ASSESSMENT OF STORM DRAIN SOURCES OF CONTAMINANTS TO SANTA MONICA BAY

VOLUME II
REVIEW OF WATER AND WASTEWATER SAMPLING TECHNIQUES WITH AN EMPHASIS ON STORMWATER MONITORING REQUIREMENTS

by

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PREFACE AND ACKNOWLEDGEMENTS

This report represents Volume II from a series of four volumes of reports which form the basis of a pollution assessment and monitoring plan for Santa Monica Bay. Volume I describes storm drainage system land use statistics, catchment areas, existing water quality monitoring data, rainfall data, NPDES permit information for existing permits to storm drains, and contaminant mass emission estimates, based upon land use modeling. Volume II reviews sampling techniques, including sampling equipment, and other aspects associated with sampling such as a quality assurance plan. Volume III presents the proposed monitoring plan. Volume IV addresses best management practices as they apply to the Santa Monica Bay area. The first draft of this volume was issued in September 28, 1992.

The contract was performed by UCLA and Woodward-Clyde Consultants (WCC). Professor Michael K. Stenstrom of the Civil and Environmental Engineering Department, UCLA and Eric Strecker from WCC's Portland office were the project managers. There were several key individuals from both UCLA and WCC who assisted with the project; they include Sim-Lin Lau and Kenneth Wong (UCLA) and Lou Armstrong, Gail Boyd, Carol Forrest, and Joan Kersnar (WCC).

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ABSTRACT

This report is a literature review of surface water and wastewater sampling techniques, with an emphasis on applications for storm drain sampling. The report discusses sampling program objectives, statistical approaches, sample types, sampling equipment, flow measuring techniques, special problems in sampling specific biological, chemical, or physical parameters, and quality control/quality assurance plans. A variety of sampling equipment is reviewed, such as bottle samplers, messenger-activated samplers and automatic samplers, among others. Additionally several case studies are presented. The case study review is based upon Woodward-Clyde Consultants' previous experience in monitoring storm drains or developing monitoring programs.

This volume complements Volume III of this four-volume report series. Volume III provides more specific information on the development of a storm drain monitoring program for the Santa Monica Bay watershed.

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1.0
INTRODUCTION

1.1 OBJECTIVES

This review outlines methodologies for sampling storm drains (urban runoff). It is not intended to address any site-specific sampling requirements. A general overview is provided, followed by several case studies of specific programs and their associated procedures and sampling equipment. It was produced as part of a contract to develop a storm drain monitoring program from the Santa Monica Bay Restoration Project to team comprised of the Civil Engineering Department at UCLA and Woodward-Clyde Consultants (WCC).

The following chapters address the sampling program, statistics, sample types, sampling equipment, sample storage and preservation requirements, flow measurement, special techniques required for certain contaminants (e.g., oil and grease), and quality assurance/quality control plans.

1.2 SAMPLING PROGRAM - OVERVIEW

The main objective of any sampling program is to collect a sample which is representative of the state of the media under study. A sample is considered to be representative if the sample possesses the same qualities or properties as the media being sampled at the point and time of collection. A set of representative samples is considered to be valid if it provides a true representation of the temporal and spatial variations of the quantity of the water body for the duration of the measurement program (Wilson, 1982).

No single sampling program can apply to all types of samples (e.g., surface water, ground water, coastal wastes, municipal wastes, etc.). However, each sampling program should consider at least the following criteria (Krajca,1989; Barcelona, 1988; US EPA, 1982) :

- objectives of sampling program
- analytes of interest
- location of sampling points
- frequency and time of sampling
- sample collection, e.g., selection of sampling equipment, sampling methods (grab or composite), etc.
- sample handling, e.g., preservation,
- field determinations, e.g., in situ analysis of unstable constituents, flow measurement, etc.
- sample storage and transport
- quality assurance/quality control (QA/QC)
- health and safety cost

In addition to the above mentioned criteria, the validity of samples in terms of the sampling sites, number of samples, time and frequency of sampling should be considered based on a statistical approach if the objective is to accurately characterize pollutant loadings and/or concentrations.. The above mentioned criteria is not all inclusive. Additional components may be added into the sampling plan depending on the objective of the project. The following section discusses the basic required criteria of sampling program.

1.3 SAMPLING PROGRAM OBJECTIVES

The objective(s) of a sampling is the first step in planning of a sampling program. In general, there are four major reasons for sampling and analyses program: planning, research/design, process control, and regulation (including detection, verification and enforcement). A comparison of the sampling program based on these four different objectives are discussed by the US EPA (1982) and is summarized in the Table 1-1. For the purposes of this report, the objective of the sampling program is to provide good monitoring procedures for the evaluation of the pollutant load to Santa Monica Bay from storm drain and runoff flows. A work shop held in conjunction with this project concluded that the proposed monitoring plan should have two objectives: assessing the mass emissions to the Bay, and providing more information on the land-use pollutant runoff characteristics. Thus, the sampling plan , which involves the selection of the types of samples (grab and composite samples), sampling techniques, sampling equipment (manual or automatic), sample preservation, field analysis (e.g., *in situ* analysis, flow measurement), etc., should be based on this objectives.

1.4 ANALYTES OF INTEREST

The selection of constituents of interest to a particular study depends on the objectives of the monitoring program. Examples of the water quality parameters (which include organics, heavy metals, nutrients, etc.) are given in the Appendix A. In cases where insufficient information is available, a staggered program is usually implemented. A full suite of parameters is generally carried out during the initial phase of the monitoring program (or during the first several storms). A reduced suite of analyses can be performed if the results of the preliminary sampling show the absence or low levels (as compare to applied criteria) of specific parameters. In addition to the parameters given in Appendix A, other constituents can also monitored if their presence is expected in the storm water.

Once the analytes of interest are chosen, appropriate analytical methods for specific parameters must be selected. This consideration is not only important for proper sample collection and handling procedures and cost minimization, but also to avoid matrix interferences for certain types of samples. In addition, the minimum sample volumes and types of sample preservation and handling procedures also depend on the detail and specificity of the proposed analytical program (Barcelona, 1988). For example, the sample volume needed for organic analyses differs from those for inorganic analyses.

The selection of methods of analysis generally is left to the experience of the analyst. General guideline for the selection of analysis method were discussed by Mancy and Allen (1982) as follows:

- total number of analyses,
- frequency and geographical scope of analysis,
- required rapidity of analysis,
- sensitivity and detection limit,
- selectivity and interferences,
- constraints on accuracy and precision.

Table 1.1 Sample Program Objectives (EPA, 1982).

Objectives	Planning	Research Design	Process Control	Regulatory
Scope	General	Specific	Specific	Specific
Goals	Establish trends Benchmarks Background levels	New developments Modifications Improvements	Operation quality control	Verification compliance enforcement
Effort	Non-intensive and unlimited	Intensive and limited	Non-intensive and limited	Non-intensive and limited

The above mentioned requirements give an insight into whether the analysis should be carried out in the laboratory or in the field. In general, in situ analysis is carried out if the conditions of the analyte of interest are unstable and need direct measurement at the sampling sites. These unstable determinads include temperature, pH, dissolved gases (dissolved oxygen).

In addition, the sampling modes, either manually, automatically or through a remote sensing system, can also be determined based on the costs and availability of manpower and equipment. Comprehensive discussion of this topic is given the *Examination of Water for Pollution Control* (1982).

1.5 SAMPLING LOCATIONS

The sampling program objectives usually define the approximate locations for sampling, e.g., the confluence of two stormdrains drains. However, the stated objectives give only a general indication, e.g., when the effect of an effluent on river water quality is of interest.

The quality of water varies from place to place in most water systems. Therefore, locations appropriate to the information needs of a particular program must be selected so that the samples collected from various sampling points can be representative as a whole of the system. No specific guidelines can be given due to the extent and nature of spatial heterogeneity that may vary with time and also differ from one system to another. However, certain general points still have to be considered when the selection of sampling locations is make.

The selected sampling locations must be representative sites. Factors influencing the selection of sampling locations are (US EPA, 1982; Wilson, 1982) :

1. Homogeneity of the water, wastewater or stormwater.
   Homogeneity is generally enhanced by the turbulence and good mixing resulting from a hydraulic jump or flow over a weir.

2. Non-homogeneity or heterogeneity of the water , wastewater or stormwater.
   Generally caused by poor mixing (e.g. vertical, thermal stratification of lakes and reservoirs), and non-homogeneous distribution of the chemicals caused by their different densities (e.g., floating oils or settling suspended solids), and also certain chemical or biological reaction (e.g., pH changes caused by the growth of algae in upper layers of a body of water).

3. Convenience and accessibility of the sampling locations.
   For stormwater such considerations include impact of vandalism, safety to workers, such entering confined spaces (e.g., manholes), and accessibility in all types of weather. Sampling in confined spaces always requires multiple team members and additional safety equipment. Another important consideration for stormwater sampling is the distance among sampling locations. Widely spaced locations may be best from the standpoint of collecting the most representative samples, but may be expensive because of travel time or the need for additional sampling teams.

4. Flow measurement.
   Flow measurement presents a particularly difficult challenge for stormwater monitoring. Often there are no provisions for measuring flow rates.

Conventional flow measuring equipment such as weirs or flumes is usually unsuitable for stormwater because of the increased head loss (resistance to flow) that the weir or flume causes. The increased head loss decreases the maximum capacity of the storm drain that may result in a loss of flood protection.

5. Other considerations
Sampling locations near the boundaries of water systems generally should be avoided except when these regions are of direct interest. Coastal stormdrains are often affected by tidal flows, which makes representative sampling nearly impossible due to the dilution of salt water. Stormdrains are often located in areas which have higher probability of violent crimes and vandalism. Extra precautions are required.

Generally, a preliminary investigation needs to be carried out to assess the degree of non-homogeneity of the proposed stormwater location. If such tests show that quality is homogeneous, one position for sampling may suffice; if heterogeneity is present, two approaches can be used to select the appropriate sampling locations (Wilson, 1982). The first alternative is to sample and test different locations until a suitable homogeneous location is found. For the second alternative, the location originally selected is used, and samples are routinely taken from several positions chosen so that they are properly representative of the quality at the location; the individual results are then weighted and averaged according to a suitable procedure (e.g., volume or flow weighting, etc.). The first alternative is usually preferable due to simplicity.

For the consideration of the spatial distribution of sampling positions, the hydraulic conditions can be characterized approximately as homogeneous, stratified, plug-flow, showing longitudinal mixing, showing lateral and longitudinal mixing, and patchy (e.g., in the distribution of photo plankton). The hydraulic conditions must be considered when selected both the location and number of samples. The number of sampling positions needed to obtain the required information tends to be smallest for homogeneous conditions and greatest for patchy conditions (Wilson, 1982).

1.6 FREQUENCY AND TIME OF SAMPLING

Frequency of sampling will be site specific and no general rules can be provided. However, several important considerations exist for determining sampling frequency: economics, regulatory requirements, and timing. The frequency of sampling is the most significant cost multiplier in a sampling operation. Certain frequencies of sampling are set by regulation and therefore, the required sampling frequency cannot be followed, even though there may be powerful incentives to modify sampling frequency. In general, if the environmental value or quality interest varies with a certain frequency, the sampling frequency must be at least twice the frequency of that variation. In addition, if the process is cyclic in nature, samples should be collected during at least one complete process cycle, or an integer number of process cycles.

For stormwater, monitoring programs often designate a specified number of storms to be sampled and a specified number of flow-weight averaged, composite samples. To obtain the required number of samples, prediction of the number of storms and the length of the storms is required. Such predictions are far from precise and some latitude and variability of sampling is necessary.

1.7 SAMPLE COLLECTION METHODS

Selection of correct sampling technique for collecting samples is very important in order for the collected samples to be representative. A good sampling collection method generally involves selection of the correct sampling techniques and equipment, trained personnel to perform the sampling procedures and correct handling of samples. This section will only discuss some general criteria involved in the selection of correct sample collection method. Detailed discussion of the types of sampling equipment available for water sampling, sampling methods (either grab or composite) and the correct sample handling (e.g., preservation, transport and storage) are discussed in the later sections of this report.

Samples can be collected either manually or with automatic samplers. Manual sampling involves minimal initial cost, but it is only suitable for collection of a small number of samples. For routine and large sampling programs, manual sampling can be costly and time consuming. Automatic samplers are increasingly being used to monitor water quality due to their cost effectiveness, minimal labor requirement, and ability to sample at greater frequency. Selection of the correct sampling collection mode, either manually or automatically, still depends on the needs of sampling programs (see Chapter 4).

In addition to the correct selection of sampling equipment, types of sample collected can be divided into two categories, i.e., grab (or discrete) and composite samples. A grab sample is defined as an individual discrete sample collected at a particular time and place, whereas a composite sample is defined as a sample formed by mixing discrete samples taken at periodic points in time or a continuous proportion of the flow (US EPA, 1982). Factors involved in the selection of sample types are discussed in the Chapter 3. The types of sample collected are also determined by the regulatory agency. In general, composite samples are required for the NPDES permit. However, grab samples may be allowed when compositing samples is difficult due to reasons such as the absence of flow during dry weather season, or analytical requirements (grab samples for certain analysis such as oil and grease or volatile organic compounds).

Poor sample collection procedures can seriously bias chemical results (Barcelona, 1988). Analyses of blanks and controls should be carried out simultaneously with samples collected from the sampling sites so that any errors, such as contamination, poor handling of sampling equipment, etc., that arise during the sampling and analytical procedures can be monitored. The efficiency with which the operator can control the operation of the sampling equipment, maintain stable, reproducible operation conditions, and recognize a malfunction all play a significant part in minimizing these errors.

Materials selection of sampling equipment can also cause unwanted bias results. Appropriate materials used for the sampling equipment should be based on the most sensitive (i.e., volatile, and reactive) chemical constituents under investigation so that any interaction of material used with the chemical constituent of interest (e.g., leaching, sorption, etc.) can be avoided.

1.8 FIELD PROCEDURES

The sampling program must also specify the various analyses to be performed on the sampling sites. Generally, determinands such as flow rate measurement, and unstable parameters such as dissolved gases, pH, temperature, and conductivity are determined on the field. Greater number of analyses can be performed in the field if a mobile laboratory is available. The mobile laboratory is especially useful when sample degradation is fast, or when immediate analysis is required, such as tracking a spill.

In addition to the collection of representative sample, field procedures must also include proper handling and preservation of samples, good housekeeping and appropriate chain of custody procedures. Factors that are commonly considered to insure good housekeeping of the field operations include (US EPA, 1982) :

- written instructions on field sampling procedures should be completed beforehand,
- sampling equipment should also be checked prior to use in order to insure good operating conditions and cleanliness. After the sampling has been completed, the equipment should be cleaned and stored properly.
- all sample bottles should be checked to avoid possible contamination. Prior to collecting the samples, sample bottles usually should be rinsed several times with sample water.
- records of breakdown in the sampling operation, the problems encountered with different equipment and how they were resolved should be maintained.

More detailed procedures are provided by the US EPA (1982).

Conditions at the time of sampling, such as climatic conditions, hydrologic conditions, hydrogeological conditions, should also be noted during the field operations. Sampling from streams and reservoirs can be influenced to a considerable extent by variations in such things as flow rate, sediment and bed loads, temperature regime, and stratification. Sampling problems can also be caused by sudden changes of climatic conditions such as intensity and type of precipitation, air humidity, temperature and pressure, wind and speed direction. For example, intense precipitation can affect the composition of sample through direct contact with the water to be sampled, resulting in dilution or contamination (Krajca, 1989). Therefore, conditions at the time of sampling should be observed.

The safety and hygiene of those collecting the samples also need to be considered. The correct handling of sampling equipment and chemicals used during sampling operation to protect sampling personnel have been discussed by Krajca (1989). Stormwater, while usually not as contaminated with pathogenic organisms as wastewater, should be treated with the same precautions as wastewater. In sampling for many trace compounds, human contact or contact of safety equipment (e.g. rubber gloves) with the sampled water is required not only for personnel safety, but also to prevent sample contamination.

1.9 SAMPLE HANDLING, STORAGE AND TRANSPORT

Correct sample handling should be performed to avoid any unwanted contamination. Most of the Quality Assurance (QA) and Quality Control (QC) guidance manuals provide sound guidance for planning the procedures for sample preservation and handling. Selection of appropriate materials of sample containers, preservation methods, maximum holding times, and sample volume are discussed in the Chapter 5.

In general, the following guidelines for sample handling and preservation should be considered (US EPA, 1982) :

- minimize the number of people handling the sample
- if possible, have the same individual perform all operations when repetitive operations are conducted
- store the sample in a manner which insures that the parameters to be analyzed are not altered, and use appropriate preservation method(s) and holding time,
- make sure the container material does not interfere with the analysis of the specific parameters.

Efforts should also be made to handle and preserved field control samples (i. e., blanks and spikes) in the same manner as the samples collected. This precaution provides more effective identification and control of post-sample collection errors.

2.0
STATISTICAL APPROACH

The number of samples and frequency of sampling need to be considered carefully while planing any monitoring program so that samples collected will be representative. The aim of this Chapter is to give a general review of the statistical approach generally employed in determining an appropriate number of samples and sampling frequency. Detailed explanation on basic statistics is beyond the scope of this study. Information of basic statistics can be found in a numbers of statistics textbooks. References such as Montgomery and Hart (1974), US EPA (1982), and Schaum Series -Statistics are also useful.

2.1 BASIC STATISTICS TERMS

Basic statistics terms that are generally used for the determination of the number of samples and frequency of sampling include the following:

1. arithmetic mean
2. median
3. standard deviation (s)
4. variance (σ or s^2)
5. coefficient of variation (CV)
6. confidence level (α)
7. Normal distribution
8. Chi-square distribution

2.2 DETERMINATION OF NUMBER OF SAMPLES

Two methods have been described by Montgomery and Hart (1974) to determine the number of samples. The first is based on the allowed sample variability while the second is based upon the accuracy of the sample mean. Examples of these two methods also describes by US EPA (1982). Standard deviation and coefficient of variation (CV) of the concentration of the constituents are needed to determine the number of samples. These two parameters are usually obtained from the previously collected data. In the absence of such information, and sometimes in spite of such information, the number and frequency of samples are controlled by cost.

2.3 FREQUENCY OF SAMPLING

As mentioned in Chapter 1, frequency of sampling generally is site specific and no specific rules can be provided. In general, if the environmental value or quality interest varies with a certain frequency, the sampling frequency must be at least twice the frequency of that variation. In addition, if the process is cyclic in nature, samples should be collected during at least one complete process cycle. A detailed description of the procedure for determining frequency of sampling is described by US EPA (1982) and Wilson (1982). Various forms of time-series analysis such as harmonic and spectral analysis have also been used to study the nature of variability of water quality. This type of analysis can be found in references such as Thomann (1967), Fuller and Tsokos (1971), Shastry et al (1972) and Edwards and Thornes (1973).

Most of the time the frequency of sampling for the monitoring program is restricted by the availability of costs, regulatory or permit requirements and sampling objectives. Monitoring programs for stormwater sampling are much newer and less information is known. Therefore a tiered sampling approach is often followed, with the objective of the program to develop appropriate sampling frequency. In such programs a certain number of storms is selected for sampling in the first period (e.g. first year or storm season). The initial number of storms must be greater than the expected number of storms to sampled in the final plan. After completion of the initial period a statistical analysis can be performed to determine the impact of reducing sampling frequency. This analysis can be as simple as analyzing a subset of the data and comparing means and variance to the full data set. The increase in variability using a smaller set of data (e.g. less sampling frequency) can be compared to the added costs of more frequent sampling. Formal methods for making such evaluations are also available and are described in several of the previously cited references.

3.0
SAMPLE TYPES

Samples collected for any monitoring program generally can be divided into two types: grab samples - those taken from a single point as individual - and composite samples - which are mixed or poured together. The distinction between these two types of sample are summarized in the following sections. Detailed descriptions and procedures are given by US EPA (1982) and ASTM (1989).

3.1 GRAB SAMPLE

A grab sample is defined as an individual discrete sample collected over a period of time (generally not exceeding 15 minutes). A grab sample represents the conditions existing only at the point and time of sampling. When the source is known to be fairly constant in composition over a considerable period of time or over a substantial distances in all directions, a grab sample may be said to represent a longer time period or a larger volume, or both (Standard Methods, 1989). Generally, the collection of a grab sample is appropriate when it is used to :

- characterize water quality at a particular time,
- provide information about minimum and maximum concentrations,
- allow collection of variable sample volume,
- corroborate composite sample,
- meet a requirement of a discharge permit.

In addition, grab or discrete sampling can also be used when (US EPA, 1982):

- the stream does not flow continuously or a spill is suspected,
- the water or waste characteristics are relatively constant,
- the parameters to be analyzed are subjected to changes with storage (e.g.micro biological parameters, dissolved gases, soluble sulfide, residual chlorine, oil and grease, purgeable organics, and pH),
- information on maximum, minimum or variability is desired,
- the history of water quality is to be established based on its state over relatively short time intervals,
- the spatial parameter variability is to be determined (e.g., the parameter variability throughout the cross section and/or depth of a stream or large body of water).

A grab sample sometimes is also called a discrete sample, spot sample, or catch sample. Sampling is considered discrete if no further sampling is planned. If a number of discrete samples are collected in sequence in time and/or space to produce a set of samples, the sampling is considered to be a repetitive sampling. The variation of determinands in time and/or space can be obtained through a repetitive sampling. Examples of repetitive sampling include zonal sampling and chronological sampling (Krajca, 1989). Zonal sampling is applied to a repetitive collection of samples which are taken from a series of horizons or levels in a source (e.g., reservoir, borehole, swallow hole or lake). When samples are taken from a single source at fixed time intervals so that changes with time can be identified, the sampling process is considered to be chronological sampling. The time interval between successive sampling depends upon the purpose of the analysis, the dynamic character of the determinand, and often the flow regime and flow rate at the sampling point.

Spot samples, another form of grab sample, are usually acquired by filling the sample container or sampler once. They can be used to determine repeatability of non-recurrent, zonal or chronological sampling.

3.2 COMPOSITE SAMPLE

A composite sample is defined as a sample formed by mixing discrete samples taken at periodic points in time or a continuous proportion of the flow. Composite samples are most useful for observing average concentrations that will be used, for example, in calculating mass/unit time loading . Composite samples should not be collected over a period exceeding 24-hours, and care must be taken to prevent the deterioration of the sample during the period of collection by using preservatives, refrigeration, storage in the dark, or other means. Preservatives are normally put into the sample container prior to sampling, so that all sub-samples are preserved at the time of collection. Generally, composite samples should be avoided for the bacteriological/microbiological examination, radiological examination (e.g., short-lived radionuclides), or for constituents/analytical components that are subjected to significant and unavoidable changes on storage (e.g. dissolved gases, purgeable organics, residual chlorine, soluble sulfide, temperature, and pH) (Standard Methods, 1989; ASTM, 1989). Analyses for those constituents that are subjected to changes should be carried out on individual samples as soon as possible after collection and preferably at the sampling points (Standard Methods, 1989; Krajca, 1989).

The number of discrete samples which make up the composite depends upon the variability of pollutant concentration and flow. Generally there are two types of composite samples, i.e. time-interval and flow-proportioned (or flow-weighted) composite samples. A time-interval composite sample is collected in a series of small aliquots in which each aliquot was collected over a fixed interval of time. Sometimes a series of periodic grab samples is collected into an individual containers and then composited to cover a longer time period. This type of sample is called a sequential composite sample. Most of the composite samples are collected using automatic samplers (see Chapter 4). Current automatic samplers can be obtained with a built-in timer, flowmeter and rain gauge. Therefore, time-interval and flow-weighted composite samples can be programmed prior to sampling.

A frequent mistake made with automatic samples is to rely to heavily upon automation. No currently marketed samplers (Stenstrom and Strecker, 1993) can be remotely programmed to collect suitable volumes over suitable intervals for varying size storms and runoff periods. This must still be done manually. Automatic samplers require electric power and may need telemetry (e.g., a phone line connected to a modem). Many stormwater locations are not easily reached with power and phone lines. Rechargeable batteries are one alternative to electricity but can be used only for short storm events.

There are six methods which can be used to composite samples (Table 3-1). Choice of composite type is dependent on the program and relative advantages and disadvantages of each composite type. For a constant volume/time proportional composite samples, previous flow records can be used to determine an appropriate flow volume increment so that a representative sample is obtained without exceeding the bottle capacity or supply. In addition, composite samples can also be prepared from time constant/variable volume discrete samples in various ways. Examples of these flow-weighted composite samples preparation are given by US EPA (1982).

3.3 BLANKS

The most commonly used analytical tools for assessing and controlling sample contamination are blanks. Blanks may be defined as samples that are expected to have negligible or unmeasurable amounts of the substance of interest. Nomenclature associated with blank samples is far from consistent in the literature, and distinguishing one type of blank from another is sometimes difficult except by context or by a more detailed description (Lewis, 1988). Generally, blanks can classified into two types: field blanks and laboratory blanks. Field blanks, which include equipment blanks and transport blanks are used to provide information about contaminants that may be introduced during sample collection, handling, storage, transport and preparation. Laboratory blanks, which include system/instrument blanks, solvent/calibration blanks, and reagent blanks, are reliable tools for assessing and controlling sample contamination that occurred in the laboratory (Black, 1988; Lewis, 1988).

3.3.1 Field Blanks

Equipment Blanks

An equipment blank is used to estimate incidental or accidental contamination of a sample during the sample collection procedure. It is also can be used to verify the effectiveness of cleaning procedures. Capped and cleaned sample containers are taken to the sample collection site. After a sample is obtained, the sampling equipment is cleaned according to the standard operating procedure prior to taking another sample. At that point, the sampling equipment is rinsed with deionized water, which is collected in a sample container for later analysis. If a preservative is used, then an equal amount is put into the container with the blank. Generally, one equipment blank should be allowed per sampling team per day per sampling equipment.

Transport Blanks

A transport blank is used to estimate sample contamination from the container and preservative during transport and storage of the sample. It is also called trip blank, travel blank or matched-matrix blank. A cleaned sample container is filled with deionized water, preservatives used in the sample are added and then the blank is stored, shipped, and analyzed with its group of samples. This blank is more important when shipping and storage consumes several days or weeks because leaching of the material from the container can become significant. One transport blank should be allowed per day per type of sample.

Table 3.1 Sample Compositing Methods (EPA, 1982).

Sample Mode	Compositing Principal	Advantages	Disadvantages	Comments
Continuous	Constant pumping rate	Minimal manual effort, requires no flow measurement	Requires large sample capacity; may lack representativeness for highly variable flows	Practical but not widely used
Continuous	Sample pumping rate proportional to stream flow	Most representative especially for high vaiable flow; minimal manual effort	Requires accurate flow measurement equipment, large sample volume, variable pumping capacity, and power	Not widely used
Periodic	Constant sample volume, time interval between samples proportional to stream flow	Minimal manual effort	Requires accurate flow measurement or reading equipment; manual compositing from flow chart	Widely used in automatic as well as manual sampling

Table 3.1 Sample Compositing Methods. (continued)

Sample Mode	Compositing Principal	Advantages	Disadvantages	Comments
Periodic	Constant time interval between samples, sample volume proportional to total stream flow since last sample	Minimal instrumentaion	Manual composition from flow chart in absence of prior information on the ratio of minimum to maximum flow, there is a chnace of collecting either too small or too large individual discrete samples for a given composite volume	Not widely used in automatic samplers but may be done manually
Periodic	Constant time interval between samples, sample volume proportional to total stream flow at time of sampling	Minimal instrumentation	Manual compositing from flow chart. In absence of prior information on the ratio of minimum to maximum flow, there is a chance of collecting either too small or too large individual discrete samples for a given composite volume	Used in automatic samplers and widely used as manual methods

3.3.2 Laboratory Blanks

System Blanks

A system blank is also known as instrument blank. It is not really a blank at all in the sense of simulating a sample. A system blank is a measure of the instrument background, or baseline, response in the absence of a sample. System blanks are often used in gas and liquid chromatographic methods to identify memory effects, or carry-over from high concentration samples, or as a preliminary check for system contamination.

Solvent Blanks

A solvent blank consist only of the solvent used to dilute the sample. It is used to identify or correct for signals produced by the solvent or by impurities in the solvent. Depending on the analytical technique, the solvent blank may be used as a calibration blank. A calibration blank is used directly to set the instrument response to zero, or is used directly as one of a series of calibration standards, where the blank represents an analyte concentration of zero.

Reagent Blanks

In addition to solvent, the reagent blank contains any reagents used in sample preparation and analysis procedure. These reagents may include color development reagents, reagents used in sample digestion steps, reagents used for pH adjustment, preservatives, or other reagents depending upon the analytical method. The reagent blank is carried through the complete analytical procedure in the same manner as an actual sample. This procedure should include all steps involved in sample preparation, such as cleanup, filtration, extraction and concentration. Because it is carried through the complete analytical method, the reagent blank is also sometimes called a method blank. It can also use to determine the lower limit of detection. A reagent blank is analyzed for each 20 samples and analyzed whenever a new batch of reagents is used. The preferred outcome of reagent blanks is a less than detection limit result for all of the analytes of interest.

3.4 CONTROLS

Basically there are two types of control samples : (1) controls used in quality control procedures to determine whether or not the analytical procedure is in control, i.e., calibration control standard, laboratory control standard and matrix control, and (2) controls used to determine whether or not a factor of interest is present in a population (e.g., a group of environmental samples) under study but not in the control, i.e., control sites (local, area, national, background) (Black, 1988).

3.4.1 Calibration Control Standard

A calibration control standard is also known as quality control calibration standard (CCS) or calibration check standard. In most laboratory procedures, this control is a solution containing the analyte of interest at a low but measurable concentration. The precise concentration of this standard need not to be known. The first sample analyzed after an instrument is calibrated is a CCS, and the result should be plotted on a control chart. Another CCS is analyzed after each 20 samples, or after each shift if fewer samples are analyzed per shift. The standard deviation of the CCSs is a measure of the instrument precision unless the CCS is analyzed as if it were a sample, in which case the CCS is a measure of the method precision.

3.4.2 Laboratory Control Standard

The laboratory control standard (LCS) is a certified standard, generally supplied by an outside agency. This standard is used to determined whether or not an analytical procedure is producing results comparable to other analytical laboratories. The National Bureau of Standards (NBS) is a good source of LCSs in which a variety of standard reference materials containing certified concentrations of elements or compounds. The Environmental Monitoring and Support Laboratory of the U.S. Environmental Protection Agency in Cincinnati is another useful source of organic standard in water or organic solvent solutions. An LCS should be analyzed with every batch of samples until 7-10 results are available. If those results are within the control limits specified by the program protocol, the frequency may then be reduced to one per day. However, several LCSs should be analyzed any time the analytical instrument is recalibrated. The mean value of all LCS results is a measure of the method bias.

3.4.3 Matrix Control

Matrix control is commonly known as field spike. A field spike may be required to obtain an estimate of the magnitude of those interferences due to a complex mixture of a sample matrix (e.g., sediments, sludges). The losses from transport, storage, treatment, and analysis can be assessed by adding a known amount of the analyte of interest to the sample during collection in the sampling site.

3.4.4 Control Sites

In addition to the controls that are used to measure the precision and bias of sampling and analysis, a control site or a control population is also very important so that the results of a study of a given area can be judged as high, low, or insignificant. For example, if the contribution of pollutants from an urban area to environmental pollution is to be assessed, then the contribution of pollutants from sources other than the urban area must be known. However, if the environmental impact of a given facility, such as a waste disposal site, is to be assessed, then the environmental levels in the absence of that facility must be known. The sites or populations that can supply control samples can be classified as local, area, or national, depending on the location selected (Black, 1988).

<u>Local Control Site</u>

A local control site is a control near in time and space to the sample of interest. Factors to be considered in the selection of local control sites include the following:

- local control sites should be upwind of the facility most of the time,
- local control sites should be upgradient from the facility with relation to surface and groundwater flow,
- the potable water source should not be affected by site effluents,

- travel between the control site and the facility should be minimal because of problems associated with transport.

Area Control Site

This control site is in the same area (e.g. city or county) as the pollutant source but not adjacent to it. The factors to be considered in site selection are similar to those for local control sites. All possible effort should be made the sites identical except for the presence of the pollutant at the site under investigation.

4.0
SAMPLING EQUIPMENT

Sampling equipment used for various types of natural waters (lake, reservoir, municipal wastes, surface waters, groundwater, stormwater, etc.) usually have common features. The sampling equipment can be divided into two major groups: surface and sub-surface sampling. Surface sampling equipment include (Krajca, 1989) :

- samplers and sampling containers (including pressure vessels) for samples collection and transportation,
- sampling accessories such as scoops on long poles, grips, and forceps and for handling samplers,
- equipment for closed pipe sampling,
- suction probes for pore water sampling,
- precipitation samplers,
- automatic sampling equipment with basic components such as automatic control blocks water distribution systems and sets of samplers or collecting vessels).

For the sub-surface sampling, the sampling equipment includes depth samplers and other equipment which parts designed to operate under water, in places that are inaccessible to the operator.

For the selection of appropriate sampling equipment, factors such as appropriate materials for sampling equipment and sample containers, type of sampling equipment (manual or automatic), cleaning of sampling equipment (Krajca, 1989). The following section discusses these criteria and the description of the commonly used water sampling equipment also included.

4.1 MATERIAL USED FOR SAMPLING EQUIPMENT AND CONTAINERS

Selection of the material for sampling equipment and sample containers should consider (Krajca, 1989):

- the material must be inert to the sample or more particularly those of its constituents which are to be analyzed,
- no biological activity occurs,
- able to withstand any sterilization, cleansing or preservation procedures.

Materials commonly used for sample containers include glass and plastics (e.g., polyethylene). Selection of the type of sample containers will be discussed in Chapter 5. In addition to glass and plastics, metals are also commonly used, especially for the sampling equipment. Stainless steel sampling equipment is usually made of chrome-nickel steel with alloying additions of tungsten and molybdenum (both non-magnetic). These alloys are corrosion resistant and able to withstand strong acidic or alkaline samples for a long period of time. Compatibility of metals with various types of water samples was discussed by Krajca (1989) (see Appendix B). However, non-metallic material (e.g. plastic) should be used for metal analysis in order to avoid leaching problems. Blank tests should always be carried out to confirm that the sample is not affected by the material of the sampling equipment or sample containers (e.g., equipment blank).

4.2 WATER SAMPLING EQUIPMENT - MANUAL

As mentioned above, there are two types of water sampling equipment: surface and subsurface sampling. Surface water samples are usually taken directly into the sample container, which is also used for transport. If it is not possible to collect the sample by submerging the container by hand, laboratory forceps or a holder with a sliding sleeve can be used. If the sample is to be taken from the mainstream by reaching out from the bank then it may be best to attach the container to a segmented rod made up to appropriate length (e.g. dip sampler). Such sampling device is usually made of stainless steel.

Subsurface sampling is generally for depth sampling. Samplers can be categorized into three general types: free-flushing samplers, non-flushing samplers and combined samplers. Free-flushing samplers consist of a tubular body which is open at both ends. This allows the sampling chamber to pass through the water on its way down to the sampling point with only a minimum disturbance or mixing. Simple flushed samplers usually can be used in the horizontal mode, e.g. for sampling open streams, provided that suspension and controls have been suitably adapted. Flushing occurs with the sampler at rest. The degree of flushing depends upon the water velocity at the sampling point. Flushed samplers are primarily suitable for homogeneous, single phase liquid samples. Their main advantage is simple design and reliable operation, even at high pressures and temperature. When sampling heterogeneous liquids, attempts to flush the sampler by repeatedly raising and lowering, can result in partial separation of the mixture because the hydraulic resistance inside the sampler may cause more the mobile phase to flow around the sampler.

Unlike free-flushing samplers, non-flushed samplers make use of reduced pressure to effect sampling in which flushing of water samples through the sampling chamber is avoided. This is achieved through a difference in pressure between the inside of the sample chamber and the water at the sampling level. Examples of non-flushed samplers include bottle samplers, bag samplers, telescopic samplers and piston samplers. The third kind subsurface samplers is the combined sampler that combines the features of two or more basic types of sampler.

4.2.1 Kemmerer Bottles (Figure 4-1)

Kemmerer bottles may be used in most situations where access to the sampling sites is from a boat or structure such as bridge or pier, and where samples at depth are required. Kemmerer bottles are a messenger-activated water sampling devices. Water flows easily through the bottle in the open position. Once it is lowered to the desired depth, a messenger is dropped down to the sample line, tripping the release mechanism which

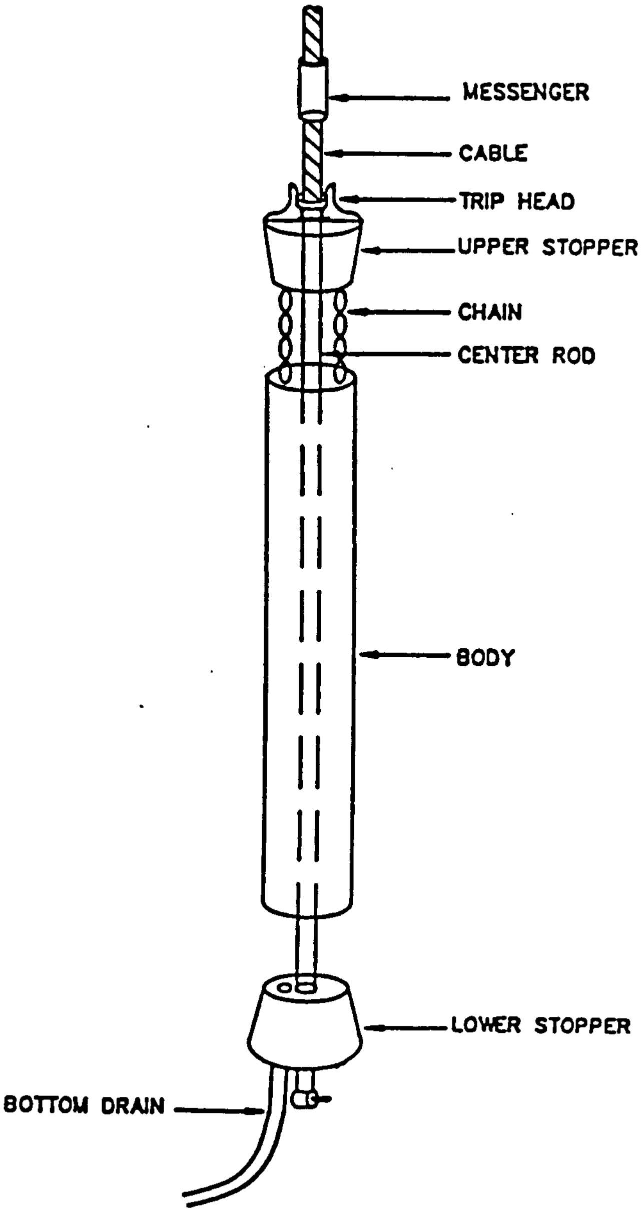


Figure 4-1 Kemmerer Bottles (US EPA, 1991)

causes the bottle to close. Both top and bottom are sealed to prevent further contact with the water column. Commercially available Kemmerer bottles are made of different types of material such as brass, plastic, stainless steel or acrylic. They can collect sample at specific depths between 3 - 600 feet.

4.2.2 Dip Samplers (Figure 4-2)

When the direct access to a sampling site is limited, such as an outfall or lagoon bank, a dip sampler is very useful for such sampling situations. The long handle on the dip sampler allows access from a discrete location. Dip sampler can be constructed of inert material such as stainless steel or Teflon.

4.2.3 Pond Samplers (Figure 4-3)

A pond sampler consists of an adjustable clamp attached to the end of a two- or three-pieces telescoping aluminum tube that serves as the handle. The clamp is used to secure a sampling beaker/container. A pond sampler is easily and inexpensively fabricated and usually not available commercially. It is commonly used to collect water samples from disposal ponds, pits, lagoons, and similar reservoirs. Grab samples can be obtained at distances as far as 3.5 m from the edge of the ponds.

4.2.4 Van Dorn Samplers

Van Dorn samplers, also known as alpha water samplers by others, are made of inert plastic tubing (generally PVC) closed with hemispherical rubber (urethane) end caps connected by a length of rubber passing through the sample chamber (available in 2,3, or 6 L capacities). When the sampler is being lowered the end caps are held open by a pair of chains attached to a 'lock' on the outside of the chamber. A messenger weight is released when the sampler is at the desired sampling depth. This will cause the end caps to snap sharply over the ends of the chamber to close it. There are two types of Van Dorn water samplers, i.e. Van Dorn-Vertical (Figure 4-4) and Van Dorn-Horizontal (Figure 4-5). The Van Dorn-Vertical is good for general water sampling. The Van Dorn-Horizontal is useful for collecting water at the sediment-water interface or sampling a thin layer of the water column. Van Dorn samplers generally are not recommended for sampling trace organics as they rely on an organic elastic closing mechanisms that can contaminate the samples.

Similar sampling mechanism as Van Dorn Samplers include Ruttner and Theiler-Friedinger water samplers. These two samplers are commonly used in Europe (Krajca, 1989). Ruttner's water samplers (Figure 4-6) are generally constructed of Perpex (plexiglass) and its open lids are in the horizontal position. Theiler-Friedinger's samplers, on the other hand, have the open lids in the vertical position and are constructed of light-metal or PVC (Figure 4-7). Both Ruttner and Theiler-Friedinger samplers have 1 - 3 L volume capacities.

4.2.5 Peristaltic Pumps

Peristaltic pumps can be used to draw in water sample through a Teflon tubing and pumped directly into the sampling containers (Figure 4-8). A medical grade silicone or C-Flex tubing is generally used as the pumping tubing. This system is highly versatile and portable. A timer can be used to provide constant sampling intervals and can also provide

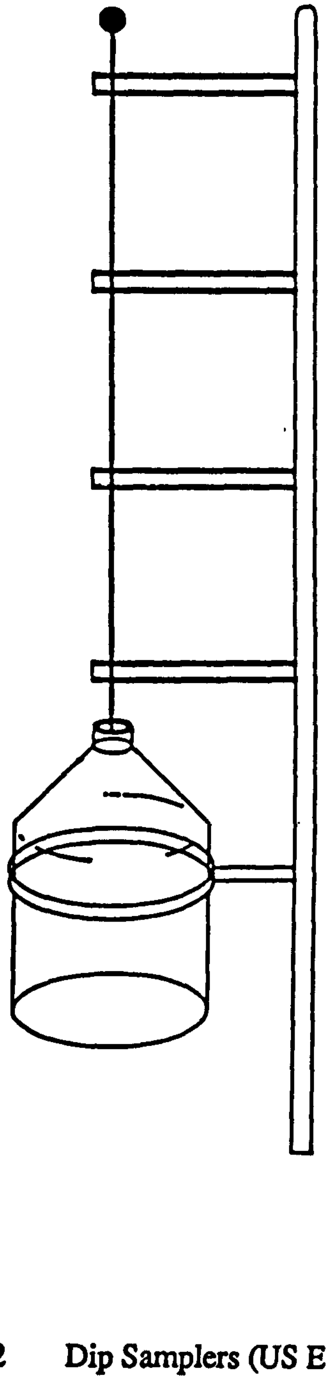


Figure 4-2 Dip Samplers (US EPA, 1991)

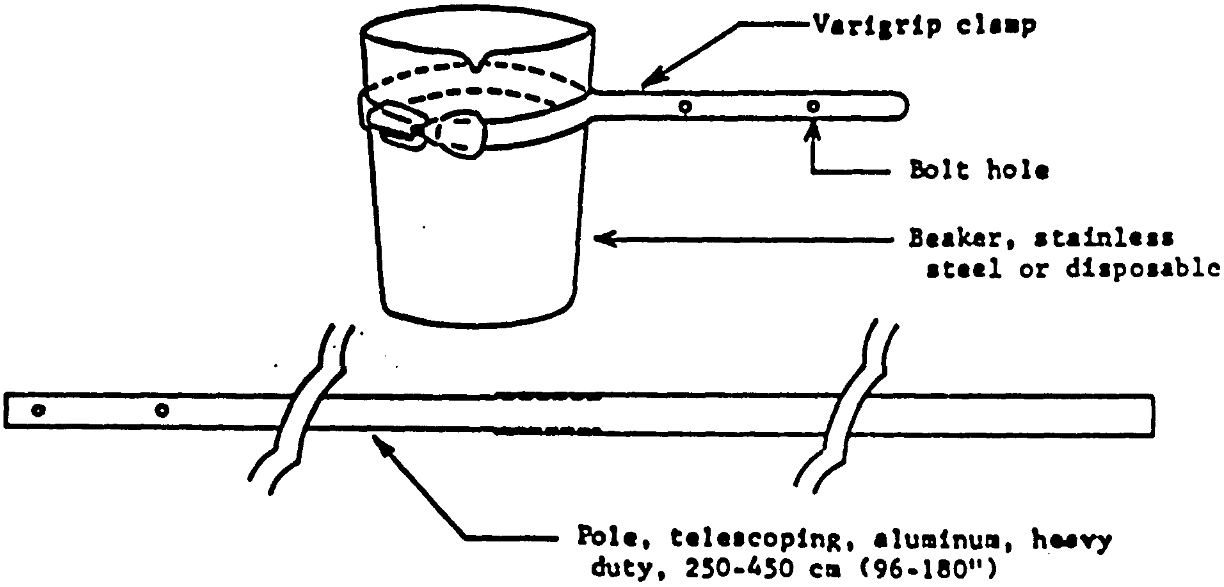


Figure 4-3 Pond Samplers (US EPA, 1984)

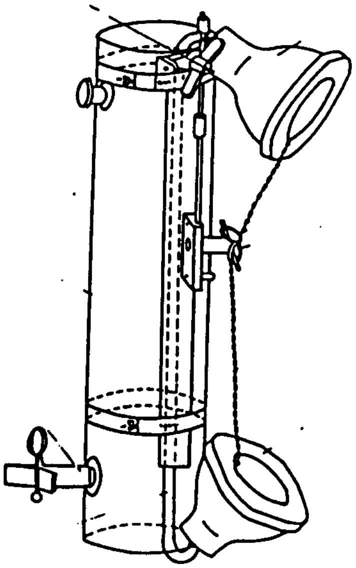


Figure 4-4 Van Dorn Vertical Sampler (Krajca, 1989)

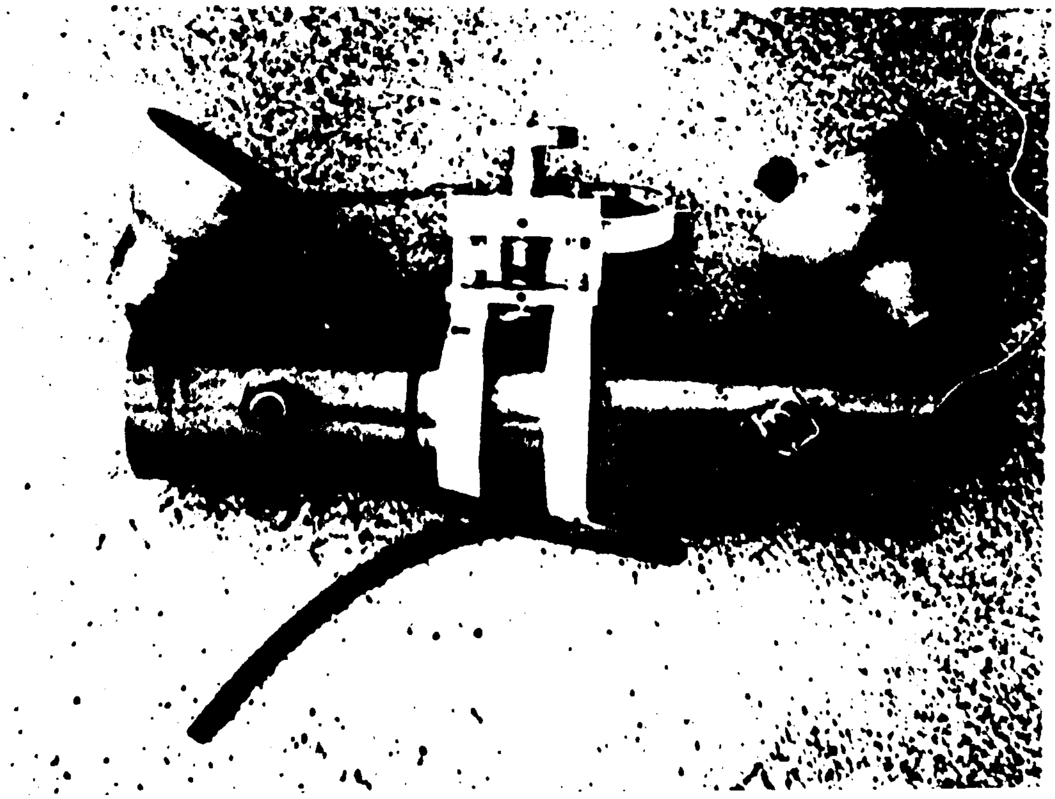


Figure 4-5 Van Dorn Horizontal Sampler (US EPA, 1982)

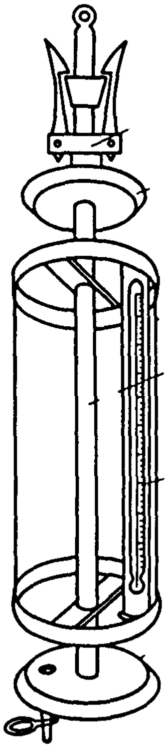


Figure 4-6 Ruttner's Sampler (Krajca, 1989)

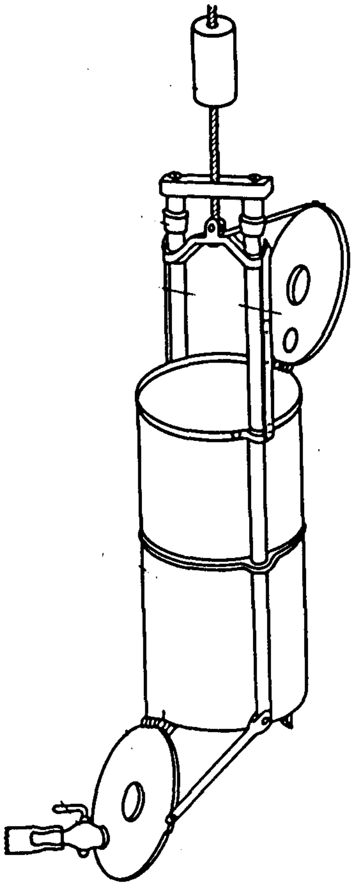


Figure 4-7 Theiler-Friedinger Sampler (Krajca, 1989)

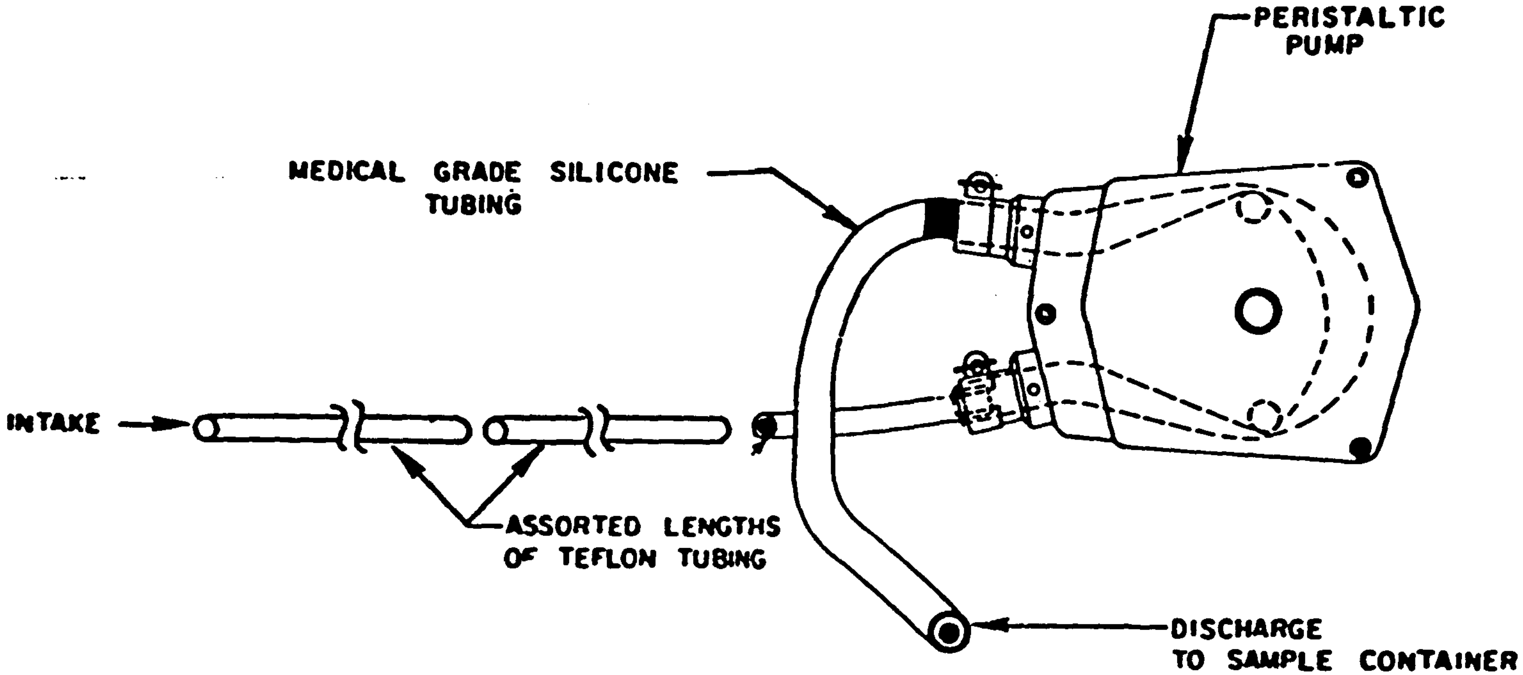


Figure 4-8 Peristaltic Pump Sampler (US EPA, 1984)

composite samples. This system allows sample collection at depths to 30 feet. The water sample contacts only tubing and stainless steel fittings. This method is not recommended for sampling volatile organics due to reduced pressure in the suction tubing, or for oil and grease due to coating of the tubing.

The system as shown in Figure 4-8 can also be altered so that the water sample is collected in a vacuum flask and does not enter the pump (Figure 4-9). The integrity of the collection system can be maintained with only the most non-reactive material (Teflon) contacting with the sample.

The main disadvantage of this method is the limited lift capacity of the pump, i.e. at ~ 30 feet. This lift capacity decreases with higher density fluids and with increase wear on the silicone pump tubing. Increased altitude decreases the pump's ability to lift. When sampling a liquid stream with a considerable flow rate, it may be necessary to weight the bottom of the suction line.

4.2.6 Knudsen Bottles

A Knudsen bottle is generally used for collection of water samples and water temperature data using up to three reversing thermometers. The sampler is constructed of nickel-plated metal with an average length and capacity of 0.5 m and 1.2 L, respectively.

4.2.7 Nansen Bottles

A Nansen bottle is similar to the Knudsen bottle, but it is designed to sample depths of ~ 3000 feet or more. The end valves is made of bronze, and the cylinder is made of brass. It is also available with either a tin-plated or Teflon-lined cylinder. A Nansen bottle has a capacity of 1.3 L and an overall length of ~ 2 feet. Several Nansen bottles can also be used in series for water sampling.

4.2.8 Simple Bottle Samplers

A simple bottle sampler is essentially a glass or polyethylene bottle and is generally used for surface sampling. The sample container is filled by displacement when the open bottle is put beneath the surface. Its advantage of this bottle sampler is its simplicity of operation mode, inexpensive, small size and weight in relation to the sample volume. However, there is no depth control using simple bottle sampler. In addition, the water sample is partially aerated which may be unsuitable for sampling dissolved oxygen (DO), carbon dioxide or other gases.

4.2.9 Niskin's Bag Samplers (Figure 4-10)

A Niskin's sampler is made of two ribbed aluminum plates connected by spring loaded hinges. It is kept in the closed position by a messenger operated mechanism. The sampling bag is fitted with pockets on each side to hold the plates, and is filled through a tube protected by a plastic casing. When the sampler is at the sampling depth, the messenger is released and activates a guillotine to cut off the cover of the inlet tube, which hangs away from the sampler body. At the same time, the two plates spring apart and the sample is sucked into the bag through the inlet. After the bag is filled, the end of the tube is automatically closed with a clamp, and the sampler can be pulled up to the surface. The

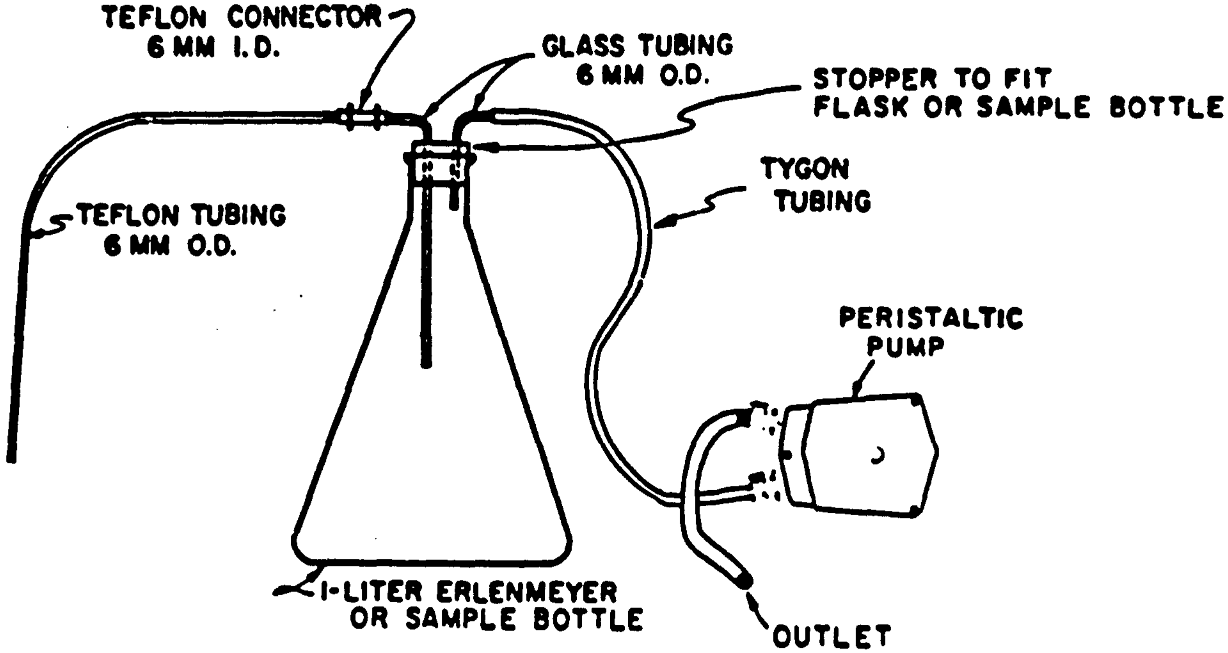


Figure 4-9 Peristaltic Pump (US EPA, 1984)

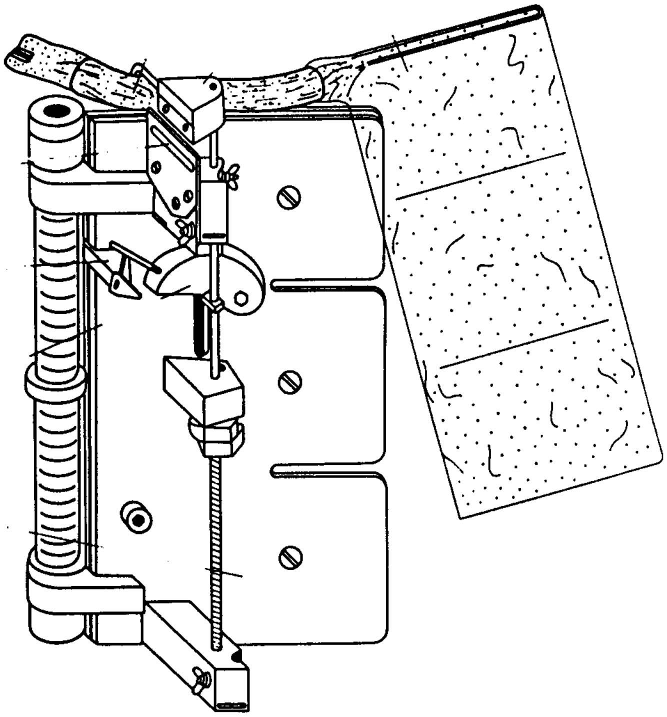


Figure 4-10 Niskin's Bag Sampler (Krajca, 1989)

bag can be used for transportation and storage, or emptied into another container. Sample contamination by this sampler is virtually eliminated, and groups of bags can be submerged as a series, on a single suspension cable either one above the other or side by side. Niskin's bag samplers are available in PVC and Teflon-lined for organics sampling. The sample volume capacity is 1.2 - 30 L.

4.3 AUTOMATIC SAMPLERS

Automatic samplers are being used increasingly in most of the monitoring programs to meet the requirements of NPDES permits. The advantages of automatic samplers include their consistency in samples collection, capability of collecting multiple bottle samples, minimal labor requirements, unattended operation, and the decrease in variability of samples caused by sample handling. However, no single automatic sampler is ideally suited for all situations. General criteria needed to be considered in selection of an automatic sampler include:

- ease of operation and repair,
- simple design with minimum operating parts and maximum long-term reliability,
- minimum number of parts in contact with water,
- resistance to corrosion, dust and sand, and low susceptibility to clogging,
- ability to use battery or main power,
- ability to tolerate varying climatic conditions,
- ability to operate a sampling schedule based on time or flow volume through the sampling chamber,
- ability to preserve samples at specified temperature for at least 24 hours.

Detailed information on the theoretical design considerations and actual field performance data for automatic samplers can be found in references such as Lauch (1976) and Shelley and Kirkpatrick (1975). The basic components of automatic samplers are a pump and a system for transporting the water sample to the collecting center (a tank or sample containers). Medical-grade silicone tubing must be used in peristaltic pumps to avoid contamination of the sample by organic peroxides used in the manufacturing of conventional grades of silicone tubing. Additionally, when sampling for toxic pollutants, the suction line must be made of Teflon (Newburn, 1988). The sample collection chamber sometimes is also connected to an autoanalyzer (e.g. flowmeter, pH and DO meter). Examples of automatic samplers used previously for stormwater sampling include ISCO models 3700 and 2900, Sigma Model 800SL, NB Model WS-1000, TN Technologies Priority Contaminant Samplers (PCS), etc. A full detailed list of automatic samplers is also given in *Addendum to Handbook for Sampling and Sample Preservation* (US EPA, 1983).

Automatic samplers are constantly being developed and improved. Recent innovations include flow and rainfall measuring equipment, and remote telemetry capability. In order to obtain the most current and correct information, manufacturers must be contacted to obtain specifications.

Automatic samplers are capable of collecting either grab or composite samples. Current automatic samplers mostly contain at least 24 sample bottles for grab sampling in which each individual sample is collected into separate sample bottle. For composite samples, small aliquots are taken at frequent intervals, usually over a 24-hours period, and collected in a single container. Most automatic samplers are also capable of gathering either timed-interval samples or samples collected proportional to flow. Timed-interval samplers have a fixed interval of time between each aliquot or sample. Flow-proportioned or flow-weighted samples are based generally on equal increments of flow as measured by the built-in flowmeter. A flow-weighted composite sample can be obtained by collecting small aliquots in a single container over small increments of flow (Newburn, 1988). However, dry weather conditions can create problems in collecting flow-weighted composite samples due to the absence of flow in the stormdrains. In such situation, only time-interval grab or composite samples can be collected.

Although automatic samplers are considered versatile and reliable in collecting samples, considerable maintenance is required for proper operation. Other disadvantages of automatic samplers include susceptibility to fouling by solids, inflexibility (fixed maximum sample volume), and possible sample contamination. Furthermore, automatically samplers cannot properly sample certain contaminants, such as oil and grease. Oil and grease can be stratified in the sample stream which makes collecting a representative sample from a single point impossible. The tubing required in the sampler's pumping system may contaminate samples (carry over from one sample to another) or may alter the sample concentration (adsorption of the contaminants to the tubing walls). Another major disadvantage of automatic samplers is their cost and susceptibility to vandalism. The sampler itself may cost as little as $1,000, but the infrastructure associated with the sampler, including telemetry, construction and flow measuring equipment may cost as much as $30,000 or more per station.

Most of the new stormwater monitoring programs are based upon automatic samplers. The cost and difficulty of manually collecting flow-weighted composite samples are prohibitive. Chapter 9 of this report includes several case studies, all of which used automatic samplers. It should be consulted for further information.

5.0
SAMPLE STORAGE AND PRESERVATION

Some properties of the samples can change, either quantitatively or qualitatively, during the interval between their collection and analyses. These changes may be spontaneous or due to the sampling handling procedures. If possible, field analysis, or *in situ* analysis, is recommended in order to avoid any possible changes. When *in situ* analysis can not be carried out, the samples should be appropriately stored and preserved to maintain parameter stability during the delays in transport and storage. The following sections will discuss the samples storage, sample preservation, recommended holding time and sample volume prior to any analysis in the laboratory.

5.1 FIELD ANALYSIS

Field analysis, or *in situ* analysis, refers to all measurements made at the sampling site. Field analysis is generally used when the parameters are known to change with time and cannot be preserved. In addition, field analysis can also be used to check the reliability and reproducibility of the sample. The parameters measured in the sampling site include temperature, pH, conductivity, buffering capacity, ferrous iron, E^o (effectively oxidation and reduction potential), some organoleptic properties (e.g., taste, odor, color and turbidity), concentrations of carbon dioxide, hydrogen sulfide and other soluble gases. Some of these parameters, such as conductivity, pH, and ferrous iron, should be determined first in the field and then in the laboratory using preserved samples. In this way, the degree of change that occurred during transport and storage can be determined (Krajca, 1989).

5.2 SAMPLE STORAGE

It is important to take proper precautions for samples storage during sample transportation from the sampling site to the laboratory. Sample containers used in storing the sample prior to analysis are very important. Selection of sample container depends on factors such as resistance to breakage, size, weight, interference with constituents, cost and availability (US EPA, 1982). The following sections discuss factors that need to be considered prior to sample storage.

5.2.1 Container Material

There are two major types of material used for sample container, i.e., plastic and glass (Hellwig, 1964):

1. Glass
    - Kimax or Pyrex brand - borosilicate
    - Vycor - generally lab ware
    - Ray-Sorbor Low - Actinic - generally lab ware
    - Corex - generally lab ware

2. Plastic:
   - Conventional polyethylene
   - Linear polyethylene
   - Polypropylene
   - Polycarbonate
   - Rigid polyvinyl chloride
   - Teflon

The above glass and plastic materials have their advantages and disadvantages (Table 5-1). For example, borosilicate glass bottles have the advantages that their internal surface is readily apparent and that they can be more vigorously cleaned. In addition, they are inert to most materials. However, glass bottles are more liable to breakage.

In general, three main considerations involve in choosing container materials (Suess, 1982):

1. the material of the containers may cause contamination of samples (e.g., sodium and silica can leached from glass, organic substances can be leached from plastics),

2. determinands may be sorbed on the walls of containers (e.g., trace metals by ion-exchange processes on glass surfaces, adsorption of benzene by plastics),

3. constituents of the sample may react with the containers (e.g., fluoride may react with glass).

The above mentioned processes generally become more important as the concentrations of determinands become smaller (e.g., less than 1 mg/L). Thus type of container used for storing samples can be critical. However, if large concentrations of constituents such as chloride, sulfate, hardness, nitrate, etc., the type of container is usually unimportant.

As a general rule, glass bottles should be used when organic compounds (e.g., pesticides, oil and grease) are to be determined. Plastic or polyethylene bottles should be used for determinands that are major constituents of glass, e.g., sodium, potassium, boron, silica (Suess, 1982; US EPA, 1982). For most bacteriological samples, bottles that can withstand sterilization temperatures should be used (ASTM, 1989).

5.2.2 Container Caps

The types of container caps used with the sample containers is also important. There are two major types of plastic used in container caps: polyethylene and bakelit with liners. Polyethylene caps are recommended for ease of cleaning unless oil and grease are to be analyzed. There are three types of liners available and their advantages and disadvantages are listed in Table 5-2. Generally caps with Teflon liners should be used for pesticides and oil and grease samples. Silicone rubber material should be avoided for trace metals due to possible zinc contamination (Gibbs, 1975; ASTM, 1989).

5.2.3 Container Structure

Wide mouth containers are mostly used. This structure permits easy filling and sample removal. It is also easily cleaned, quickly dried, and can be stored inverted. A narrow

Table 5.1 Glass and Plastic Advantages and Disadvantages (EPA, 1982).

	Borosilicate Glass	Conventional Polyethylene
Interference with sample	Inert to all constituents except strong alkali	Good for most constituents except organics and oil and grease
Weight	Heavy	Light
Resistance to breakage	Very fragile	Durable
Cleaning	Easy to clean	Some difficulty in removing adsorbed components
Sterilizable	Yes	In some instances
Space	Takes up considerable space	Cubitainers - substantial space savings during extended field studies

Table 5.2 Bottle Cap Liner Advantages and Disadvantages (EPA, 1982).

Liner Type	Advantages	Disadvantages
Wax coated paper	Generally applicable to most samples, inexpensive	Must be inspected prior to each because of deterioration. Cannot use with organics
Neoprene	Same as wax coated paper	Same as wax coated paper
Teflon	Applicable for all analyses Minimizes container/sample interaction	High cost

neck bottle is recommended when the interaction with the cap liner or outside environment is to be minimized. For pesticide sample collection, a solvent cleaned glass container should be used (Hellwig, 1976).

5.2.4 Disposable Containers

When the cost of cleaning is high, disposable containers generally are recommended. These containers should be precleaned and sterile. The most commonly used disposable container is the molded polyethylene container which is shipped nested and sterile to the buyer (US EPA, 1982).

5.2.5 Container Cleaning

Cleaning of sample containers prior to sampling is another important step in order to avoid any unnecessary contamination. Chromic acid is often suitable for glass, and hydrochloric acid (approximately 1 mole/L) can be used to clean polyethylene. The use of concentrated nitric acid should be avoided for cleaning plastic bottles as it may cause the formation in the plastic of chemical groups with ion-exchange properties (Suess, 1982). Non-phosphate or biodegradable detergent can also be used. Glass bottles that have contained samples with chromate or heavy metals should be rinsed with dilute nitric acid before final thorough rinsing with water. After the final rinse the pH should be checked to assure that toxic acids or chromate are not present (ASTM, 1989).

5.2.6 Container Preparation

In addition to the above mentioned cleaning procedure, special precaution should be taken to avoid adsorption and contamination due to interaction with container walls. Special procedures to prepare the sample containers for metals, organics and microbiological samples are outlined below (US EPA, 1982) :

1. Metals : A solution of one part nitric acid to four parts water should be used to rinse the container, and then followed with a rinse using distilled water. If phosphorous is to be analyzed, a solution of one part hydrochloric acid to one part water is used instead. The container caps are treated in similar way.

2. Organics : When oil and grease or pesticides are to be analyzed, methylene chloride should be used to rinse the containers, followed by acetone. For pesticide analysis, pesticide grade acetone or hexane should be used. The containers should have been previously treated with chromic acid solution. The caps are also treated similarly.

3. Microbiological : For microbiological analyses, the containers and its cap/stoppers should be sterilized by autoclaving at 121°C for 15 minutes or by dry heat at 180°C for 2 hours. The bottles should also be wrapped in Kraft paper or covered with aluminum foil before sterilization so contamination can be avoided.

5.3 HOLDING TIME

Holding time is defined as the time interval between collection and analysis. More reliable analytical results will be obtained with shorter holding time. It is, however, difficult to determine the maximum time that is allowed to elapsed between sample collection and analysis before any deterioration of sample occurs. The characteristics of the samples, analysis that are to be performed, and the conditions of the storage are among the factors that need to be considered in determining the holding time. There is some variability among various authors on the maximum allowable holding times for various analytes. Recommended maximum holding times for various analytical parameters, which have been compiled by the US EPA (1974), are listed in Appendix C.

5.4 SAMPLE VOLUME

The volume of sample collected generally is not important as long as it is sufficient for all the required analyses and there is enough leftover in case some analyses need to be repeated. In general, approximately 8 liters (about 2 gallons) are required for a fairly complete analysis. The volume of sample required for specific types of pollutants analyses, which has also been compiled by the US EPA (1974), are shown in the Appendix C.

However, certain points need to be considered while collecting the samples (Suess, 1982) :

- the sample containers should be completely filled for determining dissolved gases, purgeable/volatile organics, pH and conductivity in weakly buffered waters,
- the sample containers should not be completely filled when samples require vigorous shaking before portions for analysis (e.g., for bacteria or undissolved materials),
- when small concentrations of determinands are present as discrete particles (e.g., dissolved materials, algae, bacteria), a minimum volume of sample may be needed to control errors arising from the statistical variations in the number of particles in a given volume of sample. The required sample volume usually will be given in the analytical method.

5.5 SAMPLE PRESERVATION

Changes of the physical (e.g., volatilization, adsorption, diffusion, and precipitation) and chemical (e.g., photochemical and microbiological degradation) conditions of the samples may occur during the time interval between sample collection and analyses. These changes can be minimize by using proper preservation techniques.

Preservation techniques are selected on the basis of their ability to minimize changes in order to preserve the integrity of the sample after collection. Preservation guidelines for certain types of sample and analyses have been compiled by the US EPA (1974). The recommended preservation methods are listed in the Appendix C. Preservation of samples has also been discussed in a number of literature such as US EPA (1982), Keith (1988), Suess (1982) and ASTM (1989). Preservation methods are generally limited to addition of preserving reagent, pH control, refrigeration and freezing. Combination of these methods are often used for the preservation of sample. The following section discusses some of the preservative methods commonly used.

5.5.1 Addition of Preserving Reagent

Stability of sample conditions can be achieved by adding a chemical reagent (or a preservative) to an empty sample container before collection. When the sample is added, the preservative disperses immediately, stabilizing the parameter(s) of concern for a certain period of time. However, when the added preservative interferes with other parameters being measured, additional samples for those parameters must be collected. For example, concentrated nitric acid added for preserving the metals would interfere with BOD, so an additional sample must be collected for BOD.

As a general guideline, acidification (usually with nitric or hydrochloric acid) of samples is carried out for trace metals analyses. Different acids and acidities can be use for different metals. The minimum acidity required for stability depends on the metal. In general, sufficient amount of nitric or hydrochloric acids should be added to give a final concentrations in the range of 0.05 - 0.1 mole/L in the sample after collection (Suess, 1982).

When the samples are subject to biological changes, addition of mercuric chloride or acidification are more frequently used. In general, mercuric chloride (20 - 40 mg/L) can be used for preserving nitrogen compounds, while sulfuric acid (1 - 2 ml/L) is used for determinands such as COD, fats, and greases (Suess, 1982).

5.5.2 pH Control

This type of preservation method usually involves acidification (or chemical addition) of the sample. For example, concentrated nitric acid is added to lower the pH to less than 2 in order to keep metal ions in a dissolved state.

5.5.3 Refrigeration

Refrigeration of samples is another common preservation method. It is commonly used for biological examination in which the samples is refrigerated immediately after collection and held at a temperature less than 4°C.

5.5.4 Special Sample Containers

Samples with photosensitive constituents (e.g., polynuclear aromatic hydrocarbons and bromo- or iodo-compounds) should be collected and stored in amber glass containers to protect them from light (Parr et al., 1988) and stored in dark areas prior to analysis. It is also possible to use collapsible containers which facilitate collecting samples with no gas space in the container.

6.0
FLOW MEASUREMENT

Flow measurement is one of the most important monitoring parameters in any sampling program. Care must be taken in selecting a site suitable for flow measurement as well as the flow measurement method. The ideal site allows flow measurements to meet program objectives, provides ease of operation and accessibility, personnel and equipment safety, and freedom from vandalism. Flow measurement is so important that site selection may be dominated by the ability to measure flow rate.

There are many flow measurement methods. The objective of this section is to present a brief overview of the current flow measurement methods and equipment appropriate for the storm drain monitoring programs and to list advantages/disadvantages. Detailed information of methods of flow measurements can be found in references such as *Flow Measurement Engineering Handbook* (Miller, 1983), *Water Measurement Manual* (USDI, 1974) and *Fluid Meters* (ASME, 1971).

The measured flow rate is generally used to determined the mass emission of contaminants (mass emission = flow rate x concentration). If the concentration of contaminants and flow rate vary with time, a flow weighted average must be determined to quantify mass emission. In addition, the number of discrete samples that make up the composite sample depends upon the variability of contaminant concentration and flow. Examples of manual compositing samples based on flow rate are given by the US EPA (1982). Inaccurate flow measurements will lead to inaccurate flow proportional composite samples.

Most of the flow measuring devices, however, have disadvantages such as:

- devices (e.g. weir) can reduce flow in the storm drain
- increase the risk of flooding,
- debris and trash can hang up on the device.

General criteria for an ideal flow measuring device include:

- no or insignificant restriction of storm drain flow,
- ability to use the device over a wide range of flows,
- no tendency to be fouled by debris.

6.1 OVERVIEW OF TRADITIONAL FLOW MEASURING DEVICES

The traditional flow measuring devices commonly used include weirs, flumes, venturis, orifices, positive displacement meters, flow nozzles, etc. These devices are generally not suited for stormwater flow measurements primarily because they restrict flow too much and require too much pressure drop for accurate measurement. In addition, they are also susceptible to clogging or fouling by the debris or suspended solids. More detailed information of these flow measuring devices can be found in the literature, but a brief overview is provided here.

6.1.1. Weirs

A weir is an overflow structure built across an open channel to measure the rate of flow. Weirs may be termed rectangular, triangular or trapezoidal, depending on the shape of the opening. The relationship between head and discharge are different for different weirs. More detailed information can be found in references such as *Water Measurement Manual* (USDI, 1974) and *Fluid Meters* (ASME, 1971). One of the parameters that affects weir flow measurements is the weir coefficient (C_w), i.e. a coefficient characteristic of flow conditions over the weir. The coefficient differs from one type of weir to another. Corrosion of the weir crest or damage caused by floating debris may alter the C_w value. Weirs also have the tendency to settle suspended particles or debris near their upstream side. This build-up will further restrict the flow in the sewer, increase the risk of flooding and bias water quality samples. In addition, the use of a weir usually results in a relatively large head loss. Therefore, permanently installed weirs are generally not suited for flow measurements in storm drains, unless they have been previously installed for other purposes and their head loss has already been accounted for in providing for flood protection. Temporary weirs are sometimes useful. The downstream side of a weir can be used a place to obtain representative samples from stratified streams, since the entire flow is mixed as it passed over the weir. In areas like Southern California, with seasonal rainfall, and dry weather runoff, low flow channels may be equipped with weirs without loss of flood protection.

6.1.2 Flumes

Flumes consist of three sections: a converging upstream section, a throat or contracted section, and diverging downstream section. The flume size is given by the width of the throat section. Flumes are considered better than weirs as most flumes have a self-cleansing feature in which build-up of particulate matters onto their upstream side can be avoided. In addition, the head loss resulted from flumes is relatively less than weirs. Commonly used flumes as flow measurement devices include Parshall flumes, Palmer Bowlus flumes and cut-throat flumes. Flumes create head loss and reduce maximum flow rate. Additionally they are expensive to construct, especially if they need to be retrofitted into existing facilities.

6.1.3 Positive-Displacement Meters

Positive-displacement (PD) meters separate the flow into discrete volumes and then sum to total volume by counting unit volume that passes through the meter. As fluid enters a chamber, an impeller, a piston, a diaphragm, or a disk rotates or moves to accommodate the entering fluid, and a known volume is discharged. Seals are required to separate the volumes, and the pressure loss across the meter provides the energy to drive the moving parts. The fluid temperature and viscosity affect the range and accuracy. Manufacturers should be consulted on temperature, pressure and viscosity limitations. Positive-displacement meters have no time basis. Therefore, they are seldom used to indicate instantaneous flow rate. They are unsuitable for storm drain monitoring because of their head loss and tendency to foul.

6.1.4 Differential Head Meters

Examples of differential head meters include venturi meters, flow nozzles, orifice plates, elbow flowmeter and pitot tubes. The measured the flow rate is proportional to the differential pressure between the undisturbed flow and the constriction section of the pipe caused by the meters. The difference of pressure may be measured with a differential manometer or pressure gauge. A straight length of pipe at least 10 diameters long is usually installed upstream of the meter. The main disadvantage of these differential head meters is the large permanent pressure loss that occurs across the section. Among these differential head metes, venturi meters have the lowest pressure loss whereas orifice meters cause the largest permanent pressure loss. Another disadvantage of these differential head meters is their susceptibility to clogging in waters with high suspended solids concentration. The head differences are also difficult to measure at low flow conditions.

6.2 ALTERNATIVE FLOW MEASURING DEVICE

Most of the traditional flow measuring devices mentioned above are considered poor in obtaining accurate results because they restrict flow too much. Alternative flow measuring devices include magnetic flowmeters, ultrasonic flowmeters and flow gauges (in which the flow is estimated using equations such as Manning, Chezy and Hazen-William's equations). These alternative devices are superior to those mentioned above due their low or negligible pressure loss.

6.2.1 Magnetic Flowmeter

The operation of magnetic flowmeter is based on Faraday's Law of Induction which essentially averages velocity over the pipe area. The voltage induced by a conductor (which is the liquid stream to be measured) moving perpendicular to flow direction and magnetic field (which is produced by a set of electromagnetic coils). The induced voltage is then detected by two flushed-mounted electrodes on a diameter of a non-conducting pipe wall. The low level millivolt signal is proportional to the average pipeline velocity. Thus magnetic flowmeters are considered ideal for all conductive fluids that operate in both laminar and turbulent flow regimes. Fluids to be measured must be a conductivity of at least 2 μmho/cm to be measurable (Miller, 1983).

Magnetic flowmeters generally are used in pipes flowing full. In addition to their ability to operate in a wide flow measurement range (laminar and turbulent flow regimes), their advantages also include accuracy of ± 0.5 - 1 %, negligible pressure loss, no moving parts, and rapid response time. However, the cost of magnetic flowmeters is high. Build-up of grease deposits or pitting by abrasive wastewaters can also foul the electrodes. Installation of magnetic flowmeters also require straight sections along the pipes with minimum length. Thus, regular inspection and cleaning of the electrodes are necessary. Built-in ultrasonic cleaning devices are the most commonly used (Hayward, 1979).

6.2.2 Ultrasonic Flowmeters

There are two types of ultrasonic flowmeters: time-of-flight and Doppler effect (Miller ,1983).

- Time-of-flight meter: In time-of-flight ultrasonic flowmeters, a high-frequency (~ 1 MHz) pressure wave is beamed at an acute angle across the pipe. The time required for the wave to reach the opposite wall depends on liquid velocity, whether it is moving with or against the flow and on the speed of sound through the liquid. Flow rate information is obtained from the measured time of travel. There are many varieties of time-of-flight meters. The main differences are usually in the number of beam paths across the pipe. A single beam instrument averages along the beam and not across the pipe area. This make the single-path measurement dependent on velocity profile. Multipath meters average along several paths, reducing profile dependency. Both single-path and multipath ultrasonic flowmeters are sensitive to swirl. They are generally used in clean fluid applications, where the ultrasonic beam is not continuously interrupted by fluid particles. Their accuracy is between ± 1 to 4 %, depending on design and applications.

- Doppler flowmeters: In Doppler flowmeters, the sound pressure front does not pass through the pipe. It is reflected back to a detector by particulate matter moving with the flow. The difference between reflected frequency and fixed transmitted frequency is used to calculate the flow rate (Miller, 1983). Doppler flowmeters depend on small particles or impurities in the flow. Therefore, its accuracy depends on particles concentration and distribution. Accuracy is also influenced by the relative velocity between fluid and particles.

The advantages of ultrasonic flowmeters are low maintenance (including cleaning), wide flow range, low headloss and relative high accuracy of measurement. However, their disadvantages include high initial cost and errors from heavy turbulence and foam (US EPA, 1982). New types of ultrasonic flowmeters can be inserted into pipes using a metal bar which holds the meter against the pipe wall. This type of installation produces the least pressure drop and tendency to catch fouling materials.

6.3 ESTIMATED FLOW MEASUREMENT METHODS

In the absence of a flow measuring device, channel or sewer bottom slope, depth of flow and flow velocity measurements can also be used to estimate the flow. Among the commonly used estimation methods are the Manning, Chezy and Hanzen-William's equations.

6.3.1 Manning Equation

$$V = \frac{1}{n}(R)^{\frac{2}{3}}(S)^{\frac{1}{2}} \qquad (1)$$

where

V = average velocity of flow (ms^{-1})
R = hydraulic radius (cross-sectional area divided by wetted perimeter, m)
S = slope of the energy grade line
n = roughness coefficient

The Manning equation can be used to estimate flow in channels or pipes.

6.3.2 Chezy Equation

$$V = C(RS)^{\frac{1}{2}} \qquad (2)$$

where

C = Chezy coefficient

Chezy coefficient is most frequently expressed as

$$C = \frac{1}{n}(R)^{\frac{1}{6}}$$

The Chezy equation generally applies to open channel only.

6.3.3 Hanzen-William's Equation

$$V = 0.85\, C_H R^{0.63} S^{0.54} \qquad (3)$$

where

C_H = Hanzen-William's coefficient

The Hazen-William's equation is generally used for pipes flowing full.

The usefulness of the above equations for flow measurement is limited due to the difficulties of assigning an appropriate value to the roughness coefficient which varies with the channel or sewer material (concrete or brick), and the surface of the channel or sewer. For sewers, it varies also with the ratio of depth of flow to the depth when flowing full. In addition, the slope of energy grade line (which is taken as the slope of the channel or sewer) may also cause the inaccuracy in flow measurement. For example, the Manning equation is only applicable when the channel slope is less than about 0.10. Various tables, nomographs, slide rules, and charts have been prepared to simplify calculation and facilitate solution of these problems (Linsley and Franzini, 1979).

6.4 FLOW MEASUREMENT CONCLUSIONS

There is no ideal flow measuring device that is suited for all sampling locations. The flow measuring devices should provide "real-time" indication of flow rate in order for automatic samplers to obtain flow weighted composites. Total flow, provided by integrators or totalizers is also very important, especially to determine the accuracy of rainfall/runoff models, which were used extensively in the design of the Santa Monica Bay monitoring plan developed as a part of this study. The flow measurement cost per sampling points may be as high as $25,000 - 30,000 (in 1991 dollars). Site-specific information on previously used monitoring equipment is presented in Chapter 9.

7.0
SAMPLING PROBLEMS

Implementation of correct sampling procedures is very important so that accurate results can be obtained. However, problems still occur in sampling, even in the hand of an experience sampling personnel. The most commonly encountered sampling problems include sample contamination (caused by sampling devices or sample containers), interaction between samples and sampler material (e.g. sorption), and problems due to stratified contaminants such as suspended solids and oil and grease.

7.1 SAMPLE CONTAMINATION

Water sample contamination is the most common sampling problem. The usual sources of contamination are the sampling devices and sample containers. Carryover between samples from the sampling devices will occur if the device is not cleaned thoroughly prior to sampling. Sampling devices are generally cleaned with detergent (non-phosphate) and hot water. Sometimes manufacturers also provide guidelines for cleaning the sampling devices and these guidelines should always be followed. The devices also should be rinsed at least three times with water to be sampled; this procedure flushes out any remaining cleaning solutions that may dilute the sample. Special cleaning procedures are often required for specific contaminants. Consult the analytical protocol for further information.

In addition to sampling devices, sample containers must also be cleaned according to appropriate cleaning procedure (e.g. the Standard Operating Procedure (SOP), and ASTM's cleaning procedures). Solvents used for cleaning sample containers include 10% nitric acid (for trace metals analyses), pesticide grade hexane or acetone (for organics analyses) and methanol. Concentrated chromate acid (typically 20 g potassium dichromate in a liter of concentrated sulfuric acid) is also commonly use to clean glass sample containers. Detailed information on the cleaning procedures of sample containers can be found in references such as ASTM and Standard Methods.

Blanks are used to assess contamination. Blank samples usually include an equipment blank and transport blank (see Chapter 3). Selections of blanks should be made by considering all likely sources of contamination for the specific situation.

7.2 SORPTION

Analyte sorption is another common sampling problem. Materials used for sampling devices or sample containers should be inert to the collected water samples (see Chapter 5). For example, PVC and plastics other than Teflon tend to sorb organics and leach plasticizers and other chemicals used in their manufacture. In addition, some pesticides and halogenated compounds strongly sorb to glass (Keith, 1991).

Tubing material used in the automatic samplers is very important. Thermoplastic materials, such as polypropylene, have the tendency of sorbing many organics. Therefore they should be avoided. Teflon tubing is recommended as the suction tubing in the automatic samplers as Teflon materials are inert to almost all constituents. Selection of an appropriate tubing material should be made based on the manufacturer's guidelines, in which compatibility of the tubing materials with certain analytes is provided.

7.3 OTHER SAMPLING PROBLEMS

Oil and grease and suspended solids usually require special techniques to avoid problems. Sampling problems caused by oil and grease include the following:

a. Adsorption of oil and grease onto the tubing wall
  - common problem in automatic samplers.
  - suitable tubing material has to be chosen in which adsorption onto the tubing wall can be avoided.
  - tubing suitable for sample may not be compatible with peristaltic pumps.

b. Sample stratification
  - free oil and grease tends to float on water surface whereas the fraction that attached to the particulates tends to deposit on the bottom.
  - at the chosen sampling location (or sampling depth) one should be able to collect samples which include the free-floating and heavy fractions of oil and grease in the water. Automatic samplers are not capable of doing that as the samples is generally collected from a specific sampling depth.
  - manual water samplers (such as Kemmerer bottles, Von Dorn Vertical bottles) are suitable to collect a sample from the water column.

Suspended solids in water may cause the following sampling problems:

a. Clogging/fouling problems in the automatic samplers
  - constant cleaning/flushing of the automatic sampler intake position is needed.

b. Fouling of flow measuring devices
  - especially in weirs in where the suspended solids are deposited onto their upstream section and restrict flow.

c. Sample stratification
  - the effects similar to those of oil and grease.
  - It is difficult to collect representation samples using automatic equipment, for the same reasons as for oil and grease. Manual water samplers such as Van Dorn and Kemmerer bottles are recommended to collect water samples with high concentration of suspended solids.

8.0
QUALITY ASSURANCE IN SAMPLING

All sampling programs should have a Quality Assurance (QA) plan. The objectives of QA plan are to make sure the generated data are precise, accurate, representative, comparable and complete. Data falling outside the acceptable levels for these criteria will results in the potential sources of error being investigated, corrected, and recorded with a repeated analysis of questionable samples. Examples of quality assurance elements include the collection of sample blanks, duplicates and spike samples (US EPA, 1984). A QA Coordinator within the organization should be assigned so that he/she can undertake activities such as quality planning, auditing and other programs to insure reliability and complete integration of the QA plan.

A quality assurance plan for a sampling program generally include the following steps:

1. The sampling program should describe details on sampling locations, sample type, sample frequency, number of samples, duration of sampling, sample volume, sample collection methods and holding times, equipment to be used for the sample collection, sample containers, pretreatment of containers, type and amount of preservative to be used, blanks, duplicates/triplicates, spiked samples, replicates, and chain of custody procedures.

2. Procedures for routine testing, maintenance and calibration of sampling equipment should be developed. Manufacturers' instructions are appropriate guides for these procedures. Information on quality assurance guidelines for field analysis, equipment calibration and documentation is given by US EPA (1977).

3. Random control checks should be performed to make sure that appropriate sampling guidelines on sample collection, handling and chain of custody are followed by the field personnel. If deviation occurs, appropriate corrective action should be taken. In addition, analytical quality control as an aid to quality assurance must be performed through duplicate, split, and spike samples. Sample preservative blanks, and known standard solutions, and accuracy may be evaluated using control chart.

The above mentioned steps are just a general descriptions of a QA plan for a sampling program. More detailed information on implementation of QA plan is given by US EPA (1980). In general, a QA project plan should address the following:

1. Title page, with provision for approval signatures
2. Table of contents
3. Project descriptions
4. Project organization(s) and responsibilities
5. QA objectives for measurement data (precision, accuracy, completeness, representativeness, and comparability)
6. Sampling procedures
7. Sample custody
8. Calibration procedures, references and frequency

9. Analytical procedures
10. Data reduction, validation, and reporting
11. Internal QC checks and frequency
12. QA performance audits, system audits, and frequency
13. QA reports to management
14. Preventive maintenance procedures and schedule
15. Specific procedures to be used to routinely assess data precision, representativeness, comparability, accuracy and completeness of the specific measurement parameters involved.
16. Corrective action

Successful implementation of a QA plan depends on the competence of the monitoring personnel. All personnel involved in any function that may affect data quality (e.g. sample collection, analysis, data reduction and quality assurance) should have sufficient training in their appointed jobs to contribute to the reporting of complete and high quality data.

9.0
REVIEW OF EXISTING MONITORING PROGRAMS

In order to facilitate the development of a comprehensive monitoring program for the Santa Monica Bay Project, existing nonpoint source storm water projects that are similar to the Santa Monica Bay Project were reviewed to provide important information on the following monitoring elements for both dry and wet weather periods:

- number of monitoring stations
- types of constituents monitored
- frequency of sampling

The following nonpoint source projects were reviewed:

1) Santa Clara Nonpoint Source Control Program
2) Alameda County Urban Runoff Clean Water Program
3) Orange County NPDES Stormwater Permit Program
4) Bellevue Urban Runoff Program

The following discussion will provide a review of each project. For each project reviewed, a brief background of the project is discussed. Next, the discussion is organized according to 1) number of monitoring stations, 2) types of constituents monitored, and 3) frequency of sampling. Lastly, a brief summary is provided. The description include the rationale for some aspects of the plan which may be repetitive with other parts of this report, but is included for emphasis.

9.1 SANTA CLARA NONPOINT SOURCE CONTROL PROGRAM

9.1.1 Background: Initial Characterization Phase

The Santa Clara Nonpoint Source Control Program (Program) was initiated in 1987 to address concerns on nonpoint source discharges from storm water into the South San Francisco Bay Region or commonly known as the Lower South Bay. The Lower South Bay is classified by US EPA and the California State Water Quality Control Board as a water quality limited segment under section 304(L) of the Clean Water Act. Because of the water quality concerns of the Lower South Bay, the San Francisco Bay Regional Water Quality Control Board (Regional Board) has pursued an active regulatory role in controlling point and nonpoint discharges into the Lower South Bay. In the 1986 Basin Plan, the Regional Board directed Santa Clara County to develop and implement an Action Plan to conduct dry and wet weather water quality monitoring "for the evaluation of both concentrations of pollutants as well as total pollutant loadings and comparison with waste loads from point source discharges".

An action plan was developed in the summer of 1987 (CH2M-Hill and EOA, Inc. 1987) and implemented by WCC in the fall of 1987, and completed by WCC in the summer of 1989. The results of the hydrologic and water quality monitoring program, and the loads estimates were presented in Volume I of the Loads Assessment report (WCC, 1991a). This report constitutes the initial characterization phase of the Program. It should be emphasized that the major objective of this phase was to evaluate dry and wet weather pollutant concentrations and loads to the Lower South Bay.

9.1.1.1 Monitoring Stations

The Study Area is approximately 690 square miles and is divided into 11 watersheds. Given the size of the Study Area, and the need to project loads from the entire area, it was not feasible to monitor the entire Study Area and thereby estimate loads based on monitoring data alone. Instead, the study was designed to develop sufficient monitoring data to calibrate and verify a watershed load prediction model, which then could be applied to estimate loads from both gauged and ungauged watersheds.

There were a total of 16 stations representing three types of stations. Figure 9-1 shows the locations of these stations, and the 11 watersheds of the Santa Clara County.

9.1.1.1.1 Land use Stations

A total of seven stations representing small, relatively homogeneous land use catchments found in the area. Two stations (L1 and L2) represented industrial land use, and three stations represented low-density single-family residential (L4 and L5), and multi-family residential (L6) land uses. One station each is represented for commercial (L3) and open (L7) land uses. Table 9-1 provides a brief description of each station. Most of these stations are manhole or open channel stations except for the open land use station (L7), which is a natural creek. Data generated from these land use stations were used to characterize water quality from specific land uses, and also used as input to the loading model.

9.1.1.1.2 Stream Stations

Four stream stations were located in the lower portions of the watersheds and had relatively large, multiple land use catchments. These stations are located near the Bay, but above the zone of tidal influence in order to eliminate the effect of backwater on flow monitoring. Two stations (S3 and S4) drain the largest watersheds located in the eastern and central regions representing about 50 % of the total area. These two stations representing two of the largest watersheds also receive substantially more rainfall than the other smaller western watersheds. The other two stations (S1 and S2) represents smaller watersheds occupying the western region of the study area. WCC evaluated the adequacy of these four stream stations in representing the 11 watersheds (WCC 1991b). WCC found that the land use distribution of all four stations not only represented their respective watersheds that they reside, but also adequately represents the overall land use composition of the Study Area.

The important distinction between the stream and the land use stations is that the stream stations support aquatic habitat and therefore water quality must meet aquatic life criteria. Both dry (from base flow) and wet weather sampling were conducted at the stream stations.

9.1.1.1.3 Reservoir Stations

Six reservoir stations were located below the upland reservoirs and were used to estimate loads associated with reservoir (spillway) releases during wet years.

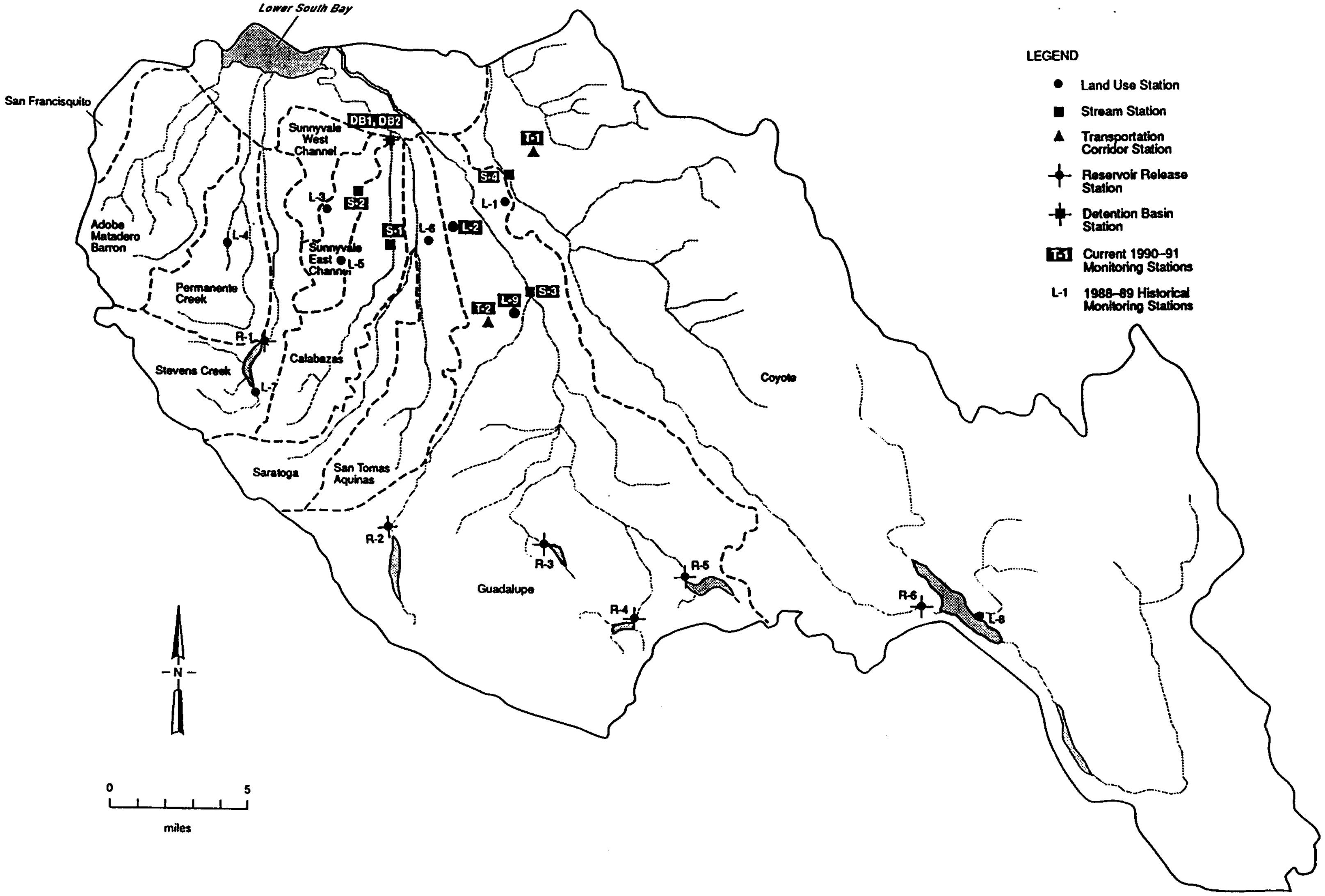


Figure 9-1 Sampling Stations and Watersheds in Santa Clara County.

Table 9.1. Description of Stations for Characterization Phase of the Santa Clara Valley Nonpoint Source Program

Station ID.	Principal Land Use	Drainage Area (acres)
A. Landuse Stations		
L1	Industrial Park	22
L2	Heavy Industry	28
L3	Commercial	265
L4	Low Density Single Family Residential	1600
L5	Single-Family Residential	2080
L6	Multi-Family Residential	85
L7	Open	8410
B. Stream Stations		
S1	Mixed (21% O, 0% I, 7% C, 71% R)	9200
S2	Mixed (0% O, 0% I, 32% C, 68%R)	3400
S3	Mixed (30% O, 4% I, 5% C, 61% R)	15900
S4	Mixed (64% O, 5% I, 1% C, 30% R)	79600
C. Reservoir Stations		
R1	Open	11000
R2	Open	24000
R3	Open	3800
R4	Open	7670
R5	Open	4600
R6	Open	125000

In comparisons with the requirements of Part II of the Federal NPDES storm water regulations, the regulations require monitoring of five to ten stations.

9.1.1.2 Constituents Monitored

The suite of constituents that were selected for chemical analyses on water and sediment samples were focused on potentially toxic contaminants, including heavy metals, organics (volatiles, semi-volatiles, pesticides and herbicides), nutrients, bacteria, and some conventional pollutants. This list of constituents were developed based on results of a Nationwide Urban Runoff Program, NURP (US EPA 1983), and also water quality excedances of specific pollutants in the South Bay. Table 9-2 summarizes the full list of constituents analyzed. This is a relatively comprehensive list when compared with the requirements specified in the Federal NPDES Part II regulations.

Metals analysis are commonly measured based on the total extractable fraction, i.e., metals that in solution as well as those associated with the suspended solids. The total fraction is used in estimating the total loads and comparisons with water quality criteria. However, the dissolved fraction, i.e., sample that is filtered through a 0.45µm filter, is the fraction that is directly available for organism uptake and therefore is more relevant for use in comparisons with water quality criteria. For two storm events, the dissolved fraction for metals was also analyzed.

This full suite of constituents was only conducted during the first storm, and sometimes in a few stations for the second storm only. Based on the results of the initial sampling a more limited suite (reduced) of analyses were performed for subsequent sampling rounds. The reduced suite of analyses is also presented in Table 9-2. The constituents that were dropped included volatile and semi-volatile organics, chlorinated herbicides, organophosphorus pesticides, and hexavalent chromium. These constituents that were dropped were mostly not detected in the storm water.

Constituents such as volatile organics have high potential to volatilize in turbulent storm waters. Unless the monitoring station is very close to the source (such as adjacent to an industrial facility that is illegally discharging volatiles), the presence of volatile organics in storm water is rarely found. For semi-volatiles, only the polynuclear aromatic hydrocarbons (PAHs) were retained for subsequent sampling analyses because PAHs are relatively toxic and some are known carcinogens. Additionally, PAHs are commonly found in petroleum by-products, and in combustion of wood and petroleum fuels. Rather than analyzing for 80 compounds in the semi-volatiles analysis, a specific PAH method using EPA 610 was used in subsequent sampling. In the EPA 610 method, a total of 16 specific PAH compounds are analyzed.

Another important secondary objective of the characterization phase was to evaluate the effects of storm water on toxicity in streams in Santa Clara County. While chemical monitoring has traditionally played an important role in evaluating water quality, toxicity monitoring using surrogate organisms is increasingly becoming a vital tool to evaluate potential impairment of receiving water bodies. Short-term chronic bioassay tests using three freshwater organisms were used to evaluate potential toxicity effects of both dry and wet weather samples. These tests are developed by US EPA (1986) and are routinely used in compliance monitoring of potential toxic effluent from industrial-treated as well as publicly-owned treatment works (POTW) wastewaters. The three surrogate organisms used in these tests are *Ceriodaphnia dubia* (an aquatic invertebrate), *Selenastrum capricornutum* (a freshwater alga), and *Pimephales promelas* (a fathead minnow fish).

Table 9-2 Full and Reduced Suites of Chemical Analysis for Water Samples.

Class	Full Suite	Reduced Suite
Organics	Total Organic Halogens	Total Organic Halogens
	Total Organic Carbon (TOC)	TOC
	Volatiles	
	Semi-volatiles	Polynuclear Aromatic Hydrocarbons (PAH)
	Organochlorine pesticides	Organochlorine pesticides
	Chlorinated herbicides	
	Organophosphorus pesticides	
Metals, Total	Arsenic	Arsenic
	Cadmium	Cadmium
	Chromium (total)	Chromium (total)
	Chromium (hexavalent)	Chromium (hexavalent)
	Copper	Copper
	Lead	Lead
	Mercury	Mercury
	Nickel	Nickel
	Selenium	Selenium
	Silver	Silver
	Zinc	Zinc
Nutrients	Total Kjeldahl Nitrogen (TKN)	TKN
	NH3-N	
	NO2 and NO3	
	Total Phosphate	
Bacteria	Total and fecal coliform	Total and fecal coliform
Other	BOD5	BOD5
	Temperature	Temperature
	pH	pH
	Total Suspended Solids	Total Suspended Solids
	Total Hardness	Total Hardness
	Turbidity	Turbidity

These tests evaluate the effects of storm water on three key organism indicators: mortality, reproduction, and growth.

9.1.1.3 Frequency of Sampling

9.1.1.3.1 Wet Weather

Figure 9-2 summarizes the types and frequency of sampling during both dry and wet weather periods. The goal of the study was to conduct sampling over two wet weather seasons (1987-1988 and 1988-1989). However, because of the extensive time required to select stations, install and test automated sampling equipment, only one storm was captured for the first wet weather season (1987-1988). A total of six storms were captured for the second wet weather season (1988-1989). Samples were collected as flow-weighted composites by automatic samplers. These samples represent average pollutant concentrations that were used to estimate total pollutant loads. Additionally, grab samples were taken during the early part of the storm for selected pollutants (such as oil and grease, volatile organics, bacteria) because of short holding times, special container requirements, or volatility. The following paragraphs discuss the rational for selecting the sampling frequency.

The wet weather season for California is about six months, starting in October and ending in April. Based on the national weather service rainfall gage at San Jose, the average storm volume for the 1948-1989 period is 0.7 inches, with most of the rain occurring during the months of November through March.

To adequately characterize storms during the wet weather season, a total of six storms collected about once every month were considered sufficient to cover the range of hydrological conditions. Of the six storms, the first storm of the wet weather season must be collected. This is because the first storm of the wet weather season is thought to have the largest pollutant concentrations. The high concentrations are attributable to the opportunity for dry deposition of pollutants on ground surfaces during the extended dry summer period, which are scoured by the first rainfall.

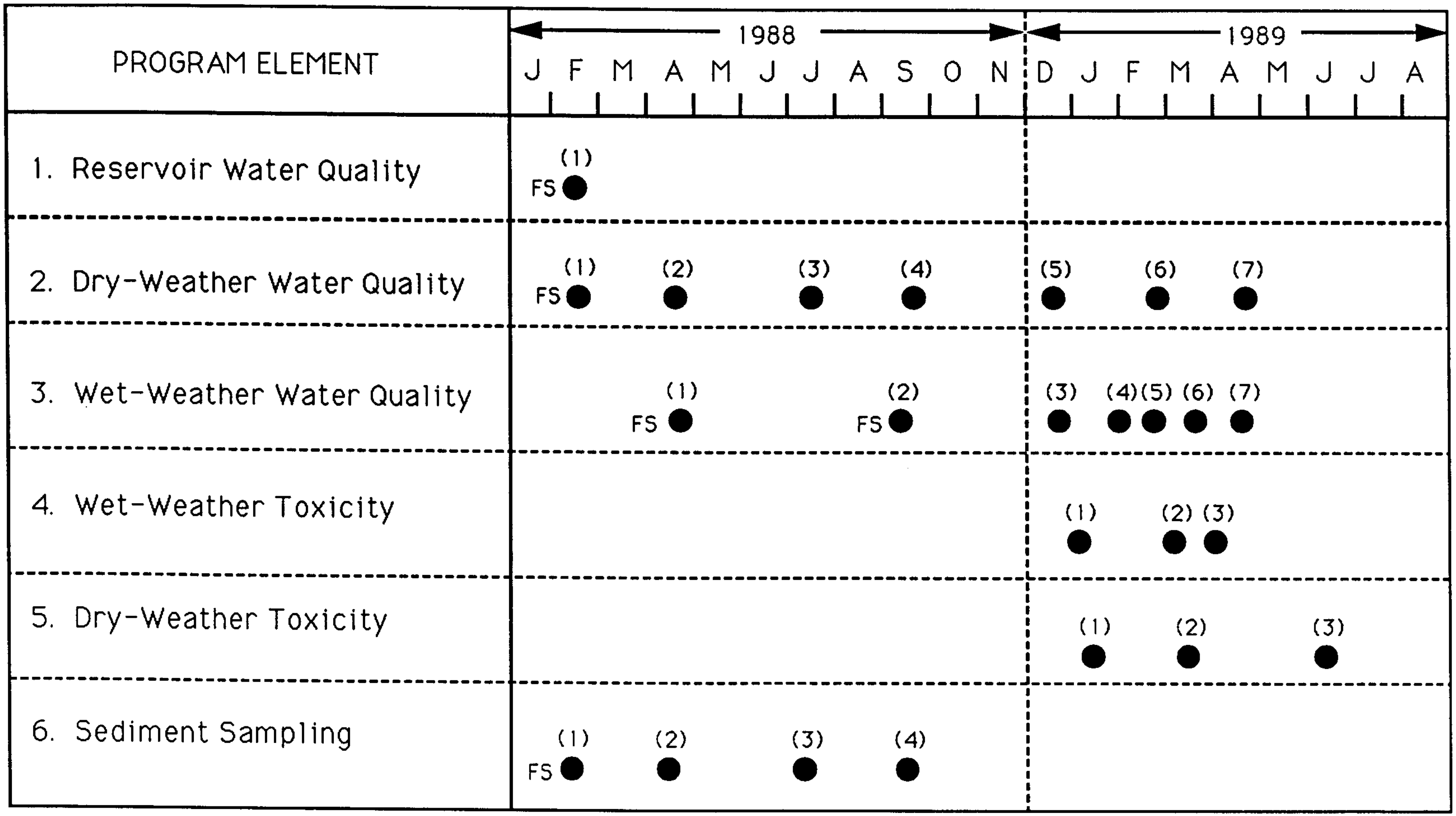
It is important to note that continued monitoring of the stream stations and specific industrial stations have to date generated about 15 to 20 data points per station. These data will be used as initial baseline conditions to be compared with additional monitoring (in future monitoring years) to evaluate potential improvements in water quality due to implementation of storm water pollution control measures across the County.

To provide a comparison with the requirements for Part II of the Federal storm water regulations, a minimum of three storm events separated by at least one month are required.

9.1.1.3.2 Dry Weather

Dry weather sampling was conducted during the summer of 1988, as well as dry weather flows during the wet weather season (i.e., in between storms). Both water and sediment samples were collected. The main objective of dry weather water sampling is to evaluate pollutant concentrations and loads during base flow from stream stations. A total of seven samples were collected; two during the summer, and five in between storms. Sediment sampling was conducted four times to evaluate sediment concentrations which serve as both sources and sinks for pollutants. All dry weather samples were collected as manual grabs.

Figure 9.2. Type and Frequency of Monitoring for Santa Clara Valley.



FS = FULL SUITE OF CHEMICAL ANALYSIS. REDUCED SUITE WAS PERFORMED AT OTHER STATIONS

9.1.2 Background: NPDES Permit Phase

Following the characterization phase, the Program applied for and obtained an NPDES storm water permit in June of 1990. From 1990 to date, WCC has continued to conduct monitoring for the Program. However, the monitoring objectives in this Permit period have expanded to include additional objectives. It must be emphasized here that the objectives of a monitoring program clearly drives the requirements for the type and frequency of monitoring.

The objectives of the monitoring program for the Permit Phase include the following:

- evaluate long-term trends in water quality
- identification of storm water pollutant sources
- comply with water quality objectives
- water quality improvements
- evaluate control measure effectiveness monitoring

Additional monitoring elements of this phase that are relevant to this discussion are summarized in section 9.1.2.1

9.1.2.1 Monitoring Stations

Table 9-3 shows the types of stations in the Permit phase. The total number of stations is ten. Five stations were retained from the characterization phase. These include four stream stations (S1 through S4), and one industrial station (L2). It was important to continue to monitor these stations because the stream stations can be considered as receiving water bodies supporting aquatic habitat, and as such can represent long-term monitoring stations. The industrial station was kept because of high concentrations of pollutants (especially chromium, cadmium, copper, lead and zinc) detected in the storm water. Continued monitoring of this industrial station will help in monitoring effectiveness of various source control measures that will be implemented in this industrial sub-catchment.

Five new stations were added. These include two stations for monitoring the effectiveness of pollutant removal of a detention basin, and another two for monitoring two major highways. The fifth station was selected to represent another industrial land use area.

9.1.2.2 Constituents Monitored

A set of constituents similar to the reduced suite was used in the permit phase, with the exception of PAHs. This reduced suite of analyses is shown in Table 9-4. Results of PAH analyses using EPA method 610 showed that most of the concentrations were less than the detection limit. Frequently, detection limits were elevated to 5 to 10 times the acceptable detection limits. A combination of high matrix interferences from salts and other natural humic organics found in the storm water, and low detection resolution by the High Performance Liquid Chromatography (HPLC) method, are likely responsible for the poor results.

A more superior method developed by Texas A&M's Geochemical and Environmental Research Group (GERG) was used for subsequent analysis of PAHs. The GERG method eliminates the matrix interference by various cleanup techniques, and uses Gas Chromatography / Mass Spectrometry (GC/MS) - Selected Ion Monitoring Mode (SIM) instrumentation to optimize detection of the specific PAHs. The number of PAHs include

Table 9.3 Description of Stations for Permit Phase of the Santa Clara Valley Nonpoint Source Program.

Station ID	Principal Land Use	Drainage Area (acres)
A. Stream Stations		
S1	Mixed	9220
S2	Mixed	3440
S3	Mixed	15900
S4	Mixed	79600
B. Transportation Stations		
T1	Paved Roadway	12
T2	Highway	35
C. Detention Basin Stations		
DB1 (inlet)	Mixed	250
DB2 (outlet)	-	-
D. Industrial Stations		
L2 *	Heavy Industry	28
L9	Light Industry	40

* The station was part of the initial characterization phase.

Table 9.4. Suite of Chemical Analysis for Permit Phase of Santa Clara Valley Nonpoint Source Program

Parameter	Units	Methodology	EPA Method (a)	Maximum Holding Time	Preservation	Target Detection Limit
INORGANICS						
pH	pH	pH electrode	150.1	Analyze Immediately	None	-
Hardness	mg/L	Titrimetric EDTA	130.2	6 months	HNO3 pH<2	1
Turbidity	NTU	Nephelometric	180.1	Analyze Immediately	Cool 4°C	1
TSS	mg/L	Gravimetric	160.2	7 days	Cool 4°C	10
METALS -TOTAL						
Arsenic	µg/L	Furnace-AA	206.2	6 months	pH <2 HNO3	1
Cadmium	µg/L	Furnace-AA	213.2	6 months	pH <2 HNO3	0.2
Chromium (Total)	µg/L	Furnace-AA	218.2	6 months	pH <2 HNO3	1
Copper	µg/L	Furnace-AA	220.2	6 months	pH <2 HNO3	1
Lead	µg/L	Furnace-AA	239.2	6 months	pH <2 HNO3	1
Mercury	µg/L	Cold Vapor - AA	245.1	28 days	pH <2 HNO3	0.2
Nickel	µg/L	Furnace-AA	249.2	6 months	pH <2 HNO3	2
Selenium	µg/L	Hydride - AA	270.3	6 months	pH <2 HNO3	0.2
Silver	µg/L	Furnace-AA	272.2	6 months	pH <2 HNO3	0.2
Zinc	µg/L	Furnace-AA	289.2	6 months	pH <2 HNO3	1
METALS - DISSOLVED						
Cadmium	µg/L	Furnace-AA	213.2	6 months	pH <2 HNO3	0.2
Copper	µg/L	Furnace-AA	220.2	6 months	pH <2 HNO3	1
Lead	µg/L	Furnace-AA	239.2	6 months	pH <2 HNO3	1
Silver	µg/L	Furnace-AA	272.2	6 months	pH <2 HNO3	0.2
Zinc	µg/L	Furnace-AA	289.2	6 months	pH <2 HNO3	1
Organics						
PAH *	µg/L	GC-MS	Texas A&M	7 day (extraction) 40 day (analysis)	Cool 4°C	0.003-0.100
TOC	mg/L	Combustion	9060	28 days	Cool 4°C pH < 2 H2SO4	1
Total Oil and Grease	mg/L	IR	413.2	7 day (extraction) 40 day (analysis)	Cool 4°C pH < 2 H2SO4	0.2

(a) Methods for Chemical Analysis of Water and Wastes (1983) EPA-600/ 4-79-020 the 16 EPA method 610 methods, and 14 additional methylated PAHs. Detection limits range from 0.003 to 0.100 µg/L, which is about more than 100 times lower than the detection limits for EPA method 610.

More sophisticated techniques to evaluate the groups of pollutants responsible for toxicity were used for toxicity testing. The 7-day short-term chronic bioassays used in the characterization phase showed that storm water from urbanized land uses were mostly toxic, especially to Ceriodaphnia. The tests, however, do not show what pollutants are responsible for toxicity.

Phase I Toxicity Identification Evaluation (TIE) tests (Mount and Carnahan, 1988, 1989a, 1989b) were used on storm water samples in the Permit Phase. If samples show toxicity (i.e., mortality), these Phase I TIE tests, using a combination of chemical and physical manipulations, are able to distinguish what broad groups of pollutants are responsible for causing toxicity. These groups tested include metals, non-polar organics, volatiles, ammonia, and strongly oxidizing agents.

9.1.2.3 Frequency of Sampling

All stations sampled for five storms for the wet weather season. Samples were collected as flow-weighted composites by automatic samplers. No dry weather water or sediment samples were conducted because of the fact that dry weather concentrations and loads were believed to be small and insignificant when compared with wet weather loads.

9.2 ALAMEDA COUNTY URBAN RUNOFF CLEAN WATER PROGRAM

9.2.1 Background: Initial Characterization Phase

In the San Francisco Bay Region, the Alameda County Urban Runoff Clean Water Program also addresses the impact of nonpoint source pollution from storm water runoff on the South Bay . The objectives of this Program is similar to the Santa Clara Valley Nonpoint Source Control Program. The Alameda Program was initiated in September 1988, and monitoring was conducted for two wet weather periods and one dry weather period between October 1989 and April 1991 (WCC 1991c).

9.2.1.1 Monitoring Stations

The Study Area is 345 square miles and 15 watersheds drain the area. There were a total of 16 stations. Figure 9-3 shows the locations of these stations. Out of these 16 stations, 10 were land use stations (L1 through L10) draining homogeneous land uses such as commercial, industrial, and residential. Another six stations were major stream or creek stations draining large mixed land uses. Table 9-5 summarizes the land uses types and drainage areas for each of the station.

9.2.1.2 Constituents Monitored

The suite of chemical analyses are similar to the Santa Clara Valley Nonpoint Source Control Program. A full suite of analyses were conducted for the first storm and a reduced suite was conducted for subsequent storms. A similar procedure was also followed for dry

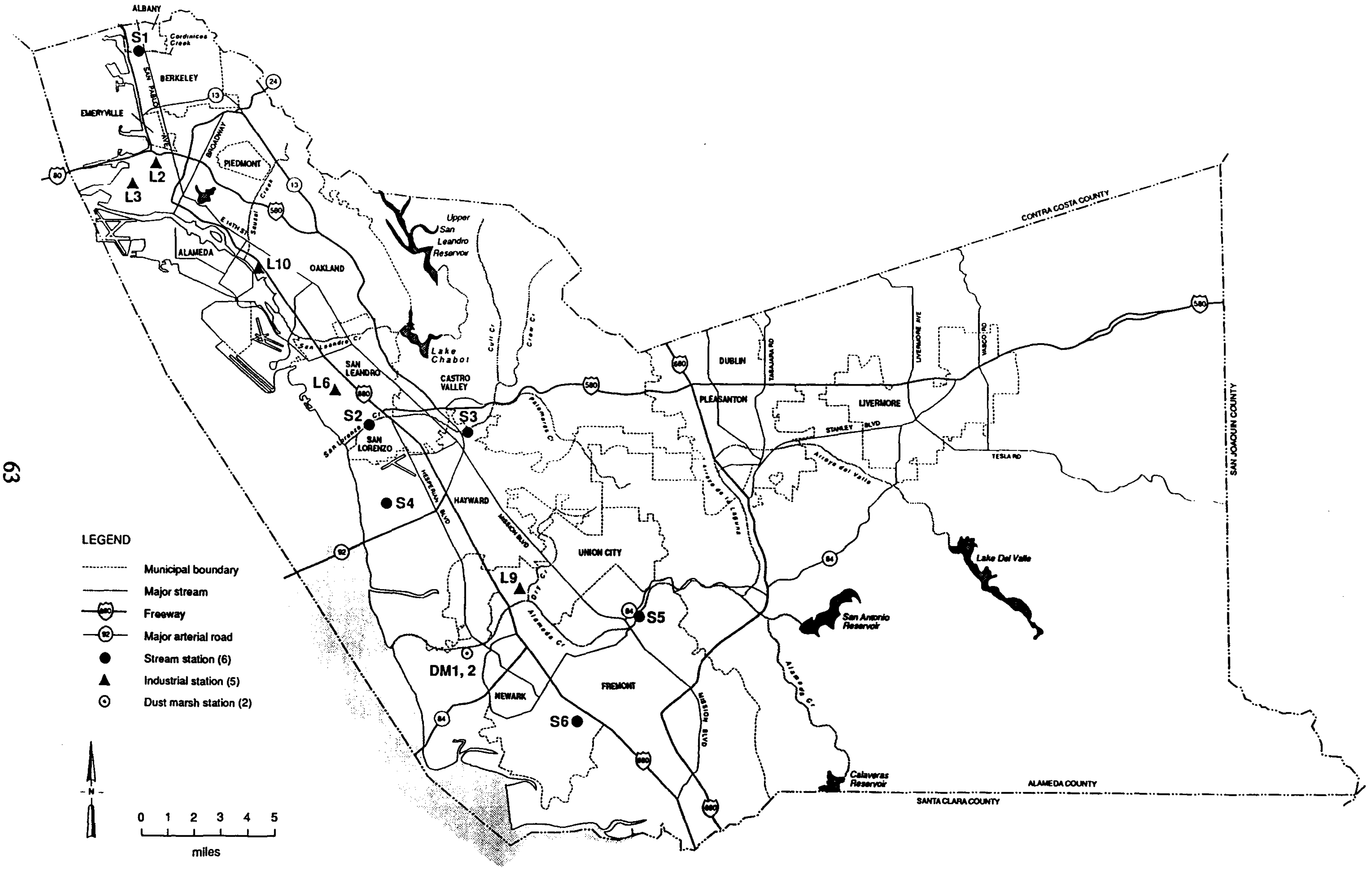


Figure 9-3 Sampling Stations and Study Area Detail in Alameda County.

Table 9-5 Description of Stations for the Characterization Phase of the Alameda County Urban Runoff Clean Water Program.

Station ID	Principal Land Use	Drainage Area (acres)
A. Landuse Stations		
L1	Open	176
L2	Mixed	950
L3	Industrial	168
L4	Residential/Commerial (59% R, 20% C)	20
L5	Residential/Commerial (83% R, 9% C)	355
L6	Industrial Park	690
L7	Residential/Commercial (33% R, 67% C)	78
L8	Open	6040
L9	Industrial Park	260
L10	Mixed (27% R, 27% C, 39% I)	140
B. Stream Stations		
S1	Mixed (88% R, 8% C)	180
S2	Mixed (12% R, 81% O)	28800
S3	Mixed (73% R, 7% C, 17% O)	3260
S4	Mixed (42% R, 21% C, 27% I)	1020
S5	Mixed	405000
S6	Mixed (68% R, 21% C)	1730

weather samples. For metals, both the total and dissolved fractions were analyzed on all samples.

9.2.1.3 Frequency of Sampling

Figure 9-4 summarizes the types and frequency of monitoring. A total of 11 storm events were conducted for the two wet weather periods. For each station, anywhere from five to nine storms were sampled.

Eight sampling events were conducted for the dry weather period at the six stream stations that had base flow. Two events were conducted during the summer (April to August 1990), and six events in between storms; three during the first wet weather, and another three during the second wet weather.

Four sediment sampling events were conducted at the six stream stations.

9.2.2 Background: NPDES Permit Phase

Subsequent to the initial characterization phase, the Program obtained a NPDES storm water permit in July 1990. The results of the characterization phase were used to direct the monitoring program for the permit phase.

9.2.2.1 Monitoring Stations

The number of stations were reduced from 16 to seven. Out of these seven stations, five of them were from the initial phase. These five stations are four stream stations (S1, S2, S3, and S5), and one industrial station (L3). The four stream stations drain the most important watersheds of the Alameda County, and also support aquatic habitat and riparian vegetation. The industrial station was retained because of the presence of elevated concentrations of metals and acute toxicity to biological organisms. Two new stations were initiated in a marsh environment to evaluate storm water pollutant removal effectiveness of the marsh.

9.2.2.2 Constituents Monitored

A reduced suite of analyses was conducted as shown in Table 9-4. Additionally, to aid in better understanding the issue of how much of the sorbed metals (attached to suspended solids) is bioavailable for organism uptake, a weak-acid extraction method, to supplement the traditional total and dissolved methods, was included. This weak-acid extraction was conducted on storm samples from one stream station for selected metals (cadmium, chromium, copper, lead, and zinc).

9.2.2.3 Frequency of Sampling

For each wet weather season, five storm events per station were conducted. Storm samples were collected as flow-weighted composites by automatic samplers.

Figure 9.4. Type and Frequency of Monitoring for Alameda County Urban Runoff Clean Water Program

MONITORING TYPE	1989			1990												1991				
	O	N	D	J	F	M	A	M	J	J	A	S	O	N	D	J	F	M	A	M
1. Wet Weather Sampling		X		X	X	X									X	X	X X	XXX		
2. Dry Weather Sampling			X		X		X		X		X					X	X		X	
3. Sediment Sampling			X		X		X									X				
4. Toxicity Testing							X		X						X X		X	XXX		

9.3 ORANGE COUNTY NPDES STORMWATER PERMIT PROGRAM

In July 1990, the San Diego and Santa Ana Regional Water Quality Control Boards issued NPDES Storm Water and Urban Runoff permits to the Orange County Storm Water Permit Program. The Program is comprised of the Orange County Flood Control District, the County of Orange, and its 29 incorporated cities. The objectives of the monitoring program are the following:

- to define the type, magnitude and sources of pollutants in the storm water system discharges within each permittees respective jurisdiction so that appropriate pollution prevention and correction measures can be identified;

- to evaluate the effectiveness of pollution prevention and correction measures; and

- to evaluate the compliance with water quality objectives established for the storm water system or its components.

The monitoring program to meet these objectives include extensive dry and wet weather sampling in four major watersheds of the County. Monitoring was initiated in January 1991. The following sections summarizes the scope of the monitoring program.

9.3.1 Monitoring Stations

There are a total of 54 stations spread over four major watersheds. These four watersheds are:

- Huntington Harbor / Anaheim, Sunset, Bolsa Bay
- Upper Newport Bay
- South County
- Santa Ana River

The types of stations are basically divided into storm channels (upstream of tidally-influenced areas) and receiving waters in the Bay. There are 34 storm channel stations and 20 Bay monitoring stations. Table 9-6 shows the list of storm channel and Bay monitoring stations in their respective watersheds. About half of these stations are located in the Newport Bay watershed. Most of these stations have been previously monitored by the Orange County Flood Control District. The bulk of the monitoring prior to the permit period was conducted during non-storm periods. Only limited data were collected during storm periods.

Out of the 34 storm channel stations, 23 are considered to be "waters of the State" and are therefore receiving waters. The other storm channel stations drains into stream tributaries that are receiving waters. Water from all these 34 storm channels ultimately drain into the Bay. Monitoring in the Bay include 20 stations.

9.3.2 Constituents Monitored

The selection of monitoring constituents was based on the analyses of past data conducted by the Orange County Environmental Management Agency, the RWQCB Toxic Substances Monitoring Program for Huntington Beach Channels and the State Mussel Watch Program. The list of constituents including nutrients, metals and organics are shown in Table 9-6.

Table 9-6 Frequency of Monitoring at Storm Channel and Bay Stations. (concluded)

Station	Nutrients	Metals (W)	Metals (S) PHP/PAH (S)
B. Harbor/Bay Monitoring Stations			
B.1 HUNTINGTON HARBOR/ANAHEIM, SUNSET, BOLSA BAY			
Sunset Aquatic Park	SEMI ST PS	ST PS	
Huntington Harbor (Chica Balsa Channel)	SEMI ST PS	ST PS	SEMI
Huntington Harbor (Warner Avenue)	SEMI ST PS	ST PS	SEMI
Christiana Bay	SEMI ST PS	ST PS	SEMI
Anaheim Bay	ST	ST	
Bolsa Bay	SEMI ST PS	ST PS	SEMI
B.2 NEWPORT BAY			
Upper Newport Bay (San Diego Creek)	M ST PS	ST PS	SEMI
Upper Newport Bay (Big Canyon Wash)	M ST PS	ST PS	SEMI
Upper Newport Bay (Shellmaker Island, N. Star Beach)	M ST PS	ST PS	
Upper Newport Bay (Newport Dunes)	M ST PS	ST	SEMI
Upper Newport Bay (PCH)	ST	ST	
Lower Newport Beach (Harbor Island Reach)	SEMI ST PS	ST PS	SEMI
Lower Newport Bay (Turning Basin)	ST	ST	
Lower Newport Bay (Rhine Channel)	ST	ST	SEMI
Lower Newport Bay (Harbor entrance)	ST	ST	
B.3 DANA PONT HARBOR			
East Basin	SEMI ST PS	ST PS	SEMI
West Basin	SEMI ST PS	ST PS	SEMI
Launch Ramp	SEMI ST PS	ST PS	SEMI
Boatyard	ST PS	ST PS	SEMI
Harbor Entrance	ST	ST	

M = Monthly Dry Weather Water Samples
ST = Storm Samples (4 for Storm Channels and 2 for Bay Stations)
PS = Post Storm Samples
SEMI = Semi-Annual Dry Weather Water and Sediment Samples
NUTRIENTS = Nitrate + Nitrite, Ammonia, Total Kjeldahl Nitrogen (TKN), Total Phosphate, Total Suspended Solids, Volatile Suspended Solids, pH, Dissolved Oxygen, Specific Conductance, Turbidity.
PAHs = Polynuclear Aromatic Hydrocarbons
PHP = Organochlorine Pesticides and Polychlorinated biphenyls, Chlorinated Herbicides and Selected Organophosphorus Pesticides
METALS = Copper, Chromium, Lead, Cadmium, Silver, Nickel, Zinc
S = Sediment
W= Water

The constituents that will be routinely analyzed for both dry and wet weather include the nutrients and metals. Nutrients, metals and organic constituents will only be analyzed on sediment samples collected during the dry weather periods. The decision to monitor only organic constituents during the dry weather is likely due to non-detectable concentrations of these organics during the wet weather.

9.3.3 Frequency of Sampling

Table 9-6 shows the frequency of monitoring for both storm channel and Bay stations. For the storm channel stations, two storms per station are proposed to be monitored for the first wet weather season for all stations. In subsequent years, three to five storms will be sampled. Two post-storm samples will be conducted to evaluate potential chronic effects of storm water for selected stations. During dry weather, water samples will be collected monthly for analysis. Sediment samples will also be collected two times during the dry weather period for selected stations.

Sampling storm water in the Bay is difficult because of tidal influence, and significant amounts of rainfall to produce a freshwater lens. An estimated rainfall of more than 0.5 inch is required for the receiving waters to exhibit a freshwater influence. The number of storms sampled per station will vary depending the weather and the amount of manpower and equipment available. Two post-storm samples (48 and 96 hours after the storm event) will be conducted for selected stations. Monthly water samples, and semi-annual sediment samples will be collected during the dry weather period for selected stations.

Water samples will be collected as discrete hourly samples for a 24 hour period by automatic samplers during storms and flow composited in the laboratory. The post storm sampling will be conducted 12 hours after the initial 24 hour sampling period. Samples will be taken once every three hours for a 72 hour period. Dry weather samples will be collected by a combination of grabs and automatic samplers, depending on the availability of the automatic samplers. Post-storm sampling and sediment samples will be collected by manual grab methods.

9.4 BELLEVU URBAN RUNOFF PROGRAM

Many aspects of urban runoff have been studied in Bellevue, Washington by the Environmental Protection Agency under the NURP study, with cooperation from the University of Washington, the US Geological Survey (USGS), the Municipality of Metropolitan Seattle (METRO), and the City of Bellevue Storm and Surface Water Utility. This section will describe briefly some of those studies and will focus on the sampling performed by the USGS.

9.4.1 University of Washington Projects

The University of Washington's Civil Engineering Department and Fisheries Research Institute performed studies of two receiving water bodies, one which had contributions from urban runoff and one that did not, to identify the impacts associated with urban development on receiving waters. Biological, chemical and physical parameters were analyzed. The main objectives of the project were:

- Document the variations (spatial and temporal) in distribution and abundance of aquatic organisms in urban streams
- Compare the condition of an urban and rural stream in the same general area
- Evaluate the biological, chemical and physical effects of urbanization on streams

9.4.2 Seattle METRO Project

The purpose of this project was to identify priority pollutants and other toxic pollutants in storm water as part of METRO's "Toxic Pollutant Inventory." The projects in Bellevue supplied samples to the Metro program for analysis. The results of this study were used to assess potential problems and evaluate best management practices. Besides identifying the toxic substances, the project also focused on identifying their sources through sampling and a literature review.

9.4.3 US Geological Survey Project

The USGS performed monitoring from 1979 to 1982 as part of the NURP study. The USGS reported the four main objective of the study were:

- Establish a consistent and accessible data base for typical watersheds

- Determine the magnitude and frequency of storm runoff loads of water quality constituents from three catchments in the city

- Develop methods for estimating storm and annual loads of water quality constituents from unsampled catchments in the study area

- Test the effectiveness of storm water quality management alternatives for the attenuation of constituent loads carried in storm water.

9.4.4 Monitoring Stations

There were a total of 8 stations within three catchments. These catchments were:

- Surrey Downs
- Lake Hills
- 148th Avenue S.E.

Five of these stations were used to monitor storm water quality and three of them were used to monitor wet and dry atmospheric deposition quality, only the storm water quality stations will be considered in this report. Table 9-7 shows the list of monitoring stations, their respective catchment, and land use breakdown. The Surrey Downs and Lake Hills catchments were predominately single family residential areas and are both approximately 100 acres. These two catchments were used to evaluate the effectiveness of street sweeping.

The 148th Avenue S.E. catchment has three main land uses: open park land, high density residential (9 dwellings per acre), and commercial. The total size of the catchment is 24 acres, however, one fourth of the catchment is occupied by 148th Avenue S.E. This catchment was used to investigate the effects of detention basins on storm water quality.

Table 9.7 Description of Stations for the USGS Monitoring in Bellevue, Washington.

Catchment	Station ID	Land Use of Catchment	Drainage Area (acres)
Surrey Downs	Catchment Outfall	91% R, 6% C, 3% O	95
Lake Hills	Catchment Outfall	90% R, 7% C, 3% O	102
148th Ave S.E.	Storm sewer below Lake Hills Boulevard	16% R, 24% C, 60% O	24
	Outlet from Detention Basin No. 3		
	Outlet from Detention Basin No. 5		

Three stations were located in this catchment. One captured storm water at the outlet of the catchment, one captured storm water at the outlet of control structure No. 3, and one at the outlet of detention basin No. 5. The samples from the outlet of control structure No. 3 were considered to be representative of the inflow into detention basin No. 5.

Water from all the catchments eventually drained into Lake Washington. The Surrey Downs catchment drains into an artificial pond, then into Mercer Slough and into Lake Washington. Lake Hills drains into Kelsey Creek, then into Mercer Slough and into Lake Washington. The 148th Avenue S.E. catchment drains into Larson Lake, then into Kelsey Creek and Lake Washington.

9.4.5 Constituents Monitored

The selection of monitoring constituents was specified by the Advisory Technical Planning Committee for the USGS and the US EPA. The list of constituents including nutrients, metals and organics is shown in Table 9-8. Also some samples were analyzed for major anions and cations, trace elements, ultimate carbonaceous biochemical oxygen demand, insecticides, herbicides, oil and grease, and total volatile residue.

9.4.6 Frequency of Sampling

Figure 9-5 shows the frequency of water quality monitoring in the three catchments. A total of 31 storm events were monitored at the Surrey Downs station and 37 storm events at the Lake Hills station. The 148th Avenue S.E. catchment was monitored for 23 storm events at the sampling station below Lake Hills Boulevard and 7 storm events at the other two stations.

Most catchment outlet water samples were collected by automatic samplers preset at 5 to 50 minute sampling intervals during storms. Each sampler filled 24 two-liter bottles in approximately 10 seconds. Samples collected at control structure No. 3 and detention basin No. 5 were collected manually using a depth integrated sampler. Depth integrated samplers were used at the outlets to collect samples for insecticide, herbicide, oil and grease, and sediment particle size analysis.

9.5 EQUIPMENT SUMMARY

Table 9-9 shows equipment used in two of the reviewed monitoring programs and three other programs known to the authors. It is included to show the types of equipment being used and specified. The inclusion is in no way an endorsement of the indicated products (some of the products are no longer available). The table indicates that automatic samplers are being used in all monitoring programs.

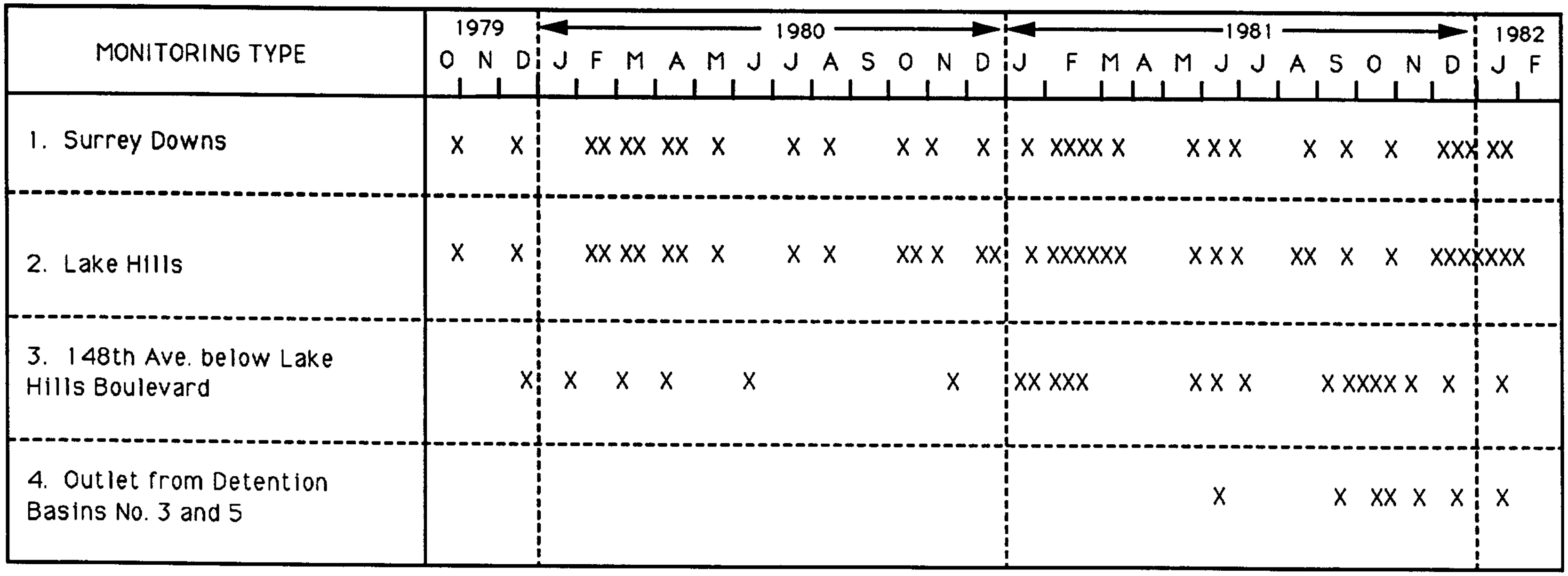
Table 9-8. Core Characteristics and Constituents Analyzed by the USGS in Belluvue, Washington.

Field determinations	Specific Conductance pH
Major Nutrients	Dissolved nitrate-plu-nitrate (as N) Dissolved ammonia (as N) Total ammonia plus organic nitrogen (as N) Total Phosphorus (as P) Dissolved phosphorus (as P)
Trace Elements	Total recoverable lead
Organic and Biological Constituents	Chemical oxygen demand Carbonaceous biochemical oxygen demand, 5-day Dissolved organic carbon Suspended organic carbon Fecal coliform bacteria
Other	Suspended solids Dissolved solids

Table 9-8. Core Characteristics and Constituents Analyzed by the USGS in Belluvue, Washington.

Field determinations	Specific Conductance pH
Major Nutrients	Dissolved nitrate-plu-nitrate (as N) Dissolved ammonia (as N) Total ammonia plus organic nitrogen (as N) Total Phosphorus (as P) Dissolved phosphorus (as P)
Trace Elements	Total recoverable lead
Organic and Biological Constituents	Chemical oxygen demand Carbonaceous biochemical oxygen demand, 5-day Dissolved organic carbon Suspended organic carbon Fecal coliform bacteria
Other	Suspended solids Dissolved solids

Figure 9-5. Frequency of Monitoring for Stations Monitored by the USGS Bellevue, Washington



MONITORING TYPE	1979 O N D	1980 J F M A M J J A S O N D	1981 J F M A M J J A S O N D	1982 J F
1. Surrey Downs	X X	XX XX XX X X X X X X	X XXXX X X X X X X X XXX	XX
2. Lake Hills	X X	XX XX XX X X X XX X XX	X XXXXXX X X X XX X X XXX	XXXX
3. 148th Ave. below Lake Hills Boulevard	X	X X X X X	XX XXX X X X X XXXX X X	X
4. Outlet from Detention Basins No. 3 and 5			X X XX X X	X

Table 9.9 Summary of Equipment Used in Previous Monitoring Programs

	Santa Clara Valley CA	Alameda County CA	Eugene OR	Portland OR	Pheonix AZ
Flow Monitoring Hardware					
ADS Quadredundant Depth Sounder			X	X	X
ADS Ultrasonic Velocity Sensor			X	X	X
Detechtronics IS Surveylogger Depth/Velocity Meter		X			
Drucks Pressure Transducer	X				
Monterdoro-Whitney Doppler Depth/Velocity Meter	X				
Sampling Hardware					
Isco 2700 Sampler	X				
Isco 3700 Sampler	X	X	X		X
American Sigma 800SL Sampler				X	

10.0
CONCLUSIONS

This report has reviewed sampling methods for water and wastewater with particular regard for stormwater. Chapters 2 through 5 discussed statistical methods, sample types, sampling equipment and sample storage and preparation. Chapter 6 reviewed flow measuring techniques. Chapter 7 discussed specific sampling problems while Chapter 8 reviewed quality assurance plans. Chapter 9 reviewed four case studies to illustrate the application of the materials presented in the earlier chapters. From this information, several conclusions are made:

1. Stormwater sampling programs may have many common procedures but many if not most of the elements are based upon site-specific considerations.

2. Stormwater monitoring programs are new and have been implemented in a development at fashion within tiered programs. The first parts of such programs usually sample a large number of stations, storm events and water quality parameters with the objective of determining the best monitoring strategy. Such programs anticipate a reduced suite of analysis and storm samples in subsequent years of the sampling program.

3. The most popular way to monitor is through automatic samplers which are set-up and programmed to sample specific storm events. Flow measuring equipment is usually provided with the automatic samplers and is usually comprised of Doppler-type flowmeters which can be installed without reducing the storm drain capacity. Traditional flow measuring equipment has little applications for stormwater monitoring.

4. Monitoring programs are created to both estimate pollutant loads as well as to better define aspects of the monitored watershed, such as land-use/pollutant concentration characteristics.

11.0
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APPENDIX A
WATER QUALITY PARAMETERS

1 Organic toxic pollutants

a. Volatiles

Acrolein
Acrylonitrile
Benzene
Bromoform
Carbon tetrachloride
Chlorobenzene
Chlorodibromoethane
Chloroethane
2-Chloroethylvinyl ether
Chloroform
Dichlorobromomethane
1,1-Dichoroethane
1,2-Dichloroethane
1,1-Dichloroethylene
1,2-Dichloropropane
1,3-Dichloropropylene
Ethylbenzene
Methyl bromide
Methyl chloride
Methylene chloride
1,1,2,2-tetrachloroethane
Tetrachloroethylene
Toluene
1,2-trans-dichloroethylene
1,1,1-trichloroethane
1,1,2-trichloroethane
Trichloroethylene
Vinyl chloride

b. Acid Compounds

2-Chlorophenol
2,4-Dichlorophenol
2,4-Dimethylphenol
4,6-Dinitro-o-cresol
2,4-Dinitophenol
2-Nitrophenol
p-Chloro-m-cresol
Pentachlorophenol
Phenol
2,4,6-trichlorophenol

c. Base/Neutral

Acenaphthene
Acenaphthylene
Anthracene
Benzidine
Benzo(a)anthracene
Benzo(a)pyrene
3,4-benzofluoranthene
Benzo(ghi)perylene
Benzo(k)fluoranthene
Bis(2-chloroethoxy)methane
Bis(2-chloroethyl)ether
Bis(2-chloroisopropyl)ether
Bis(2-ethylhexyl)phthalate
4-Bromophenyl phenyl ether
Butylbenzyl phthalate
2-Chloronaphthalene
4-Chlorophenyl phenyl ether
Chrysene
Dibenzo(a,h)anthracene
1,2-Dichlorobenzene
1,3-Dichlorobenzene
1,4-Dichlorobenzene
3,3'-Dichlorobenzidine
Diethyl phthalate
Dimethyl phthalate
Di-n-butyl phthalate
1,2-Dinitrotoluene
2,6-Dinitrotoluene
Di-n-octyl phthalate
1,2-diphenylhydrazine (as azobenzene)
Fluroranthene
Fluorene
Hexachlorobenzene
Hexachlorobutadiene
Hexachlorocyclopentadiene
Hexachloroethane
Indeno(1,2,3-cd)pyrene
Isophorene
Napthalene
Nitrobenzene
N-nitrosodimethylamine
N-nitrosodi-n-propylamine
Phenanthrene
Pyrene
1,2,4-trichlorobenzene

d. Pesticides

- Aldrin
- alpha-BHC
- beta-BHC
- gamma-BHC
- delta-BHC
- Chlordane
- 4,4'-DDT
- 4,4'-DDE
- 4,4'-DDD
- Dieldrin
- alpha-endosulfan
- beta-endosulfan
- endosulfan sulfate
- endrin
- endrin aldehyde
- Heptachlor
- Heptachlor epoxide
- PCB-1242
- PCB-1254
- PCB-1221
- PCB-1232
- PCB-1248
- PCB-1260
- PCB-1016
- Toxaphene

2. Other toxic pollutants (metal and Cyanide) and Total Phenols

- Antimony, Total
- Arsenic, Total
- Beryllium, Total
- Cadmium, Total
- Chromium, Total
- Copper, Total
- Lead, Total
- Mercury, Total
- Nickel, Total
- Selenium, Total
- Silver, Total
- Thallium, Total
- Zinc, Total
- Cyanide, Total
- Phenol, Total

3. Others parameters

Total suspended solids (TSS)
Total dissolved solids (TDS)
COD
BOD_5
Oil and grease
Fecal Coliform
Fecal streptococcus
pH
Total Kjeldahl nitrogen
Nitrate-Nitrite
Dissolved phophorus
Total phosphorus

APPENDIX B
COMPATIBILITY OF VARIOUS MATERIALS

Non-Ferrous Metals

Ability to withstand	Non-soldered copper	Brass	Bronze
Max. dry heat			
short -term	Above achievable water/steam sample temperatures		
long-term	Above achievable water/steam sample temperatures		
Hot neutral salt solution	Good, but unsuitable for determining metal and sulfuric acid content		
Weak acid	Varies with acid	Varies with acid	Varies with acid
Strong acid	Surface attacked	Surface attacked	Surface attacked
Weak alkali	Varies with alkali	Varies with alkali	Varies with alkali
Strong alkali	Metal surface attacked by the alkali		
Liquid organic solvents	Resistant to all known solvents		
Hydrocarbon diffusion	Resistant to diffusion at achievable water/steam sample temperatures		
Natural gas diffusion	Resistant to diffusion at achievable water/steam sample temperatures		

Ferrous Metals

Ability to withstand	Mild steel	Non-soldered corrosion resistant martensitic steel	Non-soldered corrosions resistant austhenitic/non-magnectic steel
Max. dry heat			
short-term	Above achievable water/steam sample temperatures		
long-term	Above achievable water/steam sample temperatures		
Hot neutral salt solutions	Good, but unsuitable for determining metal content		
Weak acid	Poor	Good	Very good
Strong acid	Surface attacked	Surface attacked	Very good
Weak alkali	Good	Very good	Very good
Strong alkali	Poor	Good	Very good
Liquid organic solvents	Resistant to all knowm solvents		
Hydrocarbon diffusion	Resistant to diffusion at achievable water/steam sample temperatures		
Natural gas diffusion	Resistant to diffusion at achievable water/steam sample temperatures		

Reference: Krajca (1989)

APPENDIX C
RECOMMENDED SAMPLE VOLUME AND PRESERVATION TECHNIQUE

Parameter	Collection technique	Container[a]	Preservation	Holding time[b]	Minimum required volume (ml)
Acidity	Grab or composite	P, G	Cool, 4°C	14 days	100
Alkalinity	Grab or composite	P, G	Cool, 4°C	14 days	100
Asbestos	Grab or composite	P	Cool, 4°C	48 hours	1000
Bacteria	Grab only	Pro, G	Cool, 4°C, 10% $Na_2S_2O_3$, EDTA	6 hours	200
Bicarbonate	Grab only	P, G	Determine on site	No holding	100
BOD	Grab only	P, G	Cool, 4°C	48 hours	1000
Bromide	Grab or composite	P, G	None required	28 days	100
Carbonate	Grab only	P, G	Determine on site	No holding	100
Chloride	Grab or composite	P, G	None required	28 days	50
Chloride demand	Grab only	P, G	Determine on site	No holding	200
Chromium VI	Grab or composite	P, G	Cool, 4°C	24 hours	100
COD	Grab only	P, G	H_2SO_4 to $pH < 2$; Cool, 4°C	28 days	50
Color	Grab or composite	P, G	Cool, 4°C	48 hours	50
Conductance	Grab or composite	P, G	Cool, 4°C	28 days	100

Appendix C (cont'd)

Parameter	Collection technique	Container[a]	Preservation	Holding time[b]	Minimum required volume (ml)
Cyanide	Grab or composite	P, G	NaOH to pH > 12, 0.6g Ascorbic acid[d]	14 days	500
Fluoride	Grab or composite	P	None required	28 days	300
Hardness	Grab or composite	P, G	HNO_3 to pH < 2	6 months	100
Hydrazine	Grab or composite	P, G	Do not analyzed immediately, collect under acid. Add 90 ml to sample to 10ml (1+9) HCl.	7 days	100
Iodine	Grab or composite	P, G	Cool, 4°C	24 hours	100
Iodine	Grab only	P, G	Determine on site	No holding	500
Metals (Except Cr VI)					
Dissolved	Grab or composite	P, G	Filter on site, HNO_3 to pH < 2	6 months, except Mg- 28 days	200
Suspended	Grab or composite	P, G	Filter on site	6 months, except Mg- 28 days	200
Total	Grab or composite	P, G	HNO_3 to pH < 2	6 months, except Mg- 28 days	100

Appendix C (cont'd)

Parameter	Collection technique	Container[a]	Preservation	Holding time[b]	Minimum required volume (ml)
<u>Nitrogen</u>					
Ammonia	Grab or composite	P, G	Cool, 4°C, H_2SO_4 to pH < 2	28 days	400
Kjeldahl (total)	Grab or composite	P, G	Cool, 4°C, H_2SO_4 to pH < 2	28 days	500
Nitrate plus Nitrite	Grab or composite	P, G	Cool, 4°C, H_2SO_4 to pH < 2	28 days	100
Nitrate	Grab or composite	P, G	Cool, 4°C, H_2SO_4 to pH < 2	48 hours	100
Nitrite	Grab or composite	G	Cool, 4°C, H_2SO_4 to pH < 2	48 hours	50
Oil and Grease	Grab only	G	Cool, 4°C, H_2SO_4 to pH < 2	28 days	1000
<u>Organics</u>					
Extractable (base/neurals and acids)	Grab or composite	G, Teflon-lined cap	Cool, 4°C	7 days until extraction, 30 days after extraction	1000
Purgeable (halocarbons-aromatics)	Grab only	G, Teflon-lined cap	Cool, 4°C	14 days	40

Appendix C (cont'd)

Parameter	Collection technique	Container[a]	Preservation	Holding time[b]	Minimum required volume (ml)
Oragnic(cont'd)					
Purgeable (acroleina nd acrylonitrile)	Grab only	G, Teflon-lined cap	Cool, 4°C	14 days	40
Pesticides and PCBs	Grab or composite	G, Teflon-lined cap	Cool, 4°C	7 days until extraction, 30 days after extraction	250
pH	Grab only	P, G	Cool, 4°C	2 hours	25
Phenol	Grab or composite	G	Cool, 4°C, H_2SO_4 to pH < 2	24 hours	500
Phosphorus					
Ortho-phosphate	Grab or composite	P, G	Filter on site, cool, 4°C	48 hours	50
Phosphorus, total	Grab or composite	P, G	Cool, 4°C, H_2SO_4 to pH < 2	28 days	50
Radioactivity	Grab or composite	P, G	$HNO_3$to pH < 2	6 months	1 gal
Silica					
Dissolved	Grab or composite	P	Cool, 4°C	28 days	50
Total	Grab or composite	P	Cool, 4°C,	28 days	50

Appendix C (cont'd)

Parameter	Collection technique	Container[a]	Preservation	Holding time[b]	Minimum required volume (ml)
<u>Solids</u> Dissolved	Grab or composite	P, G	Cool, 4°C	7 days	100
Volatile Dissolved	Grab or composite	P, G	Cool, 4°C	7 days	100
Suspended	Grab or composite	P, G	Cool, 4°C	7 days	100
Volatile suspended	Grab or composite	P, G	Cool, 4°C	7 days	100
Total	Grab or composite	P, G	Cool, 4°C	7 days	100
Volatile Total	Grab or composite	P, G	Cool, 4°C	7 days	100
Settleable	Grab or composite	P, G	Cool, 4°C	48 hours	100
Sulfate	Grab or composite	P, G	Cool, 4°C	28 days	50
Sulfide	Grab or composite	P, G	Cool, 4°C, 2 ml zinc acetate plus NaOH to pH > 9	7 days	500
Sulfite	Grab or composite	P, G	Determine on site	No holding	50
Surfactants	Grab or composite	P, G	Cool, 4°C	48 hours	250
TOC	Grab or composite	G, Teflon lined-cap	Cool, 4°C, HCl to pH < 2	28 days	25

Appendix C (cont'd)

Parameter	Collection technique	Container[a]	Preservation	Holding time[b]	Minimum required volume (ml)
TOX	Grab or composite	G, amber, Teflon-lined cap	Cool, 4°C, add 1 ml 0.1 M sodium sulfite	7 days	100
Turbidity	Grab or composite	P, G	Cool, 4°C	48 hours	100

Note:

[a] P = Polyethylene G = Glass Pro = Polypropylene

[b] The holding time are those listed in *Technical Additions to Methods for Chemical Analysis of Water and Wastes*, EPA-600/4-82-055 and *Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater*, EPA-600/4-82-057.

Reference: US EPA (1984)