

UNIVERSITY OF CALIFORNIA

Los Angeles

Particle Size Distribution in Highway Runoff:
Measurement, Characteristics, and Management Implications

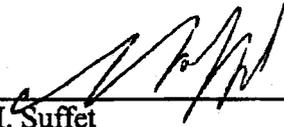
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requirements for the degree Doctor of Philosophy
in Civil Engineering

by

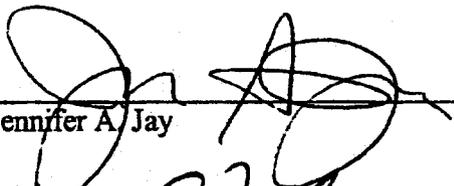
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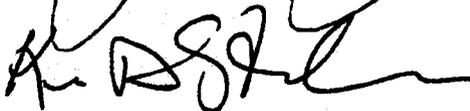
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To my parents Hongsheng Li and Wenge Yu

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ABSTRACT OF THE DISSERTATION

Particle Size Distribution in Highway Runoff: Measurement, Characteristics, and Management Implications

By

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Professor Michael K. Stenstrom, Chair

Stormwater has become the major pollution source to the receiving water bodies in many urban areas due to increased development and improved control of point source pollution. Since most of the stormwater treatment facilities target solids removal, understanding particle characteristics has become the most important step to choose suitable treatment facilities (e.g. Best Management Practices).

PSD in highway runoff was measured in seven storm events in 2002-2003 rainy season. An experimental protocol was developed to measure PSD carried by highway runoff in order to achieve repeatable and reliable results. Sample contamination, sample

representativeness, sample storage time and temperature, and PSD reproducibility were evaluated. PSD changed with time and temperature and particle size analysis must be performed within six hour of sample collection to minimize the change of PSD. Composite samples collected by auto samplers were not suitable for particle analysis purpose due to the change of PSD.

A total of 172 grab samples were analyzed from the three monitoring sites. Particle concentration decreased rapidly to 6 mm of accumulated rainfall, and then declined more slowly throughout the storm. Particle concentration was correlated with total suspended solids (TSS) and turbidity. A two-compartment settling tank was proposed as a BMP and was effective in removing both small and large particles when simulated using the measured PSD. Particle first flush was observed and the associated pollutants also demonstrated a first flush.

Optimization of the two-compartment settling tank design was evaluated by fixing the total volume of two compartments and changing the volume ratio between them. When the design storm for the total volume of the tank is only a few millimeters, no storage compartment produced the highest particle removal efficiency. When the design storm for the total volume of the tank is more than 10 mm, a volume ratio 3:1 of the storage compartment to continuous flow compartment produced the highest particle removal efficiency. Maximum metal and toxicity removal efficiencies increased rapidly with the increasing total design storm size up to 13 mm design storm size, and decreased slowly thereafter.

1. INTRODUCTION

Nonpoint source (NPS) pollution has become the major cause of the deterioration of water bodies (USEPA 2003). This has occurred because of improved control of point source pollutions and continuing urbanization and development. Nonpoint source pollution results from stormwater or snowmelt moving through or across developed areas, picking up pollutants and discharging into surface waters. Recognition of NPS pollution is not recent and was cited in the 1972 Amendments to the Clean Water Act. The National Urban Runoff Program (NURP) was established in 1978 to facilitate investigation and research of NPS or stormwater pollution. Numerous studies have been conducted under this program and showed that stormwater runoff from highways, industrial, commercial, residential, and agricultural areas contained significant conventional and toxic pollutants (USEPA 1983; Lord 1987).

Reports to congress document that urban stormwater runoff in the United States of America contribute to 13% of impaired river and stream miles, 21% of impaired lake acres, 55% of impaired ocean shoreline miles, and 46% of impaired estuary square miles (USEPA 2000). It is estimated that one third of California's beach closure was due to stormwater pollution.

More recently, a little noticed provision of the US Clean Water Act (§ 303) has been resurrected, to require permitting authorities to develop pollutant load allocations

known as total maximum daily loads (TMDLs) for all discharge sources of pollutants to water bodies that are causing or contributing to impairment of beneficial uses, including stormwater runoff. This method of allocation requires that the total pollutant load from stormwater runoff be managed, and stormwater loads can no longer be considered only as single, episodic events of large runoff volume of short duration. With the increasingly stringent regulations for water quality control, such as TMDL programs and the establishment of the final rules for Phase II of the National Pollutant Discharge Elimination Program for stormwater, the need for suitable treatment methods (best management practices or BMPs) will remain significant for many years to come (Zhen et al. 2004).

Among various NPS sources, runoff from transportation or highways is one of the most notorious due to the appearance of heavy metals and organics which show toxicity in short term and accumulation in long term. Dissolved heavy metals are usually considered bioavailable, while particulate heavy metals usually accumulate in the sediments of receiving water bodies, and can be remobilized later by natural or human activities (Lin et al. 2003). Since heavy metals cannot be degraded in the environment, accumulation from the large volumes of runoff is of concern, and reducing heavy metal loadings to ecosystems has become a priority. Hydrocarbons, nutrients, and pesticides are also important pollutants associated with highway runoff (Colwill et al. 1984; Driscoll et al. 1990; Ball et al. 1994; Barrett et al. 1995; Young et al. 1996).

Many studies have demonstrated that runoff from highways, especially those with heavy traffic load (e.g. more than 30,000 average vehicles per day or ADT), should be treated before allowed to enter receiving water bodies (Aldheimer and Bennerstedt 2003). Most BMPs, such as ponds, wetlands, detention basins and slow sand filters, remove particles. Particle removal is important, not only for the removal of the particles themselves, but also for the pollutants that are adsorbed to the particle surfaces. Metals and polynuclear aromatic hydrocarbons (PAHs) are known to concentrate on particle surfaces (Oliver et al. 1974; Herrmann 1981; Ongley et al. 1981; Hoffman et al. 1985; Hewitt and Rashed 1992; Andral et al. 1999; Legret and Pagotto 1999; Bäckström 2002; German and Svensson 2002). Therefore knowledge of particle characteristics in highway runoff, especially those related to settling velocity such as PSD, shape, and specific gravity, is of critical importance for BMP selection.

This dissertation focuses on understanding particles in highway runoff and included three major parts: PSD measurement protocol development, dynamic characteristics of particles, and application to BMP designs. The objective is to obtain more knowledge on PSD in highway runoff and to use it for runoff treatment and stormwater management. Specifically, the first objective is to obtain reliable and repeatable PSD results. The second objective is to characterize PSD as a function of storm characteristics and to use it for BMP design. The third objective is to achieve maximum removal efficiency of particles and associated metals and toxicity using PSD information.

This dissertation contains five chapters. Chapter 1 briefly summarizes the problem and describes the organization and objective of the dissertation. Chapter 2 discusses PSD measurement protocol development and PSD results for the first three events in 2002-2003 rainy season. Particle first flush phenomena are also included. Chapter 3 reports the dynamic characteristics of PSD of 172 grab samples in seven events from three monitoring sites in 2002-2003 rainy season. Correlation between particles and other water quality parameters are also investigated. A two-compartment settling tank design is proposed as an improved BMP design. Chapter 4 describes an optimized two-compartment settling tank design based on removals of particles, heavy metals and toxicity. Chapter 5 provides the overall conclusions of this dissertation.

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2. PARTICLE SIZE DISTRIBUTION IN HIGHWAY RUNOFF- EXPERIMENTAL PROTOCOL DEVELOPMENT

Abstract

Particles in highway runoff contain various sorbed pollutants, and many best management practices (BMPs) are selected for particle removal efficiency. Particle removal efficiency is a function of particle size and density, which makes particle size distribution (PSD) a crucial BMP design parameter. PSD was quantified for three rainfall events during 2002-2003 rainy season at three highway sites in west Los Angeles. Rainfall, runoff flow rate, and a large suite of water quality parameters were also measured. An experimental protocol was developed for bottle cleaning, sample storage and mixing that provided repeatable results. A naturally occurring particle aggregation occurred which required samples to be analyzed in less than six hours; the concentration of small particles decreased with a corresponding increase in the concentration of larger particles in stored samples. The PSD changed throughout the storm, and the particle concentration decreased as the storm progressed. The number of large particles decreased more rapidly than the total number of particles. Particles between 2 μm and 1000 μm demonstrated a strong first flush. On average, 40% of the particles were discharged in the first 20% of the runoff volume.

Keywords: Stormwater; Highway; Runoff; Particle size distribution; Best management practices; Pollutants.

2.1 Introduction

A great proportion of pollutants in highway runoff such as heavy metals and polynuclear aromatic hydrocarbons (PAHs) are bound to particles (Oliver et al. 1974; Herrmann 1981; Ongley et al. 1981; Hoffman et al. 1985; Hewitt and Rashed 1992; Legret and Pagotto 1999). Most of the particles are characterized as suspended solids (Uchimura et al. 1997). The large surface-to-volume ratios of particles in highway runoff provide reactive locations for partitioning and transport of pollutants, and may serve as reservoirs of these pollutants in downstream locations (Oliver et al. 1974; Thomson et al. 1997; Cristina et al. 2002). In addition, pollutants sorbed to particles generally have less mobility and bioavailability than in their dissolved form. Consequently, understanding characteristics of particles in highway runoff is crucial for future runoff management and BMP selection.

Particles in highway runoff arise from roadway maintenance operations, atmospheric deposition, corrosion and erosion, and various kinds of traffic activities such as tire abrasion, vehicular wear, fluid leakage, and pavement degradation (Kobriger and Geinopolos 1984; Thomson et al. 1997; Legret and Pagotto 1999; Grant et al. 2003). Tire and pavement wear produces numerous particles with diameters from several nanometers to several millimeters. Their properties range from quickly dissolving to insoluble (Sansalone and Buchberger 1997a)

Tire and pavement abrasion is the source of many of the particles (Muschack 1990; Sansalone and Tribouillard 1999). Kobriger and Geinopolos (1984) reported the distribution of particles from vehicle-related deposition processes: 37% arise from pavement wear; 37% from tire wear, and 18.5% from abrasion of vehicle parts, such as brakes and engines. Deposition from settleable exhaust accounts for 7.5% of the total particulate mass.

The focus of this study is to characterize particles size distribution (PSD) of highway runoff with major emphasis on developing a protocol to insure proper particle analysis and reproducible results. In addition, runoff samples were collected throughout the hydrograph and particles were analyzed to verify the existence of particle first flush.

2.2 Review of Particle-sizing Technique

Several particle-sizing techniques have been utilized to characterize stormwater. Sieving techniques use screens for analyzing dry or wet particles. Sedimentation methods have been used for particles in the water column (Gromaire-Mertz et al. 1999). A large variety of instruments have been developed for characterizing particles in the water column, and their advantages and disadvantages are shown in Table 2.1.

Table 2.1. Particle Sizing Techniques Commonly Used in Stormwater Area (Grant et al. 2003)

Particle's (P's) Property Measured	Aspect Measured	Advantage	Limitation	Sample Instruments
Transport property: sedimentation	Gravity	Directly applicable results to sedimentation basin design.	Slow	MICROMERITICS Sedigraph
Electrical property: differential resistance	Voltage pulse (proportional to P's volume)	Change of particles in sub-size region has no effect elsewhere. Results are not affected by P's shape, nature, gravity, and refractive index.	Carrier fluid influence (e.g. coagulation); May disrupt fragile fflocs.	COULTER Multisizer 2
Light obscuration (blockage)	Voltage pulse (proportional to P's maximum cross sectional area)	Change of particles in sub-size region has no effect elsewhere. Results are not affected by P's, nature, gravity, and refractive index. Optical analogue of resistive pulse technique but without electrolyte.	May disrupt fragile flocs.	NICOMP AccuSizer 780 PACIFIC SCIENTIFIC INSTRUMENTS Model 9703
Light diffraction property: light intensity	Light intensity	Do not require calibration step.	Concentration of solution has great influence on results.	SEQUOIA LISST-100 MASTERSIZER S Laser Particle Size Analyzer
Dynamic light scattering property: Time or spatial fluctuations in scattering intensity	Hydrodynamic effect – photopulse signal	Good for small particles till 1nm.	Need long time to get stable	NICOMP PSS 170

Sieving methods are used for larger, dry particles (generally larger than 45 μm). Ellis and Revitt (1982) used oven drying and sieve analysis for sediments from roadway runoff. Lau and Stenstrom (2001) reported PSD of samples collected during dry weather from roads; they used air drying and mechanical screens over a range of 43 to 2,200 μm . Sansalone et al. (1997b, 1998) collected sediments from individual storm events and measured PSD by drying the sediments at 110° C and sieving with mechanical screens. The drying step required before sieving can alter particle size and character (Krein and Schorer 2000). In addition, due to potential aggregation among particles, PSD in sediments does not necessarily represent the PSD in runoff (Slattery and Burt 1997).

Roberts et al. (1988) utilized a Coulter Counter with electrical resistance technique to measure particle sizes and employed scanning electron microscopy to characterize the alteration of runoff-entrained pavement solids transported through a pipe sewer during rainfall runoff events. Sansalone et al. (1998) investigated PSD in highway runoff ranging from 2 μm to 300 μm using a HIAC/ROYCO light obscuration instrument. Drapper et al. (2000) employed a Mastersizer laser particle size analyzer to determine the PSD of roadway runoff samples taken from sites in southeast Queensland, Australia. The instrument uses light diffraction technique.

Hargesheimer et al. (1992) proposed an experimental particle-sizing protocol for enumerating the total number of particles in wastewater effluents, and described sample collection, handling and analysis and storage procedures. They found that although carefully cleaned caps and freshly dispensed parafilm contaminated samples with small

particles (most less than 1 μm in diameter), glass bottles, cleaned by hand, dishwasher or super-cleaning procedures, were satisfactory sample containers when counting particles as small as 0.5 μm in diameter. Plastic and teflon bottles were unsuitable containers when counting particles less than 5 μm in diameter, regardless of cleaning methods. Gentle inversion, sonication, and inversion-sonication-inversion were satisfactory mixing techniques, producing similar particle counting results. Gentle inversion was preferred because of its simplicity. They found that the variability of particle counts increased with storage time and results were most reproducible immediately after sample collection. Although several researchers have measured PSD in highway runoff or stormwater (Characklis and Wiesner 1997; Sansalone et al. 1997b, 1998; Legret and Pagotto 1999), no consistent experimental method has evolved. In addition, few researchers have systematically measured PSD over a wide range (2-1000 μm) and over entire storm events. Both of these topics are the focus of this paper.

2.3 Methodology

2.3.1 Site Description

Three monitoring sites in west Los Angeles were selected with catchment areas ranging from 0.39 to 1.69 hectares and annual average daily traffic (AADT) of over 260,000 vehicles per day. These three sites were chosen as typical small catchment area sites with heavy traffic load, and were within 15 minutes travel time to the lab at University of California, Los Angeles (UCLA). The sites were so small that there was very little delay between the peak rainfall and peak runoff (i.e. 5 minutes or less). All sites were equipped

with American Sigma (Loveland, Colorado) 950 Flow Meters, tipping bucket rain gauges and composite auto samplers. For additional information on composite sampling equipment, the reader can refer to Kayhanian et al. (2003). Additional site descriptions are summarized in Table 2.2.

Table 2.2. Site Description Summary

Site ID	Location	AADT (vehicles/day)	Catchment Area (hect)	Number of Lanes (/direction)	Drainage Pipe Diameter (mm)	Approximate Impervious (%)
Site 1	Hwy 101, Van Nuys	328,000	1.28	6	508	100
Site 2	Hwy 405, Getty Center Exit	260,000	1.69	5	610	95
Site 3	Hwy 405, Santa Monica Blvd.	322,000	0.39	5	600	100

2.3.2 Sample Collection Procedure

Grab samples were collected manually with a polypropylene container from a free waterfall as runoff exited the drainage pipe, and stored in 4L narrow mouthed amber glass bottles. Collection began immediately after the beginning of runoff, usually within a few minutes of the beginning of rainfall. Subsequent samples were taken during the first hour at 15-minute intervals. After the first hour, grab samples were taken at 1-hour intervals for the following 7 hours. Some storm event durations in the study area were more than 8 hours. For storms lasting longer than 8 hours, one or two additional grab samples were collected. Flow-weighted composite samples were collected using several

4L glass bottles by composite auto samplers. The grab samples collected within the first hour were delivered to the lab (15 minutes or less travel time) once the fifth grab sample was taken. PSD was analyzed as soon as the samples reached lab and completed within the next 2 hours. The samples collected from the second hour until the end of the storm event were periodically taken to the lab, and all were analyzed for PSD within 6 hours of collection. Composite samples were also brought to the lab at the end of storm event and were analyzed within 6 hours of collection. The logic behind the PSD analysis within 6 hours is discussed in the following section.

2.3.3 Particle Size Analysis

A Nicomp (Santa Barbara, California) PSS AccuSizer 780 Optical Particle Sizer module equipped with an auto-dilution system and a LE1000-2SE Light Scattering/Extinction sensor was used for particle size analysis. This instrument was selected for its wide range (2 to 1000 μm), speed (< 2 minutes/sample analysis) and auto dilution capability. A representative sample ranging in volume from 1 to 10 ml was removed from the 4L sample bottle using a wide-bore glass pipette, after gently inverting the 4L bottle 5 to 6 times, and then injected into the AccuSizer. Between samples, the system was flushed at least three cycles, which reduced background particle concentrations to less than 3/ml.

2.4 Results and Discussion

2.4.1 PSD Protocol Development

As discussed in the previous section, no standard protocol exists for measuring PSD in stormwater. A series of experiments was performed to establish a standard protocol with known accuracy and repeatable results. These experiments were performed to understand four key sampling concerns: PSD reproducibility, sample contamination, sample representativeness, and sample storage time and temperature. These parameters were studied for three months using stored samples, before beginning similar experiments with fresh highway runoff samples. Each experimental parameter is discussed in the following sections.

2.4.1.1 PSD Reproducibility

The reproducibility of the PSD obtained by AccuSizer was demonstrated by measuring duplicate stormwater samples. Fresh samples were randomly obtained from 3 storm events. The difference between each duplicate pair was represented by a difference proportion (DP), calculated as follows:

$$\text{Difference proportion} = 100 \frac{2|N_1 - N_2|}{(N_1 + N_2)} \quad (2.1)$$

Where N_1 and N_2 are the number of particles in a specific size range for the first and second samples. The mean and variance of DP values of eleven duplicates are shown in Table 2.3.

Table 2.3. DP Values of Duplicate Samples (11 duplicates)

	Particle Diameter Range (μm)										Total
	2-3	3-5	5-7	7-10	10-20	20-30	30-50	50-100	100-200	200-1000	2-1000
Mean	9.5	4.5	6.1	8.3	9.6	9.7	20.4	35.4	66.9	75.6	5.0
Variance	0.5	0.1	0.2	0.5	0.8	0.9	2.4	12.0	24.4	64.2	0.1

The difference for duplicate samples was within 10% for particles less than 30 μm . The DP increased for larger particles, and the difference was approximately 76% for particles in the range of 200 to 1000 μm . This resulted in part because there were less particles in this size range. The number of particles with diameter from 200 to 1000 μm ranged from 0 to 57/ml. This means that even a small difference in particle number will produce a large DP. For the 2 to 3 μm size range, the number of particles averaged 166,000/ml. To decrease the variability of the large particle measurements, larger sample volumes should be collected or the measuring range should be modified to include more particles. We did not modify our procedure to reduce the variability of larger particle measurement since the smaller particles ($<200 \mu\text{m}$) were most abundant and are the focus of our study and many other recent projects (Furumai et al. 2002; German et al. 2002; Sutherland 2003).

2.4.1.2 Sample Contamination

We investigated four possible sources of particle contamination. These four sources include: grab sampling device (i.e., scoop 16 \times 12 \times 20 cm), sample bottle (4L glass bottle and cap), transfer pipette, and instrument (dilution chamber and stirrer). The

sampling scoop was eliminated as a source of contamination by rinsing the scoop in fresh runoff prior to sample collection. The particle-sizing instrument was eliminated as a source by flushing the chamber through at least three cycles with deionized (DI) water filtered through a 0.2 μm membrane filter, which usually reduced particle counts to less than 3/ml (Table 2.4) Contamination from sample bottles and glassware was evaluated by counting particles in cleaned bottles and beakers. Sample bottles were cleaned by soaking overnight in detergent, rinsing with hot water five to six times, rinsing with 10% nitric acid, rinsing with dichloro-methane, rinsing in DI water and oven drying. Four bottles (4L) and three 200-ml beakers were evaluated. The beakers were cleaned by soaking overnight in detergent, rinsing with hot water five to six times, and rinsing with nanopure, particle free water (NPPFW) obtained from a Barnstead Nanopure Infinity Water System with a 0.2 μm filter. All bottles and beakers were filled with NPPFW.

Each container was sampled with a 10-ml pipette and analyzed. The results are shown in Table 2.4.

Table 2.4. Particle Number Concentration Based on Contamination Experiment (mL^{-1})

Sample	Particle Diameter Range (μm)										Total 2-1000	
	2-3	3-5	5-7	7-10	10-20	20-30	30-50	50-100	100-200	200-1000		
Instrument ^a I1	2	0	0	0	0	0	0	0	0	0	2	
	I2	1	0	0	0	0	0	0	0	0	1	
Beaker	B1	12	10	6	5	6	2	3	1	2	2	49
	B2	12	8	6	3	3	1	2	1	1	1	38
	B3	13	8	3	3	3	2	4	1	1	1	39
4L Bottle	Bo1	14	10	9	5	8	3	4	0	1	1	55
	Bo2	45	33	16	8	5	2	2	0	0	1	112
	Bo3	81	75	34	20	12	2	1	1	3	2	231
	Bo4	27	29	16	13	11	4	3	0	0	1	104

^aWithout sample injection

After cleaning, the instrument was essentially particle free, which was treated as background concentration. The beakers had very few particles, ranging from 38 to 49/ml. The bottles had particle concentrations ranging from 55 to 231 /ml. This procedure evaluated the combined contamination sources of cleaning, bottle, cap, and pipette.

Particle concentration decreased with increasing particle diameter. Instrument particle concentration was 2/ml or less, which was satisfactory. The washing procedures cleaned the bottles to less than 250/ml total particles in all size fractions. The cleaning method was adopted since runoff particle concentrations were usually in excess of 10,000/ml.

2.4.1.3 Sample Representativeness

Sample representativeness is very important to characterize highway runoff PSD because particle-sizing instruments typically need only a small amount of sample injection. In addition, runoff from highways usually contains particles that will settle in a 4L bottle within 10 to 20 seconds or less. Complete mixing of samples is therefore an essential step to assure a representative sample. Four procedures were used to mix the 4L sample bottles: (1) no mixing; (2) inversion by gently inverting the 4L bottle five to six times in 30 seconds; (3) gentle inversion-decanting-stirring by using gentle inversion as in (2), following by removing 100 ml of sample into a beaker on a magnetic mixer and agitating for 1 minute at 400 rpm; and (4) gentle inversion-decanting-blending, similar to (3), except that 200 ml of sample was poured into a clean blender (Waring commercial blender) and blended at 3500 rpm for 1 minute. In each procedure, the end of a large-bore

pipette was inserted 2 cm below the liquid surface to collect a 1 to 10 ml sample immediately after the final mixing step, and injected into the particle sizing system for measurement. Figure 2.1 shows the PSD of the above four analytical preparation techniques. Without inverting the sample bottle, the particle measured concentration was far less than measured with mixing, suggesting sedimentation in the bottle. Gentle inversion and gentle inversion-decanting-stirring produced similar PSD results. Blending destroyed many large particles, producing many additional small particles.

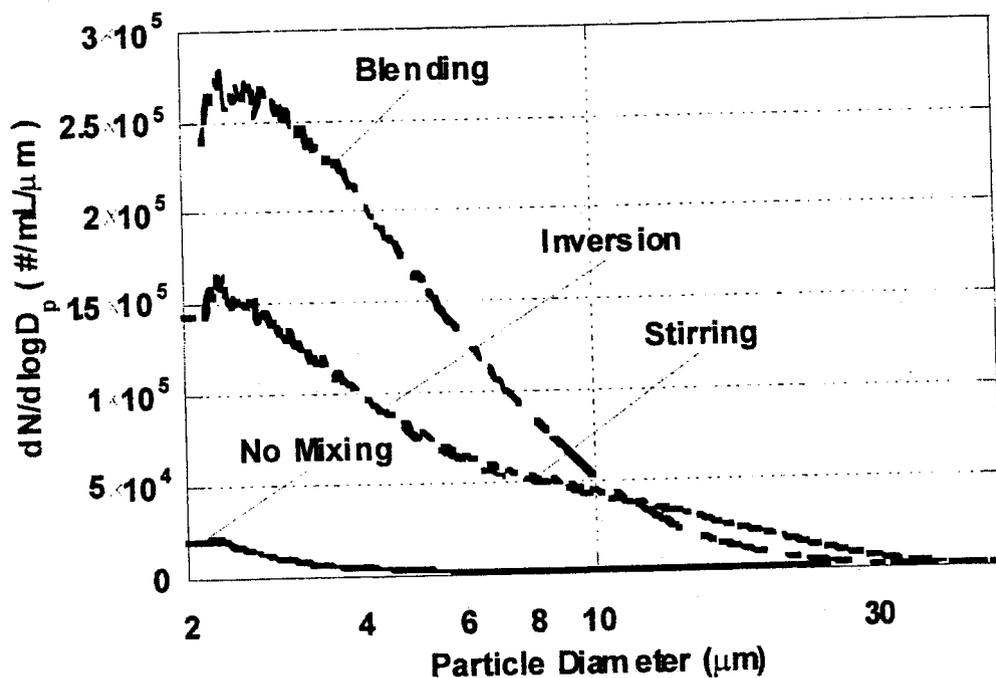


Figure 2.1 Comparison of different mixing methods (labels describe the various methods – see text for their description; dN = number of particles per ml within certain size range D_1 to D_2 , $d \log D_p = \log D_2 - \log D_1$).

Table 2.5. Concentration Difference Evaluation Using Inversion and Stirring Methods

Diameter Range (µm)	Sample 1			Sample 2			Sample 3			Sample 4		
	Inversion	Stirring	DP	Inversion	Stirring	DP	Inversion	Stirring	DP	Inversion	Stirring	DP
2-1000	176601	181548	2.8	611184	603383	1.3	94741	95276	0.6	96090	95533	0.6
2-3	42294	44351	4.7	309057	307472	0.5	39423	39959	1.4	42813	41785	2.4
3-5	57797	60073	3.9	222907	220401	1.1	34558	34921	1.0	36709	36435	0.7
5-7	31622	32492	2.7	50004	48569	2.9	10865	10902	0.3	10518	10845	3.1
7-10	23712	24054	1.4	19234	17744	8.1	5557	5418	2.5	4167	4507	7.8
10-20	17698	17316	2.2	8461	7918	6.6	3497	3304	5.7	1749	1829	4.5
20-30	2407	2213	8.4	983	782	22.8	594	499	17.4	97	99	2.0
30-50	827	802	3.1	341	338	0.9	215	225	4.5	31	27	13.8
50-100	207	209	1.0	120	115	4.3	29	42	36.6	4	4	0.0
100-200	31	34	9.2	48	42	13.3	3	5	50.0	1	2	66.7
200-1000	6	4	40.0	29	2	174.2	0	1	200.0	1	0	200.0

To further evaluate gentle inversion and gentle inversion-decanting-stirring, PSDs of four samples were analyzed using both methods, and the results are shown in Table 2.5. Concentrations of particles with diameters between 2 and 1000 µm measured with the two methods produced DP values less than 3. The large DP values of particles with diameters greater than 100 µm are due in part to the sample volume, as described before in the reproducibility analysis. The gentle inversion and gentle inversion-decanting-stirring methods produced identical results and gentle inversion was adopted for this study.

2.4.1.4 Sample storage time and temperature

PSD may change with storage time because of particle aggregation or dissolution. To quantify the changes in PSD with storage time, seven grab samples taken on November 7th and December 15th, 2002 were kept in a 4° C cooling room. At the same

time, 200 ml of sample were poured into beakers from each of the seven grab samples after gentle inversion, and kept at room temperature (20° C), open to the atmosphere, but protected from dust fall or any other contamination. Figure 2.2 shows the PSD over time for one sample, stored at 4°C and 20°C. It can be seen that the particle size generally increased over time at both storage temperatures. The size of the particles in the sample stored at room temperature increased at a much higher rate. Particle size measurements were terminated after 60 hours under room temperature due to particle breakup during analysis.

To illustrate the changes in particle sizes, the numbers of particles in specific size fractions at different times were normalized by dividing by the initial particle concentration. The normalized concentrations of all seven grab samples were averaged and plotted as ratios. Figure 2.3 shows the refrigerated samples. Concentrations of particles in the smallest fractions increased for the first 50 hours and then decreased.

The particles stored at room temperature (Figure 2.4) showed the same trend but at a much more rapid rate with larger increases in concentration. Particles larger than 7 μm at both temperatures showed a monotone increase in particle numbers through the period of observation.

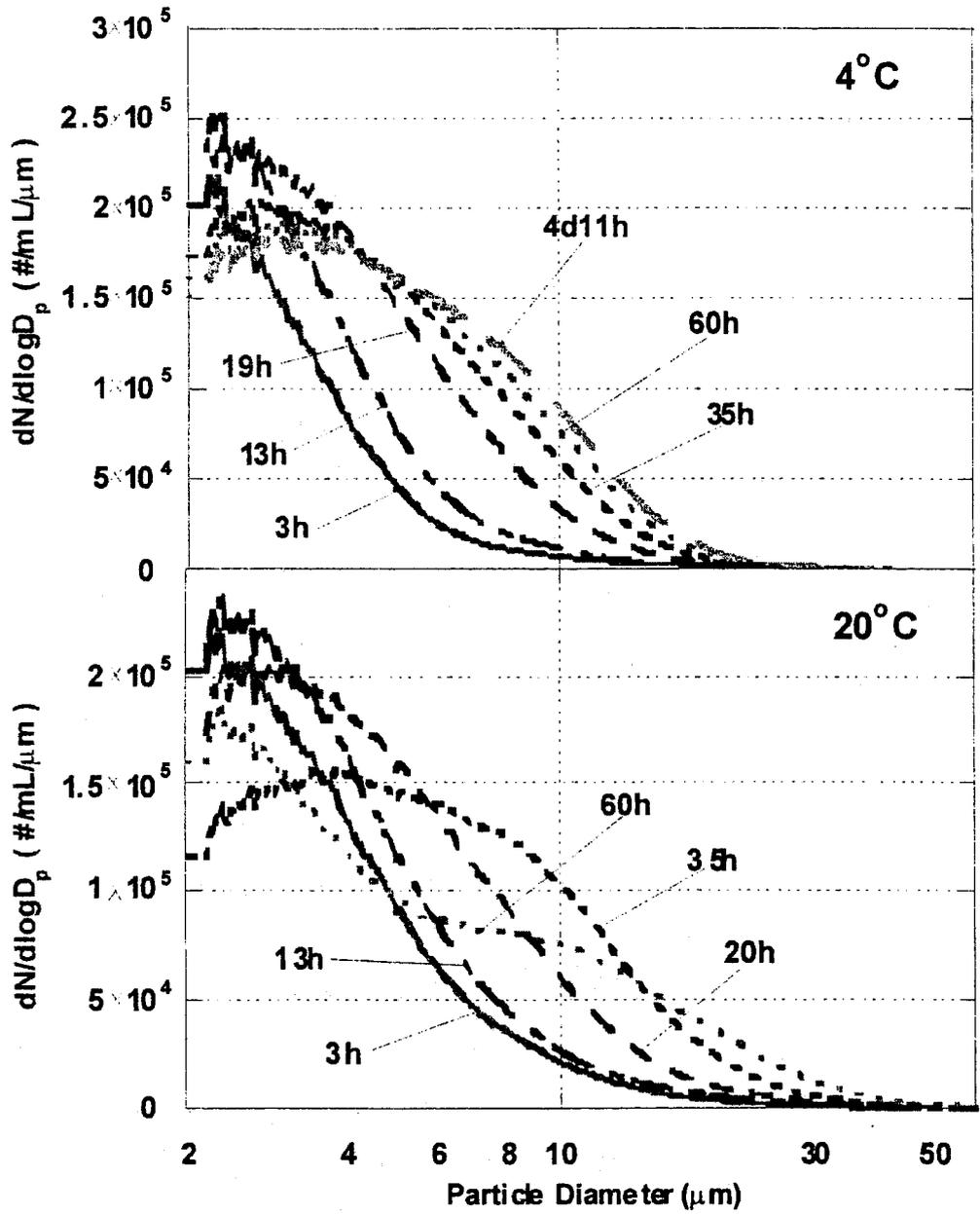


Figure 2.2 Sample storage time and temperature influence (Site 3, event 12/15/02, grab sample No. 2, labels show storage time in hours)

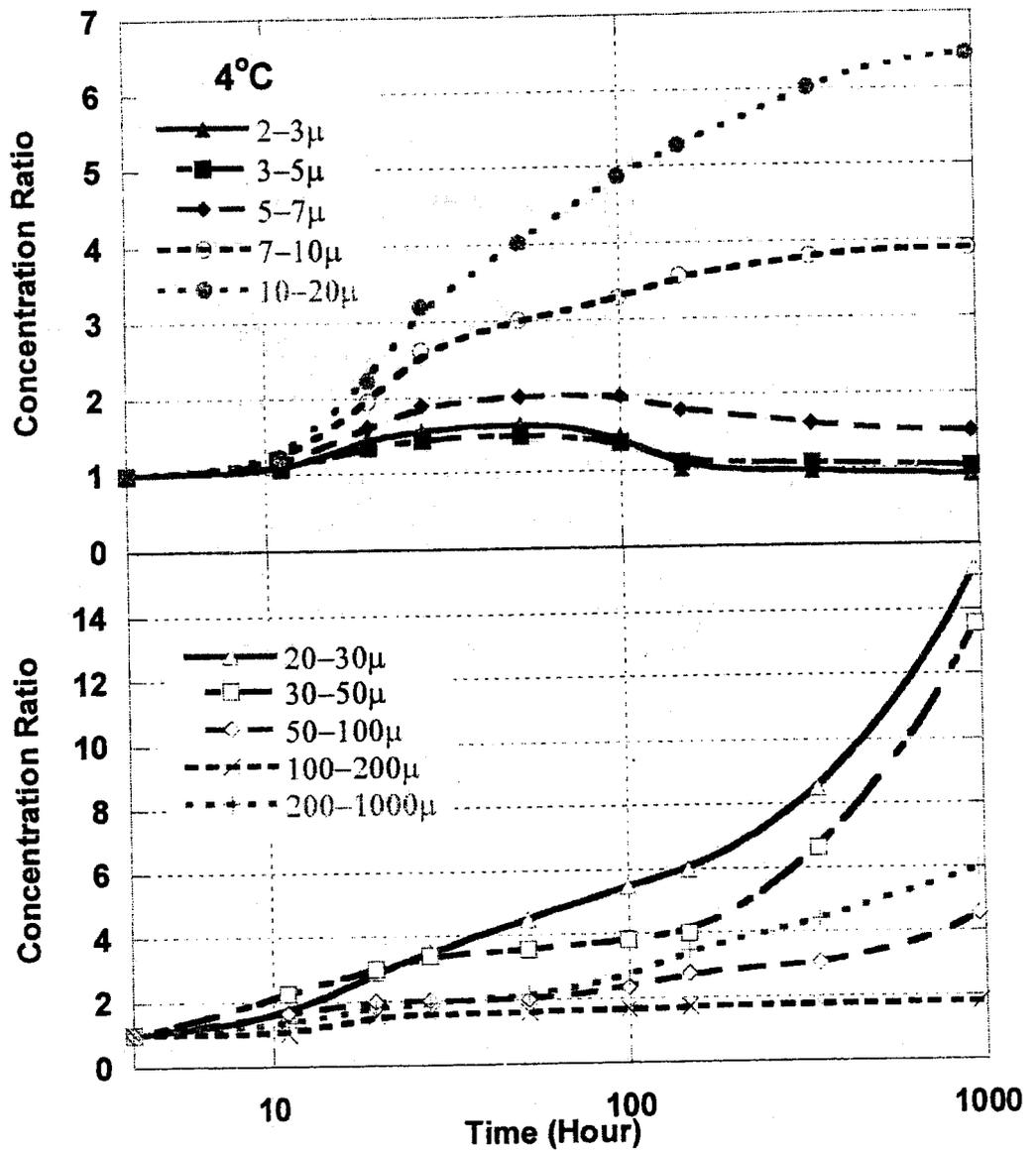


Figure 2.3 Average concentration ratio vs. time (4° C)

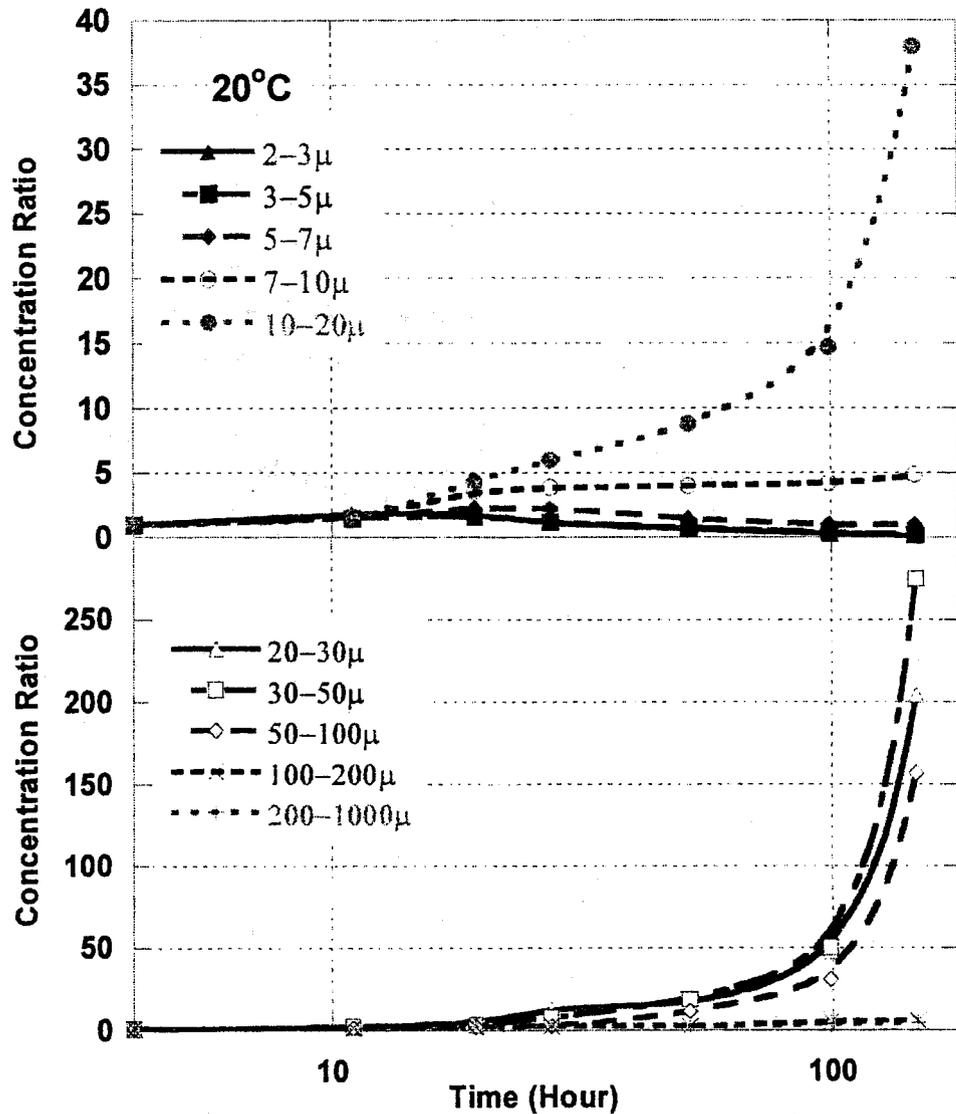


Figure 2.4 Average concentration ratio vs. time (20° C)

The rapid growth in particle size suggests a naturally occurring coagulation/flocculation mechanism. The presence of naturally occurring flocculation and an increase in particle size can have profound impact on sample storage and hence on designing stormwater treatment systems (e.g. BMPs). Based on these results, all samples for PSD analysis were analyzed within six hours of collection. Treatment systems that

hold the stormwater for appreciable amounts of time may have improved sedimentation rates due to particle growth.

The number of particles in the range of 2 to 7 μm increased in all samples at the beginning of storage. Particle numbers continued to increase for 13 to 50 hours, depending on sample. After this time, the numbers gradually decreased. This suggests that new particles were being formed from precipitation, or that particles too small to be counted were increasing in size and appearing in the smallest fraction. Future work should investigate this phenomena, since particles in this range will likely escape most treatment devices except those that providing soil infiltration. . Accelerating particle aggregation should help overall BMP effectiveness for the removal of solids and pollutant load that are associated with those solids.

2.4.2 PSD with Respect to Hydrograph and Partial Water Quality Parameters

Table 2.6 summarizes three events where PSD was monitored. Fourteen grab samples were collected at all three sites on November 7th. The other two storms were shorter and fewer samples were collected. Turbidity, conductivity and total suspended solids (TSS) were measured and are reported in this paper. A large suite of other parameters were measured and reported elsewhere (Ma et al., 2002).

Table 2.6. Event Summary (First three events in 2002-2003 rainy season)

Monitoring Site	Event Date	Grab Sample Number	Antecedent Dry (days)	Event Day Rainfall (mm)	Runoff Volume (m ³)	Max Intensity (mm/hr)	Rainfall Duration (hr:min)	Runoff Duration (hr:min)
1	11/7/02	14	40.1	29.0	210.5	10.16	47:31	44:09
2	11/7/02	14	41.2	58.7	825.8	14.22	46:29	46:43
3	11/7/02	14	40.2	71.4	178.0	12.19	47:05	47:38
2	11/29/02	5	20.2	1.8	23.3	3.05	7:44	8:14
3	11/29/02	6	20.2	1.5	0.7	2.03	6:52	7:21
2	12/15/02	8	16.1	2.5	30.3	2.03	3:20	4:38

Figure 2.5 shows the PSD, rainfall, runoff, TSS, turbidity and conductivity for Site 1, event November 7th, 2002 as a representative example of the three events. The concentration of particles (2 to 1000 μm) in 61 grab samples of all three events ranged between 50,000 and 3,742,000/ml with a median value 204,000 /ml. For all events, the highest particle concentration always occurred within the first hour, and decreased rapidly thereafter.

The lower two graphs in Figure 2.5 show PSD for the composite sample and various grab samples. The data are plotted on two axes for clarity. Each distribution has a time label that can be compared to the top of Figure 2.5 to show the point on the hydrograph when the sample was taken. The trends shown are typical of most samples. The very first sample did not have the highest particle concentration (number of particles per base-10 logarithm of particle diameter per ml), which probably resulted because runoff had not developed this early in the storm. Particle concentration increased to a maximum over the next 15 to 45 minutes, and generally decreased in later samples. The

vast majority of the particles were less than 10 μm , and after several hours particles larger than 10 μm were reduced in concentration. The median particle size decreased as the storm progressed, which shows a more rapid washout of larger particles.

In many of our previously sampled storms, we observed increases in contaminant concentrations after rapid increases or "spikes" in runoff flow. At approximately 13 hours such a spike occurred for example (Figure 2.5), which increased particle concentration and turbidity. An examination of many data sets does not reveal a strong correlation between instantaneous runoff flow rate and pollutant concentrations, but there are many examples of spikes in flow rate followed by spikes in concentration (Sansalone et al. 1998), particularly suspended solids. It is believed that there is a cause and effect relationship between instantaneous runoff rate and contaminant concentration, but a quantitative relationship has not yet been found.

Conductivity decreased rapidly as the storm progressed, and is typical of many of our observations; conductivity usually exhibits a significant first flush, which was evaluated with mass first flush (MFF) ratio developed by Ma et al. (2002). MFF ratio was defined as the normalized mass fraction divided by the normalized volume fraction at any given point along the normalized or fractional runoff diagram. It is thought that the low conductivity rain water eventually dilutes out the salts being flushed from surfaces.

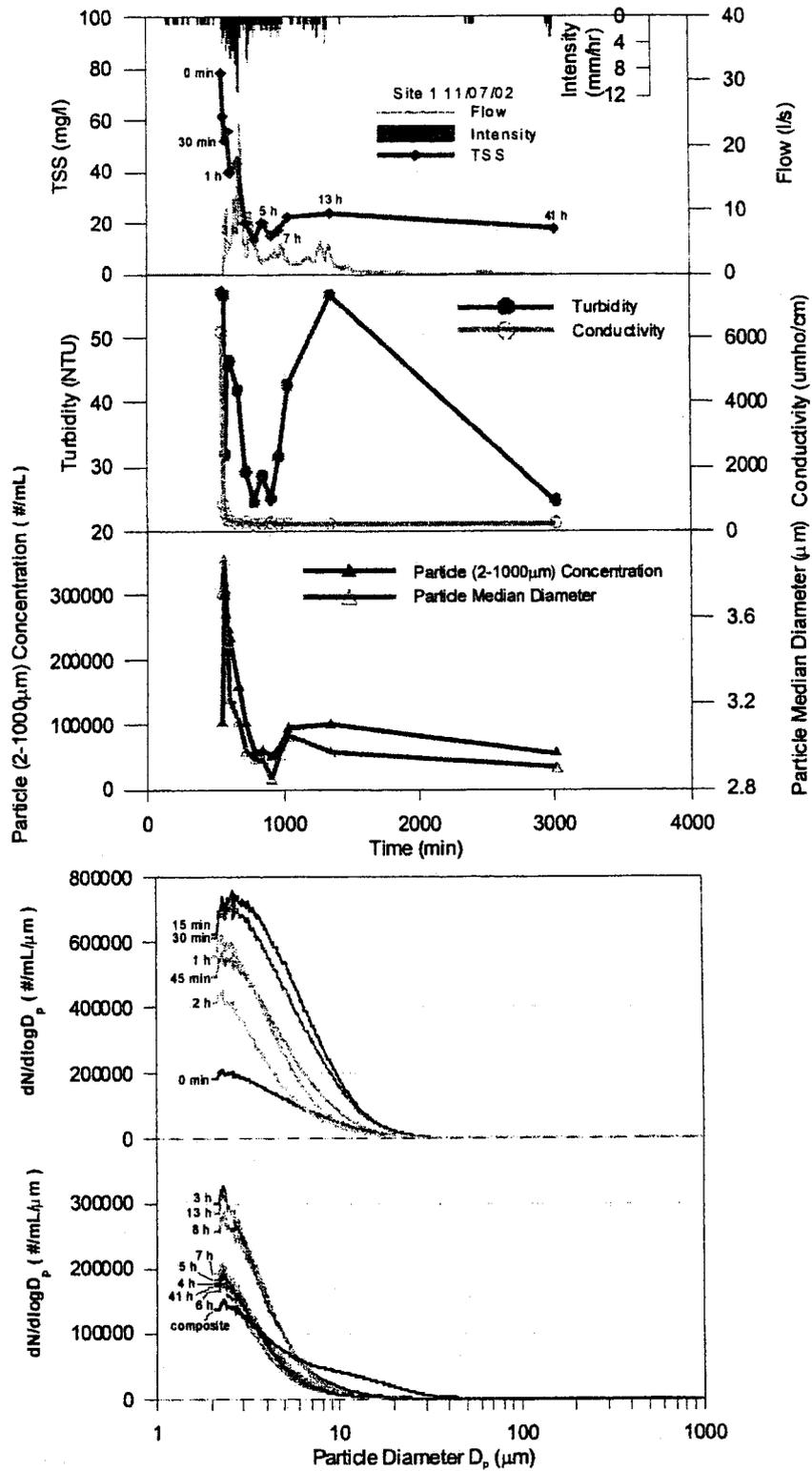


Figure 2.5 Hydrograph with TSS, turbidity, conductivity and PSD for site 1, event 11/07/02

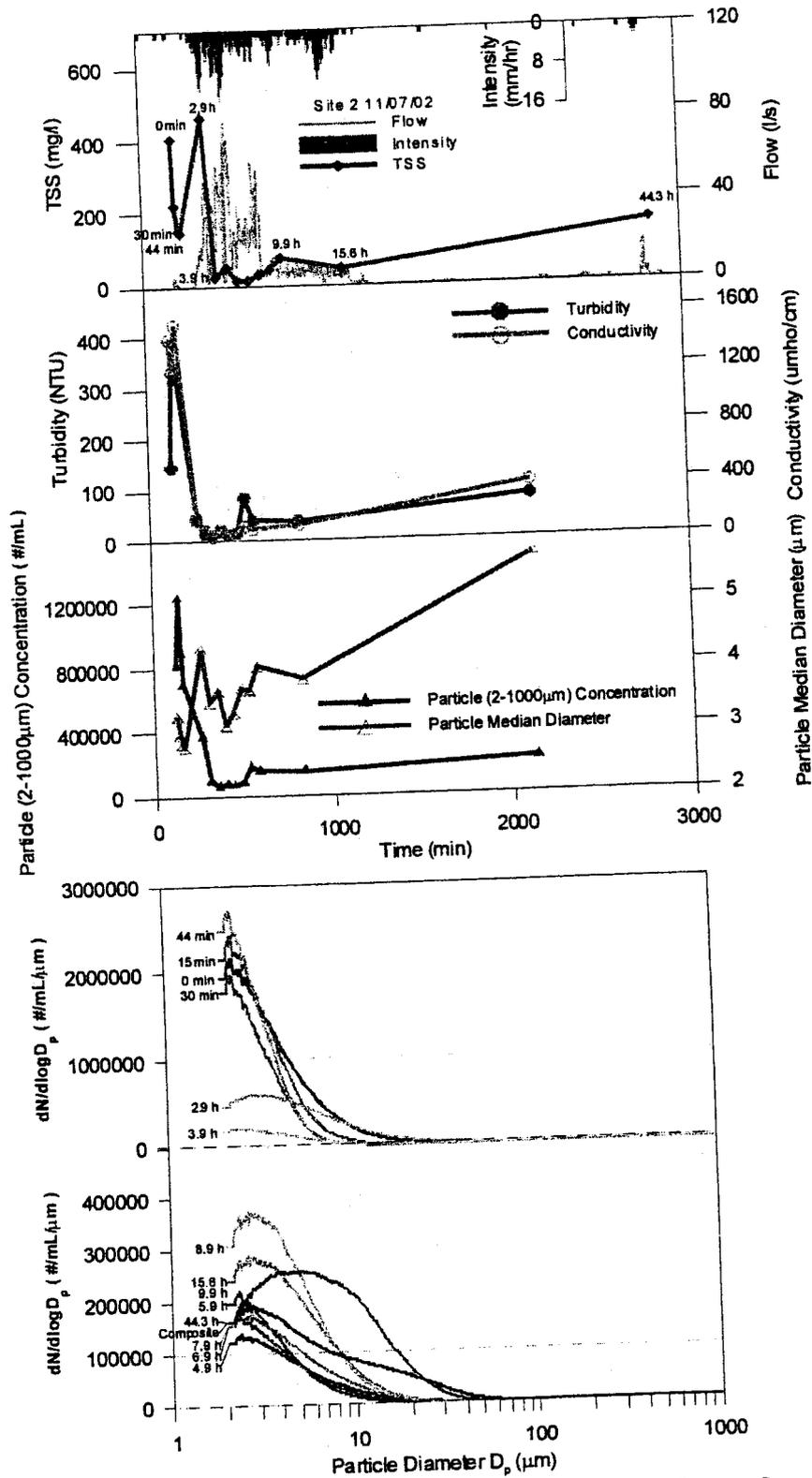


Figure 2.6 Hydrograph with TSS, turbidity, conductivity and PSD for site 2, event 11/07/02

Figure 2.6 shows similar results for Site 2, event November 7th, 2002. Early samples had the greatest particle concentration. Median particle diameter did not decline but increased slightly. The increase at the end of the storm is due to the brief, intense rainfall at 44 hours. The rainfall is responsible for increases in TSS, turbidity and particle concentration.

The particle concentrations in composite samples are also shown in the proceeding Figure 2.5 and Figure 2.6. They are lower than most grab samples, and should have a particle concentration between the lowest and highest. The composite sample concentrations were only between 34% and 94% of the corresponding flow-weighted averages of the grab samples. This large difference suggests that aggregation or some other phenomena is occurring. Composite samplers may not be the most appropriate method of collecting samples for PSD analysis due to potential aggregation between particles.

These results can be compared to other results if particle number concentrations are converted to mass concentration by assuming spherical particles and uniform particle specific gravity for particles with diameter between 2 and 1000 μm . Lau and Stenstrom (2001) recovered particles from dry pavement, and found that only 3% of the particle mass occurred in particles smaller than 50 μm . Sansalone and Tribouillard (1999) observed less than 10% of total particle mass in particles smaller than 50 μm . This research suggests that nearly 30 to 60% of the particle mass is found in particles smaller than 50 μm (Figure 2.7).

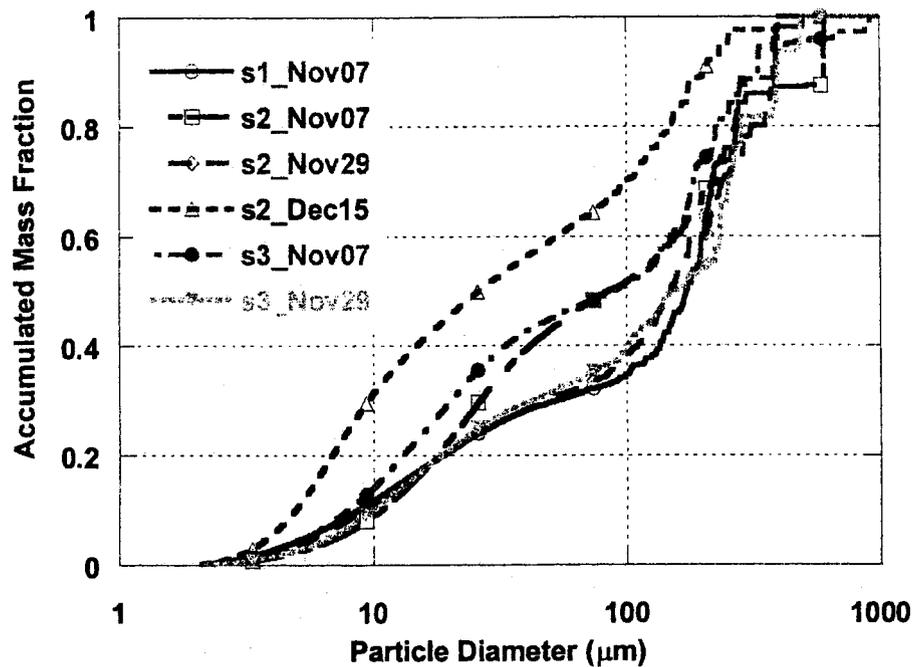


Figure 2.7 Accumulated particle size distribution by mass (Assuming spherical particles with uniform density through all size ranges)

The removal of particles by BMPs is highly dependent on the particle size, shape and specific gravity. It is also important to know pollutant distribution among the various particle size fractions. The combination will allow BMPs to be selected to optimize pollutant removal as well as particle removal. This topic is currently under investigation in our laboratory.

2.4.3 First Flush of Particles

First flush phenomenon is a controversial topic in stormwater management (Characklis and Wiesner 1997; Deletic 1998). Certain researchers (Saget et al. 1995;

Barrett et al. 1998) found that the overall first flush effect of highway stormwater runoff was small or negligible, while other researchers (Vorreiter and Hickey 1994; Gupta and Saul 1996; Sansalone and Buchberger 1997a; Lau et al. 2002; Ma et al. 2002) observed moderate or strong first flush. Generally, smaller catchment areas exhibited stronger first flushes (Characklis and Wiesner 1997). In addition, no consensus definition exists for first flush (Bertrand-Krajewski et al. 1998) and different researchers have used different definitions (Geiger 1984; Thornton and Saul 1987; Ashley et al. 1992; US EPA 1993; Vorreiter and Hickey 1994; Saget et al. 1995; Gupta and Saul 1996; Sansalone and Buchberger 1997a,b; Deletic 1998; Ma et al. 2002). In this discussion, we extend the MFF ratio developed by Ma et al. (2002) to particle first flush, and present it as particle number first flush (PNFF) ratio.

The PNFF ratio is defined as the normalized number of particles divided by normalized volume fraction at any point of normalized runoff diagram. It is similar to the first flush definition proposed by Bertrand-Krajewski et al. (1998).

Let x represent the x percent runoff volume at a certain time t_1 . Then

$$x \% = \frac{\int_0^{t_1} Q(t) dt}{V} \quad (2.2)$$

$$\text{PNFF}_x = \frac{\int_0^{t_1} C_p(t) Q(t) dt}{N} \div \frac{\int_0^{t_1} Q(t) dt}{V} \quad (2.3)$$

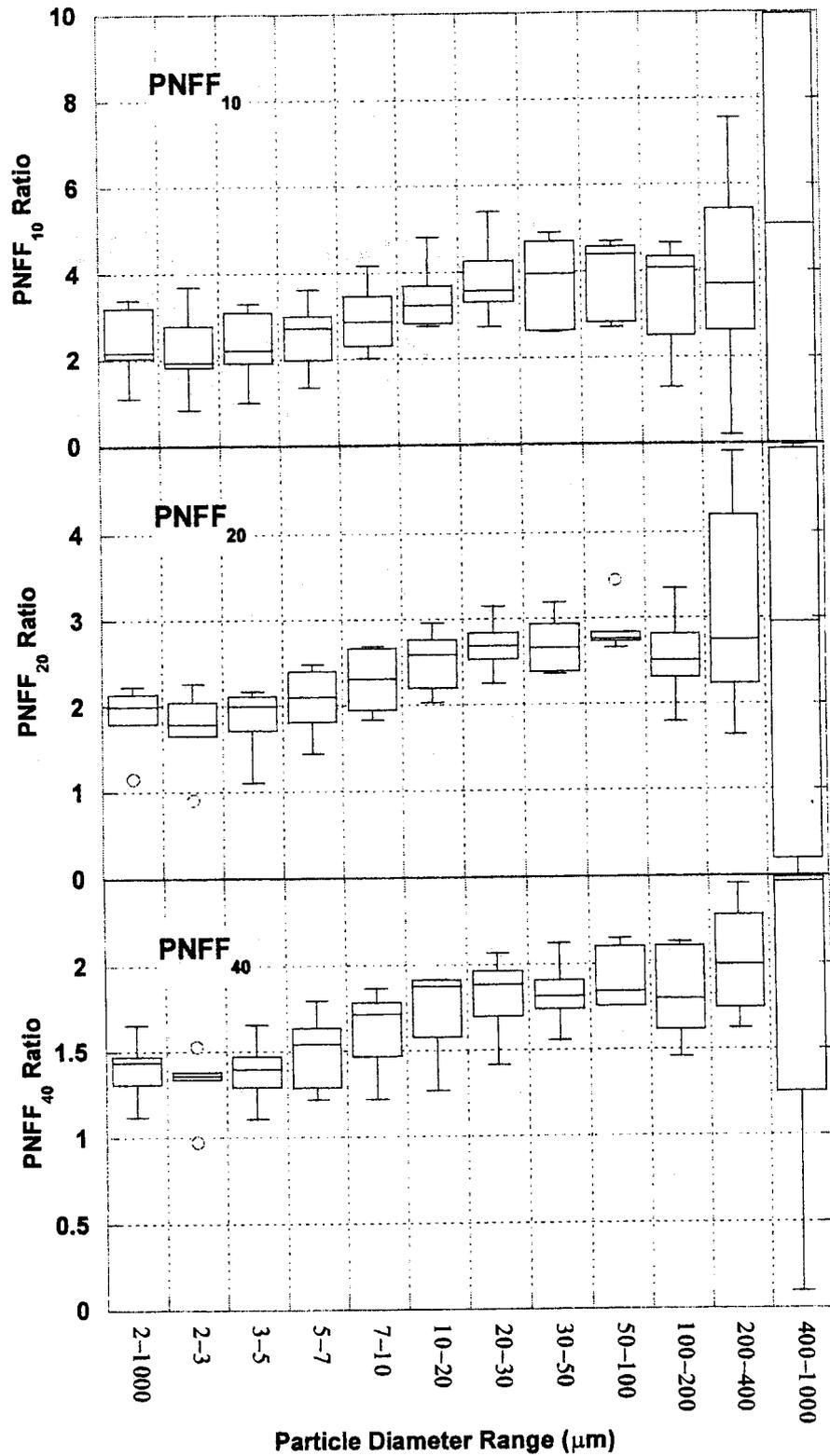


Figure 2.8 Boxplots for different Particle Number First Flush Ratio

Where $Q(t)$ = runoff flow rate, $C_p(t)$ = particle number concentration, V = total runoff volume and N = total number of particles in an event.

The ratio can be calculated for any specific point in the storm, and approaches 1.0 by definition at the end of the storm. The ratio allows convenient characterization of first flush. For example, $PNFF_{20} = 2.5$ means that when the accumulated runoff volume reaches 20% of total runoff volume, it contains $20\% \times 2.5 = 50\%$ of total particle count in an event. The MFF ratio is also defined by equation (2.3), except that concentration is used instead of particle number.

Figure 2.8 shows the number first flush ratios ($PNFF_{10}$, $PNFF_{20}$, $PNFF_{40}$) for particles in different size ranges. The top and bottom of the box mark the limits of $\pm 25\%$ of the variable population, and the horizontal line is the median. The whiskers represent the maximum and minimum observed values, unless there are outliers. Figure 2.8 illustrates median $PNFF_{10}$, $PNFF_{20}$, $PNFF_{40}$ values generally increase with increasing particle diameter. The $PNFF$ ratio is generally larger than the analogous MFF ratio for other water quality parameters such as TSS and turbidity (Ma et al. 2002). This suggests that BMPs that can completely capture the early runoff will be more effective than BMPs that treat a portion of the runoff throughout the storm.

2.5 Conclusions

Particle size distribution (PSD) was characterized in three storm events at three sites. It was necessary to develop an experimental protocol to insure representative samples. A hand washing procedure for glass bottles was a suitable method for

preventing contamination of samples being analyzed for PSD; gentle inversion (five to six times) of the sample bottle was an appropriate mixing method that prevented sedimentation or particle shearing. Particles showed a natural aggregation, which required analysis as soon as possible but within 6 hours of sample collection. Particle concentrations in samples collected by the automatic samplers were lower than a flow-weighted average of the grab samples. Results suggest that automatic composite samplers should not be used to collect samples for PSD analysis until further development is completed.

More than 97% of the particles were less than 30 μm . Particle concentration and size generally decreased rapidly as the storm progressed. Rapid increases in particle number occurred after rapid increases in rainfall or runoff, and were accompanied by increases in turbidity and TSS concentration. Particles showed an obvious first flush, with median of PNFF_{20} of approximately 2, indicating that 40% of total particles were carried in the first 20% of runoff volume. Larger particles showed stronger first flush than smaller particles.

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3. DYNAMIC CHARACTERISTICS OF PARTICLE SIZE DISTRIBUTION IN HIGHWAY RUNOFF: IMPLICATIONS FOR SETTLING TANK DESIGN

Abstract

Stormwater has become a major pollution source to the deterioration of water bodies and stormwater management is growing in importance in most urban areas. Since many stormwater treatment facilities target suspended solids and pollutants sorbed to their surfaces, the dynamic characteristics of particle size distribution (PSD) is of critical importance in designing best management practices (BMPs). To understand PSD and the potential for a first flush of particles from highway sites, PSD was monitored in seven rainfall events in the 2002-2003 rainy season at three highway sites in west Los Angeles. Most of the particles were less than 30 μm in diameter and more than 90% of particles were less than 10 μm in diameter. Particle concentration decreased rapidly to 6 mm of accumulated rainfall, and then declined more slowly throughout the storm. Particle concentration was correlated with total suspended solids (TSS) and turbidity. Grab sample particle median diameter also increased with increasing TSS due to the large particles' greater contribution to TSS. A two-compartment settling tank was evaluated using the measured PSD, and was effective in removing both small and large particles. Capturing and retaining the first 20% of the runoff volume on seasonal average can

remove approximately 30% to 40% of the total particulate pollutant load. If the holding compartment is coupled with a similar size continuous flow clarifier, the total pollutant removal efficiency can reach 65% to 90% for the metals investigated. Particle first flush was observed and the associated pollutants also demonstrated a first flush.

Keywords: Stormwater; Highway; Runoff; Particle size distribution; Best management practices; Pollution; Settling velocity; Heavy metals; First flush.

3.1 Introduction

Stormwater has become a major pollution source to many urban waters (Characklis and Wiesner 1997; Barrett et al. 1998; Davis et al. 2001; German and Svensson 2002; Vaze and Chiew 2004) and highway runoff has received much attention due to the appearance of heavy metals, hydrocarbons and fuel additives (Furumai et al. 2002). Particles in highway runoff carry the majority of pollutants from highways, and most runoff treatment facilities such as ponds, detention basins, and wetlands are evaluated based on particle removal (Oliver et al. 1974; Herrmann 1981; Ongley et al. 1981; Hoffman et al. 1985; Hewitt and Rashed 1992; Andral et al. 1999; Legret and Pagotto 1999; Bäckström 2002; German and Svensson 2002). Therefore particle characteristics are a critical issue for highway runoff treatment (Andral et al. 1999; Furumai et al. 2002; Li et al. 2004).

Research has been performed on particle characteristics in road or highway runoff in recent years. Sediments in channels and detention basins as well as particles transported in the runoff or collected from street surfaces were investigated. Due to

possible aggregation and differential sedimentation, particle size distribution (PSD) and associated pollutant distribution in sediments are not the same as those of the suspended solids in the runoff (Slattery and Burt 1997; Roger et al. 1998; Li et al. 2004). Suspended solids carried by highway runoff are usually smaller in size than sediments recovered from channel or detention basins (Roberts et al. 1988). Andral et al. (1999) investigated both groups of particles for the same event and showed that the PSD of suspended solids carried in runoff was identical to the PSD in recovered sediments for particles smaller than 100 μm in diameter and quite different for particles larger than 100 μm . The PSD of sediments has been analyzed by sieving after drying (Sansalone and Buchberger 1997b) or before drying (Roger et al. 1998; Andral et al. 1999), and no consensus exists about the superiority of methods. Pollutant distribution across different particle size ranges has also been studied (Sansalone and Buchberger 1997b; Roger et al. 1998). Finally, it has been noted that particles in highway runoff are not stable, and the PSD changes with time, which requires analysis within six hours of sample collection (Li et al. 2004).

Recent field studies showed that fine particles accounted for most of the total suspended solid (TSS) load and solid pollutant load in highway runoff. Several studies (Vignoles and Herremans 1995; Roger et al. 1998; Andral et al. 1999) demonstrated that particles less than 50 μm in diameter were 70 – 80% of TSS load carried by runoff by weight. Furumai et al. (2002) showed that particles less than 20 μm accounted for more than 50% of the particle mass. In addition, the finest particles in highway runoff had the highest concentration for many pollutants, especially metals, and the finer particles contained most of the pollutant load (Hoffman et al. 1984; Pitt et al. 1995; Sansalone and

Buchberger 1997b; German and Svensson 2002). Based on a composite runoff sample reported by Sansalone and Buchberger (1997b), Furumai et al. (2002) showed that the loads of certain pollutants such as zinc, lead and copper sorbed to particles smaller than 100 μm in diameter accounted for more than 50% of the total particulate pollutant loads in the runoff. This was much higher than the mass of the smaller particles, which was just over 10% of the total mass. Vaze and Chiew (2004) showed that most of the particulate total phosphorus (TP) and nitrogen (TN) were sorbed to particles between 11 and 150 μm in diameter, with 30 - 60% of particulate TN associated with particles less than 20 μm , and 30 - 50% of particulate TP associated with particles less than 20 μm . These findings suggest that removal of small particles is an important issue in the design of highway runoff treatment facilities (Furumai et al. 2002; Vaze and Chiew 2004).

Settling was effective in removing pollutants and reducing toxicity in runoff (Pitt et al. 1995). In order to evaluate pollutant removal efficiency by sedimentation, knowledge of particle characteristics and pollutant concentration as a function of particle sizes is essential. A number of researchers have investigated the settling characteristics of particles in runoff (Bachoc 1992; Butler et al. 1992; Andral et al. 1999; Jacopin et al. 1999; Bäckström 2002; Furumai et al. 2002; Vaze and Chiew 2004). Tables 3.1 and 3.2 summarize data on particle characteristics. Table 3.1 shows particle densities, and Table 3.2 shows metal concentrations as a function of particle size, with metal concentrations increase with decreasing particle sizes. For additional metal allocation with different

particle size ranges, readers can refer to Biggins and Harrison (1980), Ellis and Revitt (1982), Stone and Marsalek (1996), and Sutherland (2003).

Table 3.1. Particle Specific Gravity

Size Ranges (μm)	Specific Gravity (g/cm^3)	Reference
<i>Stormwater suspension</i>		
<50	2.38-2.65	Andral et al. 1999, Kérault Region, France
50-100	2.53-2.86	
100-500	2.5-2.82	
500-1000	2.51-2.7	
All	2.19-2.56	Bachoc 1992, Toulouse, France
<i>Stormwater sediments</i>		
All	2.10-2.51	Butler et al. 1992, London
All	2.20-2.27	Jacopin et al. 1999, Bordeaux, France
<i>Street sweeping</i>		
<75	2.61	Bäckström 2002, Luleå, Sweden
75-125	2.58	
All	2.70-3.01	Sansalone and Tribouillard 1999, Cincinnati, Ohio

Table 3.2. Metal concentrations for different particle size ranges

Size ranges (μm)	Heavy metal concentration ($\mu\text{g/g}$)								Remarks	References
	Al	Cd	Cr	Cu	Fe	Ni	Pb	Zn		
0.45-2				2894	29267		199	13540	Urban stormwater suspension	Morquecho and Pitt 2003, Birmingham and Tuscaloosa, Alabama.
2-10				4668	18508		868	13641		
10-45				735	26221		229	1559		
45-106				1312	14615		226	2076		
106-250				2137	21730		375	3486		
>250				50	28604		117	266		
25-38	16.8			364			265	1189	Highway runoff sediments	Sansalone and Buchberger 1997b, Cincinnati, Ohio
38-45	17.2			353			236	996		
45-63	17.3			364			266	1027		
63-75	16.3			333			258	1057		
75-150	15			312			248	1014		
150-250	9.2			204			195	574		
250-425	8			78			65	325		
425-850	9.5			48			53	314		
850-2000	9.7			45			37	259		
<50	60000		350	420		230	1570	4370	Highway runoff sediments	Roger et al. 1998, Hérault region, France
50-100	45000		400	250		250	1480	1700		
100-200	38000		410	200		220	1550	1100		
200-500	35500		150	100		220	850	930		
500-1000	37500		140	50		220	460	930		
<43	5	46	220		65	350	960		Street sweeping	Lau and Stenstrom 2004, Los Angeles, California
43-100	5	58	230		50	300	805			
100-250	2	38	230		40	210	500			
250-841	na	12	240		5	44	150			
Average	1	28	238		25	142	360			
<75				470			410		Street sweeping	German and Svensson 2002, Jönköping, Sweden
75-125				270			230			
125-250				340			190			
250-500				200			120			
500-1000				50			70			

The objective of this study is to characterize PSD in highway runoff and its correlation with other water quality parameters such as TSS and turbidity. Using this information, better sedimentation basin designs are proposed.

3.2 Methodology

3.2.1 Site Description

Three sites in west Los Angeles were monitored in 2002-2003 rainy season. These three sites were chosen as typical highway sites (0.39 to 1.69 hectares) with heavy traffic load (above 260,000 vehicles per day) and within 15 minutes travel time to the lab at the University of California, Los Angeles (UCLA). Close proximity to UCLA was important to facilitate rapid analysis of the PSD as well as other parameters. PSD was always measured within 6 hours of sample collection. Rainfall and flow rate were recorded by American Sigma (Loveland, Colorado) 950 flow meters and tipping bucket rain gages installed at each site.

3.2.2 Sample Collection Procedures and Particle Size Analysis

Grab samples were manually collected with a polypropylene scoop at a free water fall where runoff exited the drainage pipe. The first grab sample was collected at the beginning of runoff, which was usually within a few minutes after the onset of rainfall. Grab samples were taken at 15-minute intervals in the first hour of runoff and at 1-hour intervals over the next 7 hours. PSD was analyzed with a Nicomp (Santa Barbara,

California) PSS AccuSizer 780 Optical Particle Sizer module equipped with an auto-dilution system and a LE1000-2SE Light Scattering/Extinction sensor. This module has a measurable range from 2 to 1000 μm . For additional information on sites, sample collection, and particle size analysis, please refer to Li et al. (2004).

3.2.3 Settling Methods

Various methods have been utilized to remove particles in highway runoff, such as sedimentation basins, ponds, wetlands, grassy swales, and slow sand filters (Nix and Daykin 1992; Hvitved-Jacobsen et al. 1994; German and Svensson 2002). All depend on particle size and the settling velocity associated with each particle size, particle shape and density. Design of these devices is complicated by site-specific issues, including available space. To evaluate the potential impact of particle size on efficiency, a simplified analysis was used, and site-specific issues were left for later consideration.

Stormwater runoff volume varies with total rainfall and for this reason the removal rate will be influenced by storm size. Therefore, an average approach must be used which addresses a portion of the storms, based upon their magnitude. Several design criteria have been considered, which include retention time, overflow rate or minimum critical settling velocity, and strategies that collect and hold a fraction of the initial runoff. In this study, we evaluated a two-compartment sedimentation design based upon our PSD measurements. Particle settling velocity was calculated using Stokes' law for particles smaller than 40 μm in diameter and Newton's law for larger particles.

3.3 Results and Discussion

3.3.1 Statistical Description of PSD

Table 3.3. Event summary

Event Date	Grab Sample Amount	Antecedent Dry Day (days)	Event Rainfall (mm)	Runoff Volume (m ³)	Max Intensity (mm/hr)	Rainfall Duration (hr:min)	Runoff Duration (hr:min)
<i>Site 1</i>							
11/7/02	14	40.1	29.0	210	10.2	47:31	44:09
12/16/02	11	16.4	29.7	348	16.3	6:00	21:58
12/19/02	13	3.3	36.1	436	20.3	7:16	14:57
2/11/03	12	44.3	23.4	235	15.2	10:32	15:04
<i>Site 2</i>							
11/7/02	14	41.2	58.7	826	14.2	46:29	46:43
11/29/02	5	20.2	1.8	23	3.1	7:44	8:14
12/15/02	8	16.1	2.5	30	2.0	3:20	4:38
12/16/02	10	1.2	59.9	826	35.6	6:02	10:17
2/11/03	12	44.3	24.4	339	10.2	11:57	13:01
4/15/03	12	27.8	21.3	311	9.7	15:59	16:14
<i>Site 3</i>							
11/7/02	14	40.2	71.4	178	12.2	47:05	47:38
11/29/02	6	20.2	1.5	1	2.0	6:52	7:21
12/16/02	8	0.3	40.6	125	27.4	3:52	4:45
12/19/02	11	3.1	32.5	108	15.2	7:05	7:40
2/11/03	12	44.1	20.1	44	10.2	15:38	12:47
4/15/03	10	27.8	19.8	53	19.3	15:38	18:26

Table 3.3 summaries the events. Li et al. (2004) described some events in greater detail, including typical hydrographs and grab sample PSD. A total of 172 grab samples were analyzed from the three monitoring sites. Total particle (2 -1000 μm) concentration ranged from 4,100/ml to 3,742,000/ml with a median value 147,700/ml. The median particle diameter of all grab samples ranged from 2.72 μm to 7.15 μm . To quantitatively describe the PSD, a number fraction was defined as follows:

$$\text{Number Fraction} = \frac{\text{total number of particles in a certain size range}}{\text{total number of particles (2 - 1000 } \mu\text{m)}} \quad (3.1)$$

The fraction can be applied to a single grab sample or an entire event. For an entire event, the total number of particles is calculated in a fashion that is analogous to calculating total pollutant mass (Ma et al. 2002).

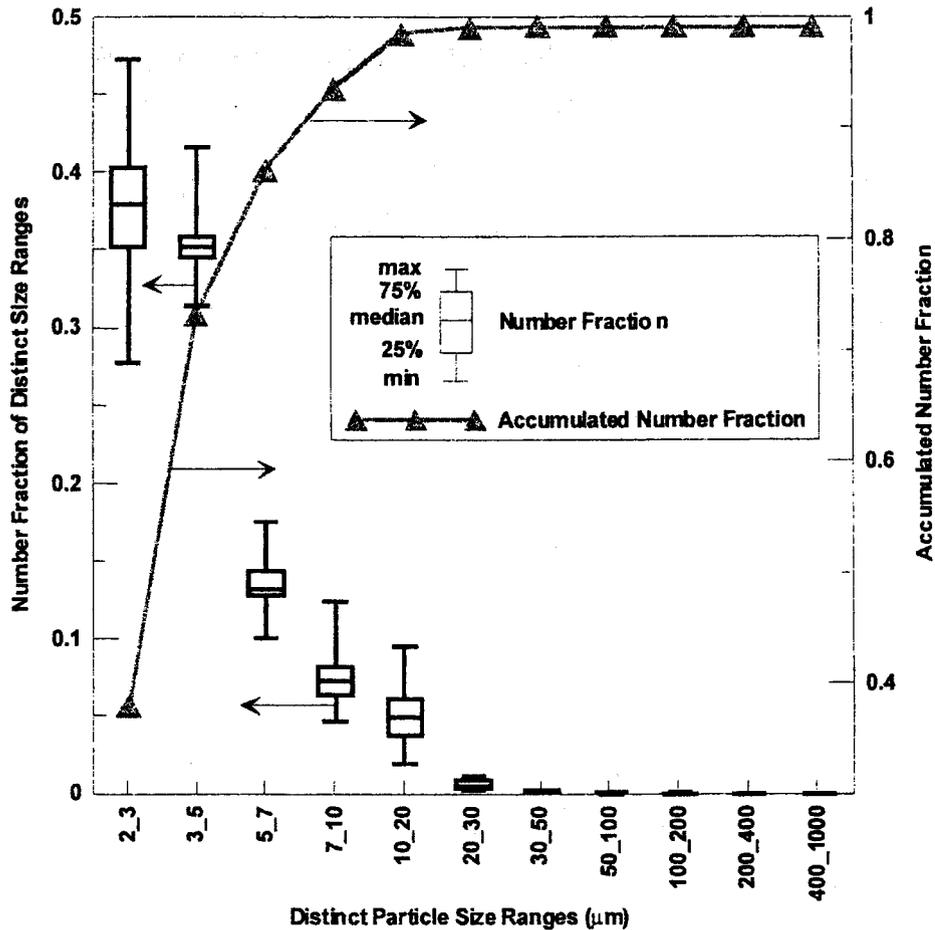


Figure 3.1 Particle number fraction of all events at three sites in 2002-2003 rainy season

Figure 3.1 shows the number fraction of particles in different size ranges. The horizontal axis indicates the individual particle diameter ranges. The box plot shows the number fraction of particles in individual size ranges for all events at three sites. The

continuous line corresponds to the right vertical axis and is the accumulated number fraction of median values of distinct size ranges. For example, among particles between 2 and 1000 μm , 27- 48% have diameters from 2 to 3 μm ; 31- 42% have diameters from 3 to 5 μm ; 10 - 18% have diameters from 5 to 7 μm ; 4 - 13% have diameters from 7 to 10 μm . Less than 11% of total particles have diameters larger than 10 μm .

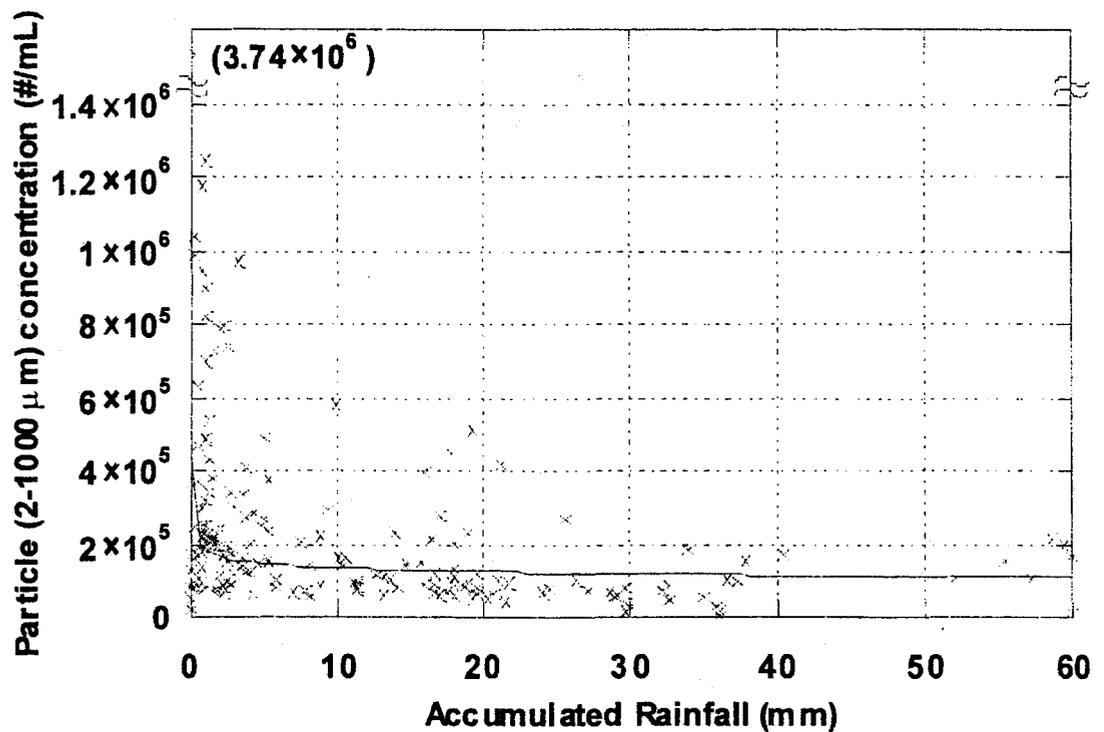


Figure 3.2 Particle (2-1000 μm) concentration of grab samples vs. accumulated rainfall

Particle concentrations decreased with increasing accumulated rainfall as shown in Figure 3.2. There was a sharp falloff in particle concentration at the beginning of the storm, which continued to about 6 mm of accumulated rainfall. After 6 mm the rate of

decline in particle concentration decreased. These results dramatically demonstrate particle first flush.

The pollutant concentration or number of particles in the runoff from the start of runoff to any point of time can be expressed by a running average, calculated in a fashion similar to the calculation of event mean concentration (EMC), and is termed the partial event mean concentration (PEMC) (Sansalone and Buchberger 1997a; Lee et al. 2002). The particle PEMC is the accumulated number of particles at any time divided by the accumulated flow volume at the same point of time, as show in (3.2):

$$PEMC = \frac{n(t)}{v(t)} = \frac{\int_0^t c_i q_i dt}{\int_0^t q_i dt} \quad (3.2)$$

Where $n(t)$ = particle number transported up to time t ; $v(t)$ = flow volume up to time t (m^3); c_i = particle number concentration at time t ($\#/m^3$); q_i = flow rate at time t (m^3/s); and t = time (s).

EMC is also defined by (3.2), when it is integrated to the end of the runoff. If the particle number and flow are normalized, the particle number first flush ratio (PNFF) is provided by (3.2) (Li et al. 2004).

Figure 3.3 shows a typical storm event, and shows the runoff, accumulated runoff, rainfall intensity, and particle PEMC. The particle PEMC peaked just a few minutes after the beginning of runoff and then decreased rapidly to an asymptotic value (EMC). The PEMC declined to 120% of the EMC after 55% of the total runoff occurred. For the

storms shown in Table 3.3, on average, the PEMC decreased to 150% of the EMC after half of the event rainfall. This implies that treating the initial portion of runoff will be more efficient than treating the later runoff, which is of critical important for BMP design.

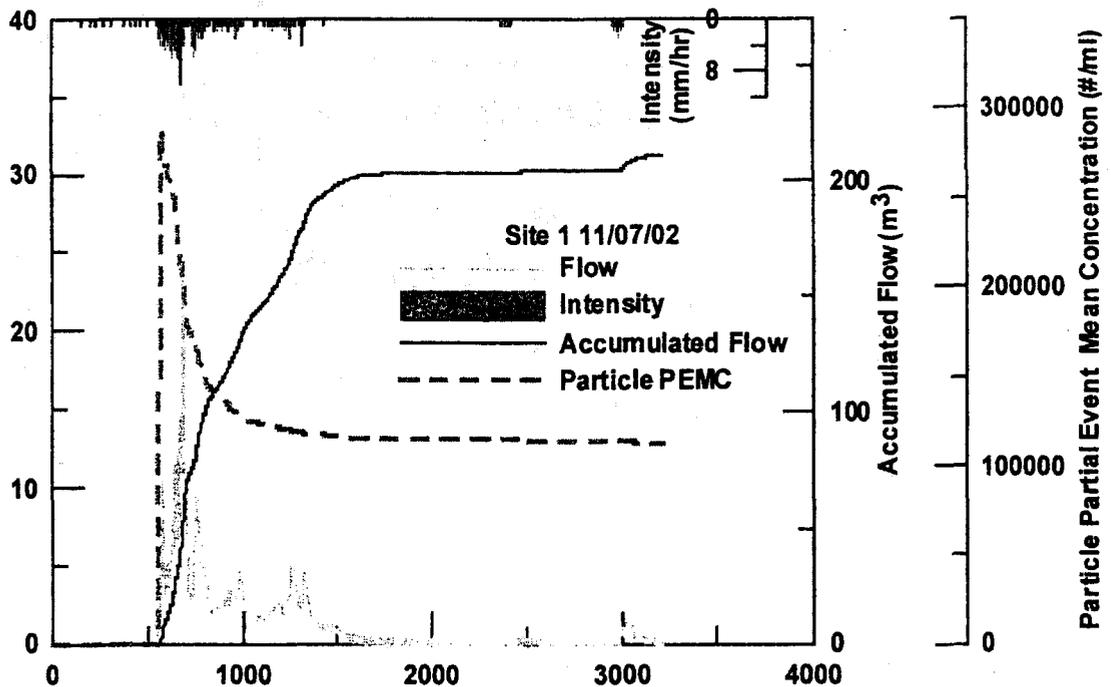


Figure 3.3 Particle Partial Event Mean concentration of event 11/07/02 site 1

3.3.2 Correlation Among Particle Concentration, Total Suspended Solids and Turbidity

TSS and turbidity concentrations increased with increasing particle concentrations as shown in Figure 3.4. The log of particle concentration was linearly correlated to log of TSS and turbidity with R^2 values of 0.689 and 0.692, respectively. TSS and turbidity were also correlated with R^2 of 0.485. The high correlation among TSS, turbidity and

particle concentration suggests that these parameters might be useful surrogates for each other. Possible pitfalls for using the correlation exist when applying it to different land uses, where the PSD or correlations might be different.

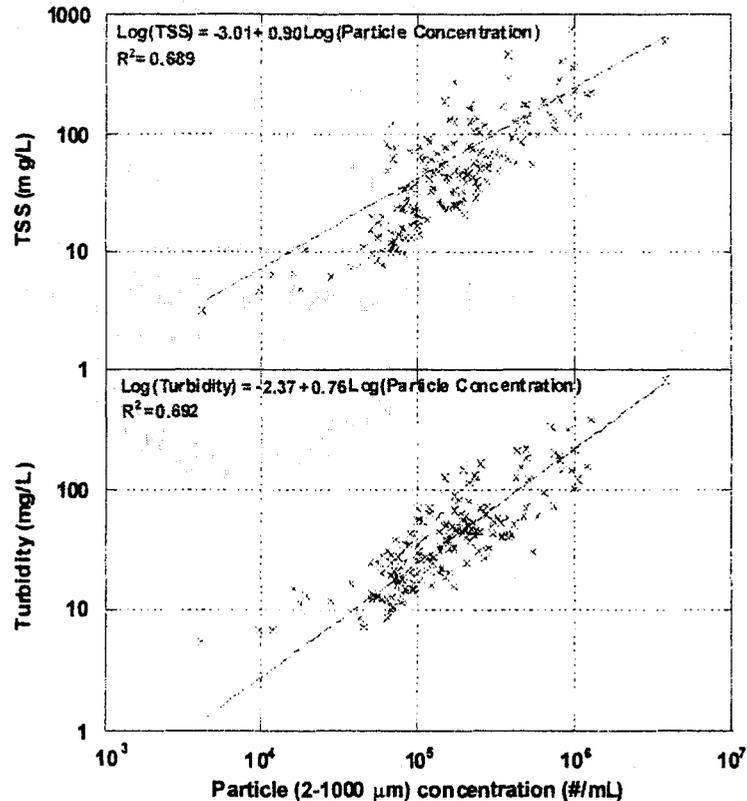


Figure 3.4 Particle (2-1000 μm) concentration of grab samples vs. TSS and Turbidity

Figure 3.5 shows particle median diameter of grab samples as a function of TSS concentration for all sites. The correlation is better for lower TSS concentrations, and is more scattered at higher TSS concentrations. This results because larger particles contribute more to TSS load than smaller particles, and the number of larger particles is much more variable than the number of small particles. For example, for TSS concentrations greater than 200 mg/L, the contribution of particles larger than 30 microns

was more than 60% (assuming spherical particles with uniform density through all size ranges).

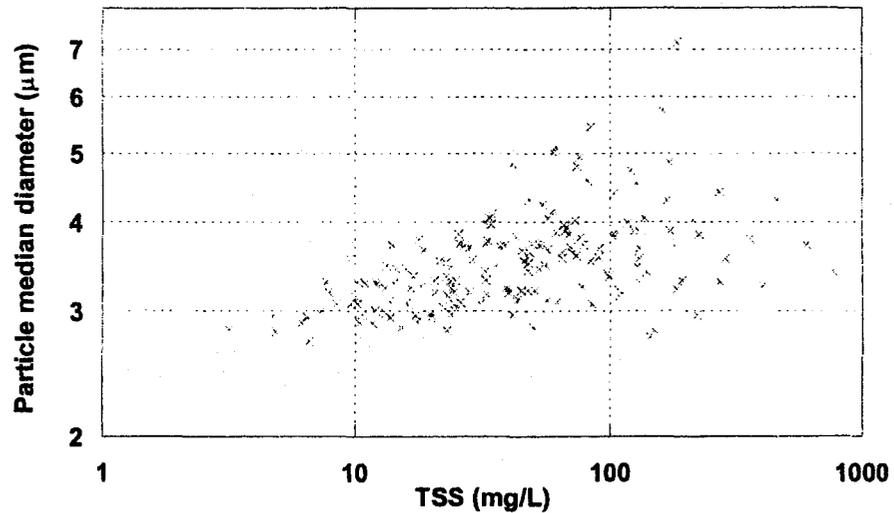


Figure 3.5 Particle median diameter of grab samples vs. TSS

3.3.3 Application of PSD to BMP Design

Knowledge of the PSD provides an opportunity to evaluate and suggest better BMP design. More importantly, if the solid phase concentration (i.e. pollutant mass per unit mass of particles) is known as a function of particle size, overall pollutant removal rates can be calculated.

We propose a two-compartment sedimentation design after evaluating several settling tank design criteria, such as retention time, overflow rate or minimum critical settling velocity, and strategies that collect and hold some fraction of the initial runoff

(Figure 3.6). The first compartment is designed to capture and retain the initial runoff for a defined period (24 hours in our example case). The extended holding time allows a greater fraction of the smaller particles to settle. This compartment removes most of the particles and associated pollutants contained in the initial part of runoff, or the particle first flush (Li et al. 2004). The second compartment is a continuous flow sedimentation tank or clarifier, which treats the later runoff that bypasses the first compartment. The continuous flow clarifier removes the larger particles. The size of the tanks can be optimized to remove the most particles for a given total volume or construction cost. The optimization will depend on the particle size distribution for each site, the target pollutant, and its concentration as a function of particle size.

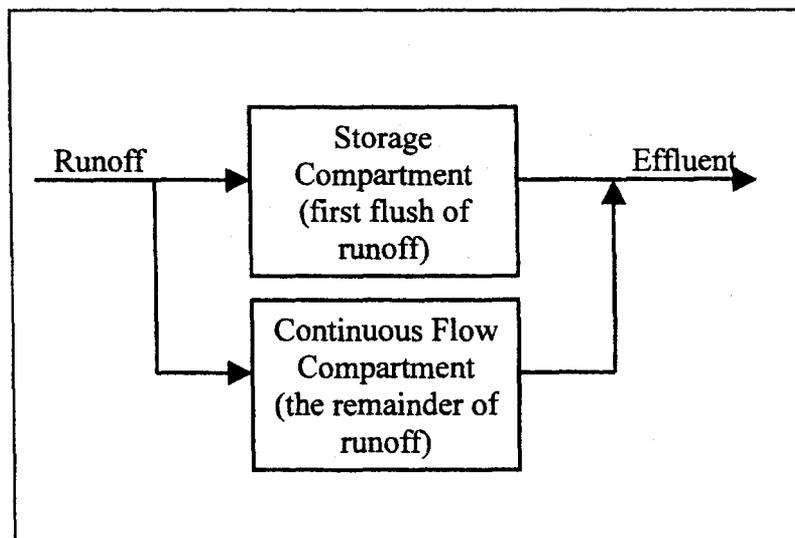


Figure 3.6 Two-compartment sedimentation design

To evaluate the pollutant removal efficiency of the proposed two-compartment settling tank, it was necessary to calculate particle removal efficiency as well as pollutant removal efficiency. The literature data presented in Tables 3.1 and 3.2 were used. We

assumed the particles to be homogenous density of 2.6g/cm^3 and to be spherical in shape. The actual shape of the particles is probably not spherical (Sansalone et al. 1998) but this assumption is considered sufficient for this demonstration.

3.3.3.1 Impact of Particle Settling Velocity

Discrete (type I) settling analysis was used to analyze the performance of the proposed two-compartment tank. The particles observed in our samples were not were flocculent and were too low in concentration to create hindered or zone settling (types, II, III and IV). The discrete particle terminal settling velocity was calculated using Newton's law or Stokes law (Tchobanoglous et al. 2003). The overflow rate (Q/A , $\text{m}^3/\text{m}^2\cdot\text{s}$) was used to determine which particles are removed. Particles with greater settling velocities are removed completely.

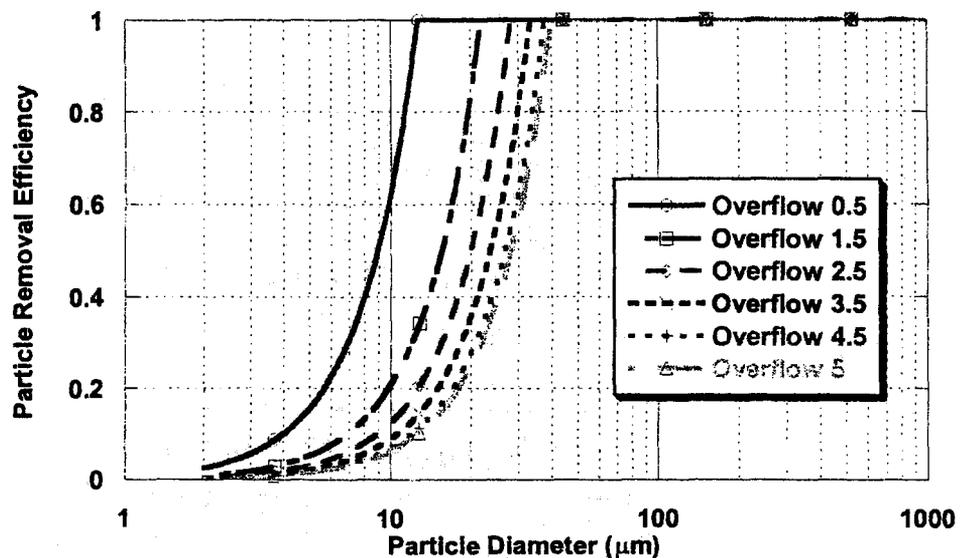


Figure 3.7 Particle removal efficiency (assuming spherical particles, specific gravity = 2.6g/cm^3 , discrete settling with Newton's and Stokes's settling velocities; overflow 0.5 refers to overflow rate of 0.5 m/h)

For a continuous overflow settling tank, in an ideal situation, particles with settling velocity equal or larger than the overflow rate are totally removed and particles with settling velocity smaller than the overflow rate will be removed at a rate equal to particle settling velocity divided by overflow rate. Figure 3.7 shows the calculated removal efficiency for particles as a function of diameter for different overflow rates. Particles with diameters larger than 40 μm are totally removed at overflow rates as high as 5 m/h while particles with diameters smaller than 10 μm are difficult to remove at any overflow rate. Additionally, the error introduced by our assumptions (uniform specific gravity, spherical shape and discrete particle settling) will be larger at smaller diameters, and the expected removal for smaller particles will be even less. Bäckström (2002) has noted this phenomenon and applying his recommendations, the particle removal efficiency decreases by up to 95% for the smallest particles. For example, Figure 3.7 shows a removal efficiency of 47% for 15 μm diameter particles at overflow rate 1.5 m/h, and using Bäckström's suggestions, the removal efficiency decreases to 10%.

For the holding compartment, removal efficiencies are also calculated using Stokes' and Newton's laws. In this case, the particles must settle from their initial height in the tank to bottom of the holding compartment. Again, Bäckström's suggestion can be evaluated, and his suggestion reduces particle (2-1000 μm) removal by less than 6% while associated pollutant removal decreases up to 32% in our sample calculation. The reason for this is that small particles have much higher associated pollutant concentration

than large particles as shown in Table 3.2, and most of the removal efficiency decrease is due to the reduced settling velocity of small particles.

3.3.3.2 Impact of Flow Variability-Design Storm

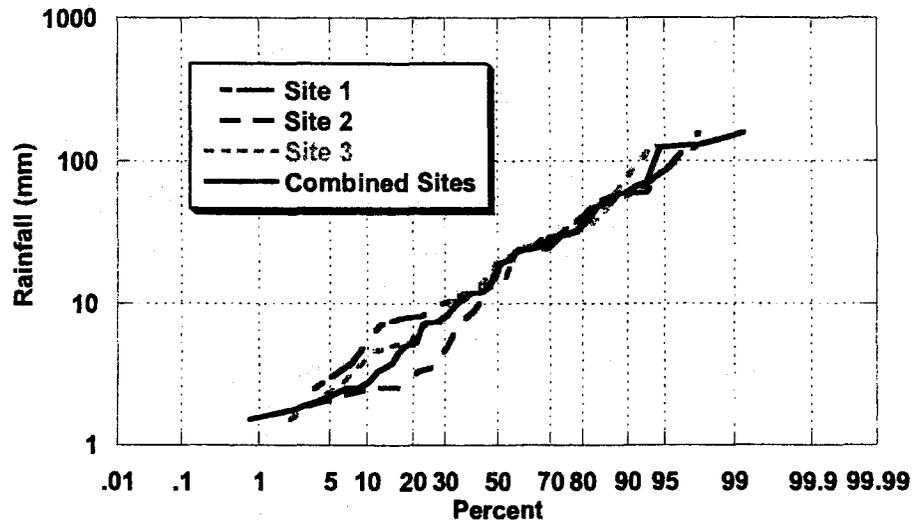


Figure 3.8 Rainfall probability for three sites monitored in 2000-2003 rainy season

Rainfall is highly variable and a probabilistic basis must be used for tank design. We chose to use rainfall probability based on total event rainfall. Figure 3.8 shows the probability of total rainfall for our 2000-2003 monitored events for the three sites taken separately and combined. For different rainfall probability, the corresponding rainfall amount is termed the design storm as shown in Figure 3.9. For example, the 50% rainfall corresponds to a design storm of 18 mm. For this design storm, assuming the runoff coefficient to be 0.95, the total runoff volume for sites 1, 2, and 3 are computed to be 219, 289, and 67 m³, respectively.

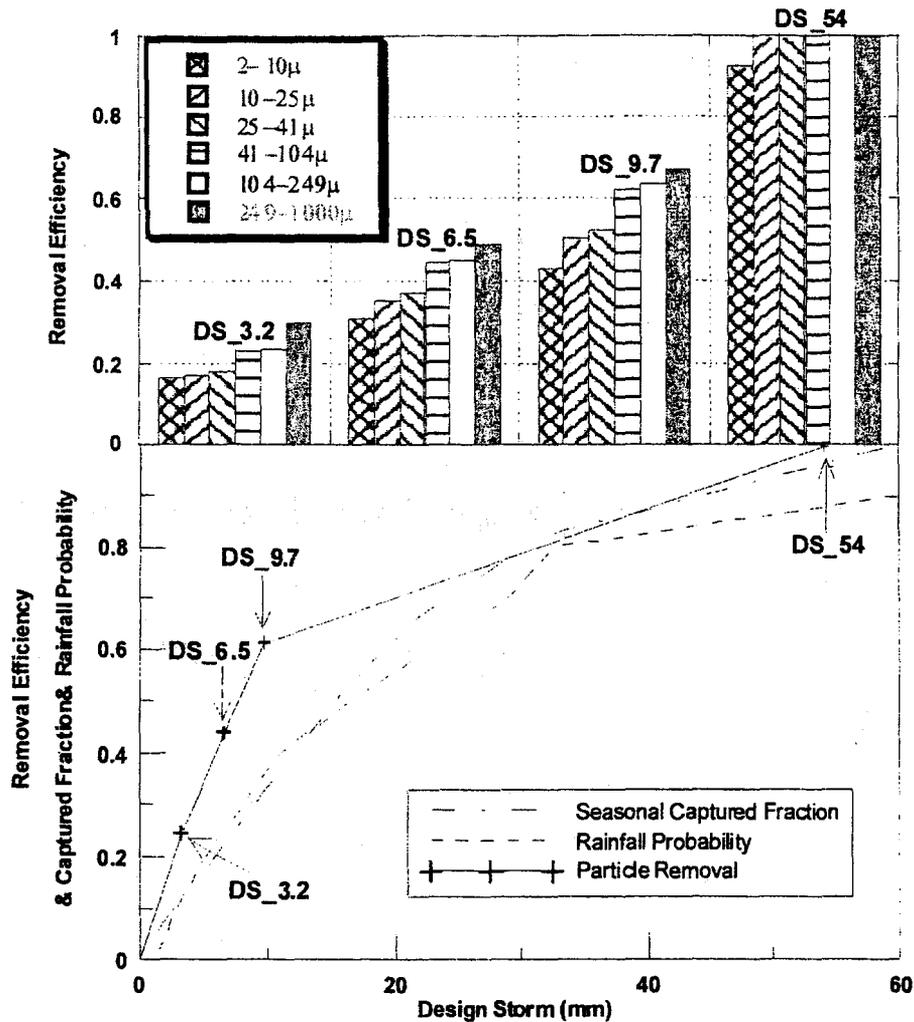


Figure 3.9 Simulated seasonal (2002-2003) particle removal efficiency with only storage compartment (e.g. DS_3.2 refer to Design Storm 3.2 mm)

3.3.3.3 Particle and Pollutant Removal Efficiency

The design procedure we propose is to set the storage compartment volume equal to the runoff from the design storm. The depth of the storage compartment is assumed to be 3 m, which also determines its area, since the volume is fixed. All storms less than or equal to the design storm are completely captured and retained. We ignore the possibility

of two storms occurring within 24 hours, which did not occur in our study. For larger storms, the excess is treated only by the second compartment, continuous flow clarifier. The method used to determine surface area of the continuous flow compartment is similar to that used for storage compartment.

Figure 3.9 shows the simulated removal of particle with only the storage compartment for the entire 2002-2003 season. The bottom shows the overall particle removal efficiency and the top shows the particle removal efficiency for particles within the defined size ranges for different design storms. The horizontal axis shows the design storm for the storage compartment. The vertical axis shows the overall particle removal efficiency, the captured fraction, the design storm's probability (bottom), and the removal efficiency for individual particle size range (top). The overall removal increases almost linearly but "leads" the runoff volume shown by the diagonal line. The impact of the first flush is shown; for example, at a design storm of 5.1 mm or 20% probability, 35% of the particle is removed by the storage compartment, while capturing only 17% of the volume. The simulation shows that the storage compartment with 24 hours retention time will remove most of the particles less than 10 μm and all the particles larger 10 μm captured. Larger particles show higher removal efficiency than smaller particles, which is due to larger particles' stronger first flush than smaller particles (Li et al. 2004).

Figure 3.10 and Figure 3.11 are similar to Figure 3.9. Figure 3.10 shows the simulated seasonal particle removal efficiency with only the continuous flow compartment while Figure 3.11 shows the removal efficiency with both compartments.

For the same size storage and continuous flow compartments, the storage compartment is better for removing particles smaller than 10 μm (e.g. 17% vs. 7% for design storm 3.2mm) and is poorer for removing particles larger than 10 μm , especially for particles larger than 25 μm . All of the particles larger than 100 μm can be easily removed by continuous flow compartment. By using both compartments, better removal efficiency for both small particles and large particles is achieved.

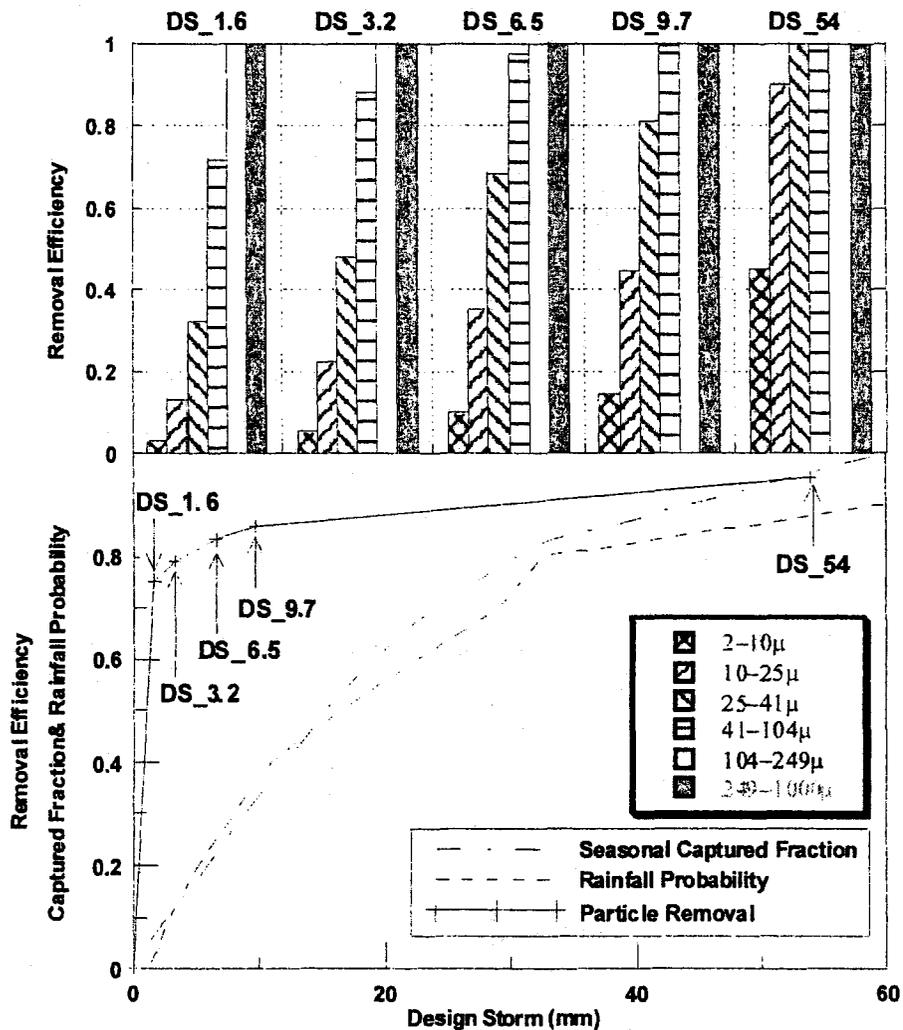


Figure 3.10. Simulated seasonal particle removal efficiency with only continuous flow compartment (e.g. DS_3.2 refer to Design Storm 3.2 mm)

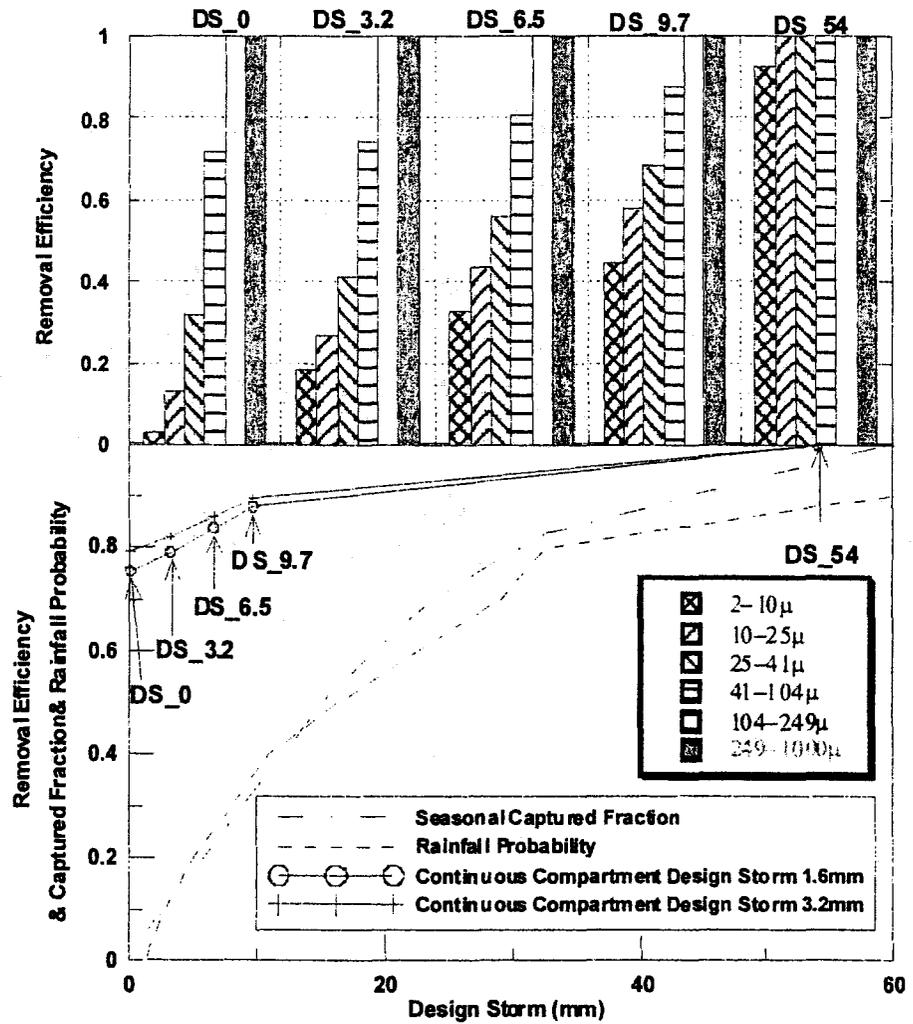


Figure 3.11. Simulated seasonal particle removal efficiency with two-compartment settling tank (e.g. DS_3.2 refer to Design Storm 3.2 mm)

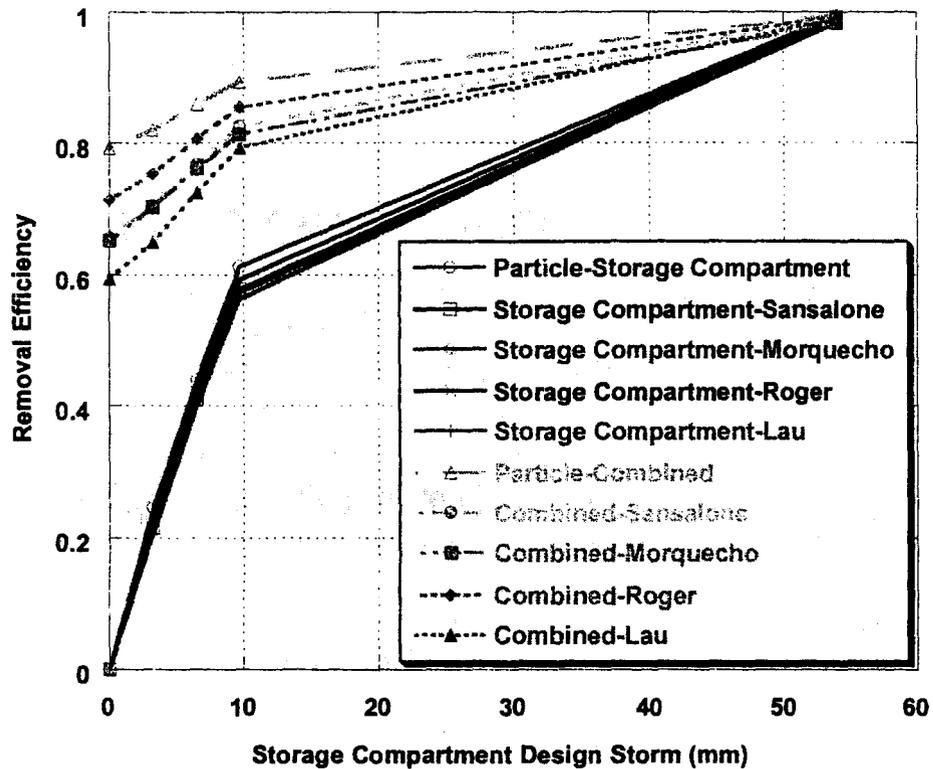


Figure 3.12. Seasonal Pb removal efficiency when continuous flow compartment design storm is 3.2 mm

To determine pollutant removal efficiency from particle removal efficiency, the pollutant concentrations on the particles as a function of size must be known. The two-compartment design will show the greatest advantage over a single continuous clarifier when the pollutants are more concentrated on the smaller particles. We evaluated removal of eight metals using five different sets of concentration versus size data as shown in Table 3.2. Figure 3.12 is an example, showing the lead (Pb) removal efficiency. The lower group of lines in Figure 3.12 shows the removal efficiency of PARTICLE and

Pb by the storage compartment and upper group of lines demonstrates removal efficiency by both compartments. The removal by the storage compartment calculated using different researchers' Pb concentration data are similar. This results because virtually nearly all the captured particles are removed in the storage compartment. The combined removals of both compartments are different results for different researchers' Pb data. For example, the overall removal of Pb is 76% for Roger's (1998) concentration and 65% for Lau's (2004) concentration. Generally, when pollutant concentrations are higher on large particles, the removal efficiency will be higher because the larger particles are removed more efficiently. In the two-compartment settling tank design, when the targeted pollutant is more associated with small particles, a larger storage tank will be preferred, and conversely, when the targeted pollutant is more associated with larger particles, a larger continuous flow compartment should be used.

3.4 Conclusions

Previous studies have shown that small particles accounted for most of the pollutant load of particles carried by stormwater runoff for certain pollutants such as total phosphorus and nitrogen. In this study, particle size distribution was measured during individual storm events over the 2002-2003 rainy season. More than 90% of the particles were less than 10 μm in diameter. Particle concentrations declined with accumulating rainfall. Log transformed particle concentrations were linearly correlated with TSS and turbidity. Grab sample median particle diameter increased with increasing TSS concentration.

A two-compartment settling tank demonstrated improved removal efficiency for both small and large particles. Pollutant removal efficiency was evaluated using several researchers' published solid phase pollutant concentrations. When the targeted pollutant was more associated with smaller particles, a larger storage compartment resulted in higher removal efficiency. When the targeted pollutant was more associated with larger particles, a larger continuous flow compartment produced better removal efficiency. The observed particle first flush more than doubled the removed particle mass, as compared to hypothetical runoff that had no particle first flush. Larger particles showed a stronger first flush than smaller particles.

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4. APPLICATION OF PARTICLE SIZE DISTRIBUTION IN HIGHWAY RUNOFF: OPTIMIZATION OF SETTLING TANK DESIGN TO REMOVE PARTICLES, METALS AND TOXICITY

Abstract

Removal efficiencies of particles, metals, and toxicity are optimized for a two-compartment settling tank, which includes a storage compartment to retain the first part of runoff and a continuous flow compartment to treat the rest. Measured particle size distribution (PSD), rainfall, and flow data from 16 storms in the 2002-2003 rainy season are used. Maximum removal efficiencies are calculated for a specific design storm size as a function of the storage and continuous flow volumes. Larger storage volumes are needed to remove the smallest particles, which is desirable because higher pollutant concentrations are associated with smaller particles. A tradeoff exists between removing small particles and removing large particles during very large storms. When the total design storm is only a few millimeters of rainfall, a design with no storage compartment optimizes overall particle removal. When the total design storm is more than 10 mm rainfall, a storage volume equal to 75% of the total tank volume produces highest particle removal efficiency.

Keywords: Stormwater; highways; runoff; particle size distribution; best management practices; pollution; settling velocity; metals; toxicity; first flush.

4.1 Introduction

Nonpoint source (NPS) pollution has become the leading cause of the deterioration of water bodies in the United States because of continuing urbanization and the reductions from point sources due to wastewater treatment plant construction. Among nonpoint sources, highway runoff is one of the most serious due to the presence of heavy metals, hydrocarbons and fuel additives (Colwill et al. 1984; Driscoll et al. 1990; Ball et al. 1994; Young et al. 1996; Barrett et al. 1998a). Due to the non-degradable, accumulative, and toxic character of heavy metals, highway runoff treatment has become increasingly important. In addition, because of the episodic nature of stormwater discharges, large variability in pollutant concentrations, and the implementation of more stringent water quality regulations such as total maximum daily loads (TMDLs), special attention is being given to mitigate pollutants from highway runoff.

Partitioning of metals between dissolved and particulate forms is important to evaluate their removal efficiencies, because most treatment facilities remove particles as opposed to soluble components. The partitioning information can be conveyed by dissolved fraction f_d values (Sansalone et al. 1997) as shown in equation (4.1):

$$f_d = \frac{D}{D+P} \quad (4.1)$$

Where D = dissolved mass of a metal element (g)

P = particulate-bound mass of a metal element (g)

Table 4.1. Dissolved fraction f_d values for metals

Al	Cd	Cr	Cu	Fe	Ni	Pb	Zn	Reference
<i>Sediments of highway runoff</i>								
0.04 (0.003-0.31)*	0.54 (0.45-0.96)		0.62 (0.31-0.71)	0.03 (0.01-0.13)		0.21 (0.18-0.45)	0.85 (0.54-0.96)	Sansalone and Buchberger 1997
<i>Suspended solid in urban runoff</i>								
	0.78	0.16	0.63	0.03		0.18	0.28	Morquecho and Pitt 2003
<i>Suspended solid in highway runoff</i>								
0.29	0.008	0.18	0.01			0.05	0.53	Pitt et al. 1995
	0.2 (0.03-0.49)		0.28 (0.07-0.53)			0.03 (0-0.17)	0.25 (0.04-0.56)	Gromaire-Mertz et al. 1999
			0.11-0.44			0.04-0.21	0.11-0.45	Furumai et al. 2002
	0.2 (0.17-0.33)		0.22 (0.13-0.24)		0.12 (0.09-0.2)	0.03 (0-0.03)	0.26 (0.22-0.32)	Westerlund et al. 2003
	0.79	0.21	0.59		0.61	0.07	0.72	Our data, seasonal average

*Data in parenthesis shows the range of observation

Large f_d values indicate that the metals are mainly in dissolved form. Table 4.1 shows some f_d values reported by different researchers. Although f_d values vary for some metals, cadmium (Cd), iron (Fe) and lead (Pb) are mainly in particulate form in highway runoff. Lower pH and higher average pavement residence time (APRT) are associated with higher dissolved metal fraction (Sansalone et al. 1997). At the same time, metal element dissolution/adsorption kinetics plays an important role in their partitioning. Sample holding time also has a significant influence on partitioning of some metal elements including copper (Cu), Pb, and nickel (Ni), with particle phase concentrations increasing with increasing holding time.

Stormwater toxicity assessment is difficult because of the ambiguous relationship between pollutant concentrations and toxic effects, and the effects of land uses, total rainfall and rainfall intensity, antecedent dry periods, and temperatures. The large suite of potentially toxic pollutants exists in stormwater runoff, such as metals and organics (e.g. polycyclic aromatic hydrocarbons or PAHs), make toxicity evaluation costly and time consuming.

Various treatment methods have been utilized to treat stormwater, including detention basins (Jacopin et al. 1999), sedimentation tanks (Aldheimer and Bennerstedt 2003), ponds (Hvitved-Jacobsen et al. 1994), wetlands (Birch et al. 2004), grassy swales (Barrett et al. 1998b; Bäckström 2003), vortex or swirl concentrators (Lee et al. 2003), and sand filters (Barrett 2003). All depend on particle size, shape and density and the

associated settling velocity. Generally, larger particles are easier to remove than smaller particles.

A number of factors influence treatment efficiency, including influent pollutant concentrations, runoff magnitude or velocity and facility size. Large variances exist in treatment efficiencies from negative to 98%, as shown in Table 4.2. The use of treatment efficiency as an indicator of performance has been questioned by Strecker et al. (2001), who believe that comparing effluent concentrations is a more robust way of comparing performance.

Some of the treatment systems such as sedimentation tanks (Sonstrom et al. 2002; Aldheimer and Bennerstedt 2003), dry detention ponds (Stanley 1996) are designed to capture the first flush of runoff and bypass higher flows, which can be a large portion of total runoff. In these cases the efficiency was calculated only based on the treated portion. Bypassed pollutant mass was not considered, which is not representative of the total mass emissions. Removal efficiency is usually greater for higher influent pollutant concentrations (Strecker et al 2001; Lau and Stenstrom 2002). Since pollutant concentrations tend to decrease with the progress of rainfall or runoff (Sansalone and Buchberger 1997; Larsen et al. 1998; Krebs et al. 1999; Li et al. 2004a), the treatment facility tends to have higher treatment efficiency when treating the initial runoff. Therefore evaluating treatment efficiencies over the hydrograph is necessary to achieve universal results (Whipple and Hunter 1981; Characklis and Wiesner 1997).

Table 4.2. Removal efficiency of different treatment methods

TSS	Turbidity	COD	Total P	Total N	TKN	Cd	Cu	Cr	Fe	Ni	Pb	Zn	Fecal coliform	TPH	O&G*
<i>Grassy swales (Barrett et al. 1998b; Bäckström 2003)</i>															
(-85-75)**															
(85-87)	(69-78)	(61-63)	(34-44)		(33-44)				(75-79)		(17-41)	(75-91)	(-477--192)		
<i>Constructed wetlands & wet ponds (USEPA 1993; Birch et al. 2004)</i>															
60-80			25-65		20-55							20-60			
-98-46			12	16	9		65	64	-84	22	65	52	76		
<i>Sedimentation tank (Aldheimer and Bennerstedt 2003)</i>															
(66-99)			(26-95)	(-26-40)		(0-92)	(18-96)	(37-98)		(0-94)	(50-99.8)	(30-97)			(-35-87)
<i>Sedimentation Chamber (Sonstrom et al. 2002)</i>															
77-88			67		18							85	-7	16	
<i>Continuous Flow Clarifier (Clausen et al. 2002; Waschbusch 1999)</i>															
21-34			20	17-29	32	27	25				24	17-60	-15	12	
<i>Oil-Grit Separator (Clausen et al. 2002; West et al. 2001)</i>															
49			74		44							45	99	37	
<i>Swirl Concentrator (Lee et al. 2003)</i>															
65-70															
<i>Filtration (Papiri et al. 2003)</i>															
							98				98	98			95

*Oil and Grease ** Data in parenthesis shows the range of efficiency

The objective of this study is to use newly acquired particle size information, complemented with literature data on solid phase concentrations of pollutants and toxicity, to optimize removal efficiency of a two-compartment settling tank. The settling tank has one compartment to capture and retain the first runoff, and a second compartment that acts as a continuous flow clarifier for the remaining runoff. Total particle removal is evaluated as well as metal and toxicity removal. The results should be useful in designing BMPs to optimize highway stormwater treatment.

4.2 Methodology

Site descriptions, sample collection procedures and particle size analysis have been discussed previously (Li et al. 2004a). Settling velocity calculation procedures and pollutant removal efficiency calculation have also been discussed previously (Li et al. 2004b). Our metal removal efficiency used f_d values calculated from our averaged mass emission rates all 16 monitored storm for three sites in the 2002-2003 rainy season. The only exception is Fe, where we used the average value reported by other researchers shown in Table 4.1.

4.2.1 Toxicity

Toxicity reduction is a very important aspect of stormwater treatment due to the toxicants' potential long term adverse effect on ecosystems. Toxicity evaluations are costly and time consuming, and require special protocols. Very few studies have been performed on the toxicity of highway runoff (Bay et al. 2003; Greenstein et al. 2004). In

order to evaluate the potential effect of metals removal on toxicity reduction, a simple toxicity evaluation methodology is developed here based upon Fairey et al. (2001)'s previous work on sediment toxicity.

A combination of pollutants was recommended to serve as the standard for calculating mean sediment quality guideline quotients (mean SQGQs) when comparing with acute toxicity to amphipods. This SQGQ is calculated as (4.2):

$$SQGQ = \frac{([Cd] + [Cu] + [Pb] + [Ag] + [Zn] + [chlordane] + [dieldrin] + [PAH_{oc}] + [PCB])}{4.21 + 270 + 112.18 + 1.77 + 410 + 6 + 8 + 1800 + 400} \quad (4.2)$$

The various numbers in the denominators of the concentration terms serve to normalize the toxicity for each pollutant. Since not all of the information for each pollutant shown in (4.2) is available as a function of particle size, which is required in our sedimentation calculation, (4.2) is simplified by using the average of available normalized pollutant concentration. Generally necessary information was available for only 3 or 4 metals, and in the case of Cd, Cu, Pb and Zn (4.2) reduces to (4.3):

$$SQGQ = \frac{([Cd] + [Cu] + [Pb] + [Zn])}{4} \quad (4.3)$$

Table 4.3. Metal concentrations for different particle size ranges

Size ranges (μm)	Heavy metal concentration ($\mu\text{g/g}$)								Remarks	References
	Al	Cd	Cr	Cu	Fe	Ni	Pb	Zn		
0.45-2				2894	29267		199	13540	Urban stormwater suspension	Morquecho and Pitt 2003, Birmingham and Tuscaloosa, Alabama.
2-10				4668	18508		868	13641		
10-45				735	26221		229	1559		
45-106				1312	14615		226	2076		
106-250				2137	21730		375	3486		
>250				50	28604		117	266		
25-38		16.8		364			265	1189	Highway runoff sediments	Sansalone and Buchberger 1997, Cincinnati, Ohio
38-45		17.2		353			236	996		
45-63		17.3		364			266	1027		
63-75		16.3		333			258	1057		
75-150		15		312			248	1014		
150-250		9.2		204			195	574		
250-425		8		78			65	325		
425-850		9.5		48			53	314		
850-2000		9.7		45			37	259		
<50	60000		350	420		230	1570	4370	Highway runoff sediments	Roger et al. 1998, Hérault region, France
50-100	45000		400	250		250	1480	1700		
100-200	38000		410	200		220	1550	1100		
200-500	35500		150	100		220	850	930		
500-1000	37500		140	50		220	460	930		
<43		5	46	220		65	350	960	Street sweeping	Lau and Stenstrom 2004, Los Angeles, California
43-100		5	58	230		50	300	805		
100-250		2	38	230		40	210	500		
250-841		na	12	240		5	44	150		
Average		1	28	238		25	142	360		
<75				470				410	Street sweeping	German and Svensson 2002, Jönköping, Sweden
75-125				270				230		
125-250				340				190		
250-500				200				120		
500-1000				50				70		

Table 4.3 lists selected particle metal concentration distribution on different particle size ranges. These concentrations can be represented by $conc_{ij}$ which is the particulate pollutant j concentration in particle size range i ($\mu\text{g/g}$). The numbers in the denominators normalize the concentrations and can be represented by f_i which means toxicity factor of pollutant i (e.g. $f_{Cd} = 1/4.21$; $f_{Cu} = 1/270$; $f_{Pb} = 1/112.18$; $f_{Zn} = 1/410$). The total particle mass (g) in each size range i , which was determined according to the available particulate metal concentration ($\mu\text{g/g}$) for different size ranges, can be represented by $mass_i$ calculated with our measured grab sample PSD and flow data (for detailed particle mass calculation method, please refer to Li et al. 2004b). Particle masses were calculated by summing the mass in all events at all three sites.

Toxicity removal efficiency was calculated for the two-compartment settling tank and was expressed with a set of equations as follows:

$$\text{Toxicity removal efficiency} = \frac{\text{removedSQGQ}}{\text{totalSQGQ}} \quad (4.4)$$

Where,

$$\text{removedSQGQ} = \frac{\sum_{i=1}^{j_{\max}} \sum_{j=1}^{i_{\max}} (r_{mass_i} \times conc_{ij} \times f_j)}{j_{\max} \times \text{totalrunoff}} \quad (4.5)$$

$$\text{totalSQGQ} = \frac{\sum_{i=1}^{j_{\max}} \sum_{j=1}^{i_{\max}} (mass_i \times conc_{ij} \times \frac{1}{f_{pi}} \times f_j)}{j_{\max} \times \text{totalrunoff}} \quad (4.6)$$

In equation (4.5) and (4.6), *totalrunoff* indicates total runoff volume of all investigated events from three monitoring sites (L); *i_{max}* is the number of particle size ranges and *j_{max}* is total number of pollutants; *r_{mass_i}* is removed particle mass (g) in size range *i*; particulate fraction of pollutant *j* *f_{pj}*

$$f_{pj} = \frac{P}{D+P} \quad (4.7)$$

Where D = dissolved mass of pollutant *j* (g)

P = particulate-bound mass of pollutant *j* (g)

To better illustrate these equations, a set of matrix is established as follows:

$$\begin{aligned} \text{removedSQGQ} &= \frac{\sum_{i=1}^{i_{max}} \sum_{j=1}^{j_{max}} (r_{mass_i} \times conc_{ij} \times f_j)}{j_{max} \times totalrunoff} \\ &= \frac{1}{totalrunoff} \times \mathbf{RMASS} \times \mathbf{CONC} \times \mathbf{FACTOR} \times \frac{1}{j_{max}} \\ &= \frac{1}{totalrunoff} \begin{bmatrix} r_{mass_1} & r_{mass_2} & \dots & r_{mass_{i_{max}}} \end{bmatrix} \begin{bmatrix} conc_{11} & & & conc_{1,j_{max}} \\ conc_{21} & & & conc_{2,j_{max}} \\ \cdot & & conc_{ij} & \cdot \\ \cdot & & \cdot & \cdot \\ \cdot & & \cdot & \cdot \\ conc_{i_{max}1} & & conc_{i_{max},j_{max}} & \cdot \end{bmatrix} \begin{bmatrix} f_1 \\ f_2 \\ \cdot \\ \cdot \\ \cdot \\ f_{j_{max}} \end{bmatrix} \frac{1}{j_{max}} \quad (4.8) \end{aligned}$$

$$\text{totalSQGQ} = \frac{\sum_{i=1}^{i_{max}} \sum_{j=1}^{j_{max}} (mass_i \times conc_{ij} \times \frac{1}{f_{pj}} \times f_j)}{j_{max} \times totalrunoff}$$

Where r is volume ratio between two compartments; V is total volume of two compartments; PSD is grab sample particle size distributions of all events; v is settling velocities of particles; flow is flow data for all events. Removal efficiency was calculated, using Stokes or Newton's laws (Li et al. (2004b)). The optimum was calculated by solving equation (4.10) for r from 0 to 1.0 in small steps. The total volume of the two compartments was fixed for a selected design storm size, represented as millimeters of rainfall. The actual volume for a particular site can be calculated by multiplying the design storm size by the site area and runoff coefficient. The effects of different pollutant concentrations (e.g., different values of the CONC) were simulated by choosing different values from the literature (Table 4.3). No optimization technique was needed because the equation can be quickly solved.

4.3 Results and Discussion

4.3.1 Particle Removal

Fig. 4.1 shows the overall particle removal efficiency of the individual compartments and combined for two different design storm sizes as a function of the relative size of the two compartments. The graph shows the results of simulating an entire season with 16 storms of varying size. The x-axis indicates the fractional volume of the storage compartment. For example, $x = 0$ indicates the storage compartment volume is zero; the entire volume is used for the continuous flow compartment. The y-axis represents particle removal efficiency.

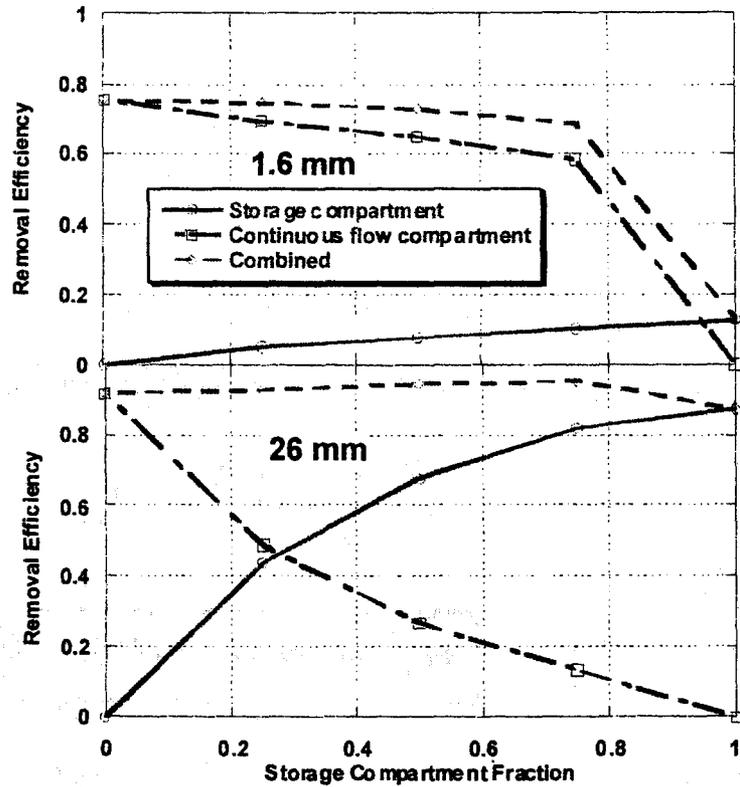


Figure 4.1 Particle removal efficiency for individual compartment and combined at design storm size 1.6 mm and 26 mm

Fig. 4.1 demonstrates that when total design storm for both compartments is 1.6 mm (i.e., a small sedimentation tank), the total particle removal efficiency declines as greater volume is allocated to storage, and most of the particle removal occurs in the continuous flow compartment. This is because volume of the storage compartment is too small and is only able to catch a small fraction of total runoff volume. When the total design storm is 26 mm, the overall particle removal efficiency slightly increases with the increasing storage until about 0.75, and then declines. The storage compartment removes more particles than the continuous flow compartment when the storage compartment fraction is more than 0.3. The large sedimentation tank allows the designer to choose

which compartment is used for treatment. For large storage tank volume, the entire flow from the smaller storms is captured, and the continuous flow tank is used only for storms larger than 26 mm. Additionally, particle first flush also has an influence on removal efficiency, which is discussed later.

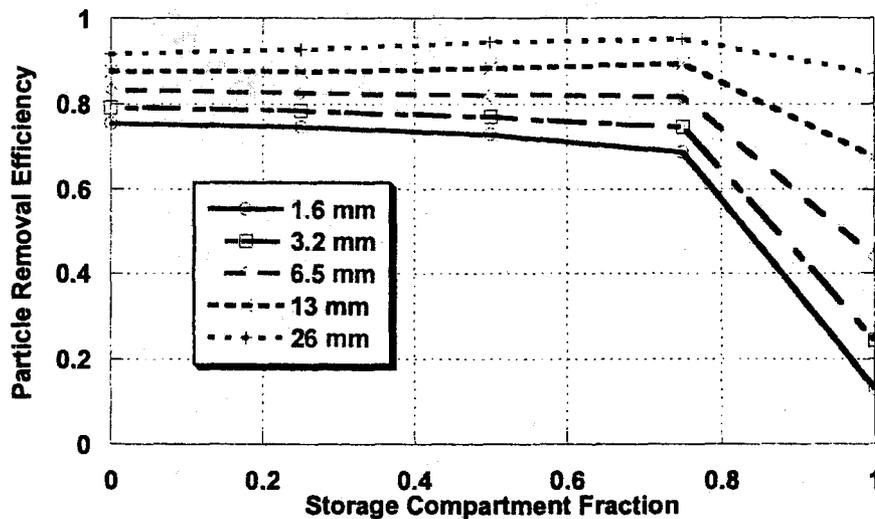


Fig. 4.2 Particle removal efficiency at different design storm size

Fig. 4.2 shows the overall particle removal efficiency of combined compartments for five different total design storm sizes. When the total design storm is 6.5 mm or less, the overall particle removal efficiency declines slightly with the increasing storage. In contrast, when the total design storm is 13 mm or more, the overall particle removal efficiency increases slightly with increasing storage. At approximately 0.75 storage fraction, the efficiency sharply declines. Although particle removal efficiency is relatively flat, a maxima exists at zero storage for low rainfall designs and at approximately 0.75 storage fraction for large rainfall designs.

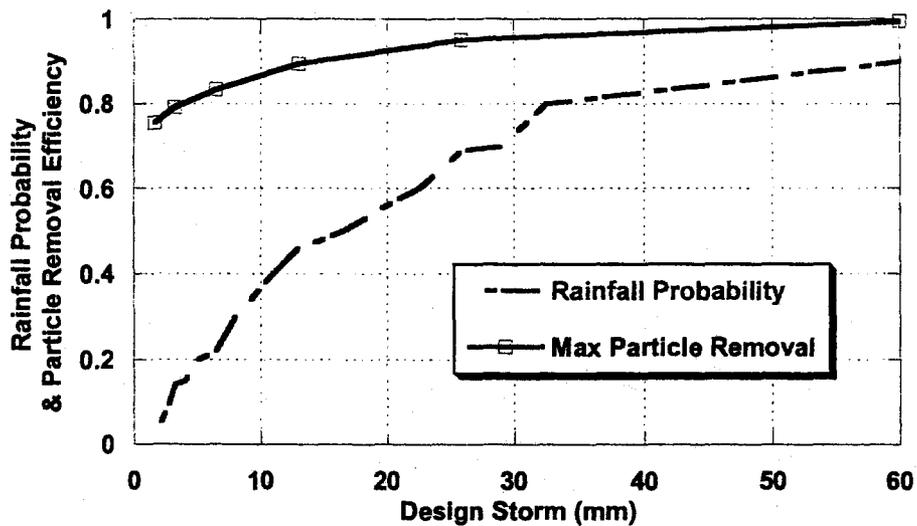


Fig. 4.3 Optimized particle removal efficiency and rainfall probability vs. design storm

Fig. 4.3 shows the optimized total removal rate as a function of design storm size. Rainfall probability is also shown on this figure. Rainfall probability is calculated from the monitored 1999-2003 rainfall data from the three sites, and shows log liner relationship with the total design storm size, although plotted in this figure on a linear axis for clarity. Maximum particle removal efficiency increases rapidly with the total design storm increase until about 13 mm and slows down thereafter. When the total design storm is 13 mm, 90% of the particles in full season can be removed by the two-compartment tank. If the design storm is doubled, the total particle removal efficiency increases to only 95%.

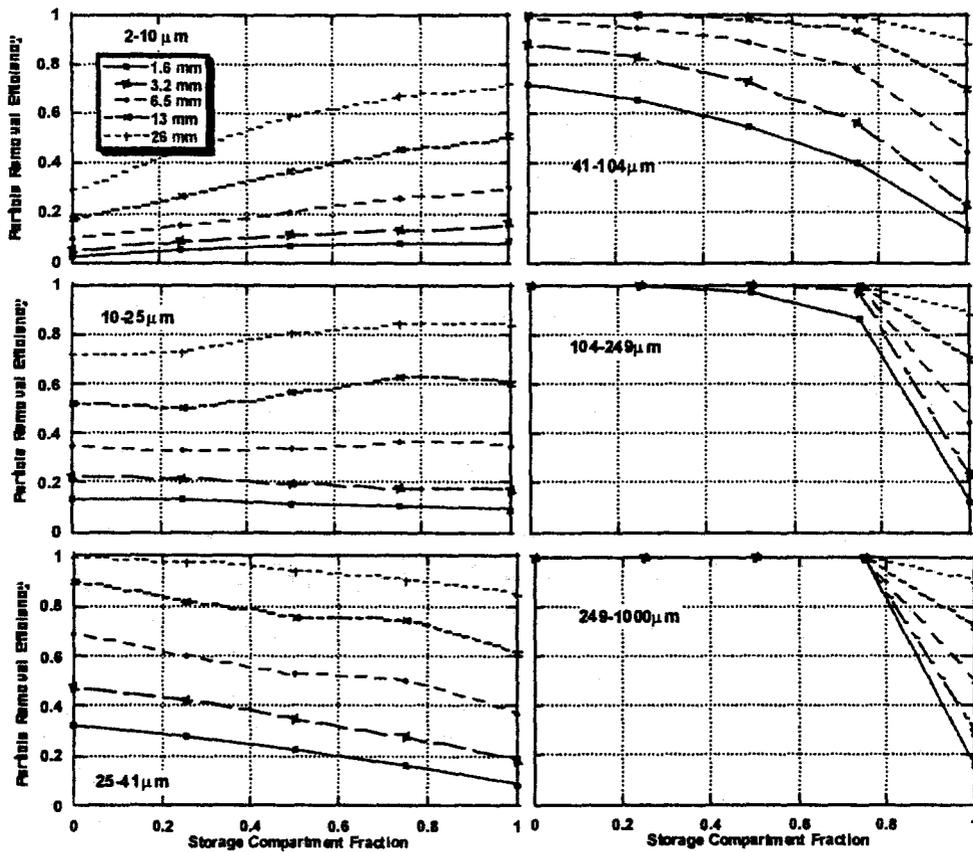


Fig. 4.4 Removal efficiency of individual particle size ranges at different design storm size

Total particle removal efficiency does not change very much with the variation of volume ratio between storage compartment and continuous flow compartment when the storage compartment fraction is less than 0.75 (Fig. 4.2). The removal of particles in a specific size range does vary greatly. Fig. 4.4 shows the change in particle removal efficiency for particles in six different size ranges, from 2-10 μm to 249-1000 μm . This graph is revealing in that it shows the differential removal of various size particles as a function of design storm size and storage fraction. Removal efficiency of the smallest particles with diameter 2-10 μm increases with increasing storage fraction. Large

particles ($>104 \mu\text{m}$) are efficiently removed with storage fractions less than 0.75, for even small design storms. Removal efficiency of medium size particles (25 to $104 \mu\text{m}$) increases with decreasing storage tank fraction. It is clear from this figure that particle storage tank volume primarily benefits removal of the smallest particles. This information will be useful if the pollutant concentrations as a function of particle size are known.

4.3.2 Pollutant Removal

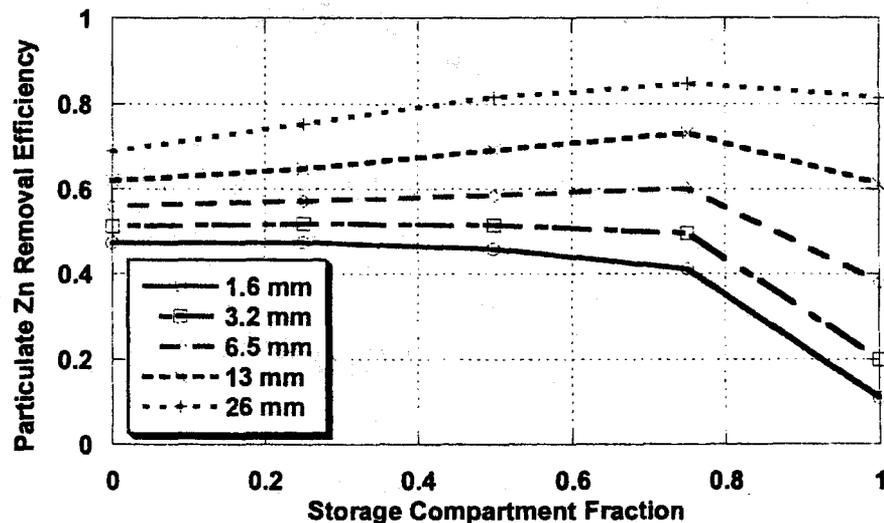


Fig. 4.5 Particulate zinc removal efficiency at different design storm size using Morquecho's zinc concentration distribution on different particle size data

Particle removal results in pollutant removal due to the fact that pollutants are sorbed to particles. Pollutant distribution on different size particles is one of the key factors that influence pollutant removal efficiency. Fig. 4.5 demonstrates particulate zinc removal efficiency for the two-compartment settling tank. For this simulation the Zinc

concentration distribution as a function of particle size was adapted from Morquecho and Pitt (2003), and is shown in Table 4.3. Particulate zinc removal efficiency increases when the storage compartment fraction increases for design storms equal to or larger than 6.5 mm. The increase is greater than the increase in particle removal efficiency, as shown in Fig. 4.2. For example, for a total design storm of 13 mm, particulate zinc removal efficiency increases from 62% to 73% while particle removal efficiency increases from 75% to 81%, when the storage fraction increases from 0 to 0.75. This results because the zinc concentration on smaller particles is much greater than on larger particle, e.g. 13,641 $\mu\text{g/g}$ for particles 2-10 μm while 266 $\mu\text{g/g}$ for particles larger than 250 μm in diameter. The higher pollutant concentration on smaller particles increases the importance of their removal, and makes increased storage important.

4.3.3 Pollutant and Toxicity Removal Optimization

Figs. 4.6 to 4.10 show the maximum metal and toxicity removal efficiencies for different design storm sizes for metal concentrations data reported by different researchers (Table 4.3). The optimal storage volume is always used, and is zero for design storms less than 6 to 13 mm, depending on pollutants and concentration distribution, and 0.75 for larger design storms. The graph includes the dissolved portion of the total metals, which is unaffected by the sedimentation tank. The large differences in metal removal are a function of the particulate fraction, f_p . Higher values of f_p allow higher metal removal efficiency. Fig. 4.6 to 4.10 shows that removal efficiencies of Cr,

Fe and Pb are much higher than other pollutants due to their high particulate fraction (f_p values of 0.79, 0.97 and 0.93 respectively as shown in Table 4.1).

Metal concentration distribution on different size particles also has obvious influence on removal efficiency. For example, with Cu concentration distribution from Lau and Stenstrom 2004 (Fig. 4.7), the removal efficiency of Cu is 0.31, but is only 0.21 using Roger et al. (1998) data. This results because there is large gradient in Cu concentration from small to large particles in Roger et al.'s data. Lau and Stenstrom's data show no gradient in Cu concentration with particle size. .

Simulated toxicity removal is greatest when using Roger's data. This is due to the high concentration and particulate fraction of Pb, which makes Pb much more influential than other metals in the toxicity calculation. The high particulate Pb fraction allows high removal efficiency which results in high toxicity removal efficiency.

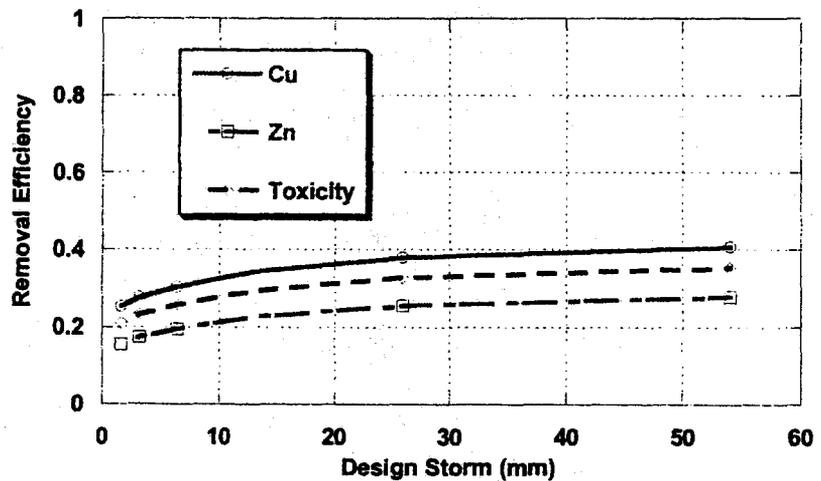


Fig. 4.6. The maximum removal efficiency for individual pollutants and toxicity using data of German and Svensson 2002.

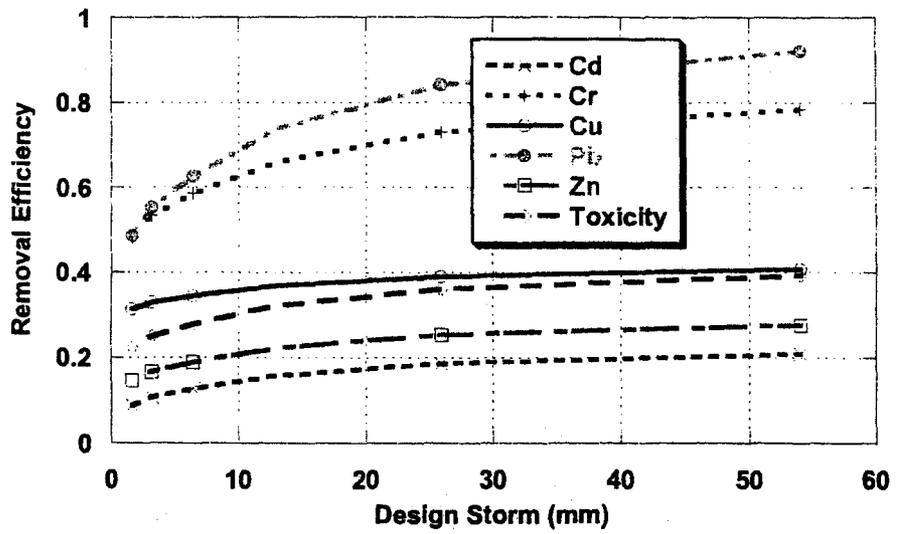


Fig. 4.7. The maximum removal efficiency for individual pollutants and toxicity using data of Lau and Stenstrom 2004.

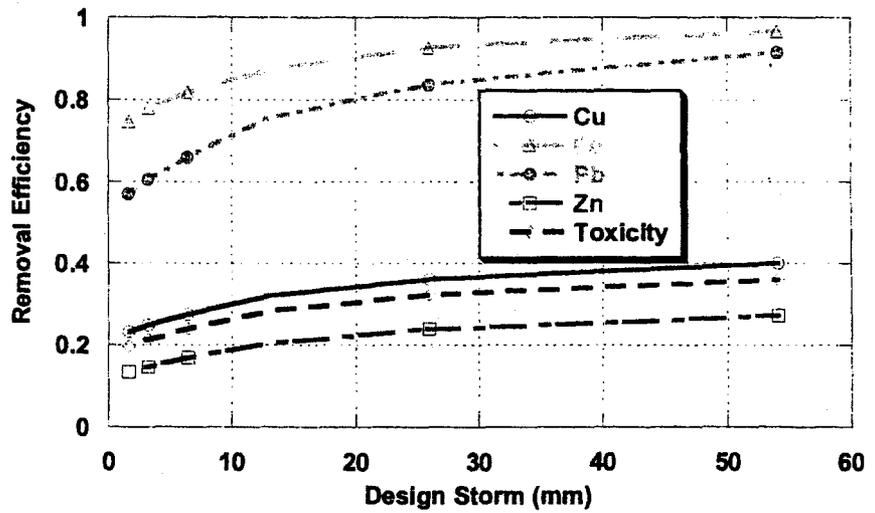


Fig. 4.8. The maximum removal efficiency for individual pollutants and toxicity using data of Morquecho and Pitt 2003.

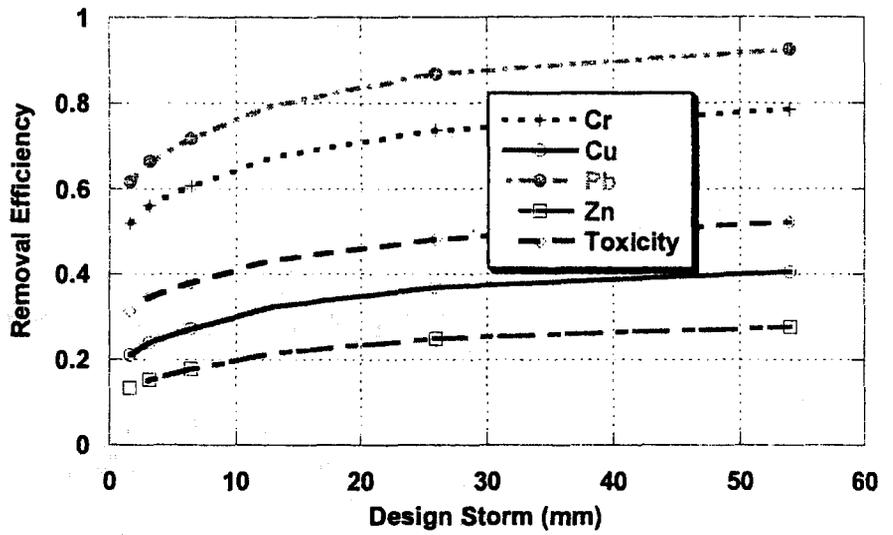


Fig. 4.9. The maximum removal efficiency for individual pollutants and toxicity using data of Roger et al. 1998.

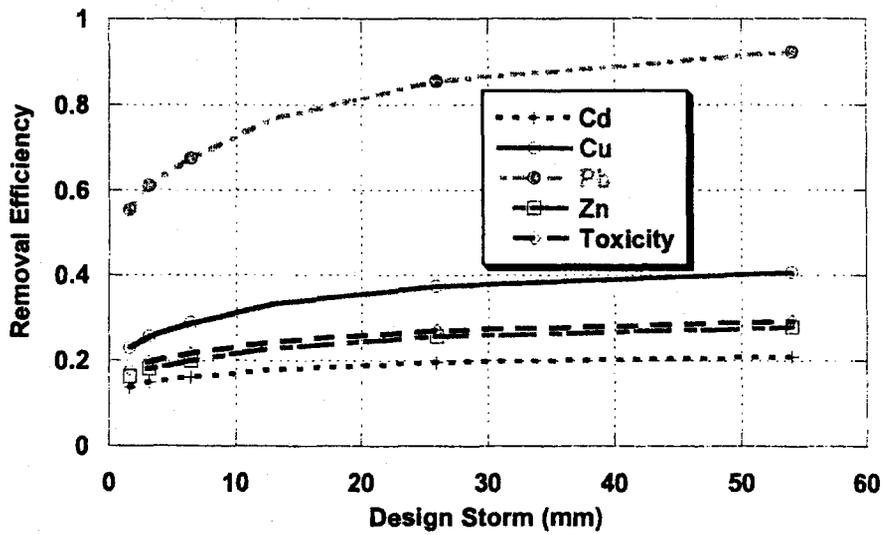


Fig. 4.10. The maximum removal efficiency for individual pollutants and toxicity using data of Sansalone 1997

4.4 Conclusions

Particle removal efficiency was optimized for a two-compartment settling tank using particle size distribution data collected from three highway sites. Removal efficiency was optimized by adjusting the storage volume for design storms ranging from 1.6 to 26 mm rainfall. When the design storm is less than 10 mm, no storage compartment produces the highest particle removal efficiency. When total design storm is more than 10 mm, volume ratio of 3:1 between storage compartment and continuous flow compartment volumes produces the highest particle removal efficiency. Particle removal efficiency increases from 75 to 90% as the design storm increases from 1.6 to 13 mm. Larger storage compartment volume increases removal efficiency of particles with diameters 2-10 μm by as much as 43%, depending on the design storm size, and may decrease removal efficiency of particles larger than 25 μm . Pb, Cr and Fe have higher removal efficiency due to their large particulate fraction. Toxicity estimates using mean sediment quality guideline quotients declines 18 to 52% depending upon design storm size.

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5. CONCLUSIONS

This dissertation has demonstrated the value of particle size distribution (PSD) in understanding pollutants highway runoff and suggesting ways of mitigating their impact through optimized sedimentation. The results are present in sequential fashion: PSD measurement protocol; characteristics and application to settling tank design, and optimization of settling tank design. The measurement protocol is a valuable reference for suspended particle sizing in stormwater. The proposed two-compartment settling tank proposed is an innovative treatment design for stormwater treatment which can be optimized using knowledge of particle size distribution and pollutant concentrations. The major conclusions in this study can be summarized as follows:

1. Particle characterization for stormwater is different from other area due to the unpredictable nature of rainfall, large variance in particle concentration, and tedious field sampling work. A PSD measurement protocol was proposed to achieve repeatable and reliable PSD results for stormwater. A hand washing procedure on glass bottles was satisfactory for cleaning sample bottles used to collect samples for PSD analysis. Gentle inversion (five to six times) of the sample bottle was a satisfactory mixing method. Composite samples taken by auto-sampler were not suitable for PSD analysis because PSD during storage in the composite sampler. Grab samples should be analyzed within six hours of sample collection.

2. More than 90% of particles in highway runoff were less than 10 μm in diameter. Log transformed particle concentrations were linearly correlated with TSS and turbidity. Particle median diameter increased with increasing TSS concentration. Particle first flush was observed and 40% of particles were transported in the first 20% of runoff.

3. Small particles less than 10 μm were the most numerous. A two-compartment settling tank was proposed to increase removal of the small particles and demonstrated high removal efficiency for both small and large particles. Particle, metal and toxicity removal efficiencies were optimized a two compartment settling tank with fixed total volume by varying the fraction dedicated to storage. When total design storm for the combined compartments was less than 10 millimeters rainfall, a design without a storage compartment produced the highest particle removal efficiency. When total design storm was more than 10 mm, a storage compartment to continuous flow compartment volume ratio of 3:1 produced the highest particle removal efficiency. Higher pollutant concentration on small particles magnified the trend in favor of larger storage compartments.

APPENDIX A PARTICLE NUMBER FIRST FLUSH FIGURES

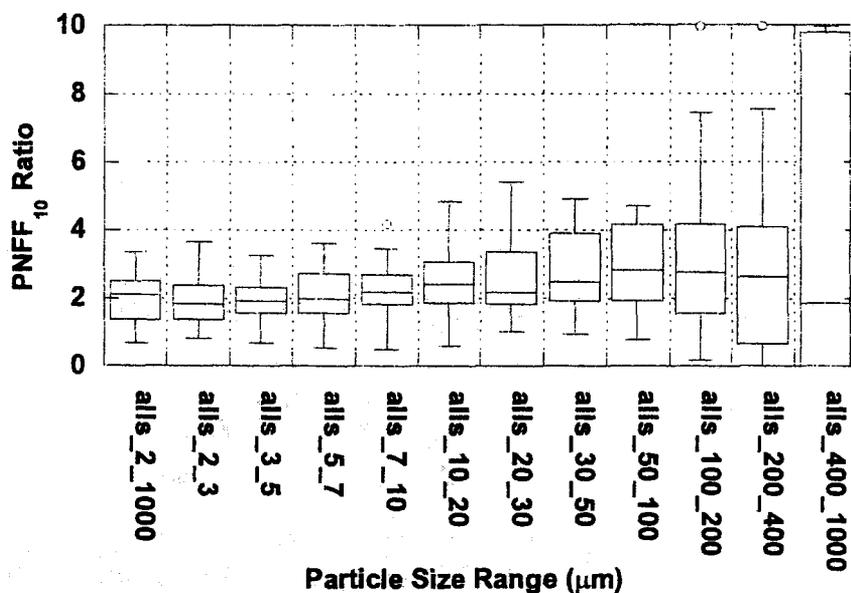


Figure A.1.1 PNFF₁₀ of Particles for Combined UCLA sites

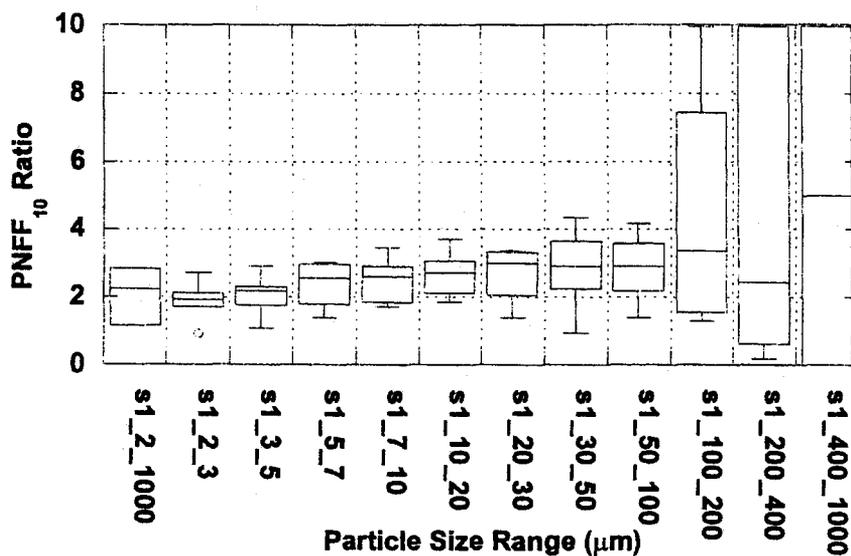


Figure A.1.2 PNFF₁₀ of Particles for UCLA 1

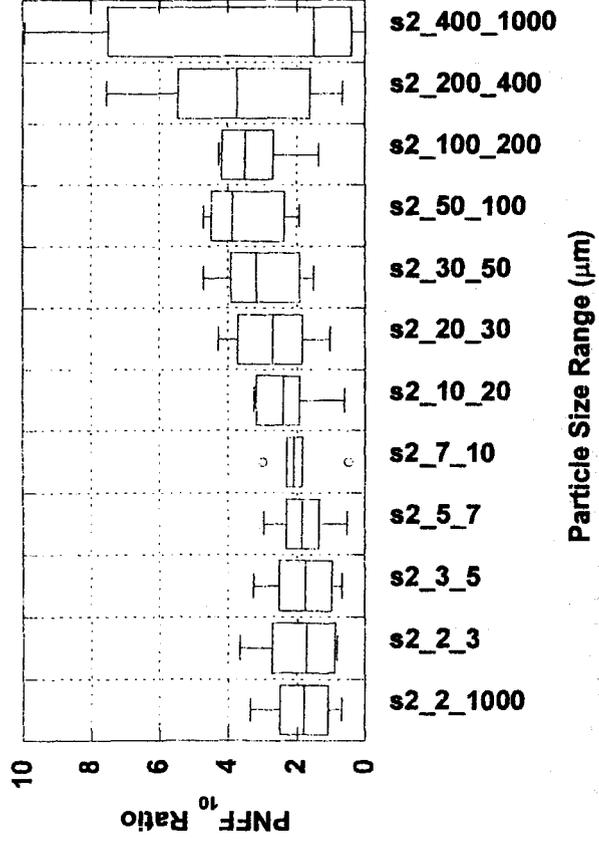


Figure A.1.3 PNFF₁₀ of Particles for UCLA 2

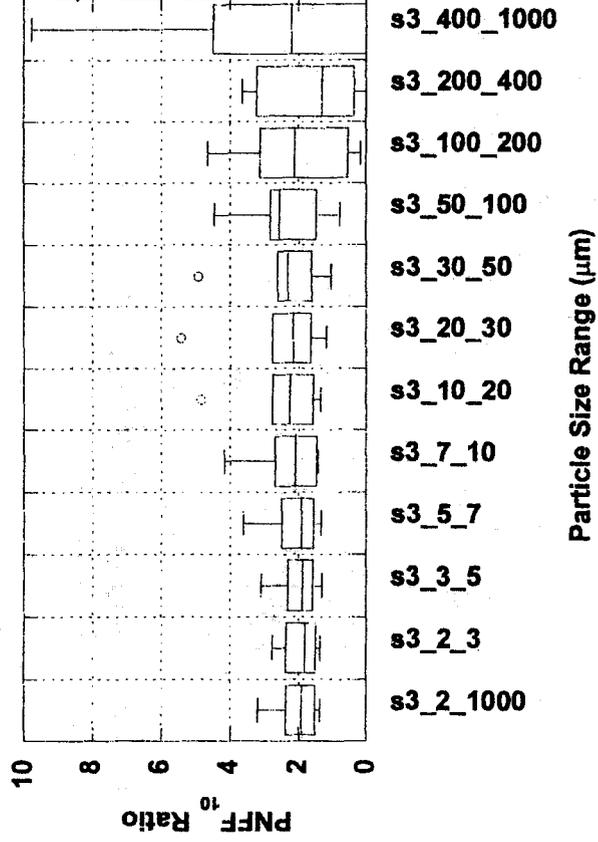


Figure A.1.4 PNFF₁₀ of Particles for UCLA 3

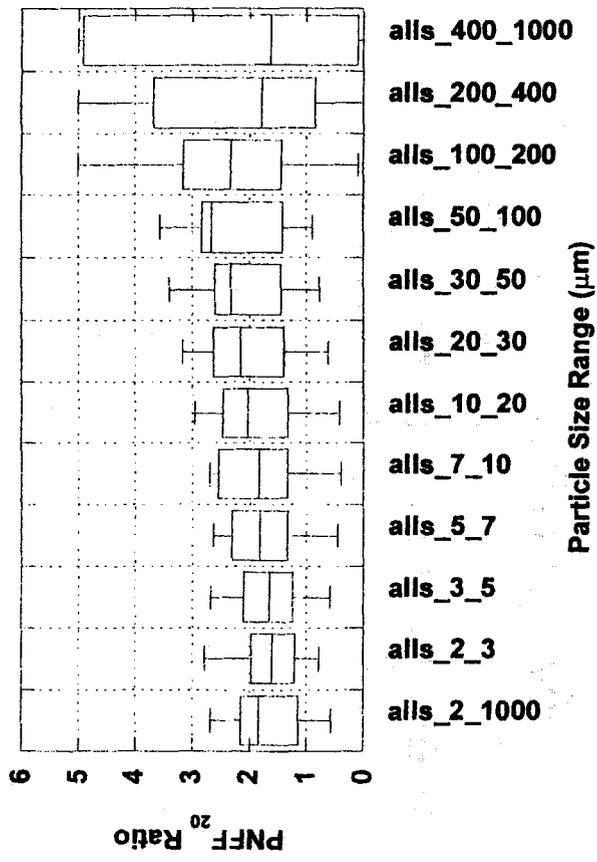


Figure A.2.1 PNFF₂₀ of Particles for Combined UCLA sites

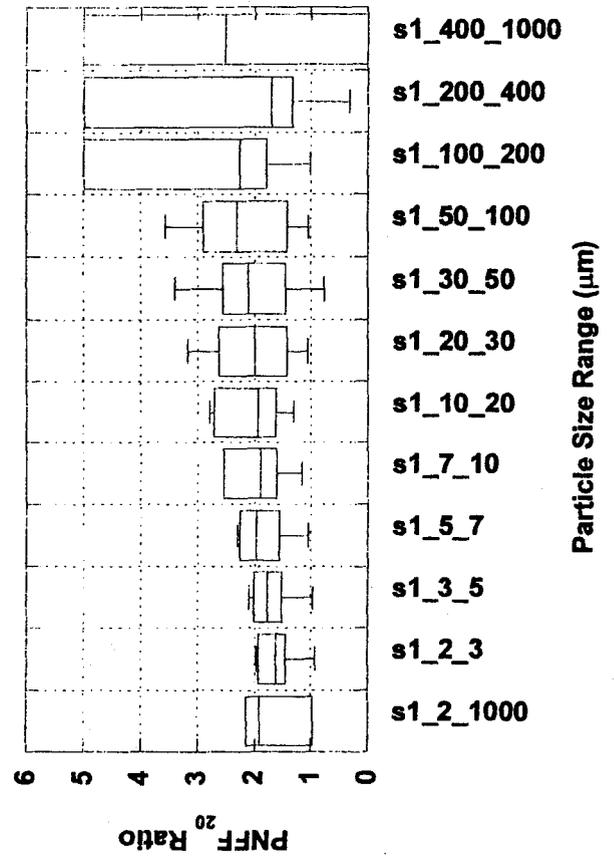


Figure A.2.2 PNFF₂₀ of Particles for UCLA 1

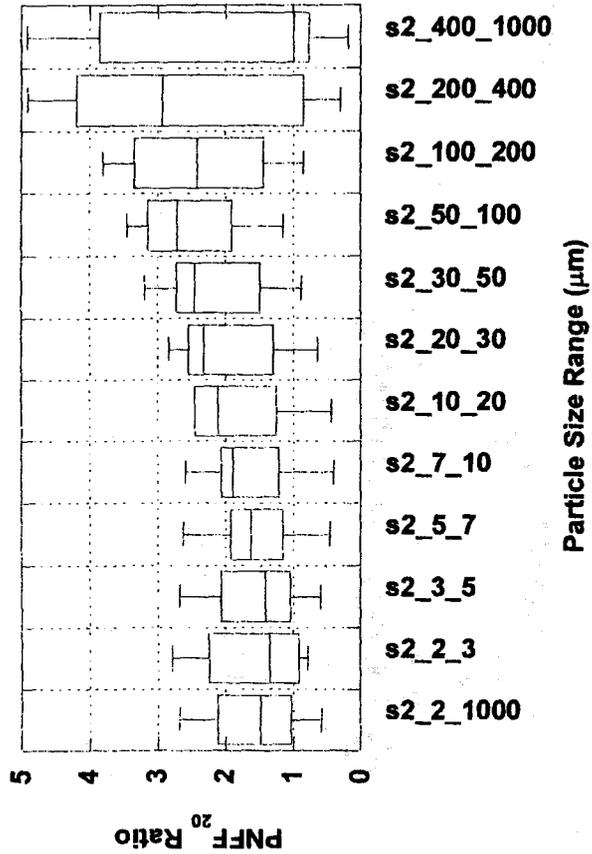


Figure A.2.3 PNFF₂₀ of Particles for UCLA 2

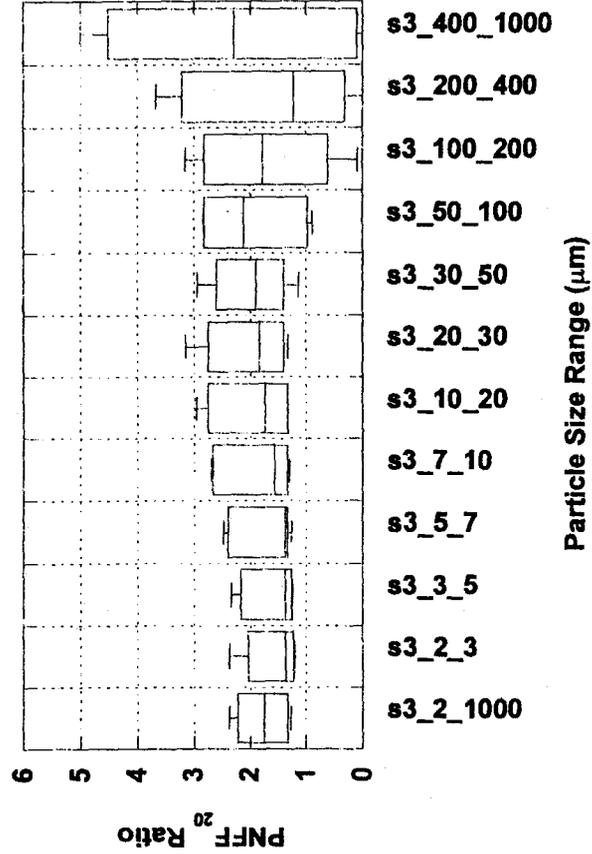


Figure A.2.4 PNFF₂₀ of Particles for UCLA 3

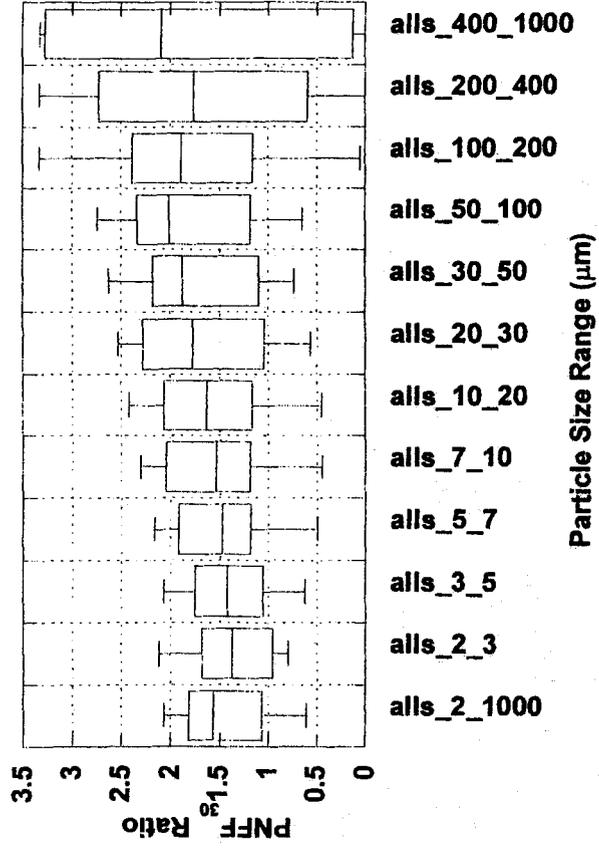


Figure A.3.1 PNFF₃₀ of Particles for Combined UCLA sites

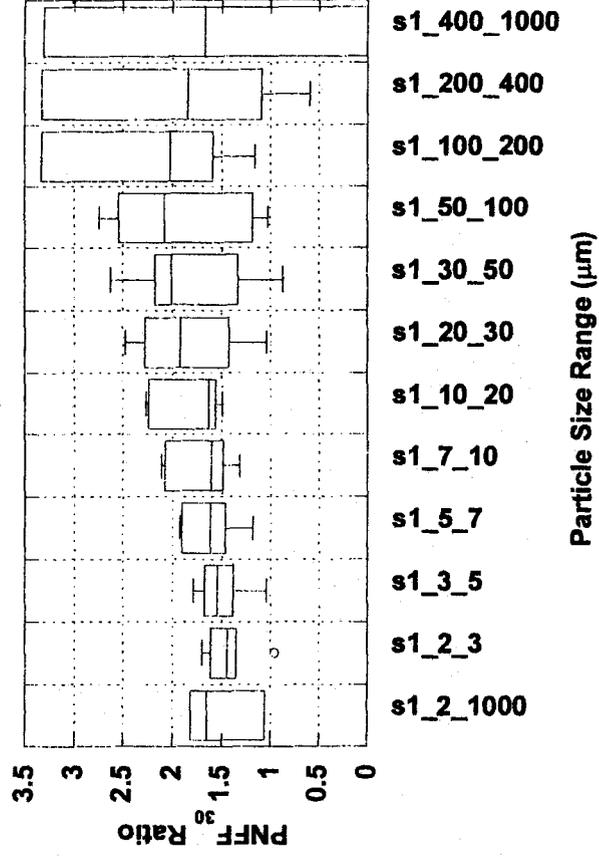


Figure A.3.2 PNFF₃₀ of Particles for UCLA 1

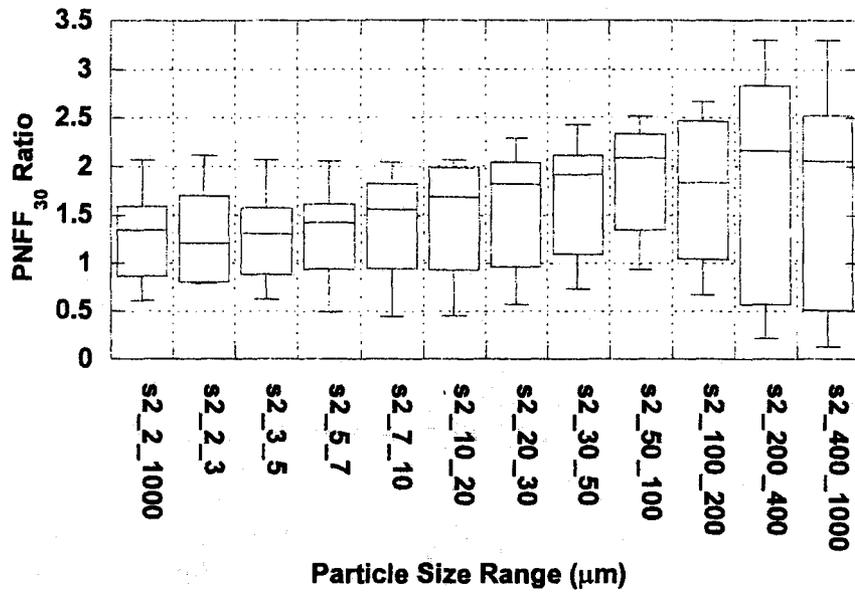


Figure A.3.3 PNFF₃₀ of Particles for UCLA 2

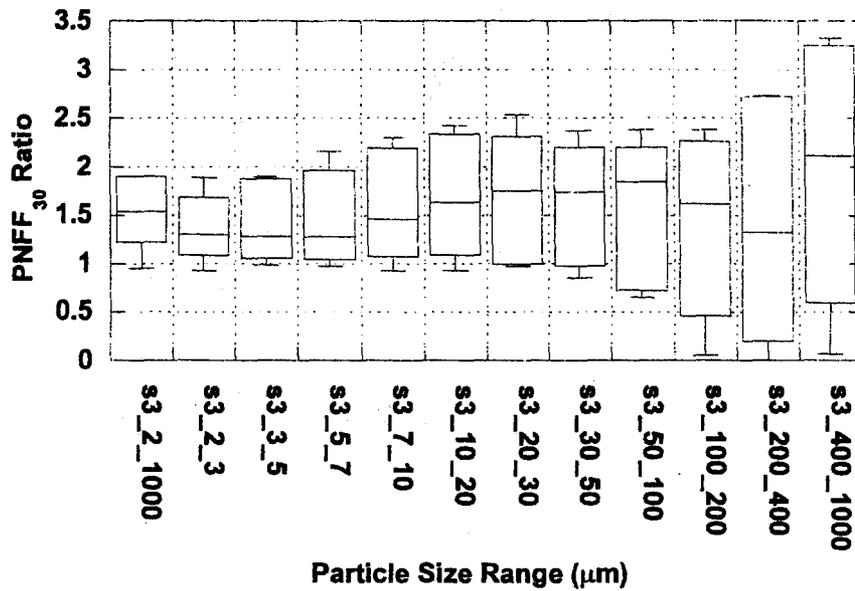


Figure A.3.4 PNFF₃₀ of Particles for UCLA 3

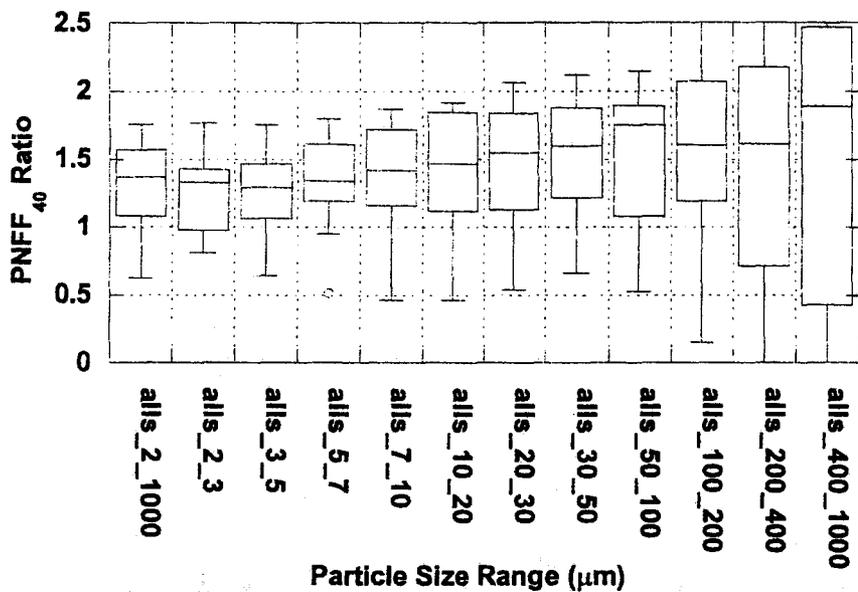


Figure A.4.1 PNFF₄₀ of Particles for Combined UCLA sites

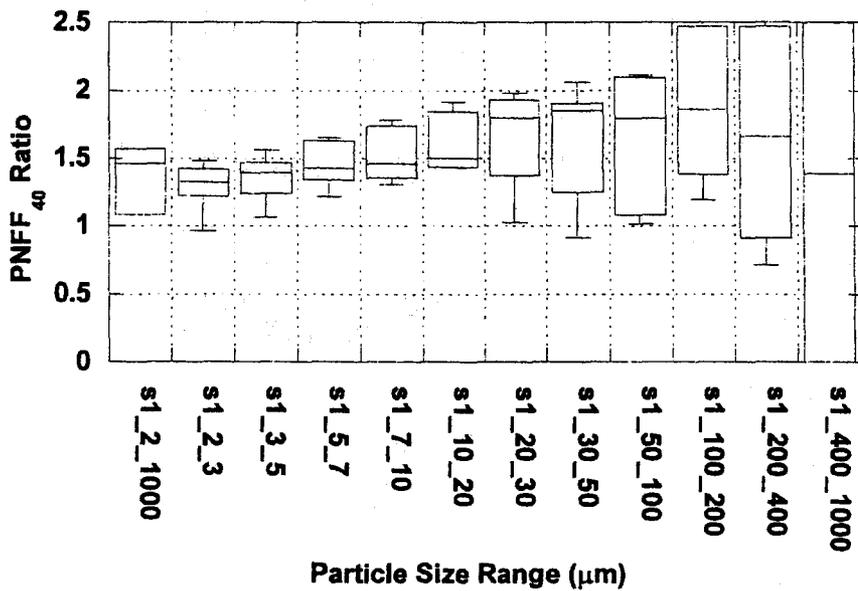


Figure A.4.2 PNFF₄₀ of Particles for UCLA 1

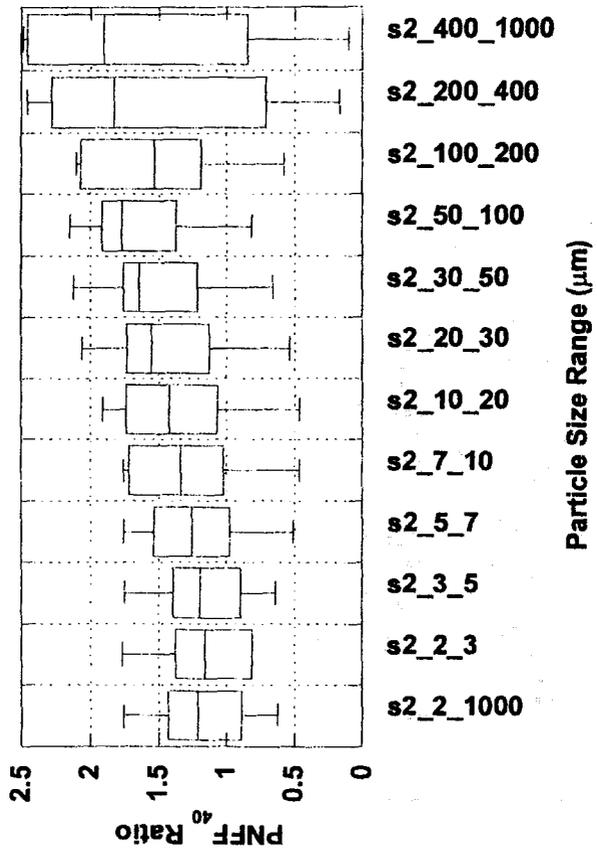


Figure A.4.3 PNFF₄₀ of Particles for UCLA 2

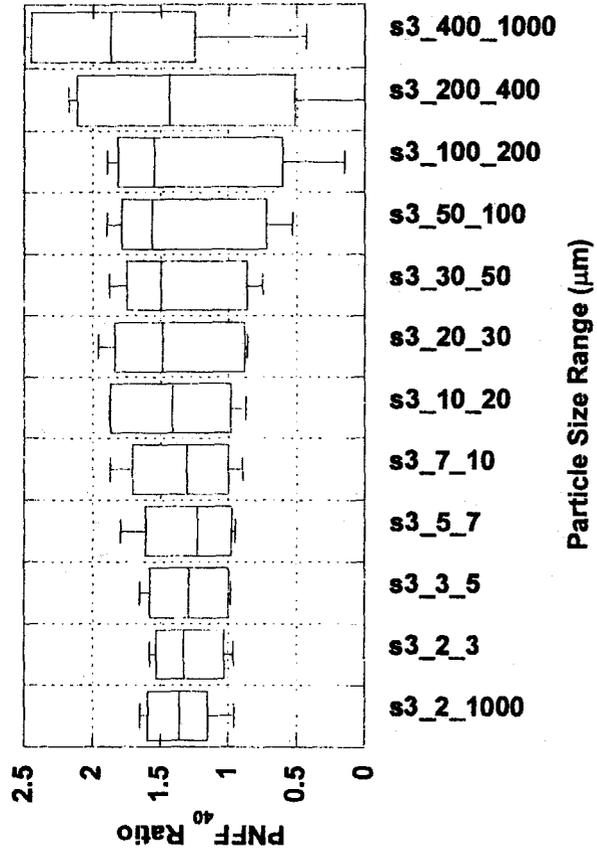


Figure A.4.4 PNFF₄₀ of Particles for UCLA 3

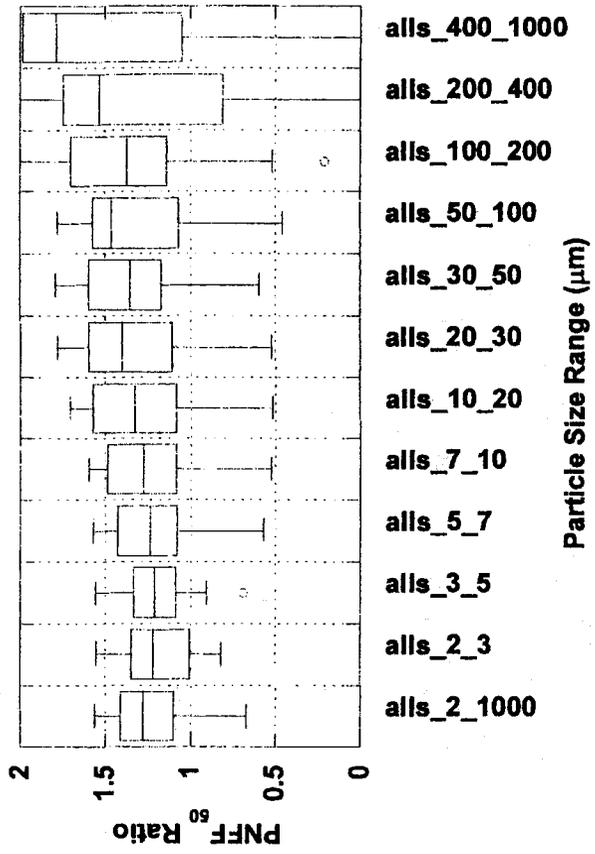


Figure A.5.1 PNFF₅₀ of Particles for Combined UCLA sites

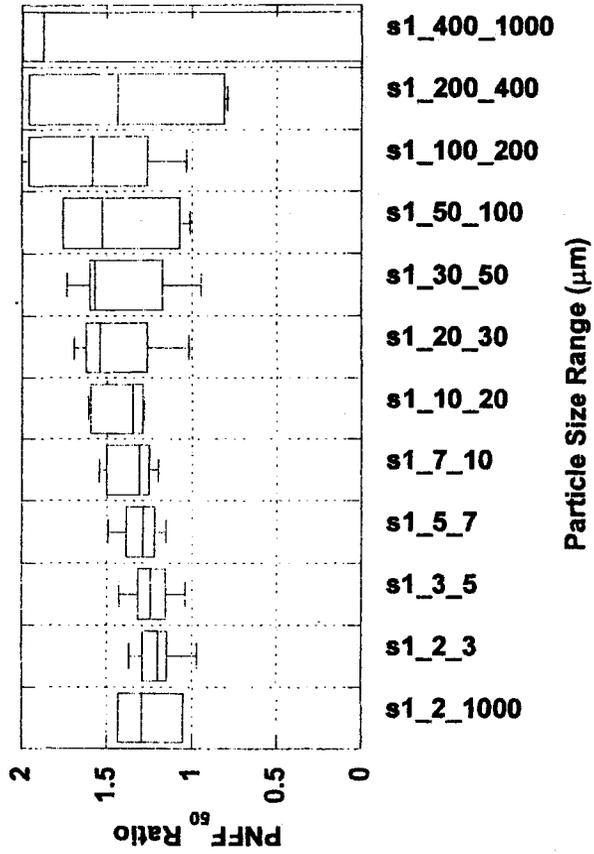


Figure A.5.2 PNFF₅₀ of Particles for UCLA 1

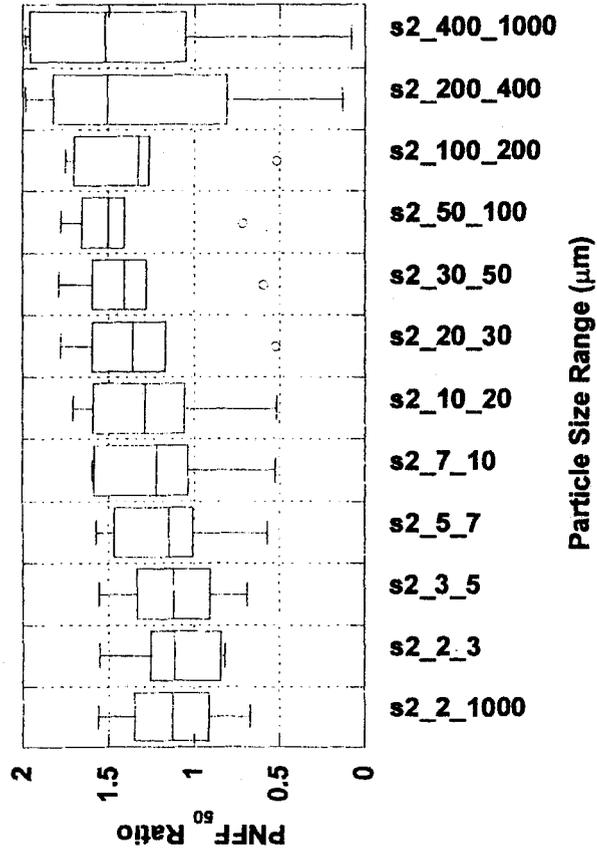


Figure A.5.3 PNFF₅₀ of Particles for UCLA 2

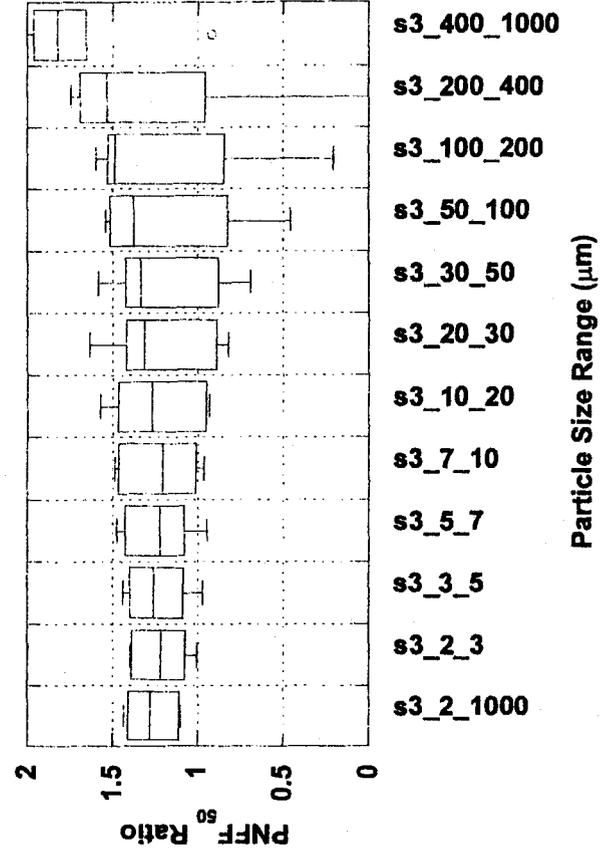


Figure A.5.4 PNFF₅₀ of Particles for UCLA 3

APPENDIX B STATISTICAL SUMMARY OF PARTICLES

Table B.1a Statistical Summary of Particle Concentration for 2002-2003 Grab Samples
(Measured with 2-1000 μ m Sensor)

Size Range ^a	Site ID	N	%D	Mean ^b	SD ^b	Median ^b	Min ^b	Max ^b
2-1000	UCLA 1	50	100	110691	81752.7	86308	4118	334846
	UCLA 2	61	100	312959	297570.9	195068	11884	1243431
	UCLA 3	61	100	290681	496650.7	157488	50727	3741716
2-50	UCLA 1	50	100	110628	81702.3	86145	4112	334610
	UCLA 2	61	100	312823	297412.9	195010	11874	1243305
	UCLA 3	61	100	290584	496528.8	157468	50719	3740831
50-100	UCLA 1	50	100	50	122.0	11	0	790
	UCLA 2	61	100	103	226.4	41	3	1698
	UCLA 3	61	100	66	81.7	35	4	436
100-400	UCLA 1	50	100	13	18.7	6	0	113
	UCLA 2	61	100	32	62.2	14	2	422
	UCLA 3	61	100	30	58.1	11	1	414
400-1000	UCLA 1	50	100	0	0.3	0	0	1
	UCLA 2	61	100	1	2.6	0	0	14
	UCLA 3	61	100	1	5.4	0	0	35
2-3	UCLA 1	50	100	44390	28568.4	35440	2306	108226
	UCLA 2	61	100	123849	138609.5	72170	6191	647787
	UCLA 3	61	100	106340	169348.2	58416	22903	1257268
3-5	UCLA 1	50	100	38031	28493.2	28756	1212	109737
	UCLA 2	61	100	111324	105845.4	70769	3564	458895
	UCLA 3	61	100	103404	178278.1	54316	17505	1341084
5-7	UCLA 1	50	100	13622	12305.9	8902	302	48777
	UCLA 2	61	100	39323	35388.2	26836	965	187625
	UCLA 3	61	100	40835	76370.7	20300	4275	577778
7-10	UCLA 1	50	100	7967	8350.9	4327	160	34031
	UCLA 2	61	100	21686	21992.2	14709	563	128652
	UCLA 3	61	100	23663	46239.5	10620	1631	348922
10-20	UCLA 1	50	100	5622	7095.6	2860	115	33713
	UCLA 2	61	100	14344	16799.2	8543	495	96576
	UCLA 3	61	100	14549	26734.4	7618	635	199596
20-30	UCLA 1	50	100	774	1356.9	269	13	7993
	UCLA 2	61	100	1811	2380.4	998	59	12704
	UCLA 3	61	100	1467	2080.4	999	54	14212
30-50	UCLA 1	50	100	222	476.0	55	2	3015
	UCLA 2	61	100	486	714.8	253	21	4486
	UCLA 3	61	100	325	364.6	205	16	1971
50-100	UCLA 1	50	100	50	122.0	11	0	790
	UCLA 2	61	100	103	226.4	41	3	1698
	UCLA 3	61	100	66	81.7	35	4	436
100-200	UCLA 1	50	100	10	17.2	4	0	107
	UCLA 2	61	100	25	49.7	11	2	353
	UCLA 3	61	100	21	30.5	9	1	189
200-400	UCLA 1	50	100	2	2.8	1	0	13
	UCLA 2	61	100	8	14.6	2	0	69
	UCLA 3	61	100	9	29.6	2	0	225
400-1000	UCLA 1	50	100	0	0.3	0	0	1
	UCLA 2	61	100	1	2.6	0	0	14
	UCLA 3	61	100	1	5.4	0	0	35

a: μ m b: #/ml

Table B.1b Statistical Summary of Particle Concentration for 2002-2003 Grab Samples
(Measured with 0.5-400 μ m Sensor)

Size Range ^a	Site ID	N	%D	Mean ^b	SD ^b	Median ^b	Min ^b	Max ^b
0.5-400	UCLA 1	24	100	4477638	2231143.8	4130536	1642456	11152890
	UCLA 2	12	100	10843326	6863006.0	10150453	2900310	25243120
0.5-0.8	UCLA 1	24	100	3276361	1694386.6	3171444	1189477	8132360
	UCLA 2	12	100	6565516	4182687.4	6254006	1796650	15329673
0.8-1.2	UCLA 1	24	100	841608	464844.4	711662	289605	2258278
	UCLA 2	12	100	2589786	1706217.9	2334026	680544	6272311
1.2-2	UCLA 1	24	100	279065	135419.6	240501	113138	637008
	UCLA 2	12	100	1123456	853932.8	885720	294747	2950148
2-3	UCLA 1	24	100	44764	23078.7	37991	16932	92013
	UCLA 2	12	100	264055	286403.4	159547	63193	1065129
3-5	UCLA 1	24	100	20639	11815.6	18316	5775	47323
	UCLA 2	12	100	158871	209876.4	83687	35234	776110
5-7	UCLA 1	24	100	7498	4898.3	6478	1213	17748
	UCLA 2	12	100	71497	112137.7	32023	12626	411207
7-10	UCLA 1	24	100	4304	2914.0	3593	618	12014
	UCLA 2	12	100	43401	77171.2	15062	4936	281061
10-20	UCLA 1	24	100	2657	2214.1	1940	314	9652
	UCLA 2	12	100	23753	41542.2	8891	2352	150865
20-30	UCLA 1	24	100	442	602.4	219	28	2548
	UCLA 2	12	100	2350	3653.5	1011	279	13262
30-50	UCLA 1	24	100	221	363.1	67	0	1382
	UCLA 2	12	100	552	810.3	289	77	2960
50-100	UCLA 1	24	100	70	120.9	19	0	414
	UCLA 2	12	100	74	90.1	61	0	323
100-200	UCLA 1	24	100	7	14.7	0	0	51
	UCLA 2	12	100	13	26.0	0	0	81
200-400	UCLA 1	24	100	3	6.2	0	0	24
	UCLA 2	12	100	2	5.8	0	0	20

a: μ m b: #/ml

Table B.2 Statistical Summary of Total Number of Particle for 2002-2003 Events
(Measured with 2-1000 μ m Sensor)

Size Range ^a	Site ID	N	Mean ^b	Median ^b	Min ^b	Max ^b	SD ^b	95%CI ^b
2-1000	UCLA 1	4	27.48	24.855	22.6	37.61	6.8958	10.973
	UCLA 2	6	91.353	66	6.2	280.41	103.44	108.55
	UCLA 3	6	13.752	11.855	0.34	25.3	9.9133	10.403
2-50	UCLA 1	4	27.473	24.85	22.6	37.59	6.8867	10.958
	UCLA 2	6	91.308	65.965	6.2	280.28	103.39	108.5
	UCLA 3	6	13.745	11.85	0.34	25.29	9.9096	10.399
50-100	UCLA 1	4	0.005	0.005	0	0.01	0.0058	0.0092
	UCLA 2	6	0.0317	0.025	0	0.1	0.0382	0.0401
	UCLA 3	6	0.0017	0	0	0.01	0.0041	0.0043
100-400	UCLA 1	4	0.0025	0	0	0.01	0.005	0.008
	UCLA 2	6	0.0083	0.005	0	0.03	0.0117	0.0123
	UCLA 3	6	0	0	0	0	0	0
400-1000	UCLA 1	4	0	0	0	0	0	0
	UCLA 2	6	0	0	0	0	0	0
	UCLA 3	6	0	0	0	0	0	0
2-3	UCLA 1	4	11.718	11.345	9.4	14.78	2.2401	3.5644
	UCLA 2	6	31.898	23.325	2.18	94.54	35.313	37.058
	UCLA 3	6	5.0333	4.46	0.13	9.94	3.5232	3.6973
3-5	UCLA 1	4	9.6225	8.685	7.99	13.13	2.376	3.7808
	UCLA 2	6	31.38	22.685	2.58	95.27	35.162	36.9
	UCLA 3	6	4.8667	4.285	0.12	9.08	3.5465	3.7218
5-7	UCLA 1	4	3.19	2.785	2.39	4.8	1.0921	1.7378
	UCLA 2	6	12.85	9.465	0.94	40.18	14.656	15.38
	UCLA 3	6	1.915	1.595	0.05	3.91	1.4554	1.5274
7-10	UCLA 1	4	1.705	1.485	1.12	2.73	0.7052	1.1222
	UCLA 2	6	8.0667	5.815	0.36	26.01	9.5232	9.994
	UCLA 3	6	1.1117	0.88	0.03	2.49	0.893	0.9371
10-20	UCLA 1	4	1.09	0.955	0.58	1.87	0.5494	0.8742
	UCLA 2	6	6.09	4.08	0.12	20.71	7.6531	8.0315
	UCLA 3	6	0.72	0.55	0.02	1.66	0.5724	0.6007
20-30	UCLA 1	4	0.1175	0.1	0.05	0.22	0.0723	0.115
	UCLA 2	6	0.8217	0.475	0.01	2.9	1.0877	1.1414
	UCLA 3	6	0.0817	0.065	0	0.19	0.0637	0.0668
30-50	UCLA 1	4	0.025	0.02	0.01	0.05	0.0173	0.0276
	UCLA 2	6	0.2	0.125	0	0.67	0.2512	0.2637
	UCLA 3	6	0.0183	0.015	0	0.05	0.0172	0.0181
50-100	UCLA 1	4	0.005	0.005	0	0.01	0.0058	0.0092
	UCLA 2	6	0.0317	0.025	0	0.1	0.0382	0.0401
	UCLA 3	6	0.0017	0	0	0.01	0.0041	0.0043
100-200	UCLA 1	4	0	0	0	0	0	0
	UCLA 2	6	0.0067	0.005	0	0.02	0.0082	0.0086
	UCLA 3	6	0	0	0	0	0	0
200-400	UCLA 1	4	0	0	0	0	0	0
	UCLA 2	6	0.0017	0	0	0.01	0.0041	0.0043
	UCLA 3	6	0	0	0	0	0	0
400-1000	UCLA 1	4	0	0	0	0	0	0
	UCLA 2	6	0	0	0	0	0	0
	UCLA 3	6	0	0	0	0	0	0

a: μ m b: 10e12

Table B.3 Statistical Summary of Particle Different Size Proportion to 2-1000 μ m for 2002-2003 Events (Measured with 2-1000 μ m Sensor)

Size Range ^a	Site ID	N	Mean	Median	Min	Max	SD	95%CI
2-3	UCLA 1	4	0.4308	0.4287	0.3930	0.4728	0.0343	0.0546
	UCLA 2	6	0.3516	0.3601	0.2776	0.3947	0.0416	0.0436
	UCLA 3	6	0.3747	0.3800	0.3162	0.4036	0.0305	0.0320
3-5	UCLA 1	4	0.3504	0.3506	0.3471	0.3535	0.0029	0.0046
	UCLA 2	6	0.3574	0.3497	0.3144	0.4161	0.0348	0.0365
	UCLA 3	6	0.3517	0.3529	0.3289	0.3666	0.0126	0.0133
5-7	UCLA 1	4	0.1146	0.1150	0.1006	0.1276	0.0115	0.0183
	UCLA 2	6	0.1440	0.1377	0.1294	0.1754	0.0176	0.0184
	UCLA 3	6	0.1383	0.1338	0.1289	0.1573	0.0115	0.0121
7-10	UCLA 1	4	0.0606	0.0614	0.0472	0.0726	0.0107	0.0170
	UCLA 2	6	0.0826	0.0788	0.0581	0.1235	0.0236	0.0247
	UCLA 3	6	0.0801	0.0745	0.0708	0.1002	0.0117	0.0123
10-20	UCLA 1	4	0.0383	0.0395	0.0244	0.0497	0.0106	0.0168
	UCLA 2	6	0.0553	0.0554	0.0194	0.0952	0.0275	0.0289
	UCLA 3	6	0.0533	0.0548	0.0418	0.0668	0.0096	0.0101
20-30	UCLA 1	4	0.0041	0.0041	0.0021	0.0058	0.0015	0.0025
	UCLA 2	6	0.0067	0.0074	0.0016	0.0108	0.0039	0.0041
	UCLA 3	6	0.0052	0.0056	0	0.0084	0.0031	0.0033
30-50	UCLA 1	4	0.0009	0.0008	0.0004	0.0013	0.0004	0.0006
	UCLA 2	6	0.0016	0.0020	0	0.0026	0.0010	0.0011
	UCLA 3	6	0.0012	0.0010	0	0.0024	0.0009	0.0009
50-100	UCLA 1	4	0.0002	0.0001	0	0.0004	0.0002	0.0003
	UCLA 2	6	0.0002	0.0003	0	0.0004	0.0002	0.0002
	UCLA 3	6	7E-05	0	0	0.0004	0.0002	0.0002
100-200	UCLA 1	4	0	0	0	0	0	0
	UCLA 2	6	4E-05	4E-05	0	0.0001	5E-05	5E-05
	UCLA 3	6	0	0	0	0	0	0
200-400	UCLA 1	4	0	0	0	0	0	0
	UCLA 2	6	6E-06	0	0	4E-05	1E-05	2E-05
	UCLA 3	6	0	0	0	0	0	0
400-1000	UCLA 1	4	0	0	0	0	0	0
	UCLA 2	6	0	0	0	0	0	0
	UCLA 3	6	0	0	0	0	0	0

a: μ m

Table B.4 Statistical Summary of PNFF₂₀ Ratios of Particles in 2002-2003 Events
(Measured with 2-1000 μm Sensor)

Size range ^a	Site ID	Mean	Median	Min	Max	SD	N>1.1
2-1000	UCLA 1	1.75	1.92	0.99	2.15	0.51	3/4
	UCLA 2	1.56	1.48	0.58	2.68	0.78	4/6
	UCLA 3	1.79	1.75	1.28	2.37	0.51	6/6
2-3	UCLA 1	1.62	1.79	0.93	1.97	0.48	3/4
	UCLA 2	1.57	1.34	0.78	2.79	0.83	3/6
	UCLA 3	1.68	1.59	1.21	2.37	0.48	6/6
3-5	UCLA 1	1.75	1.96	0.97	2.10	0.53	3/4
	UCLA 2	1.53	1.41	0.59	2.68	0.77	4/6
	UCLA 3	1.77	1.75	1.27	2.34	0.49	6/6
5-7	UCLA 1	1.91	2.14	1.06	2.30	0.58	3/4
	UCLA 2	1.57	1.63	0.46	2.63	0.74	5/6
	UCLA 3	1.90	1.89	1.34	2.49	0.59	6/6
7-10	UCLA 1	2.05	2.25	1.17	2.55	0.66	4/4
	UCLA 2	1.67	1.89	0.40	2.59	0.76	5/6
	UCLA 3	2.01	2.01	1.31	2.70	0.67	6/6
10-20	UCLA 1	2.14	2.22	1.32	2.80	0.74	4/4
	UCLA 2	1.80	2.12	0.43	2.46	0.81	5/6
	UCLA 3	2.09	2.07	1.33	2.96	0.72	6/6
20-30	UCLA 1	2.21	2.13	1.43	3.17	0.82	4/4
	UCLA 2	1.99	2.33	0.63	2.84	0.85	5/6
	UCLA 3	2.14	2.00	1.40	3.15	0.69	6/6
30-50	UCLA 1	2.27	2.11	1.45	3.41	0.85	4/4
	UCLA 2	2.20	2.46	0.88	3.19	0.85	5/6
	UCLA 3	2.17	2.11	1.40	2.94	0.57	6/6
50-100	UCLA 1	2.40	2.31	1.42	3.57	0.95	4/4
	UCLA 2	2.51	2.71	1.15	3.45	0.85	6/6
	UCLA 3	2.22	2.43	0.99	2.83	0.73	5/6
100-200	UCLA 1	1.83	1.89	1.01	2.55	0.64	3/4
	UCLA 2	2.38	2.42	0.84	3.80	1.12	5/6
	UCLA 3	2.07	2.14	0.63	3.15	0.93	5/6
200-400	UCLA 1	1.27	1.48	0.33	1.79	0.65	3/4
	UCLA 2	2.69	2.94	0.30	4.92	1.86	4/6
	UCLA 3	1.95	1.74	0.31	3.68	1.32	4/6
400-1000	UCLA 1	2.51	2.51	0.00	5.00	2.85	2/4
	UCLA 2	2.14	0.99	0.19	4.92	2.10	2/5
	UCLA 3	2.38	2.29	0.00	5.00	2.36	3/5

a: μm

Table B.5 Event Mean Concentrations of Particles for UCLA 1, 2 and 3

Event	Site ID	Grab no	Volume (gal)	Total Rain (in)	2-1000 (10e6/l)	2-50 (10e6/l)	50-100 (10e6/l)	100-400 (10e6/l)	400-1000 (10e6/l)	0.5-400 (10e6/l)	0.5-0.8 (10e6/l)	0.8-1.2 (10e6/l)	1.2-2 (10e6/l)
11/7/02	UCLA 1	14	55608.2	1.14	112.85	112.83	0.01	0.01	0	na	na	na	na
12/16/02	UCLA 1	11	92023	1.44	107.95	107.91	0.03	0.02	0	na	na	na	na
12/19/02	UCLA 1	13	115286	1.4	59.48	59.47	0.01	0	0	na	na	na	na
2/11/03	UCLA 1	12	62165.4	0.92	96.05	96.02	0.02	0.01	0	na	na	na	na
3/15/03	UCLA 1	12	776213	2.62	na	na	na	na	na	3332.01	2217.86	760.21	274.43
5/2/03	UCLA 1	12	85159.9	1.98	na	na	na	na	na	4441.64	3428.14	786.15	197.46
11/7/02	UCLA 2	14	218146	2.25	143.55	143.48	0.05	0.01	0	na	na	na	na
11/29/02	UCLA 2	5	6149.99	0.07	471.08	470.95	0.08	0.04	0	na	na	na	na
12/15/02	UCLA 2	8	8017.99	0.08	204.25	204.22	0.02	0	0	na	na	na	na
12/16/02	UCLA 2	10	218116	2.32	339.62	339.46	0.12	0.04	0	na	na	na	na
2/11/03	UCLA 2	12	89618.3	0.96	288.12	287.97	0.11	0.04	0	na	na	na	na
4/15/03	UCLA 2	12	82227.1	0.84	110.06	110.01	0.04	0.01	0	na	na	na	na
11/7/02	UCLA 3	14	47030.7	2.81	142.1	142.07	0.02	0.01	0	na	na	na	na
11/29/02	UCLA 3	6	188.484	0.06	477.53	477.37	0.12	0.04	0	na	na	na	na
12/16/02	UCLA 3	8	33014.1	1.62	198.9	198.82	0.06	0.03	0	na	na	na	na
12/19/02	UCLA 3	11	28487.1	1.31	82.27	82.25	0.02	0.01	0	na	na	na	na
2/11/03	UCLA 3	12	11682.5	0.79	335.52	335.41	0.08	0.03	0	na	na	na	na
3/15/03	UCLA 3	12	108520	0.65	na	na	na	na	na	4354.38	2657.24	1016.55	459.71
4/15/03	UCLA 3	10	14010	0.87	156.49	156.39	0.07	0.03	0	na	na	na	na

Table B.5 (Continued)

Event	Site ID	2-3 (10e6/l)	3-5 (10e6/l)	5-7 (10e6/l)	7-10 (10e6/l)	10-20 (10e6/l)	20-30 (10e6/l)	30-50 (10e6/l)	50-100 (10e6/l)	100-200 (10e6/l)	200-400 (10e6/l)	400-1000 (10e6/l)
11/7/02	UCLA 1	53.36	39.71	11.37	5.32	2.76	0.26	0.06	0.01	0.01	0	0
12/16/02	UCLA 1	42.42	37.69	13.78	7.85	5.37	0.64	0.15	0.03	0.01	0.01	0
12/19/02	UCLA 1	26.27	20.63	6.6	3.47	2.21	0.23	0.05	0.01	0	0	0
2/11/03	UCLA 1	39.94	33.95	11.41	6.17	3.99	0.45	0.11	0.02	0	0	0
3/15/03	UCLA 1	45.85	20.75	7.32	3.73	1.71	0.12	0.03	0.01	0	0	na
5/2/03	UCLA 1	19.94	6.9	1.58	0.84	0.45	0.12	0.05	0.01	0	0	na
11/7/02	UCLA 2	52.91	49.6	18.93	11.75	8.71	1.26	0.33	0.05	0.01	0	0
11/29/02	UCLA 2	185.88	176.63	61.19	30.15	15.32	1.43	0.36	0.08	0.03	0.01	0
12/15/02	UCLA 2	71.91	85.09	30.86	12.02	3.96	0.3	0.08	0.02	0	0	0
12/16/02	UCLA 2	114.5	115.39	48.66	31.51	25.08	3.51	0.82	0.12	0.03	0.01	0
2/11/03	UCLA 2	109.48	101.99	38.09	21.81	14.43	1.71	0.46	0.11	0.03	0.01	0
4/15/03	UCLA 2	30.55	34.6	19.3	13.6	10.48	1.19	0.28	0.04	0.01	0	0
11/7/02	UCLA 3	55.82	51	18.34	10.06	6.09	0.64	0.13	0.02	0.01	0	0
11/29/02	UCLA 3	175.23	170.66	66.45	39.29	23.23	2.05	0.46	0.12	0.03	0.01	0
12/16/02	UCLA 3	62.86	69.58	31.31	19.93	13.25	1.52	0.37	0.06	0.02	0.01	0
12/19/02	UCLA 3	31.06	28.99	10.76	6.26	4.5	0.56	0.13	0.02	0	0	0
2/11/03	UCLA 3	125.85	123.11	45.95	24.73	14.08	1.35	0.33	0.08	0.02	0.01	0
3/15/03	UCLA 3	105.52	60.84	26.66	16.33	9.98	1.15	0.31	0.06	0.01	0.01	na
4/15/03	UCLA 3	63.15	51.44	20.24	11.23	8.69	1.28	0.35	0.07	0.02	0.01	0

APPENDIX C MATLAB CODE FOR PARTICLE REMOVAL EFFICIENCY

CALCULATION

```
% loading file and preparation
%% prepare vectors: diameter, setvele6 (setting velocity*10e6)
[diameter setvel setvele6]=textread('diameterVel.txt','%f %f %f', 'headerlines',1);
%% prepare flow related vectors: sample, flowvol (gal/min)
load flow.txt;
sample=flow(:, 7); flowvol=flow(:, 6); rainfall=flow(:, 3);
%% prepare concentration related vectors: ptvolume
load conc.txt
pvolume=diameter.^3*pi/6;[m,n] = size(conc);
for j=1:n;
    ptvolume(:,j)=pvolume.*conc(:,j);
end
% PART0-EMC calculation
[M,N]=size(flow);
J=0;
for i=1:M
    if sample(i)~=0;
        J=J+1;
        Mlocation(J)=i;
    end
end
%% concentration index (cindex)
cumflow=cumsum(flowvol);
cindex=ones(M,1);
for i=Mlocation(1,J):M
    cindex(i,1)=J;
end
for j=1:J-1
    halfsum=cumflow(Mlocation(1,j),1)+(cumflow(Mlocation(1,j+1),1)-
cumflow(Mlocation(1,j),1))/2;
    for i=Mlocation(1,j):Mlocation(1,j+1)
        if cumflow(i,1)<=halfsum
            cindex(i,1)=j;
        else cindex(i,1)=j+1;
        end
    end
end
%% EMC
for j=1:m
    for i=1:M
```

```

    mass(i,j)=flowvol(i,1)*conc(j,cindex(i,1));
end
end
cummass=cumsum(mass);
for j=1:m
    for i=1:M
        massv(i,j)=flowvol(i,1)*ptvolume(j,cindex(i,1));
    end
end
cummassv=cumsum(massv);
cumtotalmassv=cummassv(M,:);
save cumtotalmassv.out cumtotalmassv -ASCII
%% fix volume need to be changed for different design
fixvolume=0;
if cumflow(M,1)>fixvolume
    i=1
    while cumflow(i,1)<fixvolume
        i=i+1;
    end
    H2location=i;
else
    i=M;
    while cumflow(i,1)==cumflow(M,1)
        i=i-1;
    end
    H2location=i+1;
end
ii=1;
while flowvol(ii,1)==0
    ii=ii+1;
end
catchtime=i-ii;
cumH2massv=cummassv(H2location,:);
save cumH2massv.out cumH2massv -ASCII
% PART1-catching and holding with stokes' settling velocity
% surface area of site1, 2, 3 is 26, 34,8m2, volume is 77.6, 102.4, 23.6 m3
%surface1 need to be changed for different runoff volume and sites
surface1=36.5;
for j=1:12
    Vchold(1,j)=cumflow(H2location,1)*3.785*0.001/(surface1*(2*j+(catchtime/120))*3600);
end
for i=1:m;
    for j=1:12;
        if setvel(i,1)>Vchold(1,j)
            setlefratiohold(i,j)=0;
        else
            setlefratiohold(i,j)=1-(setvel(i,1)/Vchold(1,j));
        end
    end
end

```

```

end
end
removedhold=1-setlefratiohold;
for j=1:12
    removedholdv(:,j)=removedhold(:,j).*cumH2massv;
end
% PART2-dynamic overflow settling ratio calculation
% "sumremoveddynamicv" is the removed volume by dynamic overflow
% surface need to be changed for different design
surface=36.5;
flowvoldynamic=flowvol*3.785*0.001/60;
Vcdynamic=flowvoldynamic/surface;
for i=1:m;
    for j=1:M;
        if setvel(i,1)>Vcdynamic(j,1)
            setlefratiodynamic(i,j)=0;
        else
            setlefratiodynamic(i,j)=1-(setvel(i,1)/Vcdynamic(j,1));
        end
    end
end
removeddynamic=1-setlefratiodynamic;
for i=1:m
    removeddynamicv(i,:)=removeddynamic(i,:).*massv(:,i);
end
cumremoveddynamicv=cumsum(removeddynamicv);
removedlaterpartv=(cumremoveddynamicv(M,:)-cumremoveddynamicv(H2location,:));
% PART4-final result
removedvolume=[removedholdv removedlaterpartv cumtotalmassv];
save removedvolume.out removedvolume -ASCII
%% for size range 2-25-41-104-249-1000um index range1-209 210-249 250-326 327-398 399-
511
rt=sum(removedvolume);
for i=1:209
    for j=1:14
        rs0m(i,j)=removedvolume(i,j);
    end
end
for i=210:249
    for j=1:14
        rs1m(i,j)=removedvolume(i,j);
    end
end
for i=250:326
    for j=1:14
        rs2m(i,j)=removedvolume(i,j);
    end
end
end

```

```

for i=327:398
  for j=1:14
    rs3m(i,j)=removedvolume(i,j);
  end
end
for i=399:511
  for j=1:14
    rs4m(i,j)=removedvolume(i,j);
  end
end
rs0=sum(rs0m);
rs1=sum(rs1m);
rs2=sum(rs2m);
rs3=sum(rs3m);
rs4=sum(rs4m);
rst=rs0'+rs1'+rs2'+rs3'+rs4';
finalresultvolume=[rs0' rs1' rs2' rs3' rs4' rst];
finalresultratio=(finalresultvolume(12,:)+finalresultvolume(13,:))./finalresultvolume(14,:);
location=catchtime;
finalresult=[finalresultratio' finalresultvolume(14,:)];
save finalresult.out finalresult -ASCII
save location.out location -ASCII Nonpoint source (NPS)

```