet as well developed nor understood.
- o As discussed in Section 4.3, migration processes in the saturated zone are (for the most part) a fully-contained subset of the unsaturated zone processes. Thus, expansion of the selection framework to encompass these additional processes will require additional decision points which must be determined largely on a site-by-site basis.

Further, this added complexity will have additional data demands which historically have seldom been satisfied in Remedial Investigations. Sections 4.7 and 3.4 contain further discussion of this issue. Little soils data was available for the McKin site to support use of a complex unsaturated-zone model at the time of the Record of Decision. Therefore, the decision was made to use a simplified, equilibrium partitioning approach to back-calculate an acceptable residual soil

concentration from the acceptable leachate input to the aquifer (C<sub>O</sub>) determined with the VHS model. Duchesneau (1985A) confirmed that sorption had been neglected in the saturated-zone modeling partly because of the lack of confirming field data, and because no batch equilibrium studies or column sorption studies had been performed using McKin soils. Furthermore, since contaminants were still migrating from source soils, Duchesneau believed that the attenuation capacity of underlying soils could be exhausted if all available sorption sites on the soil particles were already occupied (or periodically occupied after contaminant "slug" releases). This implies that a partitioning approach based on equilibrium conditions would provide a conservative value.

As will be discussed further in Section 6.2.3.3, E.C. Jordan (1985) asserted that retardation in the saturated zone due to sorption should have been considered at McKin in selecting the cleanup level, since they believed that the site soils had a higher organic carbon content than the 5 percent estimated by Camp, Dresser and McKee (1985E; see Section 5.6). Therefore they expected that McKin soils had a higher organic carbon content than the 5 percent the actual K<sub>d</sub> was probably more than 1.1. This would have allowed a higher residual soil concentration, since more TCE

would thus be expected to remain sorbed on the subsurface matrix than accounted for by EPA's consultants in the Record of Decision.

In Attachment A to the Record of Decision, Camp, Dresser and McKee (1985E) had estimated a soil organic carbon content of 5 percent at McKin using "typical" values estimated by EPA for developing soil covers (EPA, 1982D) and for running its Hydrologic Evaluation of Landfill Performance (HELP) model (Schroeder et al., 1984). Duchesneau (1985A,B) felt that this value was already somewhat nonconservative, since it was developed for agricultural soils unlike those on the site, which are "typically low in organic carbon." He cited a study by Sutton and Barker (1985), who measured a total organic carbon content of 0.05% in a similar sandy aquifer in Ontario, and who noted little sorption of four organic compounds, butyric acid, pentachlorophenol, dimethyl phthalate, and phenol. The Koc of TCE falls within the range of Koc's of these compounds.

For Canonie's recalculations using the VHS model,
Gerken (1986A) cited biotransformation studies of TCE in
granular soil materials taken from two California sites
with TCEcontaminated ground water. McCarty et al.
(1986) studied sorption and biotransformation of TCE and
other halogenated organics in columns of granular
aquifer materials whose physical characteristics Gerken

considered similar to the sandy subsurface matrix at McKin, and found (soil:pore water) mass ratios for TCE ranging from 20 to 61 (mean of 44). Gerken (1986A) used this mean, assuming a porosity of 0.35 and specific gravity of 2.6 for the McKin soil, and calculated a soil partition coefficient of 9.1, as follows:

$$K_d = \frac{(44 \text{ lb TCE } / 2,850 \text{ lb soil})}{(1 \text{ lb TCE } / 590 \text{ lb water})}$$
 (6-2)

This value was used to revise the "acceptable" TCE concentrations for site soils in support of the 1 ppm excavation target, as discussed in Section 5.10 (Gerken, 1986A).

When EPA and Camp, Dresser and McKee questioned the applicability of McCarty et al.'s data to McKin, Gerken (1986B) presented additional parts of the study to justify Canonie's position. McCarty et al. (1986) had added TCE solutions, ranging from 50 to 161 ppb, to six water-saturated laboratory columns over a period of months, after which sorption had equilibrated at a ratio of about 44 g TCE/g soil. Gerken (1986B) claimed that partial saturation of the soil pore spaces should not change the K<sub>d</sub> value, and that if diffusion is the primary contaminant transfer mechanism during rainfall events at McKin, TCE desorbs from the soil particles to infiltrating rain water wherever the water droplets are

in contact with TCE- contaminated soil particles in a manner described by this distribution coefficient with sufficient accuracy for this analysis.

Duchesneau (1986) considered this change in  $K_{\rm d}$  the most significant factor causing the differences between Camp, Dresser and McKee's and Canonie's model results. He disputed the applicability of McCarty et al.'s (1986)  $K_{\rm d}$  value to McKin on several grounds:

- Differences in soil physical characteristics—Duchesneau compared the boring logs for the California soils with the McKin logs, and found that the California soils contained significant amounts of clay or silt, compared with the fine sands and silty sands at McKin. No measurements of clay content had been provided by Canonie for either site, however, Duchesneau asserted that the higher apparent clay contents of the California soils could indicate much higher sorptive capacity than at McKin.
- Discrepancies in the K<sub>d</sub> calculation— Canonie had calculated a distribution coefficient based on average TCE sorption observed in 23 experimental columns, only 5 of which were biologically inactivated. Further, the average included 5 columns to which no TCE had been added. Thus, averaging all columns neglected the biological effects and increased the apparent sorption (Duchesneau, 1986). However, McCarty et al. had reported an average distribution coefficient of 0.35, some 26 times lower than Canonie's value of 9.0 (Gerken, 1986A).
- Discrepancies in the porosity estimate— McCarty et al. had determined a soil pore volume of 35 ml per 120 ml soil column through bromide tracer tests, yielding a porosity of 0.29, yet Gerken (1986A) used a porosity of 0.40 to calculate his K<sub>d</sub> of 9.0.
- O <u>Use of column vs. batch studies</u>— Duchesneau noted that Canonie's porosity estimate, if accurate, left an

unaccounted-for pore volume in McCarty et al.'s columns. This could cause the TCE removal rate due to sorption to be overestimated, since it is calculated by mass balance. He argued that the advantage of determining  $K_{\rm d}$  through batch studies would have been to avoid the constantly changing volumes and the difficulty in establishing equilibrium concentrations inherent in the column tests.

O Loss in sample collection—Duchesneau noted that McCarty et al. (1986) had collected samples from their columns beneath an iso-octane layer to eliminate volatilization losses, yet the low solubilities and high octanol-water partition coefficients (Kow) of the experimental species likely resulted in their partial removal by the iso-octane itself prior to analysis. This would further increase the apparent measured sorption. Duchesneau (1986) did not estimate the magnitude of this potential loss.

Duchesneau cited Schwartzenbach and Westall's (1981) laboratory study of sorption of various nonpolar organic compounds on various natural aquifer media, which seemed to show that Gerken's (1986A) proposed  $K_d$  of 9.0 was much higher than found for related compounds such as tetrachloroethylene, whose measured  $K_d$  was 0.56. It fell more into the range of  $K_d$  values for highly hydrophobic polychlorinated benzene compounds (e.g., the  $K_d$  measured for 1,2,3,4tetrachlorobenzene was 10.48), when measured in similar soil matrices to those at McKin.

6.2.2 Choice and Application of Model Parameters

As was stated earlier in this chapter, many of the

disagreements about the modeling and the soil cleanup level occurring during the Remedial Design phase at McKin were focused not so much on the choice of model, but on its application. In this regard, all the assumptions and input parameters used in the VHS model came under scrutiny by the agencies, their consultant Camp, Dresser and McKee, and the consultants for the Responsible Parties, E.C. Jordan and Canonie. As a result, the experts came to differing conclusions regarding the model results, and regarding the appropriateness of the soil cleanup level calculated in the Record of Decision.

#### 6.2.2.1 Downgradient Receptor Distance (X)

As with several other decisions discussed in Section 6.2.1, the lateral distance between the soil source and the downgradient ground water receptor should be a relatively straightforward decision, one that is essentially independent of the decision steps in the SOCEM framework. However, it is a critical issue in the overall selection of remedy.

For example, if site remediation is intended to be so thorough as to allow unlimited future land use without deed restrictions, access prevention, or other constraints, the decision might be made to clean soils to such a level that leachate exiting the soil source

should not contain contaminants at levels exceeding health-and-environment-based standards. That is, unlimited future use could demand residual soil levels safe for all exposure pathways at the immediate point of contact, with no allowance whatsoever for dilution and attenuation in the unsaturated and/or saturated zones, i.e., X=0, thus  $C_X=C_O$ . No ground water model would be required in such circumstances.

However, at McKin, site response objectives were set so that on-site soils must have residual levels safe for direct contact exposures, i.e., inhalation, ingestion, and dermal contact. Additionally, they must not leach contaminants to ground water at levels exceeding the health-based ground water performance targets given in the Record of Decision at the site boundary (EPA, 1985J; Camp, Dresser and McKee, 1985E). Security fences, signs, and monitoring were intended to prevent future ground water exposures within the site boundaries. Thus, contaminant attenuation in the unsaturated and saturated zones was allowed to occur between the soil source and the site boundary, providing the rationale for back-calculating the soil level using the VHS model.

An unusual dimensional notation was used in the VHS transport equation by the original authors (Domenico and Palciauskas 1982), and retained by EPA (1985N) when they

published the model in the <u>Federal Register</u> for evaluating RCRA delisting petitions. Y was used to describe contaminant motion in the downgradient direction of flow, and X was used to represent the transverse dimension of the spreading ground water plume in map view perpendicular to the dominant flow direction, in conflict with hydrogeologic convention. In applying the VHS model at McKin, Camp, Dresser and McKee reversed the notation to conventional axes, as described in equation 5-3. They used X=800 feet for model calibration, based on the distance to the nearest downgradient receptor well off-site (B-1) from which contaminant concentration data were available; and X=200 feet for prediction of cleanup levels. Z represented the vertical dimension in all analyses.

E.C. Jordan (1985) challenged Camp, Dresser and McKee's use of X=800 feet to the "alternative boundary," claiming that this allowed too much contaminant concentration reduction by vertical dilution between the source and well B-1, "or, conversely, too high an initial source concentration." This argument was then used by E.C. Jordan to assert that a "mixing length" (L') much shorter than 800 feet must be accounted for at McKin, requiring use of a different form of the VHS equation, and a different value for X. The mixing length concept was introduced by Domenico and Palciauskas

(1982) in separate discussions from their description of the VHS equation, as described in Section 6.2.2.4.

Duchesneau (1985A) responded that, while E.C.

Jordan disputed Camp, Dresser and McKee's 800-foot X

value, no alternative was offered; and that E.C. Jordan

had implied that X must be assigned the value of L'.

This neglected the fact that horizontal dispersion of

the contaminant plume would continue downgradient beyond

the point at which it spread vertically to occupy the

entire saturated thickness (i.e., at X greater than the

mixing length L').

Both arguments somewhat missed the point. The alternate boundary selected by EPA was 200 feet, the minimum distance from the downgradient edge of the contaminated soils source area and the site boundary. EPA and Camp, Dresser and McKee considered this the nearest point of potential future ground water exposure, since the site itself was fenced and protected. The 800-foot value represented the actual distance to offsite well B-1, used for calibration of the model, since TCE measurements were available in ground water at that point. Further, neither party conclusively established the actual value of L', the mixing length distance of Domenico and Palciauskas (1982). The issue of mixing length is a related, but separate issue, as will be discussed in Section 6.2.2.4. Further data collection

would be necessary to determine the mixing length distance through actual measurement of aquifer core material, or through be necessary to determine the mixing length distance through field measurement of the parameters used to calculate an accurate mixing length value.

As discussed in the next section, Canonie postulated that two separate sources were responsible for the ground water contamination, Areas 3 and 6 (Gerken, 1986A). The center of each area was taken as the center of the contaminated soils mass within Areas 3 and 6 at an elevation of 265 feet above mean sea level (MSL), which Canonie estimated as the elevation of the ground water table beneath each source area. Based on this data, Gerken (1986A) determined the distance to the site perimeter from the approximate center of each area, 230 feet for Area 3 and 90 feet for Area 6, as input values for Canonie's revised VHS model runs.

#### 6.2.2.2 Width of Contaminant Source Area (Y)

In their initial modeling, Camp, Dresser and McKee assigned a value of 200 feet to Y, the width of the leachate front entering ground water at the downgradient edge of the contaminant source perpendicular to the direction of flow. Recall that Domenico and Palciauskas (1982) originally transposed the axes, calling this term

X, as described in Section 6.2.2.1. This was based on the assumption that several areas contributed to the ground water contamination leaving the site.

E.C. Jordan (1985) used a value of Y=50 feet, based on their assumption that the identified ground water contamination originated from Area 3, near the northern boundary of the site. Duchesneau (1985A,B) noted this, stating that E.C. Jordan was neglecting other potential sources, especially the lagoon area. However, neither party had field data available at the time of the Record of Decision pinpointing the exact locations of leachate migration.

Canonie's additional data indicated that two separate sources were responsible for the ground water contamination, Areas 3 and 6 (Gerken, 1986A). For purposes of transport modeling, the width of each area was taken as the width of its contaminated soils mass with TCE concentrations above 1 ppm. This was measured on each area's lateral cross-section at an elevation of 265 feet MSL, which Canonie estimated as the elevation of the ground water table beneath each source area.

Based on this data, Gerken (1986A) used a width of 90 feet for Area 3 and 40 feet for Area 6 as input values for Canonie's revised VHS model runs.

Questions 10, 13, and 15 in the proposed SOCEM decision framework might have led the agencies to

consideration of a different model, had they been asked earlier in the process. These questions ask about the dimensionality required to simulate flow and transport, and whether the source is being simulated as a point, line, area, or volume source. See Section 4.8.4 for a detailed discussion of this topic. However, this assumes the source characterization conducted by Canonie during the pilot study and Remedial Design had been done up-front in the Remedial Investigation.

As stated elsewhere in this section, the detailed data was not available to support such decisions at the time of the Record of Decision, and it is not feasible to estimate the alternative outcomes had such decisions been made, based on data available in the site files.

This would require more detailed characterization of the uncertainties in the definition of the source term, which could be a subject of future research. However, the outcome at McKin does suggest that the additional data obtained during the remedial design and construction could have led to a different cleanup level in the Record of Decision, had the additional data been available earlier in the process.

# 6.2.2.3 Definition of Z Term in Model

In their comments for the Responsible Parties, E.C. Jordan (1985) claimed that EPA's consultants had defined

the Z term incorrectly in the Record of Decision attachment, as the entire saturated thickness H. In the original VHS reference, Domenico and Palciauskas had defined Z as the vertical depth of penetration of the leachate into the saturated zone at the downgradient edge of the source area or waste management boundary (see Figure 17). According to E.C. Jordan, the value of Z should be determined by addition of vectors describing downward velocity of leachate as it contacted the water table and horizontal flow of ground water, assuming continuous, constant fluxes of both.

E.C. Jordan calculated a Z of 2.1 feet. This was based on (1) a ground water velocity of 94 feet/year, estimated by Camp, Dresser and McKee (1985E) using Darcy's law; (2) a leachate vertical velocity of 4 feet/year, based on an infiltration rate of 12 inches/year reported by Camp, Dresser and McKee (1985E) and a porosity of 0.25 as reported by Camp, Dresser and McKee; and (3) a Y value (the width of the source area or leachate infiltration zone perpendicular to the ground water flow direction) of 50 feet, which E.C. Jordan stated was the width of Area 3. E.C. Jordan cited a mass balance approach presented in an earlier portion of the Domenico and Palciauskas (1982) article as additional support for their Z value based on the mixing length (L') contaminant concentration, as

discussed in Sections 6.2.2.1 and 6.2.2.4.

Duchesneau (1985A,B) disagreed, stating that E.C.

Jordan's approach was too simplistic, and citing the
following reasons why Camp, Dresser and McKee had used a
Z value equaling the saturated thickness of the
surficial zone (H) beneath the site:

- Density considerations—— Camp, Dresser and McKee postulated that much of the TCE originally deposited in the on-site source areas, especially in the lagoon, was in the form of relatively pure liquid product (Duchesneau, 1985A). Since TCE's density is 1.46 g/l, Camp, Dresser and McKee expected that it would sink through the entire saturated thickness beneath the site over time, in contrast to the situation presented in Figure 17. Camp, Dresser and McKee argued that the vectoral calculation neglected this density consideration, and attempted to account for it by using Z=H=15 feet.
- O Vertical spreading of source into saturated zone-Mackay et al. (1985) estimated that as a relatively
  insoluble contaminant entered an aquifer, 0.3 5.0
  percent of the pore volume could retain
  contaminants in the matrix pore spaces as described
  in Sections 4.3.1.2 and 4.4.2, and provide a
  continuing source of aquifer contamination as small
  amounts dissolved continuously into past-flowing
  ground water. Therefore, Camp, Dresser and McKee
  argued that, beneath the source soils, the
  appropriate value for Z must in any case be greater
  than E.C. Jordan's 2 feet. However, they lacked
  soil core measurements taken from aquifer material
  beneath the site to establish a field value at the
  time of the Record of Decision.
- o <u>Source literature</u> Domenico and Palciauskas (1982) did not specify using the "mixing zone" calculation to establish Z later in their article when they presented the VHS model.
- o <u>Lack of field verification</u>— Duchesneau calculated a C<sub>o</sub> =960 ppm when he used Z=2, which was inconsistent with field measurements of 130 ppm TCE

in well DEP-7 on-site (Gerber, 1982). Therefore, he argued that E.C. Jordan's value could not be supported by calibration data.

Two important observations follow from this analysis. First, neither side had actual measurements to support particular Z values, e.g., soil cores at the downgradient source boundary showing actual penetration depth of contaminant into the aguifer matrix. appropriate support in terms of field concentrations could not be gained by examining ground water TCE concentrations at the DEP-7 well, since this represents only the dissolved contaminant concentration and not the amounts retained within aquifer pore spaces. analysis of TCE in aquifer matrix core samples would be necessary to provide accurate representations of these values, and such information had not been obtained as part of the Remedial Investigation. Thus, only estimates based on best professional judgement not been obtained as part of the Remedial Investigation. were available.

However, some additional data was collected during the pilot study. Miremadi (1986) examined the boring logs for wells B-1, B-2, B-3, and B-5, together with 1985 and 1986 ground water elevation data, and estimated the total saturated thickness near the site to be 8.5 feet. Gerken (1986A) used this value of total saturated

thickness as Z when Canonie repeated the VHS modeling in September 1986. The issue of contaminant penetration into the aquifer was not examined further by the responsible parties.

#### 6.2.2.4 Dispersivity and Mixing Length

In Attachment A to the McKin Record of Decision, for purposes of modeling, Camp, Dresser and McKee assumed that vertical and transverse dispersivities were identical, i.e., isotropicity. Longitudinal and transverse dispersivity were defined as the dispersion coefficient for each direction divided by ground water velocity (Freeze and Cherry, 1979). In the absence of field data, Camp, Dresser and McKee used transverse dispersivity values given by Yeh (1981) for silty sand materials.

It should be noted, however, that for his regional-level flow and transport modeling, Gerber (1982) had assigned values of 50 feet and 15 feet for longitudinal and transverse dispersivity, respectively, based on values used by Fried (1975) and others for "regional models involving several thousand feet of flow in stratified sand and gravel aquifers" (Gerber, 1982; see Table 18 and Section 5.3). This data clearly was available to Camp, Dresser and McKee in the Record of Decision (in fact, Gerber reran his models using the

updated Remedial Investigation data as part of the Feasibility Study).

E.C. Jordan (1985) challenged the assumption of isotropicity, stating that the layers of silts and clays in the McKin delta soils would be expected to lead to slower contaminant dispersion in the vertical direction than in the horizontal. No field data were provided in support of this position; rather, E.C. Jordan offered an argument for an alternative dispersivity value by suggesting an inverse position; rather, E.C. Jordan offered an argument for an relationship between transverse dispersivity and the "mixing length", L'.

E.C. Jordan introduced its own modification of the mixing length equation originally given in equation 7 of Domenico and Palciauskas (1982), as follows:

Domenico and Palciauskas (1982)

E.C. Jordan (1985)

$$L' = \underline{V_C(H - L_2)^2} \qquad \qquad L' = \underline{\alpha_T(H - L_2)^2} \qquad \qquad (6-3)$$

V<sub>C</sub> = contaminant velocity, assumed equal to ground water velocity, i.e., no retardation;

H = saturated thickness (surficial zone)

 $L_2 = Z$  at X=L' (see Figure 6-17)

 $\alpha_{\overline{m}}$  = transverse dispersivity

For unknown reasons, E.C. Jordan omitted V<sub>C</sub>, as shown, and calculated an L' of 50 feet for a dispersivity of 3.3 feet (as used by Camp, Dresser and McKee), and 170 feet for a dispersivity of 1 foot. E.C. Jordan proposed that a dispersivity of 1 foot at McKin was more in keeping with Bear's (1979) observation that mixing in an aquifer occurs at a downgradient distance from the source approximately equaling 10 to 15 times the saturated thickness (15 feet, as given by Camp, Dresser and McKee, 1985E). Finally, E.C. Jordan postulated that the contaminant concentration at X=L' should be "relatively insensitive to the choice of dispersivity."

E.C. Jordan's argument appeared unclear in at least three areas. First, L' was calculated incorrectly, without using V<sub>C</sub> as given in the original reference. Second, while they cited Bear in support of a lower dispersivity value, they finally used Camp, Dresser and McKee's 3.3-foot value in their calculation, although this implies the inconsistent 50-foot mixing length value using their calculation for L'. Third, if dispersivity and mixing length are in fact related inversely, it does not seem possible that the downgradient contaminant concentration could be insensitive to the dispersivity value. No evidence was provided to support the latter claim.

Duchesneau (1985A) disputed E.C. Jordan's arguments, citing the following factors in support of Camp, Dresser and McKee's choices of parameters:

- The 1-foot dispersivity value preferred by E.C.
  Jordan falls in the low range of typical
  dispersivities for silts, according to Yeh (1981).
  However, Duchesneau asserted that "the composite
  well log for the area indicates the material to be
  a sand. Soil augering conducted confirms the
  material in the upper 10 feet of the unsaturated
  zone to be a uniform fine sand with some
  inconsistent thin clay lenses."
- o Camp, Dresser and McKee's 3.3-foot dispersivity estimate was also based on the collective experience of many of the firm's modelers, and on examination of estimates in the literature for sites with similar subsurface settings. For example, Pinder (1973) used a dispersivity of 14 feet for a similar glacial outwash zone with thin lenses of fine to medium sands and silts interbedded in coarser gravels.
- o E.C. Jordan nevertheless used the 3.3-foot value in their "corrected" cleanup level calculations.
- Duchesneau reemphasized that Camp, Dresser and McKee's value yielded results consistent with measured ground water concentrations, and that obtaining verifiable results represented a more reasonable approach than basing dispersivity estimates on "a general observation water concentrations, and that obtaining verifiable of Bear and a [probably incorrect] mixing length calculation."

During the pilot study and the preparation of the excavation plan, Canonie performed falling-head permeability tests and particle-size distribution analyses on samples from Areas 3 and 6 to determine a transverse dispersivity value for input to the VHS model

(Gerken, 1986A). The falling-head tests indicated permeabilities of 1.0 x 10<sup>-2</sup> cm/sec and 3.0 x 10<sup>-3</sup> cm/sec for Areas 3 and 6, respectively. When the permeability was calculated from the particle-size distributions using Hazen's equation, values of 3.2 x 10<sup>-2</sup> and 4.0 x 10<sup>-2</sup> cm/sec were obtained for Area 3, and 2.5 x 10<sup>-3</sup> was calculated for Area 6. Gerken (1986A,B) concluded from this data that dispersivity values of 1 meter (3.3 feet) and 0.4 meter (1.3 feet) were appropriate for Areas 3 and 6, respectively, on the basis of Yeh's (1981) "typical aquifer parameters" used initially by Camp, Dresser and McKee (1985E) to calculate the cleanup levels in Attachment A to the Record of Decision.

Gerken (1986B) noted that these values were estimates. However, even using slightly lower and higher estimates for Areas 3 and 6 respectively, his calculations appeared to show that a 1 ppm cleanup level still provided a conservative margin of safety for ground water exposures beyond Canonie's recalculated "acceptable" soil residual limits.

# 6.2.2.5 <u>Effective Porosity</u>

In Attachment A to the McKin Record of Decision (Camp, Dresser and McKee, 1985E), EPA's consultants used an effective porosity of 0.25. This was based on typical

values tabulated by Yeh (1981) for similar materials.

E.C. Jordan claimed that the hydraulic conductivity of McKin soils should lead to selection of porosity values given for silts (i.e., 0.05-0.1 according to Yeh, 1981), but considered Yeh's values somewhat low. E.C. Jordan further asserted that the porosity value would have little effect on the final concentration calculation.

The porosity value is critical to estimates of velocity in both the vertical and horizontal directions, and therefore to estimates of dispersion (see Section 4.3.1). Using Domenico and Palciauskas's (1982) argument, this would also strongly affect  $Z_X$  (depth of leachate penetration at a given distance X) and therefore the accurate determination of mixing length, L', as discussed in Sections 6.2.2.3 and 6.2.2.4.

Canonie assumed a porosity of 0.35, and in some documents 0.40, to calculate the K<sub>d</sub> (Gerken, 1986A).

This was disputed by Duchesneau (1986), as discussed in Section 6.2.1.4. However, Gerken estimated permeability based on falling-head tests and on particle size distribution analyses, as discussed in Section 6.2.2.4. This permeability value was then used to estimate a transverse dispersivity value for their revisions to the VHS modeling.

As discussed in previous sections, the SOCEM framework's questions on isotropicity and regularity of

the flow domain clearly could have driven the agencies' consultants to collect this type of data as part of the Remedial Investigation, which could have supported use of a different model or allowed substitution of more confidently known values of porosity, and thereby, of dispersivity and other key parameters.

# 6.2.3 Other Model Assumptions

As discussed in Chapter 5 and Section 6.1, the VHS model was selected and used, in part, based on the assumptions of continuous source term; no attenuation of contaminants in ground water due to volatilization, degradation, sorption or other retardation mechanisms; no dilution by recharge infiltration downgradient of the soil source. Equilibrium between leachate concentrations in the vadose zone beneath the source and concentrations at the phreatic surface beneath the soil source likewise was assumed.

E.C. Jordan (1985) disputed these as being "several individually conservative assumptions which are generally not valid in the real world," for example, the assumption that the ground water receptor would be located on a streamline oriented with the center of the contaminant source. Canonie disputed the sorption assumptions as well. In rebutting these disputes, Camp, Dresser and McKee was forced to support

its adherence to each assumption, and reevaluate its validity as new information became available during the Remedial Design phase.

#### 6.2.3.1 Constant Source Term

Questions 10 through 14 of the proposed SOCEM decision framework (i.e., steady or transient flow, need to simulate different contaminant phases/ densities/ viscosities, source spatial configuration, and especially, intermittent vs. continuous source) individually or together might have led EPA to consider a different source term at McKin, and therefore a different model than the VHS. The conceptual model of a limited source of residual contaminants in site soils that continued to leach intermittently to ground water following precipitation events was developed originally by Gerber (1982). It was refined in the Remedial Investigation/ Feasibility Study (Camp, Dresser and McKee, 1985 C,D), as indicated by Duchesneau's comments on the choice of the Z term based on sinking of TCE through the saturated thickness of the surficial aquifer, discussed in Sections 5.3, 5.8, and 6.2.2.3.

The VHS model assumes a continuous contaminant source providing a steady-state leachate flux into the aquifer, as presented by Domenico and Palciauskas (1982). This was an intentionally conservative

assumption at McKin (Duchesneau, 1985A), as will be discussed in the following paragraphs. E.C. Jordan (1985) considered this assumption inappropriate at McKin, inferring incorrectly from Gerber's (1982) predictions that the source would "... dissipate in about 10 to 12 years."

In fact, Gerber referred to some evidence, for example contaminant concentrations in on-site surficial zone wells, suggesting that contaminant amounts leaving the site had been decreasing since 1980. However, he could not be certain whether the onsite storage tanks, still present and still containing some liquids at the time of his field studies in 1982, were leaking into soils. He presented no determinations or estimates of the rate of decline of the source term. The model runs suggested that, if the source were isolated or removed, after 10-12 years most areas of the surficial aquifer would contain less than 30 ppb TCA, except in the low-permeability soils northwest of Boiling Springs; and that TCA concentrations in the bedrock aquifer would diminish after 10-12 years to levels below 15 ppb.

Duchesneau (1985A) stated that modeling a decreasing source term would be accurate only if its rate of decline could be determined accurately. Samples collected by Camp, Dresser and McKee in mid-1985 showed relatively constant TCE levels in several off-site wells

compared to earlier data, supporting the constant source assumption. Duchesneau also pointed out that the goal of the model effort for the Record of Decision was to determine environmentally acceptable levels of residual soil contamination, not to predict "long-term" (10-15 year) ground water contaminant levels following a given remedial action. As such, this assumption was intentionally conservative, as discussed in Camp, Dresser and McKee (1985E).

However, both goals were interrelated in this effort at McKin, since the real objective of the modeling was to determine a residual soil TCE level that, if left unmanaged, would never contaminate ground water beyond the site boundary at levels greater than those discussed in Section 5.6. The model decision framework in Section 4.8.4.14 would indicate that, if the source term were not constant, or could not be reasonably treated as constant in the model, a more complex model would be required. Several simplified approaches for simulating a declining source were discussed by Domenico and Robbins (1985), among others.

# 6.2.3.2 Effect of "No Recharge" Assumption

The VHS model is based, and was used by Camp,

Dresser and McKee (1985E) at McKin, on the simplifying

assumption that no recharge enters the aquifer to dilute

the contaminant plume between the source boundary and the receptor point. In their critical review of the EPA/Camp, Dresser and McKee modeling, E.C. Jordan (1985) postulated that at McKin, on average, approximately four leachate volumes of recharge would enter the surficial zone over the 200-foot distance separating the source and the receptor point, providing an additional dilution factor of 1.7.

Duchesneau (1985B) agreed that recharge dilution likely occurs, but it was not homogeneous over the seasons, and likely did not mix completely with the contaminant plume in the vertical dimension, as implied by E.C. Jordan. Instead, Duchesneau pointed out that first, the dense contaminant likely was sinking as it moved laterally downgradient, limiting the effectiveness of infiltrating recharge in diluting it. Second, recharge varies seasonally as indicated by the precipitation record given in Gerber (1982). During winter months, snow and frozen ground prevent recharge infiltration, while much infiltration likely occurs during spring thaws (Duchesneau, 1985A; Gerber, 1982). This was supported by water balance studies and potential evapotranspiration measurements conducted at the nearby Charles George Superfund site in Massachusetts (Duchesneau, 1985A,B), which indicated that virtually all recharge occurred during a 3 month

period of rains and snowmelt around March of each year. This temporal variability was neglected by E.C. Jordan. Camp, Dresser and McKee, in consultation with EPA regional and headquarters analysts, chose to neglect this effect due to the variability and uncertainty associated with it.

Note also that the variability of recharge relates directly to the nature of the source term, as discussed in Section 4.8.4.14 and 6.2.3.1. Recall that Gerber's (1982) conceptual model of the ground water contamination suggested that the main source was TCE that continued to be released intermittently from unsaturated zone soils by rainfall events. Canonie's soil borings taken during the pilot study and other portions of the Remedial Design phase showed TCE contamination extending to the top of the ground water table in some locations (see Section 6.2.2.2; Canonie, 1986B), which supported this conceptual model.

It should be noted that in one portion of their original article, Domenico and Palciauskas (1982) discussed ways to consider effects of recharge dilution; however, they did not include it in the VHS equation.

EPA's analysts should consider whether this factor, if it had been accurately represented and supported by field measurements, might have dictated use of a different model altogether, according to the model

selection framework as discussed in Sections 4.8.4.3, 4.8.4.4, and 4.8.4.11. The choice of alternative model and any changes in the outcome of the remedy resulting from such a choice cannot be determined with certainty based on the currently available information.

# 6.2.3.3 Sorption and Retardation

As discussed in Section 5.7, the VHS model is a simplified analytical method, lacking a mechanism to account for retardation due to sorption or other mechanisms. E.C. Jordan (1985) asserted that sorption within the saturated zone should have been considered at McKin in selecting the cleanup level, since they believed that the site soils had a higher organic carbon content than the 5 percent estimated by Camp, Dresser and McKee for the Record of Decision (1985E). Therefore they expected that retardation in ground water due to sorption could be significant enough to be accounted for in the model.

This could have allowed a higher leachate influx  $(C_0)$  and therefore a higher residual soil concentration, since more TCE would thus be expected to remain sorbed on the subsurface matrix than accounted for by EPA's consultants in the Record of Decision analysis. Canonie argued for a different  $K_d$  to account for partitioning in the vadose zone soils, as was

discussed in Section 6.2.1.4. Duchesneau (1985A)

pointed out that sorption had been neglected in the

modeling partly because of the lack of confirming field

data, and because no batch equilibrium studies or column

sorption studies had been performed using McKin soils.

As described previously, this was an intentionally conservative assumption. Question 17 in the SOCEM framework therefore was addressed at the time of the Record of Decision. It should be noted that while debates continued over appropriate sorption values for the McKin site, neither party collected field values to resolve the issue. Instead, the cleanup was delayed while each party debated their choices of partition coefficients, supported by literature from other sites. Had field data or laboratory studies been performed on the McKin soils, the result could have changed substantially; however, the magnitude of this impact cannot be assessed with any certainty since no field values were obtained at McKin.

The importance of sorption in the debates surrounding appropriate estimation of organic transport and fate at McKin demonstrates the value of obtaining some actual data on partitioning at this site, as would have been highlighted in Question 17 of the SOCEM framework. Preferably the uncertainty surrounding site-specific sorption as a retardation mechanism in both the

unsaturated and saturated zones could have been minimized by obtaining this information (and perhaps employing a decision framework) during the Remedial Investigation, and in any event, prior to the Record (and perhaps employing a decision framework) during the of Decision.

# 6.2.3.4 Attenuation by Degradation

Question 18 in the third phase of the proposed SOCEM framework examines the need to simulate degradation (whether chemical or biological), and to track daughter products of the breakdown processes. A "yes" answer to these questions at McKin clearly could have driven the agencies to consider use of a geochemical or biological transport model, since Camp, Dresser and McKee (1985E) had themselves used the high biodegradation potential of several of the McKin source contaminants to eliminate them as indicator parameters in the model (see Section 6.2.1.3). However, data limitations were a major constraint at the time of the Record of Decision, as discussed previously in this section.

E.C. Jordan (1985) complained that reduction of ground water (and source) concentrations due to chemical and biological degradation was not being accounted for at McKin by using the VHS model. Duchesneau (1985A)

stated that Camp, Dresser and McKee neglected degradation because they felt it was not likely to be significant. He cited studies by Wilson (1984) who found little degradation of aliphatic hydrocarbons in ground water. Reduction of TCE in "active" samples did not differ significantly from concentration changes in autoclaved blanks. Thus, Camp, Dresser and McKee considered this a conservative but realistic assumption.

It should be noted that McCarty et al.'s (1986) sorption studies, used by Gerken (1986A,B) to support the elevated partition coefficient (see discussion in Section 6.2.1.4), were intended to determine biotransformation potential of chlorinated aliphatic hydrocarbons in ground water at the California sites. As pointed out by Duchesneau (1986), the study design had inherent limitations in separating sorption effects from biodegradation effects.

However, while this may be an important transformation process at McKin, the lack of field data makes it difficult to determine its importance relative to other processes. Again, site-specific data, even a bench-scale screening study, would have been valuable in seeking a resolution to this issue. Such data was never obtained at any point during the study and cleanup process at McKin.

# 6.2.3.5 Attenuation by Volatilization

Ouestions 17 and 18 in the SOCEM decision framework presented in Section 4.8.4 provide examples of decision points based on the relative importance of such transformation and transport processes as sorption and degradation at the site to be modeled. The need to simulate processes such as volatilization may be more or less important than these; therefore, these questions could be substituted for the ones presented in Phase III of the prototype SOCEM framework, as dictated by the individual site situation, the level of knowledge of the site incorporated into the analyst's conceptual model, and the expertise and sophistication of the analyst. Some sort of sensitivity or uncertainty analysis could be used to determine semiquantitatively which processes should be examined in the model decision framework used at a particular site, but early in the remedial process, such decisions will be made qualitatively, based on judgement and experience.

As for other parameters discussed previously, strict adherence to the decision framework could have led some analysts to consider other models that incorporate volatilization processes, especially had EPA elected to use a mathematical model to simulate vadose zone contaminant transport. However, that would have

been unlikely at the time of the Record of Decision, given the paucity of site-specific data on the importance of volatilization available at that time.

At McKin, E.C. Jordan (1985) argued that volatilization of the organic contaminant should also reduce TCE concentrations significantly, but that volatilization from the source soils or the aquifer was not accounted for by the VHS model. E.C. Jordan offered no data or quantitative estimates suggesting what effect volatilization had on fate and transport of TCE and other volatiles at McKin.

Duchesneau (1985A) pointed out that contaminant volatilization from the McKin soils probably was affected by many factors including vapor pressure, solubility, concentrations, rates of air flow through soil pores and over the soil surface, density, porosity, temperature, humidity, and a variety of other factors. Further, volatilization would vary greatly with the seasons, and with the contaminant in question. He felt it likely to be negligible during winter periods of snow cover on the site. Many of these factors were discussed in Section 4.3, and general reviews can be found in Jury (1986B), Jury and Valentine (1986), and Sims (1986).

Duchesneau stressed that many uncertainties surrounded any attempt at reasonably estimating these factors, especially since their influences at McKin

would be quite variable and little field data was available for many of the important factors. Thus, volatilization was neglected by Camp, Dresser and McKee in the initial Record of Decision modeling as a conservative assumption. Duchesneau also observed that volatilization of TCE from ground water was likely to be negligible, since contaminants would have to migrate upward through as much as 85 feet of overburden in some areas.

# 6.2.4 Effects on the Final Remedy

The reevaluations of the cleanup level modeling done by the agencies and the Responsible Parties and their contractors did not result in changing the remedy selected, but did lead to a number of refinements to increase its reliability and its effectiveness. Overall cost-effectiveness and overall protectiveness of the remedy were simultaneously enhanced through the extensive additional site characterization that occurred during this phase, because while the soil contaminant was discovered to be more extensive than was known at the time of the Record of Decision, it was also carefully mapped such that only those soils requiring treatment were so targeted. Uncontaminated soils were set aside without aeration or left undisturbed, optimizing the implementation of the remedy. Further,

the cement stabilization added additional factors of safety and reliability not envisioned when the remedy and the cleanup level were initially selected in the Record of Decision, thus compensating for some of the uncertainties inherent in the cleanup level analysis.

McKin therefore does not provide an example of situations where reevaluation and additional data collection, whether or not it was prompted by use of a SOCEM-type decision framework, led to a change in the remedy itself. At other sites, however, such could be the case. Further study would be needed to define these situations, and establish criteria and thresholds where the agencies might shift to a "fallback" remedy.

The other significant result of the additional site characterization and the reevaluation of the VHS modeling was that the cleanup level was changed, once sufficient support for its relaxation had been supplied to the agencies. As discussed previously in this section, this was done through reinterpretation of the model, its parameters, and its underlying assumptions, and not because an alternate model was used. It is beyond the scope of this study and the limitations of the available site data to determine with any degree of certainty which of the circumstances outlined in this section could have led to choice of a different model at McKin, which model or models might have been selected, or

what cleanup level might have been calculated using these models.

However, use of a SOCEM-type decision framework could have led some analysts to a different model choice at the time of the Record of Decision or at several points thereafter, as discussed in the preceding sections. The use of such a framework at McKin might at least have led to additional data collection in the Remedial Investigation or at the time of the Record of Decision, which would have saved time in the long run by resolving several of the controversies on input parameters before they started.

# 6.3 Uncertainty and Decision Analysis at McKin

The other principal component of the SOCEM framework described in Section 4.10, in addition to the decision framework proposed in Section 4.8.4, is the use of a method such as decision analysis for tracking and semi-quantifying the uncertainties in parameters, assumptions, and outcomes in the modeling process. Clearly, decision analysis was not used at the McKin site to select or implement the model. Uncertainties were identified at various points in a combination of qualitative and quantitative ways, and many of the uncertainties at the McKin site were not explicitly identified by either party's analysts.

In order to apply decision analysis to the model selection and use process at McKin or other Superfund sites, a three step procedure would have to be followed:

- 1. All processes of fate and transport that could significantly affect the cleanup level at the site must be identified (which requires a decision criterion for what constitutes a significant or noteworthy effect).
- Expert judgement must be canvassed to assign relative confidence levels to both the typical or likely values for each process parameter and to their importance in the modeling to be performed.
- 3. The site analyst's expert judgement must be canvassed to determine alternative outcomes of each decision: selecting a different model, choosing a different cleanup level, getting more data, or switching remedies. Probabilities and utilities, i.e. the expected values in terms of health risks, cleanup costs, time, etc., must be assigned to each alternative outcome.

The importance of various processes and parameters to fate and transport was described generally in Chapter 4. The relative importance of various processes at McKin, as judged by either party's experts, was discussed in the preceding section. The discussion illustrated that a decision framework applicable to all sites having a soils/ground water exposure pathway necessarily would have to be as general as that given in Section 4.8.4. Additional and/or different decision points may be needed to address fate and transport processes important at an individual site.

Determination of the most appropriate decision points,

especially regarding vadose zone processes and appropriate parameter values, should be an important subject for future research.

The analyst must collect sufficient data to determine which processes and factors are operating at a given site, and to select/use a model that will adequately account for each. Many uncertainties are associated with these decisions, including the following:

- o Heterogeneity of site conditions in terms of temporal and spatial variability of key parameters;
- o Accuracy of measurement of the key parameters;
- o Adequacy of known/measured parameter set for meeting the study objectives, whether for site characterization, remedy comparison, or cleanup level estimation; and
- o Appropriateness of model selected to simulate a given process or zone.

These uncertainties are not identified in any consistent or formalized way in current CERCLA cleanup decisions, but they would have to be in the future in order to apply decision analysis concepts to the Remedial Investigation/ Feasibility Study.

It was mentioned in Section 6.2.1.4 that sorption and partitioning were considered the most important factors contributing to the Responsible Parties' documentation for relaxing the soil cleanup level. It was also clear that several controversies surrounding

soil partitioning and other key processes could have been resolved more quickly and conclusively had additional site-specific data been obtained. Use of a quantitative or semi-quantitative decision or uncertainty analysis method could have expedited the McKin cleanup by identifying earlier which parameters were most sensitive or most in need of field verification on the site.

As discussed in Section 4.9.4, such an analysis could have assisted the EPA decisionmakers by providing a more rigorously determined and more quantitative assessment of the incremental ground water risk associated with the decision to relax the cleanup level. It might also have allowed for an estimate of the probabilities of observing the excess risk within some confidence range. Then, one could compare the "reasonable worst case" assumptions with the Responsible Parties' more "nominal-case", but in their view, more realistic, assumptions and input values.

This would have allowed the tradeoffs between the different decisions to have been more quantitatively compared. However, utility functions were not developed to describe the alternate modeling outcomes at McKin, per Section 4.10.2.2. Although costs of excavation to various cleanup levels were calculated by Canonie, as presented in Table 21, they postulated that risks

associated with the ground water targets established in the Record of Decision would not be exceeded by relaxing the soil cleanup level as they had proposed (see Section 5.10).

Additionally, while the use of the VHS model at McKin conformed to several of the principles of SOCEM given in Section 4.10.3, the fit of others was not as evident. For example, Camp, Dresser and McKee reasonably supported their position that they had matched the model to the available data at the time of the Record of Decision, based in some respects on best professional judgement. The experts for each party clearly differed in their subsequent interpretations of parameters and results, and it was pointed out that other experts reasonably could have made different model selection decisions with the same set of facts and assumptions. Many, but not all, of the questions in the SOCEM framework given in Section 4.8.4 were asked during the rebuttal/ reevaluation period, and others not shown in Figure 8 were discussed. This illustrates the need for maintaining flexibility in the framework by considering different decision nodes in the model framework, as needed, on a site-by-site basis.

The agencies felt that the conservatism in the soil cleanup level was appropriate to the level of precision of the chosen analytical methods. However, the lack of

confidence ranges or boundaries on the calculated values, coupled with the evidence presented by Canonie that an order-of-magnitude change in soil cleanup level would not change the predicted ground water concentration, does not provide an opportunity for independent validation of this position.

Finally, since a steady-state equilibrium transport model was used, the McKin analysis did not quantitatively identify the needs for verification monitoring. The VHS model predicts steady-state long term ground water levels, not the time pattern of likely contaminant reduction in the aquifer due to soil treatment, nor breakthrough times for untreated contaminants at certain ground water receptor locations. That would have required a numerical analysis of the type performed by Gerber (1982; Camp, Dresser and McKee, 1985D).

Likewise, the VHS model provided no predictions of geochemical or biological transformations to allow selection of, say, daughter products as indicator compounds. Uncertainty ranges around the calculated ground water risks were not given, nor were probabilities of occurrence of alternative risk levels estimated. Therefore, the temporal and spatial design of an appropriate ground water verification system, in terms of well depths, sizes, and design, sampling

frequencies, and analytes, cannot be determined solely on the basis of the modeling analysis that was performed at McKin. Verification designs will be developed as part of the design and implementation of the ground water remedy at the site, which currently is being negotiated (Serian, 1988).

The decision analysis element of the SOCEM approach could have had several applications at various points within the overall model selection decision process at McKin. These applications should be considered for future Superfund investigations, including bounding the uncertainties of each decision point when choosing among models, and estimating the overall uncertainties or the quality/ validity of the calculated soil cleanup level.

Others include estimating the value of obtaining additional data and/or selecting different models, in terms of their potential effects on intermediate decision outcomes or on the overall outcome. The most important iterative decision in this category concerns the identification of when to back up and reassess whether to collect more data/ use better model, or revisit goals/ use simpler model. Such applications should be considered in future model selection decisions at other Superfund sites, if a SOCEM type framework is incorporated into the site characterization process on a program-wide basis.

# 6.4 <u>Developing the Decision Approach for Selecting</u> the Remedy

The preceding discussion illustrated the extent to which the McKin soil cleanup followed SOCEM type model selection decisions, and suggested ways in which the cleanup could have been more speedily or effectively implemented, or the modeling decisions more rigorously supported, had a formal decision framework been used early in the site investigation, or later in the remedial design and implementation stages. The uncertainty analysis components were not thoroughly developed or tested, but should be in order to make such a method useful for model selection decisions at future sites.

Further, this concept of a decision framework coupled with semi-quantitative identification and tracking of uncertainties could be helpful in other aspects of the Superfund site cleanup process, for example, in designing and performing the risk assessment for other exposure pathways than ground water; for designing the sampling and analysis workplans for the Remedial Investigation; and for comparing and selecting remedies in the Feasibility Study.

# 6.4.1 <u>Criteria for Choosing Appropriate Models</u> It was pointed out in Section 4.8 that no one model

can account for all significant processes of fate and transport of water and contaminants from soils to ground water. This has several major consequences:

- The analyst must link several models to represent the complete soil/ground water exposure pathway. The models may be for different compartments, for example the unsaturated zone and one or more saturated zones; for flow versus physical/ chemical/ biological transport processes; and so on.
- o Each submodel likewise is limited in terms of how accurately and precisely it simulates a given process over the area or time frame of interest. The analyst selects each model to account for the processes contributing most significantly to contaminant exposure.
- The analyst's understanding of the major fate/
  transport processes at a site must be sufficient to
  select and use these models appropriately, or to
  opt not to model all or part of the soil/ground
  water pathway. This requires a continuous string
  of decisions throughout the cleanup level
  estimation process about the tradeoffs between
  collecting more data and using less precise models
  for decision making.

Ideally, the same models should be used both in the initial exposure assessment to calculate the ground water threats/ risks from site soils, i.e., the "forward" calculation, and to back-calculate residual soil cleanup levels. This would maximize consistency.

Since a unique solution is necessary for effective back-calculation, this may not be possible at sites where numerical models are used for the forward calculation, due to intrinsic properties of the process

equations and solution methods. This may also exclude the use of stochastic techniques and discrete parcel random walk methods from back-calculation applications. This is analogous to the benchmarking problem with numerical models. In many ground water investigations, analytical models have been used to validate the numerical model's results, although they usually do not describe the physical system as completely or precisely (Keely, 1987A).

The preceding discussion also illustrated that no one decision framework is likely to be capable of accounting for all possible combinations of site factors. Otherwise, it would be so complex as to be unmanageable, and understandable to only a few experts. This defeats the intended purpose of most expert systems or decision frameworks, as discussed in Section 4.10. Therefore the decision framework must be flexible, both in terms of the models to be selected (the possible outcomes of the decision points) and the decision points themselves.

## 6.4.2 Criteria for Selecting Cleanup Level

The discussion in Chapters 3 and 4 supported the contention that soil cleanup levels should be selected on a site-specific basis, and that if one assumes health-and-environment-based numerical cleanup levels can

be developed for each exposure pathway of concern, then fate and transport models could be used to set cleanup levels that would prevent exposures above these "safe levels." There are many problems attendant to selecting or developing the appropriate chemical dose levels on which to base cleanup levels in each medium. The uncertainties surrounding these are many and complex, and a discussion and analysis of these uncertainties, or a quantitative comparison with the uncertainties of various aspects of contaminant fate and transport, is beyond the scope of this study. See National Research Council (1983); Research Triangle Institute (1987); Schultz et al. (1987); EPA (1986A); and others for a discussion of this issue.

A principle underlying the SOCEM approach is that where the conceptual model of the site is limited or vague, one must necessarily use a simpler, and therefore more conservative, model. The simpler the model, the more conservative (stringent) will be the cleanup level it predicts, and the greater the need for mechanisms to compensate for the broad uncertainties. These compensating mechanisms should include monitoring sufficient in scope and duration to verify the assumptions and parameters used in the model.

Also included should be some kind of land use or access restrictions, or more extensive long-term manage-

ment of the site following cleanup, until verification is completed. In some instances verification could be made before concentrations diminished such that any possible exposures to soils or ground water would not yield risks above the predetermined "safe levels."

Likewise, any remedy leaving unsafe levels of residuals in place should have provisions for a fallback remedy, to be employed if verification monitoring fails to bear out the fate and transport predictions, or if unanticipated events occur subsequent to site cleanup. At McKin, long-term monitoring, site security and access restrictions, and alternate water supplies were all provided for in the two Records of Decision (EPA, 1983C, 1985J).

In the as-built remedy, Bell and Antommaria (1987) included several compensating mechanisms which further reduce the uncertainties introduced by the simplified VHS fate and transport analysis by reducing the potential for future contaminant leaching to ground water in excess of the predicted levels. These included cement stabilization of treated soils prior to redeposition on-site. Future cleanup of the contaminated ground water on and off site will further compensate for the uncertainties in the agreed-to 1 ppm TCE cleanup level in site soils. As discussed in Sections 5.10.3 and 5.10.5, EPA also intended to treat

an additional "buffer zone" of soils containing trace levels of contaminants below the selected cleanup level, as added compensation for the uncertainties in the soil cleanup level. However, the arguments and additional level, as added compensation for the uncertainties in the data presented by Canonie enabled these uncertainties to be reduced, or compensated by other means. This allowed the size of the "buffer zone" excavation to be minimized, saving time and resources.

Since the choice of model did not change, it cannot be stated with certainty whether use of more data in a more sophisticated model up-front in the remedial process would have reduced these uncertainties, or allowed for some other soil cleanup level. More studies would be necessary to attempt such a determination, and data collected by Canonie during the Remedial Design would have been needed much earlier in the Remedial Investigation/Feasibility Study process.

# 6.4.3 <u>Criteria for Choosing Appropriate Remedial</u> <u>Actions</u>

In the Remedial Design phase at McKin, the additional data collected allowed optimization of the selected remedy. First, the thorough soil characterization allowed the excavation and treatment to be focused on areas requiring treatment, and elimination

of relatively uncontaminated areas from unnecessary treatment. This optimized the cost-effectiveness, protection, and "permanence" of the remedy as implemented. Second, it allowed the treatment process parameters to be refined, so that full-scale treatment could proceed at optimum speed while not compromising the safety of site workers or off-site receptors.

While the process design data would have been difficult to obtain during the Feasibility Study, more thorough soil characterization earlier in the site study could have affected final remedy decisions and saved time. At McKin, it would have meant spending more time and resources on the Remedial Investigation/Feasibility Study, but probably would have saved approximately a year on the overall cleanup. The two-year period from Record of Decision to completion of the source control action could have been shortened by obtaining data on the disputed parameters and assumptions, thus preventing the disputes and shifting the focus of the design earlier.

## 6.4.4 Criteria for Selecting Cleanup Approach

Use of a SOCEM type framework earlier in the process might have affected the site cleanup approach. For example, had the agencies and the public wished to clean up the site to allow unrestricted access and no future monitoring or long-term care requirements, a more

stringent cleanup level might have been selected that did not introduce uncertainties of fate and transport. Concerns about other risks caused by on-site treatment could have led to greater consideration of an off-site treatment/disposal remedy, or soils could have been capped and contained in place, with much greater long-term care requirements than posed by the selected remedy.

This would mean trading off capital costs versus operation and maintenance costs, as the more capital-intensive treatment remedies may destroy more contaminants and thus require less long-term management of residuals than less capital-intensive remedies involving containment, limited treatment, or less stringent cleanup levels. However, the agencies' ability to make and defend such tradeoffs could depend greatly on the utilities assigned to these various outcomes in the decision analysis process.

As discussed in Sections 4.9 and 4.10, the political and economic disagreements that would result from any attempt to assign these utilities may make such a calculation unlikely in future cleanup decisions. EPA has not been willing to commit to such risk-benefit analyses in the Superfund program to date, and may be prevented from doing so under the SARA statute. For additional discussion of this point, see the preamble to the National Contingency Plan (EPA, 1985A) and the Office

of Technology Assessment (1985).

## 6.5 Implications for the Superfund Program

Despite the difficulties in assigning expert-derived utilities to various decision outcomes at Superfund sites, and the tremendous uncertainties of fate and transport at each step in the pathway from the contaminated soils source through soils and ground water to the human or environmental receptor, the preceding discussion suggests that adoption of some type of formal decision framework would be helpful to Superfund site investigators and decision makers. As was mentioned in Section 4.8.2, the modeler and the remedial project manager are faced with conflicting pressures. On the one hand, the Congressional mandate (as given in SARA) to streamline and accelerate the remedial process includes site cleanup quotas. These dictate a more rapid and less detailed Remedial Investigation, as the Agency pushes to streamline the Remedial Investigation/ Feasibility Study process to avoid "studying sites to death." At the same time, the Agency is pressured to collect high quality data to support the increasingly more complex remedial decision making process, and to assure the selected remedy's compliance with applicable requirements and with the statutory preference for permanent solutions (Camp, Dresser and McKee, 1987A).

Many of these pressures have arisen when Agency critics failed to recognize that much historical slowness in the Superfund program resulted partly from the many uncertainties regarding what kinds and how much data are needed to characterize sites sufficiently to select appropriate remedies and cleanup levels.

Further, the approach to site characterization has been evolving continuously. Keely (1987A) and others have argued for more "state of the art" site data collection in the Remedial Investigation to better achieve both goals in the long run. A SOCEM type approach could provide such an organizing framework to the site characterization process.

The potential benefits to the program are many. The program is moving more and more toward use of more effective but capital-intensive treatment remedies. Achievement of the Superfund statutory cost-effectiveness requirement could be better addressed if a quantitative basis was available for comparing relative risk reductions afforded by different alternatives, especially when attempting to compare shortterm risks of excavation and treatment with the long-term, lower-level risks of chronic exposures to contained or uncontrolled contaminants.

McKin was typical of many recent Superfund sites where soil cleanups are interim remedies or operable

units, as compared to a "permanent," final, integrated site remedy. Use of a SOCEM type approach could reduce the need to defer setting cleanup levels to a subsequent action by addressing this requirement from the start of the study. By reducing (and explicitly identifying) the uncertainties related to the chosen cleanup level, the likelihood is much greater that the site will be cleaned up effectively the first time, and will not need to be revisited later. Currently, costs and probabilities of revisiting a site are seldom analyzed or considered. The revisit will always be more expensive, because the problem may be more complex and/or extensive than before, e.g., due to an expanding ground water plume, and costs will have become inflated.

Soil and ground water cleanups could be integrated by addressing both source control and management of migration problems at a site in a single study where practicable, using the same data set and, if possible, the same model suite. This expedites completion of the overall site cleanup, and enhances economies of scale in terms of the resources (both human and material) spent on the site study, and on design and construction of the remedy.

At some sites, sensitivity analyses may show uncertainty ranges for final soil cleanup levels that are so broad that the additional quantitative analysis

involved in implementing SOCEM is not worth it. It must be noted that the sites most amenable to this method are those that generally have the most straightforward, easy-to-characterize, subsurface environments, and perhaps the simplest lateral contaminant distributions. These are the sites that need such approaches the least. A classic paradox faced in Superfund cleanups is that the highly complex, difficult-to-characterize sites are in greatest need of such cleanup decision approaches.

Therefore, basic research addressing the fundamental aspects of fate and transport in the subsurface must be continued, focusing especially on definition and characterization of key unsaturated zone processes. Likewise, field personnel need to sharpen their understanding of the spatial and temporal heterogeneities in subsurface physical and chemical transport processes, so that sampling plans can be better designed to yield truly representative data that can be used effectively in the commonly available models.

A phased site characterization process, as recommended in Camp, Dresser and McKee (1987A), and in Sections 4.8 through 4.10 herein, will help address this problem and limit the additional time requirements for the Remedial Investigation. It would simultaneously yield lower overall costs and time if the remedy is examined in total, from Remedial Investigation through

completion of construction. Several specific areas for future research are suggested in Chapter 7.

It should be evident from the discussion in Sections 5.10 and 6.2 that many of the supposedly "state-of-the-art" modeling decisions presented in the SOCEM framework in Section 4.8.4 were addressed either implicitly or explicitly at McKin. Some might arque that the framework would not be particularly useful to a trained hydrogeologist or modeler. In fact, they do not represent the primary intended users of such a framework. The SOCEM approach will be more directly useful to the interdisciplinary remedial site manager and/or decisionmaker, by enabling them to track and justify how each individual analytical decision was reached, and the expected level of confidence they can have in obtaining the desired outcome of that decision. The outcome, coupled with the confidence level or probability and the expected value or utility of that outcome, could then be compared objectively with the value of obtaining additional data at any point in the site analysis.

The decisions would also be more accessible to agency program managers and to the public. Depending on the "acceptable" level of confidence the agencies will place on data and decisions, they may be better able to withstand challenges by interest groups or by responsible

parties. However, this depends on the agencies' willingness to make its decision making process accessible to the public at such a fine level of detail.

Modelers and hydrogeologists still may gain some benefit from a SOCEM type framework, in that it would provide an organizing structure to their analytical and decision making process, enhancing the consistency from site to site in terms of how site analysis and soil cleanup decisions are reached. This would heighten the consistency in Remedial Investigation data collection from site to site, and might help to bring earlier resolution to disagreements between experts regarding individual parameters and assumptions, or varying interpretations of a given set of data.

Such a process would be very useful in enhancing consistency from site to site, given the relative scarcity of modelers and hydrogeologists available to EPA and the states who have sufficient training and experience to integrate the many individual decisions into an effective site cleanup. This scarcity of human resources may be a limiting constraint in the effectiveness of SARA's implementation as well (Keely, 1987A; Office of Technology Assessment, 1985, 1988).

#### 7.0 CONCLUSIONS AND RECOMMENDATIONS

#### 7.1 Conclusions

As discussed in Chapters 1 through 4, contaminated soil cleanups at uncontrolled or abandoned hazardous waste sites historically have been complex and difficult to accomplish, due to a variety of technical and institutional factors. Controversy exists as to how cleanup levels should be defined. No federal soil standards exist, and few are available for ambient chemical concentrations in other media (air, water). The consequences have been inconsistent soil cleanups from site to site, in an attempt to satisfy various requirements of other laws to meet Superfund's protectiveness requirement.

Because of the many limitations in applying existing standards for other media to soils, it was proposed that cleanup levels can best be addressed on a site-specific basis. This approach should use standards, or existing EPA-approved health- and environment-based numbers, for other media and modify them to address soil appropriately. This is premised on the assumption that EPA will have approved healthand-environment-based numbers available for all compounds of concern at a given site. Site-specific soil cleanup levels would be selected based on the most limiting exposure pathway

at each site, for each compound of concern. The exposure assessment is the primary component of this site-specific risk assessment approach.

For the purposes of this study, it was assumed that ground water ingestion is the most limiting exposure pathway at most CERCLA sites; i.e., soil contaminants leach to ground water, and migrate to drinking supply wells. Models would be used in the exposure assessment, to help assess risks from soils, and to estimate soil cleanup levels by back-calculating soil levels from "safe" ground water concentrations.

In order to select and use a model to back-calculate soil cleanup levels, one must identify and understand the processes governing the transport and transformation of contaminants migrating from the soil source to the ground water receptors through several distinct subsurface zones. Transport and fate processes in each zone are many and complex. Physical, chemical, and biological processes occur interdependently. Different processes may occur at different sites, or in different locations at a given site, and their relative roles affecting a given contaminant are not yet well understood. Site, waste, and human factors can affect any or all of these processes at a given site. Most sites have highly complex, hard to characterize, and heterogeneous subsurface conditions.

No one model accounts for all significant fate and transport processes carrying water and contaminants from soils to ground water, as discussed in Sections 4.8 and 6.4. If models are to be used in exposure assessments to set site-specific soil cleanup levels, consistency across sites will not be obtained by cleaning up to the same soil concentration nationwide, or using one model at all sites. Rather, consistency could be best obtained through the use of a similar decision making process from site to site for selecting and applying models. The analyst must collect sufficient data to determine which processes and factors are operating at a given site, and to select/use a model that will adequately account for each. Many uncertainties are associated with these decisions, as discussed in Chapters 3 through 6.

The Soil Contaminant Evaluation Methodology (SOCEM) concept was proposed in this study as a candidate modeling decision process. A prototype decision framework is presented in Section 4.8.4. It has two main elements: the set of model selection decisions representing currently accepted hydrogeologic practice; and decision analysis principles, which can provide a semi-quantitative method to estimate and track the uncertainties associated with each decision in the model selection process, i.e., to identify which processes and

parameters affect the final cleanup level at a given site. The "state of the art" model selection decision rules could be assembled into an expert system.

The quality of this methodology's results will be highly dependent on the quality and appropriateness of the decision rules, and the accuracy with which alternative outcomes of each decision step are presented and mapped into a framework. Uncertainties in current knowledge of how the various subsurface processes interact may be a key limitation on the breadth of site situations to which any proposed decision framework could be applied. The decision analysis element of the SOCEM approach has several potential applications at various points within the overall model selection decision process, as discussed in Sections 4.9, 4.10, 6.4, and 6.5.

The McKin Superfund site in Gray, Maine, was described in Chapter 5 as one of the first sites in which a numerical soil cleanup target was developed upfront in the remedy selection process, and presented to the public in EPA's Record of Decision (ROD). It was also one of the first sites where the author advised EPA project managers in selecting and using an analytical ground water transport model to back-calculate this cleanup level, based on potential ground water exposure to trichloroethylene (TCE) and 1,1,1-trichloroethane

(TCA) from site soils. This was the Vertical and Horizontal Spread model of Domenico and Palciauskas (1982).

McKin was not a traditional case study in terms of providing an example of all aspects of SOCEM as described, for several reasons, including that the pre-ROD selection of the model, and of the TCE/TCA cleanup levels, was made without considering all available site data. Chapter 6 discussed what could have been done at the Record of Decision stage using a more formal decision process. However, many of the questions and decisions presented in SOCEM to reevaluate the model choice and use did occur after the McKin Record of Decision was signed, as the responsible parties challenged the model choice and EPA rebutted.

The choice of model might have changed had the SOCEM criteria been used formally. The additional site characterization data gathered during Remedial Design could have allowed for modeling with more sophisticated methods. Information in the site files did not allow a clear determination regarding whether the added information would otherwise have led to selecting a different cleanup level. Conversely, formal use of SOCEM or another decision process would have dictated collection of more and different kinds of data before, rather than during, the Remedial Design phase of the

project. SOCEM could show that additional data and/or a better model can, in some cases, lower the total project costs. For example, in certain instances, it could lead to selection of a more "permanent" remedy, as defined in SARA and in Chapters 1 and 3, or a different remedy.

Very few of the uncertainties were analyzed or presented quantitatively at McKin, especially when compared with SOCEM would suggest that uncertainties should be handled. Examples included verification of model assumptions and estimates of key parameters; needs/uses of verification monitoring and site use restrictions; and compensatory "overkill" mechanisms in the implemented remedy, such as cement stabilization of treated soils.

## 7.2 Recommendations

The SOCEM analysis undertaken partly after the fact at McKin suggests that generally, the more accuracy and certainty EPA wants in soil cleanup levels, the more and better the data that must be obtained. Thus, Remedial Investigations will cost more and, probably, take longer. However, if good data quality objectives are developed and the approach is implemented early in the site study, the time and resource increase could be minimized. This is because a SOCEM type decision framework could provide an organizing structure to the site study, and a formal,

consistent means of constantly reassessing the value of more information. As Keely (1987A) argued, more spent on site characterization means less spent on cleanup, with significant overall savings to EPA.

If a framework like SOCEM was adopted on a national level, identical cleanup levels would not be selected from site to site, but the different levels would be obtained by applying a similar analytical process. The process would allow semi- quantitative justification of how the selected remedy/ cleanup level achieves statutory goals and requirements. A consistent basis would be provided for EPA managers to select remedies and cleanup levels. Their decisions could better withstand challenge by responsible parties, citizens, etc. than at present.

Locational considerations would be taken into account in remedy selections in a more quantitative manner, because use of a SOCEM-type decision framework could allow for a model-based assessment of risks of transporting excavated or treated soils to an off-site location. In many cases, such risk estimates could drive the decision to select a lower cleanup level and treat materials on-site. Further study should focus on the following:

 Additional characterization of major physical, geochemical, and biological fate and transport

#### processes;

- o Construction of a broadly applicable geochemical data base that could be applied at a variety of sites with reasonable levels of confidence;
- Determination of whether, under any conditions, a unique solution could be obtained using a numerical model for back-calculation, if the final ground water concentrations are fixed. This is not likely to be possible with iterative solution methods if one specified certain error margins to define "acceptable" convergence of the solution, which gives nonuniqueness to the "forward" calculation output;
- o Identification and testing of quantitative methods for identifying appropriate indicator compounds for fate and transport analyses, when exposure pathways other than ground water may control overall soil cleanup levels (see Section 6.4.1.3);
- o Identification of the appropriate circumstances, if any, in which sensitivity analyses should be used to set the error margins acceptable for selection of a numerical model for a back-calculation type of application. If such conditions exist, one must establish how (or if) the decision criteria for nonconvergence should be used to reject the numerical method, or create new ones;
- o Additional identification of uncertainties related to the commonly used contaminant fate and transport models;
- compilation of Superfund site experience in fate and transport model applications and their results, including long-term verification monitoring, on an ongoing basis. Its purpose would be to clarify inconsistencies, pitfalls, and other application experience, and document it for inclusion into a structured knowledge/inference base. Such a system might be maintained at the International Ground Water Modeling Center, for inclusion in MARS, their model selection database;
- o Development of a more structured expert system/ artificial intelligence application of this decision framework, that would provide an interactive environment to assist analysts and decisionmakers; and

o Additional evaluations of decision analysis in this application, with a range of levels of available data, to determine the breadth of its applicability for performing uncertainty analysis of model selection decisions. In some applications, other techniques for uncertainty analysis discussed in Section 4.9 might be more useful and less dataintensive. Comparison studies of several of these methods should be made in the Superfund model selection context.

Further study is needed to determine whether or how EPA could adopt this approach as one of many tools to help it make decisions while minimizing possible negative consequences of its use. The issues include the following:

- o Identifying methods to help the public understand the many uncertainties associated with the selected remedy/ cleanup level if presented explicitly by SOCEM;
- o Studying whether use of SOCEM would impede EPA's ability to negotiate private cleanups through abuse or misinterpretation of the analyses in litigation; and
- o Determining whether EPA management would be willing to adopt, and make public, a more structured decision process, due to the likelihood of its being perceived as unduly constraining EPA's flexibility in unique and difficult cases.



### 8.0 REFERENCES

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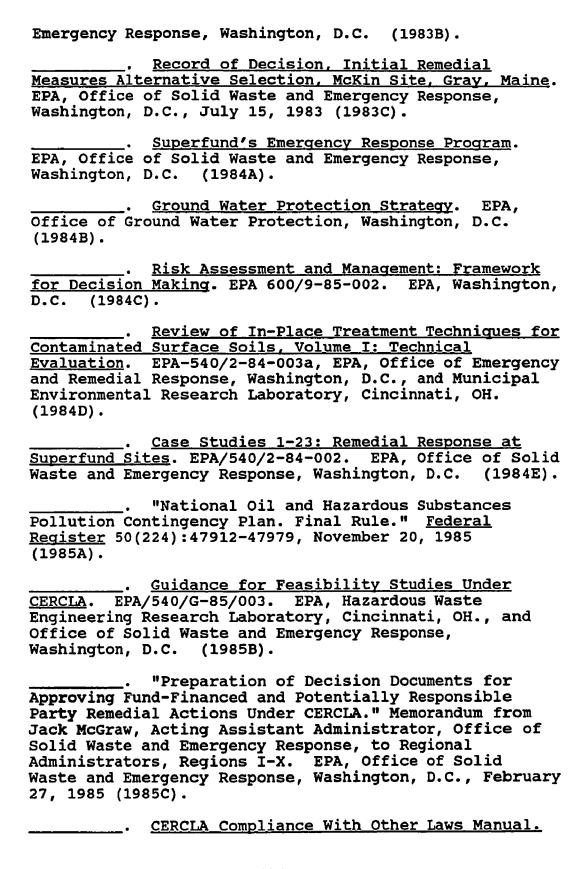
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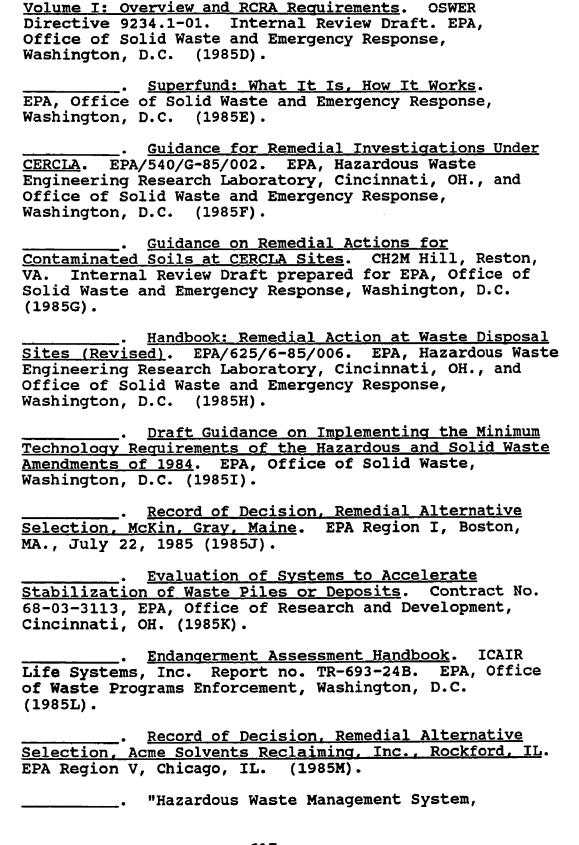
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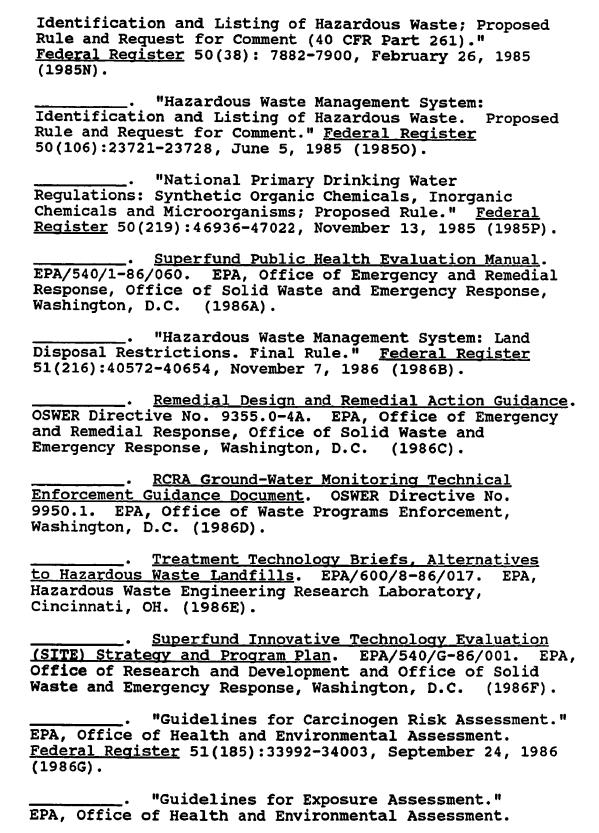
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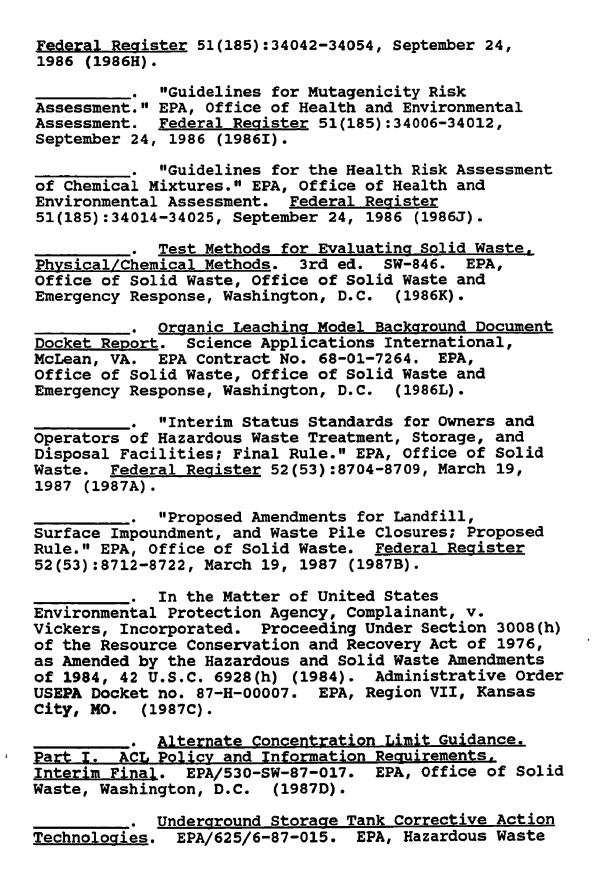
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## APPENDIX I

Summary Table of Superfund Records of Decision Concerning Soil Cleanups

(Adapted from EPA, 1987F)

647

THEFAT!
sell contaminated with VOCs including TCE and PCE
Du. Su. soil.  and sediments  continuinated  with  instants.  instants.  and metals
Cal and set! centaminated with PCBs and vocs including TCE

SITE HAME. ST	SIG BATE	OPERABLE UNIT	TWRAT/ PROBLEM	ESTIMATED HASTE QUANTITY	MAJOR COMPONENETS OF SELECTED REMEDY	STARGMCD5/ GDALS	CAPITAL COSTS
Bridgeport. #3	151 00/11/21	156 - 7161	Gu. Su. seil. and sediments contaminated with VOCs and PCBs	met provide	bispess of oily maste, sediment, and sludge via envite includentation; removal and dispess of contaminated mater using ensite treatment; drum encavation with of site removal; maintenance pumping; removal and efficie dispess of tents and maste; and installation of an alternate mater supply pipeline	GA must saot vec 1 mat of 80 co/1 on a 10 day 2verage	57, 572, 696
Surnt 61y Edg. #3 31/16/83		<b>5</b>	GA, SM, and soil centaminated with PCBs, wocs, and metals	Met provided	Excavation and offsite dispess? of liquids. sludges. asphalt piles, drums, and contaminated sell from lapsens and nevietnes of eviginal site contamys and vegetation; and suplementation of a laplementation of a laplementation of a laplementation of a laplementation.		2,200,000 (Choso I) (Choso II)
Calduall Trucking, 83	69/15/86	<b>1</b>	Gu and soil contaminated with organics including PANs and PCS . VOCs . VCC . Increase and extals including lead including lead	88. 90. 28.	Excavation and heat addition treatment of soil and weste materials with ensite disposal; Gd treatment using air stripping; and provision of an alternate mater supply	previous dad	<b>ଖରଉ'</b> ୧୯୬' ସ

SIVE MAME, SV	ROD SIG BATE	DPERABLE UNIT	THREAT/ PEODLEM	ESTIMATED MASTE QUANTITY	MAJOR COMPONENCIS OF SELECTED REMEDY	STAMBAEDS/ GOAL S	ESVIRATED CAPBTAL COSUS (8)
Army Creek Landfill, BE	99/01/60	151	Car, Sul, soil, and sediments contaminated with VOCs, thornamics, and metals	1. 900. 000 yd	Capping; demogradient (Su pumping with (monitering; and possible upgradient controls	Bet provided	12.010.000 cr 12.140.060 (woorddon)
Clescost I	<b>29/13/16</b>	151	Gu. Su. and soil centaminated with PCBs. WCBs. WCBs. Including benzene and TCE. and positicides	Rol provided	Excavation and remays of buried drums and other materials with MCBA office disposal; alternate water supply; GV pumping with emsity; Captured; captured; supply out the SM diversion and sauce reduction program.	Containated codio will attain a torest fish. Cod will initially to treated to Atta. then to levels established by	11,000,000 - 15,000,000 056/E5/66 055/E5/66
Fruin Legeth, PA	A 66/02/02	151	GJ. Sy, and soll conteminated with asphalt sludge, acid liquids, waste all, resins, fly ash, coal fires, sufferic and sufferic and suffericum waste	Mat previded	Access and efficient dispess of liquid lapsan contents with physical stabilization of lapsand. efficant pend cleanup, and dispession.	Net provided	8,456,6 <del>90</del> 0.
Bruin Lagoon, PA	PA 09/23/64	2nd - Final	Soils and bedrack contaminated with acidic sludges and	17,500 yd3	Stabilization of studies and perched liquid zone; in-situ hedrock treatment; and capping	bet provided	3.695,000

SITE MANE. ST	SIG BATE	\$ -	IHRE AT / PROBLEM	ESTIMATED MASTE QUANTITY	HAJOR COMPONENETS OF SELECTED REMEDY	STAMOAIDS/ COALS	ESVIRANTED CAPITAL COSTS
Chisabn Creek, VA	<b>36</b> /06/40	3	(M, sall (disposal) plis with fly ash), and Su contaminated with trace metals and inorganics	6 A	Capping (2 pits); capping and upgraters and diversion of one pit; alternate union supply, possible dead restrictions; and Gu drai:ppc and ensite irealment	Action for checkel complies with the MACE for presention of fresh water 1100 1100 1100 1110 1110 1110 1110 11	119.630
Delamire City PVC, 86	151 99/91/66	<u> </u>	GM, SM, and soil confaminated with WCS including ICE	25, 680 yd <sup>3</sup>	Excavation and removal of containated soils and Sludges with offsite dispessi; capping; But purp and treatment; and alternate water supply	Mecentry ualls will operate concentrations of vor. (BC. and VCC rests.) e.g.,	
Beuglassville. PA	<b>4</b> /2/4		Sail and sediments contaminated with VGCs. pesticions. organics including PAMs and PCBs. and metols	Hat provided	Contablidation of contablidati	Bot previded	\$\$\$ <b>.</b> \$\$\$

SITÉ MANÉ, ST	ROB SIG BATÉ	GPERABLE UNIT	THREAT/ PROBLEM	ESTIMATED HASTE QUANTITY	HAJOR COMPONENETS OF SELECTED REMEDY	STANDACES/ GDALS	ESTERNIEB CAPITAL COSTS (Å)
Burlington Morthern, Mi	96/94/96	136 - Final	GN and soil contaminated with organics	6	Excavation and onsite aerabic breakdown and transfermation of centaminated soils and sludges; and ensite MCRA capping	fessible goals ord detailitation of sells as delined by the microton test and achieve test by and bensen extractable concentrations to the treatment ord than cencentrations present in the	\$5.2. 00.00
Sualtation, HI	<b>4</b> /ec/ <b>4</b>	lst - final	GA. Su, sell, and sediments contaminated with metals and transpanies including cyenide	6 p	Excevation. salidification/ fixation, and offsite dispess of metal hydraxide sludges; and GV pump and treatment	Gu cleanus based on current lemost regulated concentrations for chemical criteria will to criteria will to chemical acceptuble Chrenic Interioration levels, and thought for levels, and thought for levels an	1.286.788 - 1.318.408 (Capanding on Obstance to Opsile REA Parting
Byren/Jahrsen Salvage, IL		<b>±</b>	Soil contaminated with VOCs. organics including PCBs, and matals including test and arsenic	Hot provided	Excavation and office disposal of drums; effsite fich disposal of EP toxic sells and, if position of treatment of liquids; and in-situ treatment of contaminated soil	Remody consists of trainment of soil that accords to times the destrict and ensite storable of soil trainment of soil tentaining trainment of soil tentaining trainment of soil tentaining	0,010,010

STIE NAME, ST	SIG BATE	OPERABLE UBIT	THREAT/ PROSLEM	ESTIMATED WASTE QUARTITY	MAJOR COMPONENETS OF SELECTED REMEDY	STANDAEDS/ GOALS	ESTIMATED CAPITAL COSTS
Cham-Dyne, OH	67/05/25 1st	lst - final	GH and soil contaminated with VOCs. erganics including PCBs. and metals	Bot provided	Gy pump and treatment; demolition of ensite buildings; removal of selected soil; and RCRA capping	Cu will be treated to cite up/l total vocs to exet background lovels.	11,600,000
Cross Brothers,	03/25/05	<b>E</b>	Soll contaminated with VOCs	Not provided	Excavation and of of site disposal of sufficial and buried waste materials, and visibly contaminated soil	Not previded	877,726
Complery Bump, MI	\$9/11/60	ž	GW and soil containated with VOCs. and organics including PCBs	Hat provided	Exception and offsite MCRA disposal of 250 drums	Bot previend	1,003,261
Charlevelk, MI	96/12/84 IEM	ē	GH Contaminated with VOCs including TCE and PCE	Het previded	Provision for a permanent alternate water supply	Hat provided	%, 550, 066
Charlevolk, MI	<b>99</b> /10/85 2nd	2nd - Finst	GA containated with VOCs including TCE and PCE	Motor of the second of the sec	Plume discharge to take Michigan under matural flow cenditions; long-term plum menticating; and institutional controls on private	Under natural flos conditions, NCE and PCE will mack 0.01 ug/l, respectively	O

SITE MANE.	. 51	809 SIG BATE	OPERABLE URIT	THREAT/ PROBLEM	ESTIMATED MASTE QUANTETY	MAJOR COMPOLEMETS OF SELECTED REMEDY	STANDAEDS/ GDALS	CEPITAL COSTS
Flalds Brook, Gt	8	98/8740	11	Breek sediments contaminated with VOCs including TCE and PCE, organics including PCBs, and metals	24. 04. 31. 31. 32. 32. 32. 32. 32. 32. 32. 32. 32. 32	Excavation, and insite disposal of contaminated sediments Excavation and thomas of contaminated sediments disposal of residuals	Sediments will be enclosed to be a concer fish or to be morting for the first or to be enclosed for the first or	36, 103, 066
Forest Wasle. MI	Ste. MI	82/29/80	ă	Soil contaminated with organics including	Hat provided	fienc t ng	#at providad	000.000
forest Waste, MI	ste, H	64/36/86	2	Soils and sediments contaminated with organics and metals	6 00 00 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1	Excavation of sludges and removal of aqueous lapsen wastes with solidification and offsite BERA disposal	Cleany lavels will achiavo on ingestion rate of 0.16/64y of soil for a 70 to ocult	1,395,000
Linke Sendy Je. III	= .* .*	<b>34/32/68</b>	lst - final	SM, soils, and sediments contaminated with VOCs, organics including PAMs, and metals	2.566 yd <sup>3</sup>	Seil capeine: alternate water supply; ensite consalidation of sediments; and institutional centrols including deed restrictions on aquifer usage	Sediments with containing the 16° brish section and containing excepted and consolidated	0.747.000
tasalle Electrical	# #	98/52/10	151	Offsite soils contaminated with VOCs. and erganics including PCBs	25, 530 yd <sup>3</sup>	Excavation and onsite incineration of offsite soils	Excevetion and incineration of soils with grouter than 6 eg/to 900s in the first 12 inches of soil and ereater than 10 mg/tg in soils	26,400,000 (present worth)

SITE HAME, ST	ROB SIG DATE	CPERABLE UNIT	THREAT/ PROBLEM	ESTIMATED MASTE QUANTITY	MAJOR COMPONENETS OF SELECTED REMEDY	Stardaeds/ Goal S	ESTINATED CAPITAL COSTS (\$)
Main Street, IN	151 <b>38/29/70</b>	35	Gu contaminated with vOCs including TCE and PCE	Kol erovided	GA treatment using air stripging with discharge to water treatment system and drinking whier distribution system	The air stripping system is dasfend to achieve a solute removal of VCE.  BL. F. removal of VCE.  removal of 1.1-CEE	1,105,000
Helemora Landfill, Hi	<b>89/30/64</b>	3	Gu and sell conteminated with VOCs including ICE and PCE, and metals	18, 158 yd <sup>3</sup>	Excavation and offsite thermal destruction of mastes from areas 1 and 4	Gu and soil cleans tergets will be established in the	qi,seo,eoa (present worth)
Harris Arsenic. Ha	35/0/0/00	1st - finel	Mone	Rone	No further action	that provided	O
Laskin Poplar Oll, OM	151 99/60/00		SM and soil contacted with VOCs. and organics including PCBs and PAMs	Hot provided	Incineration of conteminated waste oil; and treatment of conteminated waste water	Het previded	0.033.088
LeHillier/Menhalo, 89/27/85 ist	. 89/27/85	lst - final	GH and soll contaminated with VOCs including ICE	not provided	Gu pump and frastment using air stripping; extension of LeMiller mater supply system to affected areas; and abandomment of	The goal of plumo extraction and trategat to consistent with the 10° center risk concentration for TCE 2.0 mg/l	000.000

SITE HAME, ST	ADB SIG BATE	OPERABLE UNIT	THREAT/ PROCLEM	ESTHATED HASTE QUANTITY	MAJOR COMPONENETS OF SELECTED REMEDY	STANDARDS/ GOALS	6511MATED CAPITAL COSTS (\$)
1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1		156 - Final	Gd, soll, and sediments contaminated with VOCs, organics, and increasics including asbestos	Mot provided	Capping: installation and operation of extraction/containment wells to demater landfill and eliminate leachate; onsite GM and leachate treatment using biological disc. sodium hydraxide precipitation, and granular activated carbon; onsite consalidation of contaminated sediumnia disc.	Mot provided	10, 79 <b>0, 600</b>
Merthernatre, MI	99/11/86	<b>2</b>	GH, sell, and sewer sediments contaminated with metals including chromium and cadmium	Mot previded	Excavation and affilts disposal af soil and sewer line to privately-emmed accent for a facility; cloaning dust and hazardeus residue from building floor; brighting up of 188 ft <sup>2</sup> af floor and dryvell, sampling soil, excavation, and disposal of any centaminated debris and backfilling of area with clean soil	Excavation of soils and soils and sodiments will meet responso objectives of chromium 50 mg/kg	75,600

SITE NAME. ST	SIG BATE	OPERABLE UNIT	THREAT/ PROBLEM	ESTIMATED WASTE QUANTITY	MAJOR COMPONENETS OF SELECTED REMEDY	STAMBALDS/ GOAL S	ESTERMTED CAPITAL COSTS (\$)
90 E E E E E E E E E E E E E E E E E E E	121 197/07/08	Bst - Final	Gu and soil contrainated with VOCs and organics including PCBs	Mot provided	disposal and offsite disposal of 95 percent of 95 percent of soil contaminants; Guerteation and treatment using granduler aquifer use restrictions; and pravision of public water supply to residences	Sells contembaled with base/noutrol companies will be removed to be to the total total to the total to the total	5,91 <b>7,890</b>
Corp., IL	15/18/84 156		Gu, sail, end river sediments containated with VOCs, and organics including PCBs	Not provided	Excavation and offsite disposal of PCB centaminated materials; construction of ensite centament cell for mederately contaminated PCB material; capeing; GM diversion; carstruction of clay-lined denatering laguent and treatment of supernatant with discharge to harber	Met provided	21,570,000 (present worth)
Deilly Tar & Chamical, PM	05/30/06 2nd	Pure Pure Pure Pure Pure Pure Pure Pure	GV and soils contaminated with VDCs and organics including PAHS		Cut pump and treatment; copping and filling of graced wastes; and discharge of anythe to sever	Frinting mater criteria for Phila mere developed through \$1810 and EPA consultations	Cost cost cost cost fully cost fully

SITE MANE, ST	800 S1G BATE	OPERABLE URIT	THREAT/ PROBLEM	ESTIMATED MASTE QUANTITY	MAJOR COMPONENETS OF SELECTED REMEDY	STANDARDS/ GOALS	ESTIMATED EAPITAL COSTS
Schmalt Bump. VI	<b>64/17/66</b> 1st	) st _	Soil contaminated with VOCs. organics including PCBs. and metals including chromium	3 . Soo ve	Excavation and office disposal of contaminated building debris and sediments with devalating	removed in the detailering process to below 8.5 ug/to	3,030,300
Seymour, In	99/30/66	15 £	Gd and soil contaminated with VOCs. erganics. and metals	161.696.666	GW extraction and trateget with discharge to POTW	Water dischargo will conform with POTM standards	300.000
Spieselberg Landfill, MI	<b>63/30/86</b>	181	Gd and soils contaminated with VOCs. erganics, and metals	5,600 yd <sup>3</sup>	Excavation of waste materials with offsite incineration of liquid paint sludges and offsite disposal of solid paint sludges.	Excavation of old materials exceeding a 10-6 excess cancer of the	15,771.000 - 10,395.000
Verona Hell Field, Hi	68/12/86	2	GH and soil contaminated with VOCs including TCE and PCE	Not pravided	Soil treatment using enhanced velatilization; and GV pump and treatment using existing air stripper	it is esthmoted that within 3 years. Gu contamination will decress to 100 ug/1 WEES	080.020,
Maucanda Sand & Gravel, II	\$1/64/60	# # # # # # # # # # # # # # # # # # #	G4. S4, and soil contaminated with VGCs, organics including PCBs, and metals	Het previded	Installation of leachaite collection drains; provision for leachait disposal at sewage treatment plant or at an offsite hazardous waste treatment facility; regrading with clean soil cover	beeviend	000 CO3 1

SITE BANK, ST	SIG BATE	OPERABLE URIT	THREAT/ PROBLEM	ESTIMATED LASTE QUANTITY	MAJOR COMPONENETS OF SELECTED REMEDY	STANDARUS/ COAL \$	CESTINATED CAPITAL COSTS (\$)
Bayes Bonfeuse.	80/12/00	184	CM, seil, and sodiaments contaminated with creesete	Mot provided	Offsite disposal of creosole maste	Mat provided	<b>039°8</b> 03
Dio-Ecalogy Systems, TX	<b>14/8/1</b>	- 5100	Seil and Su contaminated with VOCs including TCE, organics including PCBs, and metals	Met provides	Construction of ensite dispesal cell with synthetic liner. leachate cellection system, and final cover; stabilization of waste and ansite placement in cell; elevation of site above 180-year flood plain; and fencing	Met pravided	D, 709, 689
Geneva Industries, TX	<b>4</b> /11/4	lst - flad	GH and soils contaminated with 90Cs including ICE, and organics including PAHS and PCBS	. 500 yd3	Excavation and offsite disposal of contaminated soil and drums; capping; and GM pump and treatment using carbon with discharge to adjacent flood control channel	Sell will to exceeded to FCDS life mg/kg. CM will bd trobted to below TCE 1 wp/1	10,090,086
Highlands Acid Pit. TX	<b>66</b> /25/84	<b>x</b>	GW. seil, and sludge conteminated with VDCs, organics, and	Kot provided	Excavation and offsite disposal of waste material; backfilling and seeding; and fencing	Bet provbead	2, co <b>), eee</b>
HDTCO, TK	03/18/08	13.	Soil and SH contaminated with organics including PCBs	Not provided	Offsite biological treatment of conteminated pit water; offsite TSCA incidention of presention of presenting the present of presenting the present of presenting the present of presen	Met previded	999 '901' 25

SITE MANE, ST	EDB SIG BATE	OPERABLE UNIT		THREAT/ PROBLEH	ESTIMATED MASTE QUANTITY	HAJOR CONTONENETS OF SELECTED REMEDY	STANDAEDS/ GDALS	ESTIMATED CAPITAL COSTS
Sikes Oispesal Pits, IX	\$8/91/6	186 - final		GM, soll, and SM SM Contaminated with VOCS and organics	150.000 yd	Excavation and onsite incineration of sludges and soils with ensite disposal of residual ash; banning usage of ensite upper aquifer during natural attenuation; and Sutrealment, as necessary, with discharge to river	Soil and Studess will be excevoled to 10 mg/kg vacs. The upper sculfor will be etternabled to 10 threan	\$02'317,CG
01d Inger. tA	<b>6</b> /57/6 <b>8</b>	lst - final	2	Gut and set! contaminates with WGS. and metals		Graite land treatment of heavily contaminated sell and sludges; ensite centainment and capaing of slightly centaminated soils; closing and sealing ungrouted ensite well; G4 pump and treatment; and fluid treatment; and fluid erfsite discharge	Previous .	D. 0 70. GGD
Tar Creek, OK	14/94/98	15t - Fi	1	EM. SM. and sediments contaminated cutt) acidic maste mater, metals, and organics	bat provided	Diversion and diking at two major infler areas; and plugging of 66 wells	net provided	<b>©</b> ©0°C00
Triangle Chemical, TX	\$ <b>0</b> /11/ <b>98</b>	. Final .		Soll containated with VOCs	Met prevides	Incineration and deep well injection of the tank and drum contents; amechanical peration of contaminated soils; decentamination of all ensite	Soil will to persion to beckpround lovels	305,06 <b>9</b>

			anor and 1997
ESTIMATED CAPITAL COSTS	thidave loped	3,580,175 ( <i>Grese</i> nt worth)	2, 455. 475.
STANDAEDS/ GDALS	Excevation and dispassive all contembrated above PAH 180 Co/ko	bot provided	ket previedd
MAJOR COMPONENETS OF SELECTED REMEDY	Demolition and purchasing of 6 homes with pravision for permanent relocation of residents; onsite censelidation of surface soil with temperary capping; excavation and disposal of PAM contaminated soils at apprapriate facility available; backfilling and cavering; and natural GM atternation	Offsite disposal of bulk liquids and sami-selles by deep well injection; and ensite drainage central	Excavation and offsite dispesal of buried wastes and centaminated soil; backfilling, of and saile; and seeding of the site; angension of the monitoring well network and blancual Ga testing; and washing interior surfaces.
ESTIMATED WASTE QUANTITY	84.996 vd3	Not previded	Hot previded
THREAT/ PROBLEM	Soils contaminated with VOCs. organics including PCP and PMRs, and inceganics including creosote	GJ and soil contaminated with VOCs and pesticides	GJ and soil contaminated with VOCs and pasticidas
OPERABLE Until	<b>1</b>	ž	2nd - Final -
BOD SIG BATE	151 36/96/60	68/24/83	- PW 18/86 500
SITE MOME, ST	United Cressating Site. TX	A146×. 1A	A166x. 1A
1			

GST BRATEB CAPITAL COSTS	920,000	000.23	go, gos, ees (grasent morth)
STANDARDS/ GDALS	Hot provided	Hot provided	<b>हैं।</b> कृपक् । हैं उठ व
HAJOR COMONENETS OF SELECTED REMEDY	Transportation of highly contaminated soil from other sites for storage in an ensite interior storage facility (to be constructed); and restoration of other sites by excavation and temperary relected residents	Callabam Promerty: stabilization and erestem central; removal and disposal of plastic cover and caver; haid-demn blocks; removal and salvaging of the barbed-wire and chain link fences; and graval removal fesalia Frametk; excavation and offsite disposal of contaminated soil, drum, cans, and ether debris; and soil testing and soil testing and	Excavation and ensite interto storage of diexin contaminated soil; and excavation, transportation, and offsite land disposal of soils containing nondiexin waste
ESTIMATED HASTE QUANTITY	Mot provided	tod trend tr	Hot previded
THREAL/ PROSLEM	Soil contembated with dioxin	Soil and Su- contaminated with WGS. organics. and pesticides	Soil contacted with VOCs. dioxins, and matals
OPERABLE UNIT	<b>3</b>	ž	<b>9</b>
816 GATE	<b>4</b> /11/10	24 - 17 - 17 - 17 - 17 - 17 - 17 - 17 - 1	99/62/60
SITE MANE, ST	Times Beach, MD (Interim Storage facility)	Entrathe, M	Ellisville, MD

ESTIMATED CEPITAL COSTS (\$)	999.08	1.912.480	PDP rospensibility	262.719	Col provided
STANGALIDS/ GDALS	Standards Cor Standards Cor Spannedial Action at Inactivo Uranium Protossing Sites*	Standards for Standards for Benedial Action at Incelvo Uranium Procossing Sites	Not provided	to EPA driction to EPA driction wher standords for arsente 0.000 mg/h	Bat provided
MAJOR COMPONENETS OF SELECTED REMEDY	Temperary leaving of centaminated material in place; institutional centrals; and routing maintenance	Excavation and offsite disposal of contominated soils and debris; or Excavation, stabilization and temperary ensite consolidation of contominated soils	Alternate mater supply; and institutional contrels prehibiting	Construction of a now well end discribution system; and flushing and testing residential plumbing systems	Replacement of household water supply appurtenances: and on-palmy testing of residential plumbing systems
ESTIMATEO MASTE QUANTITY	E D. 805.01	7.660 yd <sup>3</sup> (sel <sup>3</sup> ) 260 yd <sup>3</sup> (demlished bulldings)	Not previded	Mak provides	Mat provided
IMEAI/ PROBLEM	Asphalt contaminated with radium	Soil and buildings contaminated with radium	Soil and Gd contaminated with inarganics including cressote, and erganics	Go and soil containated with metals including arsenic	CM and sell contracted with metals including arsenic
OPERABLE UNIT	12	P.	151	*	2
SIG BATE	\$0/52/00	29/30/80	<b>99</b> /32/ <b>60</b>	18/11/00	FE 19/10/18
SITE MANE, ST	Derver Radium Site Streets, CO	Derver Redium/ NORCO. CO	Libby Ground Mater, MT	Militam. Mf	Militan, M

SITE NAC. ST	SIG BATE	OPERABLE UNIT	THREAT/ PROBLEM	ESTIMATED WASTE QUANTETY	MAJOR COMPOSEMETS OF SELECTED MEMEDY	Starbaeds/ Coals	ESTIGATED Capital Costs (\$)
Union Pacific Railroad, un	98/35/98	ī	Ch and soll contaminated with organics including free, and increasing creesele	Greater than 706,000 yd	Mochanaling of creets of pump and treatment with carbon adsorption with discharge to river; and slurry wall barrier construction	Mot previend	<b>0</b> 99° C33° ℓ
Modbury Chemical, CO	67/19/85	121	GH, soil, and sediments contaminated with pesticides, metals, and erganics	Mot previded	Excavation, offsite transportation, and incinuitation of highly contaminated rubble and soil with disposal of residual asts; and backfilling with clean soil, regrading, and reventation	Contaminated soils will be treated to 3 mg/kg and contaminated ruchble to late   gastichics   100 mg/kg	8,45 <b>0,0</b> 00.
Celter Chamical Morts, CA	16/96/91	Ma	Gu, Su, and soil soil centralnated sith metals and mining waste	Hat provided	Offsita transpertation and dispession telling piles and contabinated soil; and conduction of RI/FS	Het provided	340 <b>,</b> 000
Calter Chemical.	<b>21</b> /36/ <b>15</b>	Znd - Final	Strand seil cententented with metals including cadelin and arsenic	Hat previded	Excavation and MCRA office disposal of contaminated soils	Action levels for sell will be based on Hallond Handr God of the based on McLa or CHIEFTA BUNGT CHIEFTA WIND CO based on Stradords for the predection	9.65 <b>5.330</b>

SITE HAME, ST	808 S1G BATE	OPERAGLE URIT	THREAT/ PROBLEM	ESTINATED HASTE QUANTITY	MAJOR COMPONENETS OF SELECTED REMEDY	STANDARUS/ GDALS	CAPITAL COSTS
Del Morte, CA	121 29/00/00	lst - final	Gu and soil contaminated with VOCs. pesticides. and metals including chremium	700 yd <sup>3</sup>	Excavation and removal of soil; GU treatment with discharge to POTM; and disposal of chromium-rich waste bring to MCRA facility	Cleans tovols will meet the le-b cancer rish level and MCLS under Stada	1,240,688
Iran Mountain, CA 10/81/86			Su runeff from mountain centaminated with acid mine dealnage censisting of sulfuric acid and metals: fish and sediment are also affected	2.5 acres (to be capped)	Capping of selected cracked and caved ground areas; and dam enlargement	Cleanup progressific be dastened to meet EPA Melor Guality Critorio for Protection of Aquatic Life For the "warst coso" condition of 1970	COST)
Jibbeca Junkyard, CA	30/44/30	ist - final	Set1 centaminated with VOCS. matuls including lead, zinc. and cepeer. and erganics including PCBs	Mat provided	Encavalies and office disposal of conteminated soils	Soils centaining lead abovo 100 mg/kg mill to ancavated	1, 46 <b>6, 686</b>
MCGoll Site, CA	04/11/64	<b>3</b>	Soil containated with VOCs and increants including sulfur disorted hydrogen sulfide, and arsent	Mot previded	Excavation and office disposal of wastes and soil	Bet previded	21,500,000

SITE MANE, ST	SIG BATE	OPERADA E URITO	THREAT/ PROBLEM	CSTINATED MASTE QUANTITY	MAJOR COMPONEIETS OF SELECTED REMEDY	STANDAESS/ GDALS	ESTIMATED Capital Costs (A)
Hountain View/ Glebe, AZ	151 12/07/99	1st - Finel	Soll Contaminated with asbestos	Not provided	Permanent relocation of residents: onsite burial of centainerized mabile homes: and fencing	Het provided	432,698
San Gabriel/ Area I, CA	93/11/50	į	Gal contaminated with VOCs including TCE and PCE	Hot previded	GJ pump and treatment using air stripping; and canduction of RI/FS	Not provided	• ଜଣ ଓ ଅଟେ
Stringfellow Acid Pits. CA	07/22/01 IBH	i	Gu, Su, and sail contaminated with astals and organics	Not provided	fercing: cap maintenance: and effice leachald dispesal	Het previdad	2,406,600 (prosent worth)
Smage ler Hount à in. CO	99/35/86 131	ī	Gu and soil contaminated with catalian and matals including lead	6 P	Excavation and permanent orste mena disposal of solis; soil capping; and alternate water supply	exite ten and exite sellent extension exite ten and exite ten and exite	6,016,860

SITE MAME, ST	SIG BATE	OPE BABA E UNIT	THREAT/ PROBLEH	ESTIMATED WASTE QUANTITY	MAJOR COMPONENETS OF SELECTED REMEDY	STANDAEDS/ GDALS	CAPINATED CAPITAL COSTS
Ponder's Corners.	<b>19/9/</b>	Z	Gu and sail contactnated with WCs including TCE and PCE	not provides	Centinued operation of MI-M2 trainment system; installation of variable-frequency controllers on well purp malers on well purp malers on well charding of for actives on trainments; charding of for actives on trainment tower; installation of now mentioning of outsition wells, upgrading of activities wells, upgrading of activities and placement of social tanks and drain field piping; and placement of social activities of social	The remedy will meet the recommended eccupational our levels for VDCs which are based on OSMA Standerds	914.916
Gueen City Farms, wh	10/24/46 156	·	SM, soll, and sediments contaminated with VOCs including TCE, or sold matching the luding and matching chromium and lead	22,080 yd <sup>3</sup>	Exception, and stabilization, and affite dispess of sludger, sediments, and caping	Bot previded	3,430,00 <b>0</b>
South Tacoms Charmel Well 12A, MA	03/10/63	<b>&amp;</b> :	Cateminated with VDCs inclusing TCE	Mot provided	Ga pump and trastment using air stripping	Hat provided	000°CO2°1

SITE MANE, ST	ECO SIG DATE	OPERABLE UNIT	THREAT/ PROBLEM	ESTIMATED MASIE QUABILTY	MAJOR COMPONEMETS OF SELECTED REMEDY	STANDAEDS/ GOALS	CSTIMATED CAPITAL COSTS	
South Tacoma Channel Hall 12A, MA	P6/01/05 2nd	Z	GJ and seil contaminated with VCs including ICE and PCE	Mat provided	Continue operation of ABM; construction of a Ed treatment system; excavation and offsite dispessions and emintenated soil with soil flushing; and emintenate of institutional centrals	Specific 634 cleans goods to vo mat been established. Att inment of the 10 fish reach frecomended	ଜଳ <b>ତ</b> ୍ତେର <b>୍</b> ଷ	
Tofidahi Brums.	151 36/66/69	1st - fiml	Hone	Bet previded	to further action with GA manifering	Not previded	O	
United Chrome, Off 69/82/86 1st	<b>4</b> /21/ <b>6</b> 0	186 - Finat	Contaminated units materials including chronium	350 tests (offsite dispersal)	Excavation and offsite disposal of sails: Flushing of sails above shallow Cu table; and Cu pump and procipitation with discharge to FGTV or Su	The chreshum cleans criterio squifer is 0.05 mg/1 end 10 mg/1 for the unconfined zeno. A freshman effluent concentration of chreshum is chreshum is expected to be	, sco, coo	