Methodology to Measure Small Particles and Associated Constituents in Highway Runoff

Draft Final Report

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Table of Contents

List of Figures

List of Tables

Abbreviations

BMP	best management practices
DOC	dissolved organic carbon
EDS	energy dispersive x-ray spectroscopy
GF/F	glass fiber filters
ICP-MS	inductively coupled plasma-mass spectrometry
LISST	Laser In-Situ Scattering and Transmissometry
NPDES	national pollution discharge and elimination system
NPPFW	nonopure particle free water
NURP	national urban research program
PAHs	polyaromatic hydrocarbons
PEMC	Particle Event Mean Concentration
PSD	Particle Size Distribution
SEM	scanning electronic microscopy
SPLITT	split-flow thin cell separation
TMDL	total maximum daily load
UCD	University of California at Davis
UCLA	University of California at Los Angeles
USEPA	United States Environmental Protection Agency
μm	micrometer or 10^{-6} meters

ADA Statement

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Acknowledgements and Disclaimer Statement

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Executive Summary

This study was undertaken to develop methods for measuring particle size distributions (PSDs) in highway runoff, understanding the changes in the PSD upon sample processing, and to determine the concentration of elements and organic compounds associated with varying particle sizes. Particles in roadway runoff are of concern for three primary reasons. First, as the repository of most pollutant mass for many organic and metallic constituents, they represent a potentially significant source of pollutant to the dissolved phase. Second, even if the solid-phase pollutants are not readily released to the dissolved phase, upcoming regulations (e.g., sediment quality objectives) may address inputs of particle-bound constituents directly. Third, if constituents need to be removed from roadway runoff, knowing their distribution among the dissolved phase and particulates of varying sizes is critical to the selection and design of treatment systems. The project was performed jointly by the Departments of Civil and Environmental Engineering at the University of California Los Angeles (UCLA) and the University of California at Davis (UCD). Major tasks performed at UCLA included: developing methods to store, preserve and mix the samples as well as establishing the holding time needed to measure PSDs accurately, characterizing the first flush of particles, fractionating particles by serial filtration, analyzing chemical constituents associated with fractionated particles, and demonstrating the practical application of particle size analysis for improving treatment methods. Major tasks performed at UCD included: developing methods to collect samples for particle size analysis and chemical characterization, determining the importance of dissolved organic carbon in mobilizing heavy metals from highway particles, testing additional methods for particle size fractionation and chemical analysis including cell sorting, gravity settling, and electron microscopy. Four highway sites were monitored to collect runoff and particle samples for this study. Three of the highway sites were located in West Los Angeles near the UCLA campus and the fourth one was located at interstate 80 near the UCD campus. A total of 37 storm events over three years was analyzed as part of this study and all relevant particle size characterization data obtained from these storm events are presented in this report.

Major findings of the study are summarized below:

Particle Size Measurement Protocol

- Particle size generally increased over time at both storage temperatures of 4^{o}C and 20^{o}C (room temperature). The size of the particles in the sample stored at room temperature increased at a much higher rate.
- 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 automatic samplers were lower than a flow-weighted average of corresponding grab samples. These results suggest that automatic

composite samplers should not be used to collect samples for PSD analysis until further development is completed.

- The reproducibility of the PSD obtained by measuring duplicate stormwater samples was represented by a difference proportion (DP):

$$DP = 100\ \frac{2\left|N_1 - N_2\right|}{(N_1 + N_2)}$$

where N_1 and N_2 are the number of particles in a specific size range for the first and second samples. 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 fewer particles in this size range. 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.

- Measurement of particle size distribution throughout the hydrograph showed that particle concentration varies significantly at different stage of storm events. In general, larger particle concentrations were observed during the early portion (first flush) of the storm events.

On Line Particle Size Measurement

Very few instruments are capable of measuring particle size distributions on line directly at storm water discharge points without sample pre-treatment. We have successfully been able to use a LISST 100 particle size analyzer to measure particle concentrations continuously under on-line, flow through conditions. On-line particle size measurement will, however, work best when the total suspended solid concentration in the runoff is below 260 mg/L.

Particle Size Fractionation

Three different methods were used in this study to fractionate various particle size ranges including: serial filtration, a cell sorter and a gravity settling column. The cell sorter was principally used to fractionate very small particles (less than 2 μm), the gravity settling column was used to sort much particles between 2 and about 60 μm and serial filtration was used to sort particles in the range of 0.5 to larger than 100 μm.

Microscopic Image Analysis of Particles

A scanning electron microscopy with an energy dispersive x-ray spectrometer was used to visualize and quantify the dimensions, shapes and elemental compositions of individual particles from highway storm water runoff and from particle samples washed from automotive brake assemblies during repair/replacement. The median runoff sample particle diameter (2.65 μm) was slightly greater than for the brake samples (2 μm). For all samples, more than 80 % of the particles were smaller than 5 μm. The maximum diameters were 32.4 to 79.0 μm. Significant variability was observed from particle to particle in the sizes, shapes and elemental compositions in both the runoff sample and the brake samples. On average, however, the brake particles were enriched in elements typically considered as roadway pollutants (copper, nickel, lead) while the runoff particles contained higher concentrations of crustal elements such as magnesium and calcium. This method may serve as an important means of identifying the contribution of varied sources to the particle loads on highways and subsequently to improved source control methods.

Heavy Metal Mobilization

The microscopic imaging study shows that individual runoff particles can contain significant concentrations of heavy metals. The release of these metals to the dissolved phase depends on the composition of the aqueous solution, particularly on pH and the presence of species (ligands) that can bind with the metals in the dissolved phase. The importance of dissolved organic carbon found in

highway runoff in mobilizing the metals found in highway particles was explored by concentrating DOC from runoff and examining how metal release from particles varied as a function of solution phase DOC concentrations. Simulations of particle-water partitioning of metals in runoff were performed over a plausible range of runoff DOC concentrations (0-40 mg/L) using metal-particle and metal-DOC binding constants determined in laboratory experiments. The fraction of metal dissolved in runoff ranged from ~0 to >85% over the tested range of DOC concentrations corresponding to changes in dissolved phase concentrations of more than a factor of 10. Virtually all of the dissolved metal in solution was associated with DOC rather than being freely dissolved. Controlling dissolved metal concentrations, which will likely be required under several upcoming total maximum daily load (TMDL) standards, therefore requires a better understanding of the sources of DOC on the highway and methods for its removal.

Correlation between Particle Concentration, TSS and Turbidity

Turbidity and TSS correlate well with particle size concentration, suggesting that these parameters might be useful surrogates for each other. The correlation was generally better for lower TSS concentrations and was more scattered at higher TSS concentration, probably because of the greater importance of larger particles with more variable concentrations in high TSS samples. For example, for TSS concentrations greater than 200 mg/L, the contribution of particles larger than 30 μm was more than 60% by mass (assuming spherical particles with uniform density in all size ranges).

Organic and Inorganic Constituents Associated with Particles

Significant fraction of most heavy metals and PAH organic compounds are found to be particle bound. In general, major concentration of both organic and inorganic constituents is associated with particle size in the range of 8 to 20 μm, although substantial fractions (5-10%) of the mass of some important elements in runoff were associated with particles smaller than 2μm.

Practical Implication of Small Particle Size Results

Particles in storm water runoff may range from below 0.1 μm to over 1000 μm with the majority (by number) being less than 30 μm. Results obtained from this study revealed that a large fraction of the total Cu, Pb and Zn for all storm events monitored during 2004-05 were associated with particles in the range of 8-20 μm. Most existing BMPs are considered to be ineffective in removing particles smaller than 20 μm. In such a case pilot investigations with expensive field monitoring will not provide additional useful information about the efficacy of treatment BMPs. In addition, the results can be useful in recommending the use of chemical treatment (e.g. coagulation) if the intent is to remove a higher mass fraction of particulate phase metal or organic pollutants.

We took advantage of the particle first flush by simulating a two-compartment settling tank design to achieve optimal particle and associated contaminant removal. The two-compartment settling tank is comprised of storage and continuous compartments. Removal efficiency was optimized by adjusting the storage fraction for design storms ranging from 1.6 to 54 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, a 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 has higher removal efficiency due to its small dissolved fraction. Removal of smaller particles through a storage compartment improved the overall efficiency of metal pollutants. In general, the removal efficiency of metal pollutants was vastly increased when higher concentrations of metal pollutants were associated with smaller particles, and when the majority of the metals were in particulate form. For metals that are mostly dissolved, conventional BMPs will not effectively remove them without flocculation, precipitation or the utilization of other advanced treatment mechanism.

1. INTRODUCTION

BACKGROUND

Particles are ubiquitous in the roadway environment, being contributed by windblown soils, tire and brake wear, vehicle exhaust, pavement degradation and many other possible sources. These particles play a major role in delivering chemical constituents to roadway surfaces, and subsequently to runoff, by one or more of the following:

- affecting how readily the contaminants are mobilized during storms,
- influencing the physical, chemical and biological transformations that contaminants undergo as they are transported to receiving waters, and
- potentially reducing the impact of the particle bound contaminants on aquatic and benthic organisms in receving waters (i.e., pollutant toxicity).

Particles in roadway runoff are of concern for three primary reasons. First, as the repository of most pollutant mass for both organic and metallic constituents, they represent a potentially significant source of pollutant to the dissolved phase. Second, even if the solid-phase pollutants are not readily released to the dissolved phase, future regulations (e.g., sediment quality objectives) may address particle-phase concentrations directly. Third, if constituents need to be removed from roadway runoff, knowing their distribution among the dissolved phase and particulates of varying sizes is critical to the selection and design of treatment systems. A thorough understanding of the size-resolved chemical composition of roadway derived particles and the rate and extent to which target pollutants can be transferred from the particles to the dissolved phase is essential to address these regulatory and design concerns.

A large fraction of the heavy metal and non-polar organic contaminant load in roadway runoff is adsorbed to particles (Oliver et al. 1974; Herrmann 1981; Ongley et al. 1981; Hoffman et al. 1985; Hewitt and Rashed 1992; Legret and Pagotto

1999). 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. Most best management practices (BMPs) for roadway runoff are configured to remove only the particulate fraction. Hence, reductions in toxicity and contaminant loads accomplished by BMPs are limited by the degree to which contaminants associate with colloidal particles, and the efficiency of BMPs in removing those particles. Neither of these topics has been the subject of previous investigations, and the dynamics of contaminant distribution between particle and dissolved phases within a BMP are not fully understood.

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). Suspended solids carried by highway runoff are usually smaller in size than sediments recovered from channels or detention basins (Roger et al. 1998). 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), but only within the range of sizes accessible by sieving (>~30 μm). Finally, it has been noted that particles in highway runoff are not stable and that the PSD consequently changes

with time as particles aggregate; this requires PSD analysis to be performed within six hours of sample collection (Li et al. 2005).

Some recent field studies showed that fine to medium particles accounted for most of the total suspended solid (TSS) load and particle-bound 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 comprised 70 – 80% by weight of the TSS load carried by runoff. Furumai et al. (2002) showed that particles less than 20 μm accounted for more than 50% of the particulate mass for runoff samples with TSS concentrations below 100 mg/L. In addition, the finest particles in highway runoff had the highest concentration for many pollutants, especially metals (Sansalone and Buchberger 1997b; Roger et al. 1998; Morquecho and Pitt 2003). 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 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).

Measurement of particle-bound pollutants in roadway runoff involves three basic steps: solid/liquid separation, solubilization of particulate bound contaminants (extraction or digestion), and analytical measurement of the solubilized contaminants. There are several different approaches available for fractionating particles by size; physical and chemical characterization of a single particle size fraction typically requires collecting large roadway runoff samples (e.g., 50 to 10,000 L). Equally important, toxicity test methods used in most roadway runoff monitoring are not adequate to assess biological impacts related to particle- bound contaminants. While procedures for measuring particle-bound contaminant concentrations and their biological impacts have been proposed in the literature, there are no regulatory approved or standardized methods for performing these measurements.

In the absence of standard methods to measure particle-bound contaminant concentrations, methods used for soil, solid waste, and wastewater quality analyses are currently employed. One classical example is the classification of contaminants as either "dissolved" or "particulate" based on whether or not they pass through a 0.45 μm filter. However, the choice of a single cut-off is arbitrary when applied to samples of roadway runoff, because the particle size distributions extend continuously from tens of nanometers to hundreds of micrometers. Results obtained from existing techniques may not be applicable in design and performance evaluation of best management practices (BMPs) for storm water runoff.

Removing the particles from runoff requires either source control or treatment (e.g., BMPs). Particle removal strategies such as coagulation and filtration depend, in turn, on the size distribution, chemical composition and surface characteristics (e.g., surface charge) of the particles. Establishing the sources of the particles is a prerequisite for source control efforts and is another reason for collecting detailed information about particle composition. The knowledge gained from particle size distribution and contaminates associated with it presents an opportunity to develop better BMPs and to estimate their performance without conducting costly, full-scale field studies. For example, sand filters without coagulation/flocculation typically remove particles larger than 3 μm in typical applications such as water and wastewater treatment. Removal of smaller particles may not be possible without the aid of flocculants. If the distribution of particles in roadway runoff can be measured, along with the pollutant concentrations on the various particle size fractions, then the performance of BMPs can be predicted. Moreover, the potential improvements in water quality as well as cost can be calculated on a watershed basis.

OBJECTIVES OF THE STUDY

This study was undertaken to develop and evaluate consistent methodology for:

1. measuring particle size distribution from stormwater runoff and the variation of PSD within and between storm events,
2. separating particles into varied size classes for subsequent chemical analysis,
3. analyzing the chemical composition of particles within specific size ranges, and
4. applying particle size analysis methods to improve stormwater treatment methods.

REPORT ORGANIZATION

This report is organized into four major sections. Section 1 presents the introduction, covering background information, study objectives and report organization. Section 2 presents the methodology employed in the study, much of it developed specifically for this investigation; the section covers major topics including particle size measurement, particle size fractionation and chemical analysis of various particle size ranges. Section 3 provides the results of the study and a discussion of their significance for highway runoff quality. Major topics presented in Section 3 include: metal mobilization, inorganic constituents associated with small particles, organic constituents associated with small particles, correlation between particle size and contaminants, first flush of particles, and practical application of the results. The references cited within the text are presented in Section 4.

STUDY TEAM ORGANIZATION

This study was jointly performed by the Departments of Civil and Environmental Engineering at the University of California, Davis (UCD) and the University of California at Los Angeles (UCLA) under the direction of Drs. Michael Stenstrom, Thomas Young and Masoud Kayhanian. Major work performed at UCD includes:

- Methodology to collect samples for particle size analysis
- Mobilization of heavy metals with respect to particles
- Cell sorting and gravimetric methods to fractionate the particles

- Microscopic imaging and analysis of particles
- Analysis of chemical constituents associated with fractionated particles

Major work performed at UCLA includes:

- Methodology to store, preserve and mix the samples as well as holding time needed to measure particle size distribution
- First flush characterization of particles
- Serial filtration methods to fractionate the particles
- Analysis of chemical constituents associated with fractionated particles
- Practical application of particle size analysis for improving treatment methods

2. METHODOLOGY

MONITORING SITE AND EVENT DESCRIPTION

Site Description

Three highway monitoring stations were used for the UCLA portion of the particle size study. These highway sites were the same sites previously used for the Department's first flush characterization study. Table 2-1 summarizes the site characteristics. These sites are identified as 7-201, 7-202, and 7-203 in the Department database.

Table 2-1 Summary description of UCLA monitoring sites

Site No.	Monitoring Location	Freeway/ Post Mile	Area (m^2)	Type	Annual Average Daily Traffic
7-201	Eastbound US 101	US 101/PM 17	12802	Grade	328,000
7-202	IS 405 Freeway and Sepulveda	IS 405/PM 34.8	16918	Fill	260,000
7-203	Santa Monica Blvd. North Bound Exit on IS 405	IS 405/PM 30.8	3917	Cut	322,000

Monitoring site 7-201 was located near the intersection of the US 101 and IS 405 Freeways, on the south side of US 101. The site was accessible from a service road, which was reached from the Haskell exit of the northbound US 101 Freeway. This site has several 20-inch diameter corrugated drainage pipes and they all have lengthy straight sections to facilitate flow measurement. The freeway is elevated at this point with sound walls. No other drainage can enter the site. There is a free waterfall as the stormwater exits the pipe to facilitate sampling.

Monitoring site 7-202 was located near the IS 405 Freeway and the Getty Center exit, on the east side of the freeway. Drainage was through a 24-inch diameter corrugated drainage pipe. The site has a single stormwater inlet with several grates, along the east shoulder. There are no sound walls, and a hill exists on the east side of the shoulder. In heavy rainfall events, it is possible for runoff from the hill to reach the shoulder and the Department's inlet. Analysis of runoff rates suggests that this rarely happened. Sampling was also possible at a free waterfall.

Monitoring site 7-203 was located on the east side of the IS 405 Freeway just south of the point where it passes over Santa Monica Boulevard. This site was previously constructed as a monitoring site by the Department. It has a 24-inch diameter plastic corrugated pipe (smooth on the inside, corrugated on the outside) which collects runoff from the northbound, east side of the freeway. The curb was opened to collect runoff from the shoulder, and no runoff can enter the site in any other way, including the freeway and shoulder south of the site. It has no sound walls. As the runoff exits the pipe there is a gap of 20 cm, which creates a free waterfall for sampling.

All three sites were virtually 100 percent impervious, and the runoff coefficient was usually 0.9 to 0.95. Each site was equipped with an American Sigma rain gage and flow meter. The flow rate and the amount of rainfall were recorded automatically in one-minute intervals. Data from each site was downloaded into a Windows-based laptop computer after the end of each storm. Several pictures of the monitoring sites are shown in Figures 2-1 through 2-3.

Figure 2-1 Photo view of the UCLA highway monitoring site 7-201

clockwise from the top: (1) site from a distance of 30 meters; (2) drainage pipe showing free waterfall and cables for level and velocity sensors, and (3) rain gage above the sound wall

Figure 2-2 Photo view of the UCLA highway monitoring site 7-202

clockwise from the top: (1) site from a distance of 15 meters, showing rain gage, rain protection enclosure, PVC pipe for cables. The discharge is obscured by the brush; (2) drainage pipe showing free waterfall and PVC pipe for cables for level and velocity sensors, and (3) freeway looking north showing the four inlet grates.

Figure 2-3 Photo view of the UCLA highway monitoring site 7-203

Clockwise from the top: (1) site from a distance of 50 meters, looking north, showing drainage pipe (an early picture, taken before our study) (2) drainage pipe showing rain gage and dry/wet collection containers from an earlier study. The free waterfall is at the end of the black pipe, and (3) site entrance from the shoulder, looking south.

As part of the UC Davis particle size study one highway site was established to collect stormwater runoff samples on westbound Interstate 80 (I-80) midway between the Campus Road and Richards Boulevard exits near the UC Davis campus. The average daily traffic at this site was about 127,000 vehicles per day and the drainage area was nearly 2000 m^2. The contributing drainage area in this site is mostly paved surface with a runoff coefficient of about 0.9. A photo of the UC Davis monitoring site is shown in Figure 2-4.

Figure 2-4 Photo view of the UC Davis highway monitoring site

Clockwise from the top: (1) site from a distance of 10 meters, looking west toward San Francisco, showing drainage sampling equipment enclosure and rain gage (2) flume and a discharge point to collect the grab samples and (3) inside the enclosure during field sample preparation.

Storm Events Monitored

Storm events monitored at the three UCLA highway sites to collect runoff samples for the particle size study are summarized in Table 2-1.

Table 2-1 Summary of storm events monitored as part of UCLA particle size study

Storm Number	Monitoring Site ID	Storm Event Date	Total Rainfall (mm)	Antecedent Dry Period (days)	Runoff Volume (L)
2002-01	7-201	11/7/2002	28.96	40.13	210250
2002-02	7-201	11/29/2002	9.65	20.23	72619
2002-04	7-201	12/16/2002	29.72	16.43	348346
2002-05	7-201	12/19/2002	36.07	3.25	436406
2002-06	7-201	2/11/2003	23.37	44.27	235322
2002-07	7-201	3/15/2003	66.55	11.68	481134
2002-09	7-201	5/2/2003	50.29	18.10	322366
2002-01	7-202	11/7/2002	58.67	41.21	825776
2002-02	7-202	11/29/2002	1.78	19.97	23280
2002-03	7-202	12/15/2002	2.54	16.11	30345
2002-04	7-202	12/16/2002	59.94	1.21	825660
2002-06	7-202	2/11/2003	24.38	44.26	339243
2002-08	7-202	4/14/2003	21.34	27.85	311264
2002-01	7-203	11/7/2002	71.37	40.16	178136
2002-02	7-203	11/29/2002	1.52	19.96	714
2002-04	7-203	12/16/2002	40.64	0.27	124972
2002-05	7-203	12/19/2002	32.51	3.09	107836
2002-06	7-203	2/10/2003	20.07	44.12	44223
2002-07	7-203	3/15/2003	123.19	11.68	410796
2002-08	7-203	4/14/2003	19.81	27.85	53034
2004-01	7-201	10/16/2004	11.94	215.0	19911
2004-02	7-201	10/26/2004	61.47	6.0	704237
2004-04	7-201	12/5/2004	14.22	8.0	53246
2004-06	7-201	1/7/2005	155.96	2.0	1847605
2004-07	7-201	2/10/2005	68.83	8.0	449613
2004-01	7-202	10/16/2004	21.84	215.0	254334
2004-02	7-202	10/26/2004	48.26	6.0	710979
2004-04	7-202	12/5/2004	17.02	8.0	250631
2004-06	7-202	1/7/2005	287.02	2.0	4392559
2004-07	7-202	2/10/2005	78.23	8.0	1011186
2004-08	7-202	3/18/2005	5.08	5.0	51587
2004-09	7-202	4/28/2005	32.77	31.0	522038
2004-02	7-203	10/26/2004	45.21	6.0	131656
2004-04	7-203	12/5/2004	14.73	8.0	24850
2004-06	7-203	1/7/2005	202.18	2.0	758139
2004-07	7-203	2/10/2005	52.07	8.0	176821
2004-08	7-203	3/18/2005	2.79	5.0	4102
2004-09	7-203	4/28/2005	29.72	31.0	104863

As indicated, 20 and 18 storm events were monitored during the 2002-03 and 2004-05 sampling campaigns, respectively. Total rainfall at these sites ranged from about 2 to 290 mm.

Characteristics of the storm events monitored at the UC Davis I-80 monitoring site are shown in Table 2-2.

Table 2-2 Summary of storm events monitored as part of the UCD particle size study

Storm Number	Storm Date	Total Rainfall (mm)	Antecedent Dry Period (days)	Runoff Volume (L)
2003-3	December 6, 2003	9.6	18	4719
2003-4	December 10, 2003	8.1	2	3418
2003-5	December 12, 2003	2.0	1	470
2004-7	February 2, 2004	16.0	25	21,886
2004-8	February 25, 2004	47.5	22	73,422
2005-1	January 8, 2005	15.0	3	NM
2005-2	February 13, 2005	11.9	17	NM
2005-3	February 19 2005	6.1	15	NM

NM = not measured

PARTICLE SIZE MEASUREMENT INSTRUMENTS

Three different particle size measurement instruments were used in this study: (1) AccuSizer 780, (2) LiQuilaz SO5-HF, and (3) LISST 100. The fundamental techniques used in each particle size analyzer are briefly described below.

AccuSizer 780 Optical Particle Size Analyzer

As part of the UCLA portion of the particle size study, a Nicomp Particle Sizing Systems (Santa Barbara, California) AccuSizer 780 Optical Particle Sizer module equipped with an auto-dilution system and a Light Scattering/Extinction sensor (Model: LE400-05SE) was used for particle size analysis. This instrument was selected for its wide range (0.5 to 400 μm), speed (< 2 minutes/sample analysis) and auto dilution capability. A representative sample ranging in volume from 0.5 to 10 ml was removed from the 4L sample bottle, or from the stirred dilution beaker 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. All glassware was cleaned by soaking overnight in detergent, rinsing with hot water five to six times, and rinsing with NPPFW.

LiQuilaz® Particle Size Analyzer

Particle size analyzer used for UCD particle size study was LiQuilaz®-S05-HF manufactured by Particle Measuring Systems, Inc. (Boulder, Colorado). LiQuilaz® were controlled by a laptop personal computer, which exports the data in a spreadsheet. The LiQuilaz® determines the size of a particle based on the magnitude and duration of light scattering (over 120° in the forward direction) as the particle passes through the measurement chamber at a known flow rate, and it provides a measure of absolute particle concentration (particles/mL) in fifteen size classes ranging from 0.5 to 20 μm in spherical-equivalent diameter. Boundaries between size classes are adjustable by the user.

The laser used in the LiQuilaz® is a 30 MW laser diode. The laser beam is focused by using a cylindrical lens before it illuminates the sample flow at the center of the capillary. This lens focuses the beam perpendicular to the flow axis of the capillary causing the entire width of the capillary to be illuminated uniformly. The variation in the light scattering that a particle causes when passing through the laser beam, is electronically detected by the photo-detector. The duration the particle is in the laser beam is measured by the detector. The signal is amplified and converted into a digital signal, after which the amplitude of the signal is converted to an equivalent particle size in a microprocessor located in the main section of the LiQuilaz®.

The manufacturer has indicated that 10,000 total (cumulative) particles/mL is the maximum. However, experiments showed that the total number of particles should be kept below 7,000 particles/mL to avoid undercounting the smaller particles. Therefore, large factors of dilution are employed for stormwater.

Absolute particle size is calibrated across the instrument's range of 0.5 to 20 μm using a set of NIST-traceable standard polystyrene beads of known dimensions (Particle Measuring Systems, 1993). In addition, periodically throughout the year, users check the instrument's particle size accuracy using a set of standard beads. Therefore, the size determination is calibrated to the shape (spherical), index of refraction (1.59), and reflectivity (high) of the beads. Actual stormwater particles are likely to vary in refraction (both higher and lower) and reflectivity (both higher and lower), so the calibration is an operational one.

LISST 100 Particle Size Analyzer

The LISST 100 particle size analyzer manufactured by Sequoia Scientific were used for on-line particle size distribution measurement. The LISST-100, Laser In-Situ Scattering and Transmissometry, is a laser diffraction device. It measures the particle size distribution, particle volume concentration, optical transmission and volume scattering function of water samples. The laser diffraction method for sizing particles is the best method for determining size distribution because light scattering is determined almost entirely by light diffracted by the particle not by the light

transmitted through the particle. Therefore the composition of the particles does not affect the laser diffraction measurements.

The main measurements of the instrument are the small-angle scattering properties of particles in water. The LISST-100 uses a 670nm diode laser connected to a laser beam collimating system, a beam manipulation and orienting system, a scattered-light receiving lens, a custom 32-ring detector and a data logger. A cut-away view of the optics of a LISST-100 is shown in Figure 2-5. Light from a laser travels through water(arrow). The receiving lens places scattered light on 32 ring detectors. Each ring measures scattering over a particular angle. A hole at center of rings passes the unscattered light to a photodiode, which measures optical transmission also.

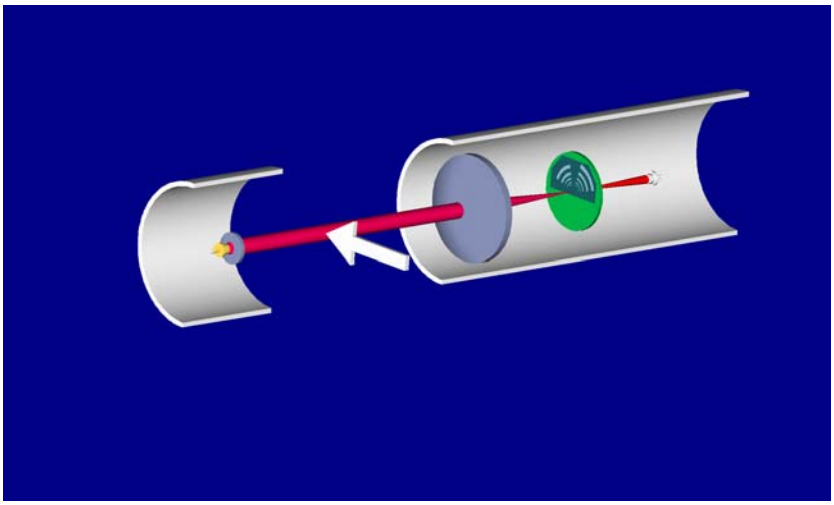


Figure 3-5 A cut-away view of the optics of a LISST-100
(Source: Sequoia Scientific Inc.)

This instrument is capable of autonomous operation with a program that sets the instrument to a specific sampling schedule. The detector of the LISST-100, which is placed in the focal plane of the receiving lens, consists of 32 rings of increasing logarithmic radii. The rings cover an angular range of 0.0017 to 0.34 radians. This corresponds to size ranges 1.2 to 250 microns. The LISST-100 also houses a data logger and is able to off-load the data from the instrument to a PC using an inversion function included in the software.

The LISST 100 instrument has not yet been used for the continuous on-line particle size measurement for stormwater runoff. With the assistance of Sequoia Scientific

engineers, we have made a few modifications to the instrument in order to measure particles continuously. Visual explanations of modified parts for LISST-100 are shown in Figure 2-6.

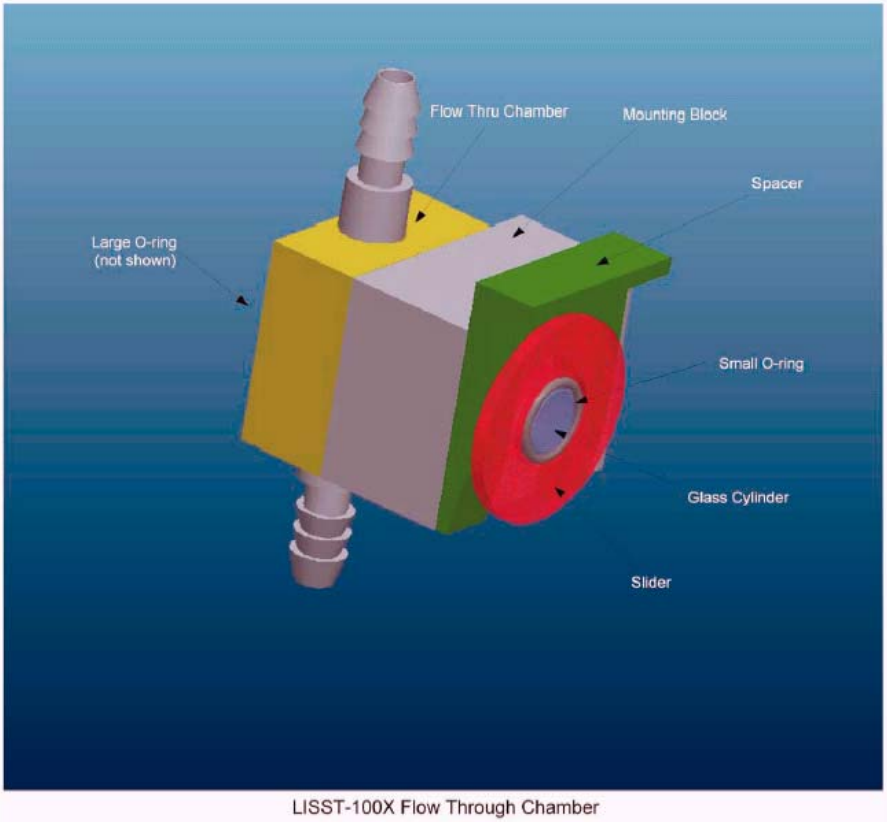


Figure 2-6 Major modified parts of LISST 100 flow through chamber (Source: Sequoia Scientific Inc.)

As shown, the major components of the modified parts include a glass cylinder, a slider, a spacer, a small O-ring, a mounting block, a flow through chamber and a large O-ring. Generally, the instrument works by being submerged in water. In this case only the flow through chamber will be filled with water. With continuous mode operation the undiluted runoff constantly passes through the flow through chamber.

PARTICLE SIZE MEASUREMENT NOTATIONS

Several notations have been used throughout the report that are unique to this study and it is important to described them before introducing the results. The major particle size notations used include: difference proportion (DP), particle first flush

ratio (PNFF), number of particles with certain diameter ($dN/d\log D_p$), number fraction (NF), and particle event mean concentration (PEMC).

The difference between each duplicate pair was represented by a difference proportion (DP), calculated as follows:

$$\text{Difference proportion} = 100\ \frac{2\left|N_1 - N_2\right|}{(N_1 + N_2)} \qquad (2\text{-}1)$$

Where,

N_1 and N_2 = number of particles in a specific size range for the first and second samples.

The PNFF ratio is defined as the normalized number of particles divided by normalized volume fraction at any point of normalized runoff diagram. Let x represent the x percent runoff volume at a certain time t_1. Then

$$x\ \% = \frac{\int_0^{t_1} Q(t)dt}{V} \qquad (2\text{-}2)$$

$$PNFF_x = \frac{\frac{\int_0^{t_1} C_p(t)Q(t)dt}{N}}{\frac{\int_0^{t_1} Q(t)dt}{V}} \qquad (2\text{-}3)$$

Where,

$Q(t)$ = runoff flow rate (L^3/T),

$C_p(t)$ = particle number concentration (L^{-3}),

V = total runoff volume of an event (L^3), and

N = total number of particles in an event.

Number of particle within a certain particle size range is defined as:

$$dN/d\log D_p = \frac{\text{Number of particles with diameters between } D_1 \text{ and } D_2 \text{ (\#/mL)}}{\log D_2 - \log D_1} \qquad (2\text{-}4)$$

Where,

N = particle concentration (#/mL) and

D_1 and D_2 = particle diameter (μm), $D_2 > D_1$.

To quantitatively describe the PSD, a number fraction was defined as follows:

$$\text{Number Fraction} = \frac{\text{total number of particles in a certain size range}}{\text{total number of particles (2 - 1000 } \mu\text{m)}} \qquad (2\text{-}5)$$

For number of particles in the runoff, 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 (2-6). Particle EMC is defined when it is integrated to the end of the runoff.

$$PEMC = \frac{n(t)}{v(t)} = \frac{\int_0^t c_t q_t dt}{\int_0^t q_t dt} \qquad (2\text{-}6)$$

Where,

n(t) = particle number transported up to time t,

v(t) = flow volume up to time t (m^3),

c_t = particle number concentration at time t (#/m^3),

q_t = flow rate at time t (m^3/s),

t = time (s).

PROCEDURES FOR SAMPLE COLLECTION AND SAMPLE PREPARATION

Sample Collection

Nearly all samples collected at the UCLA highway sites were obtained by grab. 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 also 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. The samples collected were periodically taken to the lab, and all were analyzed for particle size distribution (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 PSD analysis within 6 hours is discussed under sample storage (holding) time.

Both grab and composite samples were also collected at the UCD highway site. The grab samples were collected by taking 1 gallon increments from the end of a corrugated pipe funneling water off the road's surface. The time for each grab sample was recorded, and then the sample was poured through a 125 µm stainless steel sieve into a glass carboy connected to a Westfalia Flow-Through Separator via Teflon compression fittings and tubing. The runoff sample was processed at the site through the centrifuge separator at a speed of ~10000 rpm and the effluent was collected and saved for humic substances extraction and other elemental analysis. 200 L of stormwater runoff was processed through the separator. The bowl containing the centrifuged particles was removed, wrapped in baked aluminum foil, and returned to the lab where it was rinsed with post-centrifuge stormwater. The concentrated particle sample recovered from the bowl (final volume ~800 mL) and the post-centrifuge stormwater were refrigerated at 4^{o}C for future experiments. The pre-centrifuge sample was analyzed for total suspended solids (TSS) and turbidity.

Sample Storage (holding) Time, and Temperature Preservation

PSD was performed immediately after grab samples back to the lab and always within six hours of sample collection. The particle size analysis within 6 hours was considered to reduce the possibility of change in PSD due to particle aggregation or dissolution. To quantify the changes in PSD with storage time, seven grab samples taken on November 7^{th} and December 15^{th}, 2002 were kept in a 4^{o} 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^{o} C), open to the atmosphere, but protected from dust fall or any other contamination. Figure 2-7 shows the PSD over time for one sample, stored at 4^{o}C and 20^{o}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 2-8 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, shown in Figure 2-9, present 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.

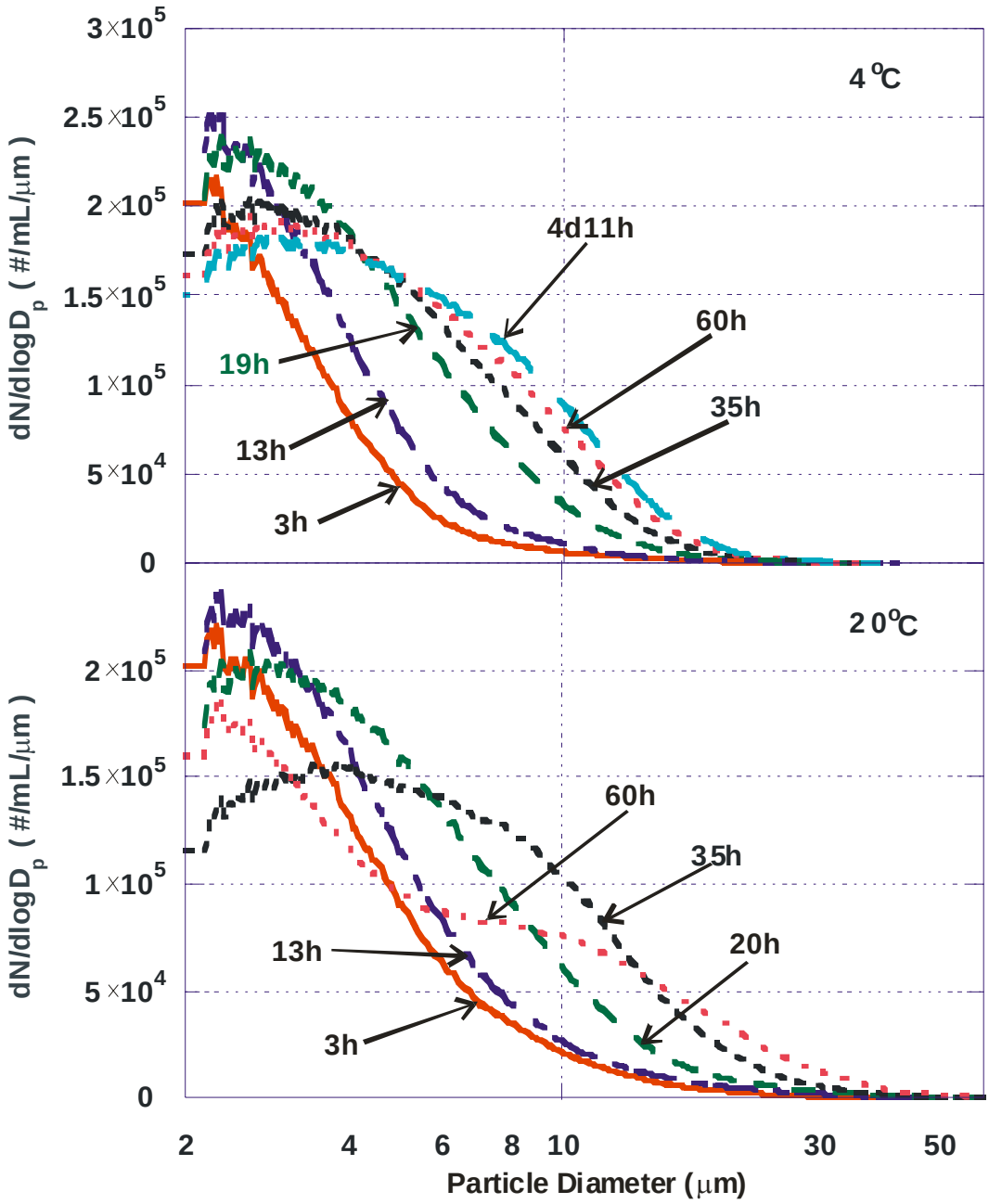


Figure 2-7 Sample storage time and temperature influence
(Site 3, event 12/15/02, grab sample No. 2, labels show storage time in hours)

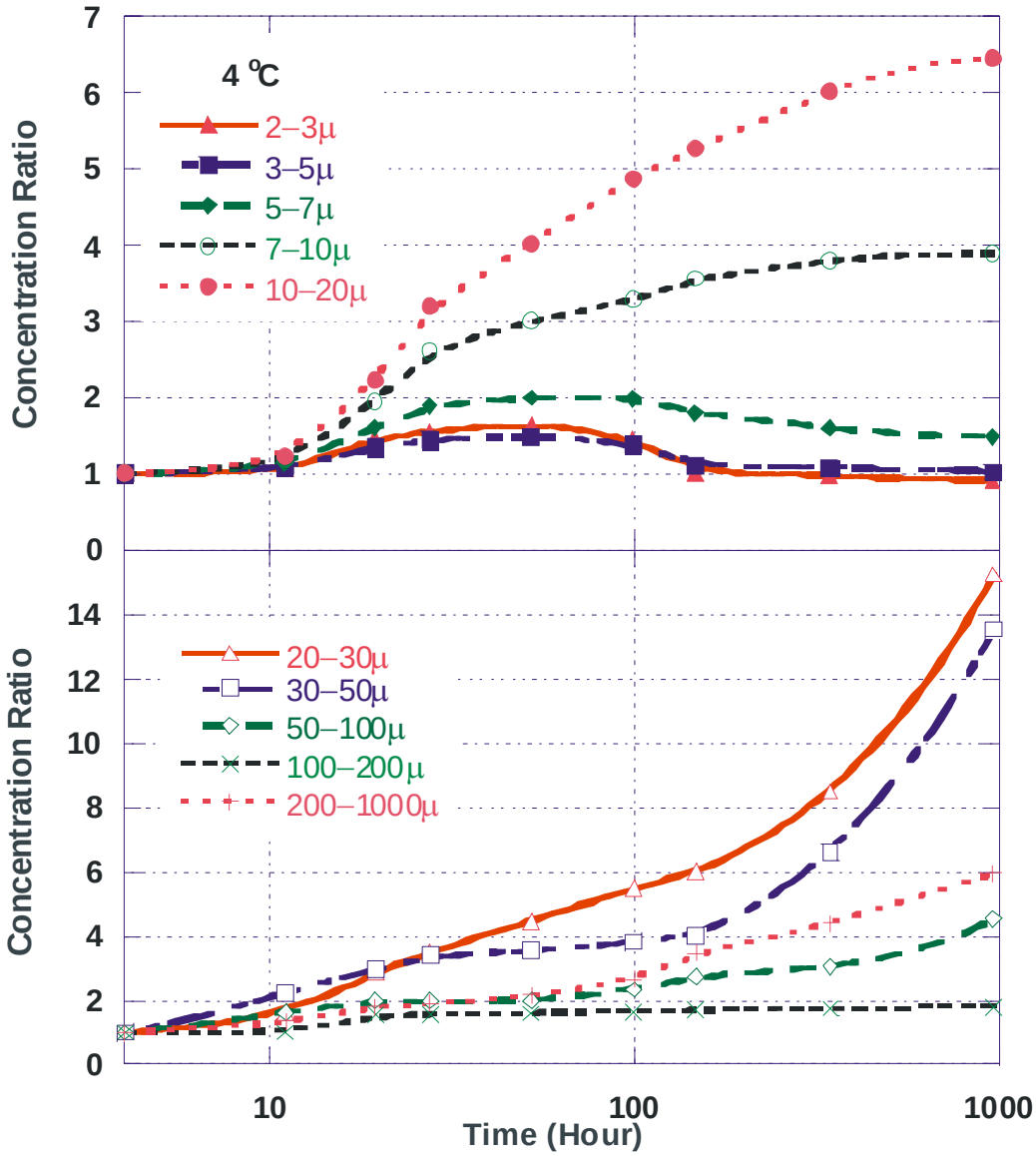


Figure 2-8 Average concentration ratio vs. time (4° C)

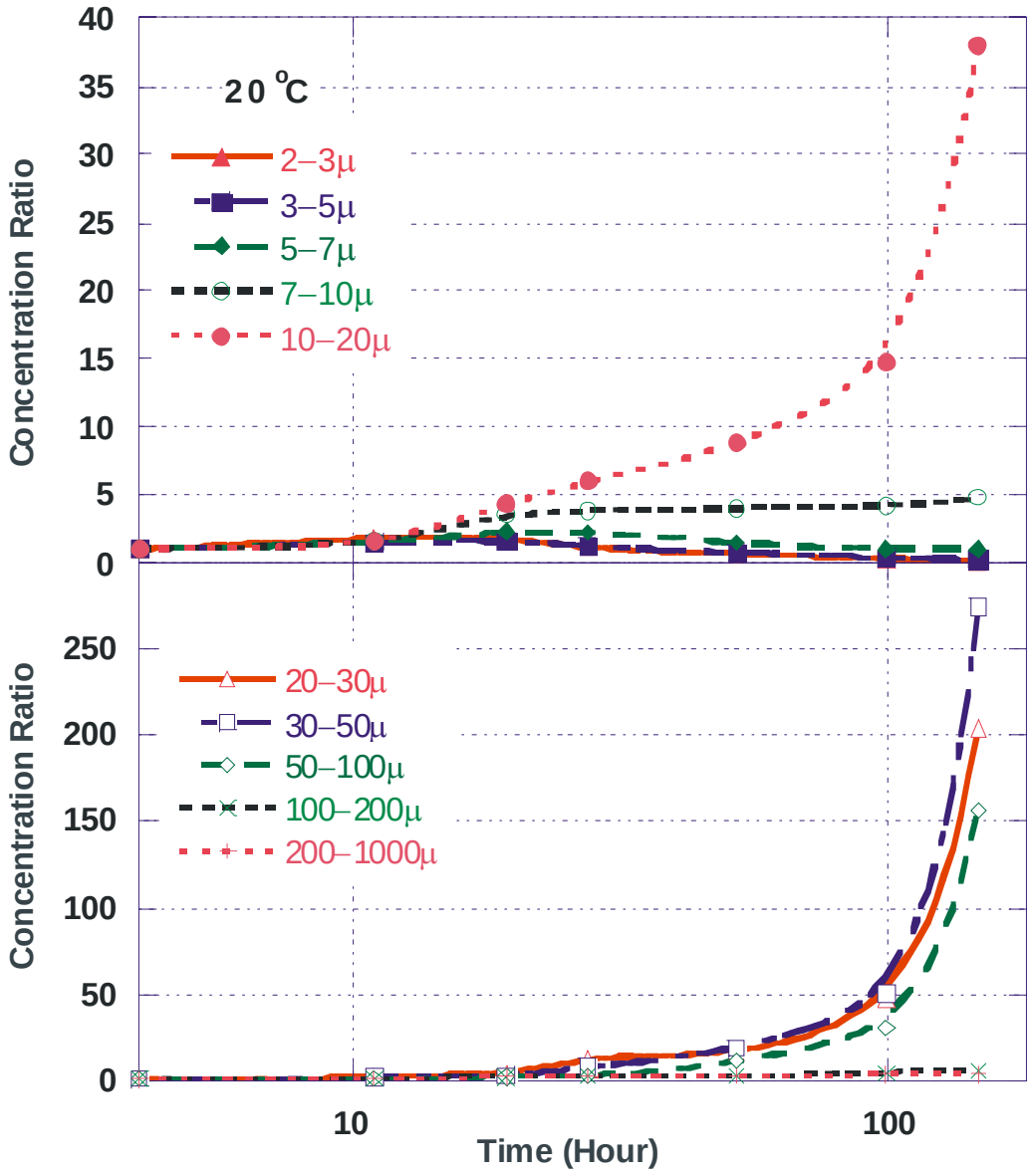


Figure 2-9 Average concentration ratio vs. time (20° C)

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.

Sample Mixing and 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 dense particles. 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) gentle inversion (five to six times); (3) gentle inversion-decanting-stirring, and (4) gentle inversion-decanting-blending. In each procedure, the end of pipette was inserted about 2 cm below the liquid surface to collect 1 to 10 ml sample immediately after the final mixing step, and injected into the particle sizing system for measurement. Figure 2-10 shows the PSD of the above four sampling techniques. With no mixing, the particle concentration measured 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.

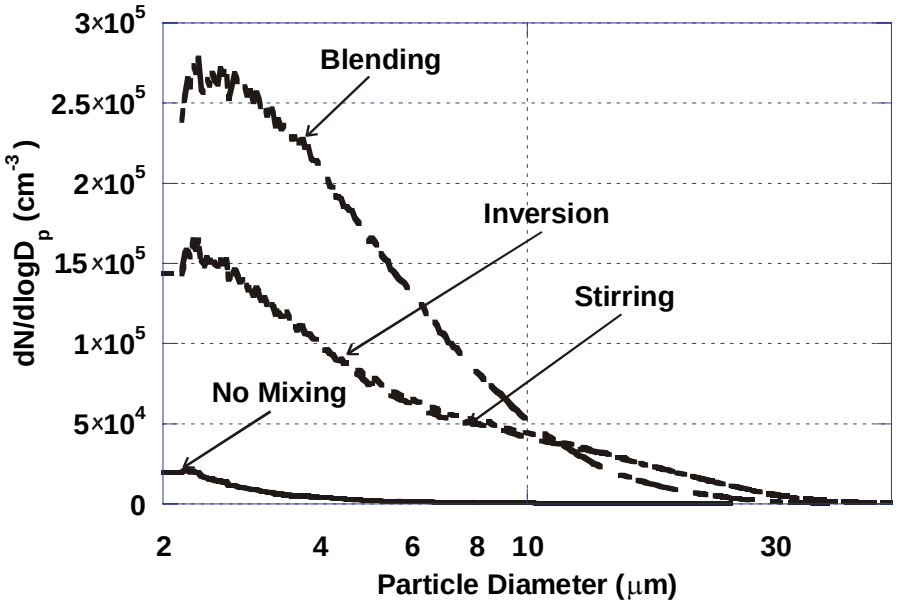


Figure 2-10 Comparison of different mixing methods.

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 2-4. 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 inversion and stirring methods produced similar results, and gentle inversion was adopted.

Table 2-4 Concentration difference evaluation using inversion and stirring methods

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

Sample Preparation

When the particle concentration was so high that the instrument would be required to provide more than a 10-fold dilution (using its autodilution mechanism), predilution was manually preformed. Pre-dilution was performed by removing 5 to 10ml sample from the 4L sample bottle with a wide-bore pipette immediately after inverting the bottle 5 to 6 times. The pipette was released into a 25 ml or 50 ml cleaned glass flask. The flask was then filled to obtain a 25 ml or 50 ml diluted sample using nanopure, particle free water (NPPFW) obtained from a Barnstead Nanopure Infinity Water System with a 0.2 μm filter. The diluted sample was poured into a clean beaker with a clean magnetic stirring bead. Next 0.5-10 ml diluted sample was removed from the stirred beaker for measurement. When the grab sample particle concentration was not very high, 0.5 – 10 ml sample was obtained directly from the 4L bottle for measurement.

To measure particles in LiQuilaz particle size analyzer, a sample is placed in a beaker or graduated cylinder, and the desired volume of liquid is drawn into the syringe. The system then expels the fluid from the syringe through the LiQuilaz® particle detector. After the analysis the sample is pumped into a waste beaker. For each water sample, four 10 mL sub-samples are drawn into the Liquilaz®. The first sub-sample is discarded and is primarily intended to flush the system. The next three 10 mL replicate samples are measured for particle size distribution. Fresh MilliQ-UV™ blank water samples are analyzed prior to, during, and at the end of each experiment to ensure quality control. The liquid is delivered to the spectrometer through a glass capillary with an internal diameter of 0.5 mm (The liquid inflow rate was set at 20 mL/min to minimize disturbance to the particles). The capillary has a window attached to one side with an Anti-Reflection (AR) coating and an AR-coated lens attached to the other side. The AR coatings help reducing the reflected light in the system. There is a Kel-Rez™ O-ring at each end of the glass capillary in order to seal the capillary to the Kel-F ™ retainer that in turn provides the 6 mm connection to the external Teflon® tubing (Particle Measuring Systems, 1993).

HYDROGRAPHIC MEASUREMENT OF PARTICLE SIZE DISTRIBUTION

Hydrographic measurement of particles related to particle size measurement at diffirent time of a storm event to determine the variability of particles throughout the entire storm spectrum. A representative hydrographic measurement of particles for storm event captured at site 7-201 during October 26th, 2004 is shown in Figure 2-11. As shown, a typical hydrographic particle size measurement includes particle concentration, rainfall, runoff flow, and particle number as a function of time. The concentration of particles (0.5 - 400 μm) shown in this plot is based on 183 grab samples collected from seven events. The lower two graphs in Figure 2-11 show PSD for the 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 2-11 to show the point on the hydrograph when the sample was taken. Particle concentration ranged between 50,000 and 3,742,000/ml with a median value 204,000 /ml.

The principal benefit of hydrographic plots is that we will be able to determine the variability of particle throughout the event. For instance, the particle size distribution shown in Figure 2-11 indicate that the highest particle concentration always occurred within the first hour (first flush) and decreased rapidly thereafter. The first flush trends shown are typical of most samples. The very first grab 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 2 μm, and after several hours particles larger than 2 μm were reduced in concentration. The median particle size decreased as the storm progressed, which shows a more rapid washout of larger particles. The information presented in Figure 2-10, would not have been possible by single or periodic discrete sample analysis for particle size distribution. The application of particle first flush is presented in results and discussion section.

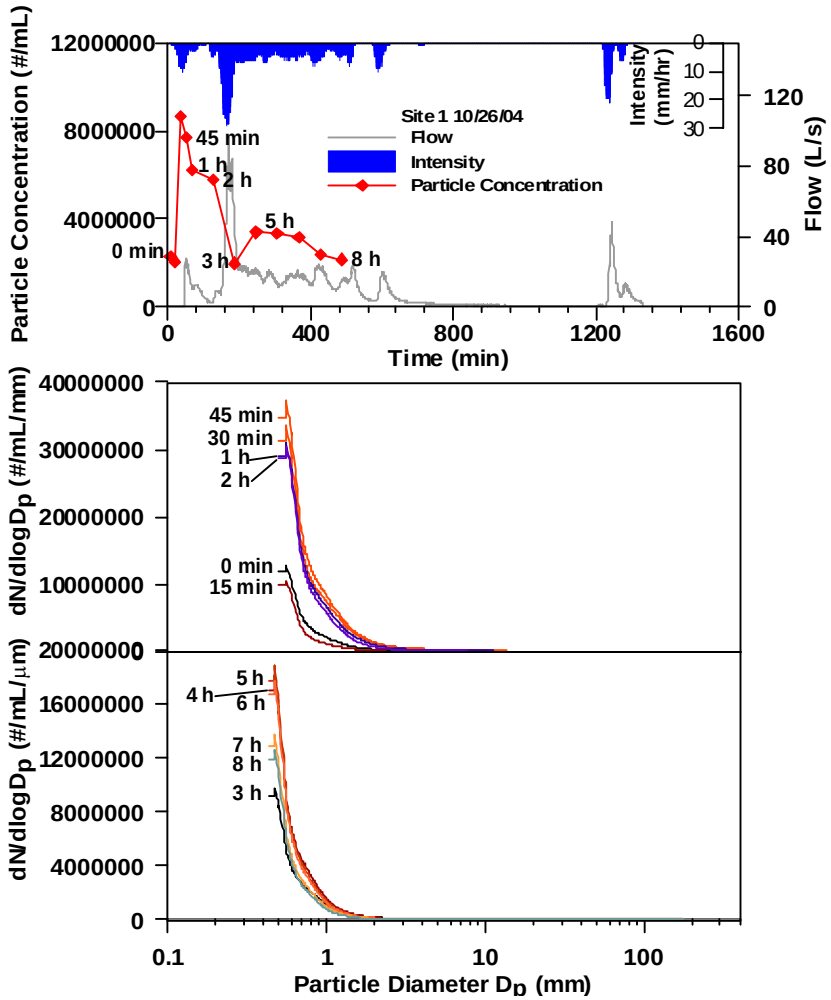


Figure 2-11 Hydrograph with PSD for site 7-201, storm event 10/26/04

ON-LINE PARTICLE SIZE MEASUREMENT

The continuous measurement of particles from storm water runoff has not been tested and at present no information is available from the literature. In this study we identified the LISST-100 Particle Size Analyzer as a unique instrument that could be used to measure particles continuously from a storm water runoff discharge point and from both influent and effluent of BMPs. Description of the LISST 100 instrument, modification made to measure particle size continuously, experimental set up and test procedures, sample preparation and sample analysis are described below.

Experimental Set-Up and Test Procedures

A photo view of the LISST 100 particle size analyzer test set up is shown in Figure 2-12. As shown the water sample is mixed with an adjustable speed mixer to assure

the representativeness of particles throughout the experiments. The continuous flow was adjusted through a peristaltic pump with various speed and flow control. The pumped water enters to LISST 100 flow through chamber. The particles in the runoff sample pass through a chamber are then measured, and the results are stored in a laptop computer. Alternatively, the particle size analysis can be stored within the LISST 100 instrument and then transported into the lap top computer upon the completion of the test.

The runoff samples used for this portion of the study were synthetically generated from section of a parking lot with area of about 20 m^2. To acquire synthetic parking lot runoff, tap water was slowly distributed over the 20 m^2 area and all runoff water was naturally directed toward a drain inlet discharge point. As the runoff gathered near the end of the slope, ten gallons of it was then collected into a container and immediately brought to the lab for analysis.

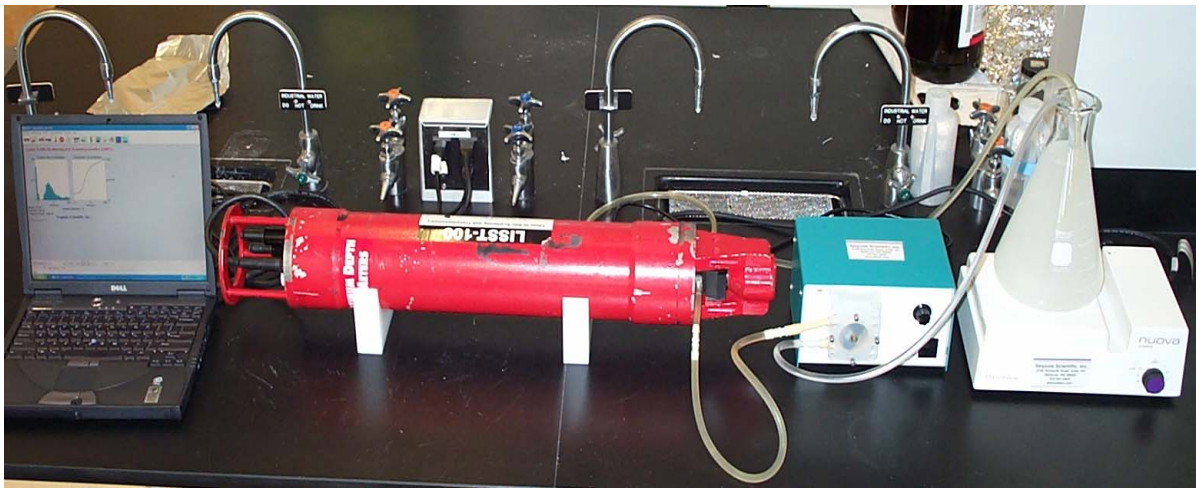


Figure 2-12 Photo view of the experimental set up using the LISST 100 continuous flow particle size measurement.

Quality Control and Assurance used for On-Line Particle Size Measurement

Prior to any continuous particle size measurements, the following quality control and quality assurance procedures were followed:

Test background particle size distribution against factory background

The factory background standard was provided by Sequoia. When testing the Milli-Q water against this factory background standard, we were able to see if the flow through chamber and the glass cylinders were contaminated or if there were obtrusive bubbles in the tubes.

Test LISST 100 instrument with a known clay particle size

Since Kaolinite is an example of a clay with a known particle size range we used it to measure the accuracy of the LISST-100. Its particle size range is known to be below 250 microns, which is the maximum range of the LISST-100. We used 2L of Milli-Q water and added .747 grams of Kaolinite. The LISST-100 was set to continuously measure the Kaolinite solution for 1 measurement every 10 seconds, up to 10 measurements. The solution was constantly mixed with the magnetic mixer and both the input and output tubes were in the solution so the volume remained steady. The results found that each measurement was almost completely similar to the one before it and all particles were under 250 micrometers. From these results we concluded that the LISST-100 was measuring a steady volume solution consistently and accurately. Figure 2-13 is an example of measurement #1 out of the 20 measurements for this Kaolinite solution.

Test LISST 100 instrument with a known particle size solution

To make sure that the LISST-100 was measuring particle sizes accurately, we decided to run the Particle Analyzer with a solution made up of 5mL of a Microbead Nist Traceable Particle Size Standard Solution (9.00 microns) and 2L of Milli-Q water. The exact diameter of the standard microbeads is 9.11 microns +/- .07 microns. The solution was constantly mixed using the magnetic mixer placed inside the solution so the particles were evenly distributed. The standard deviation of the 9 micron solution, according to the manufacturer, is 0.478 microns. The results, shown in Figure 2-14, were found to be within the range of particles close to the known 9 micron particle size solution.

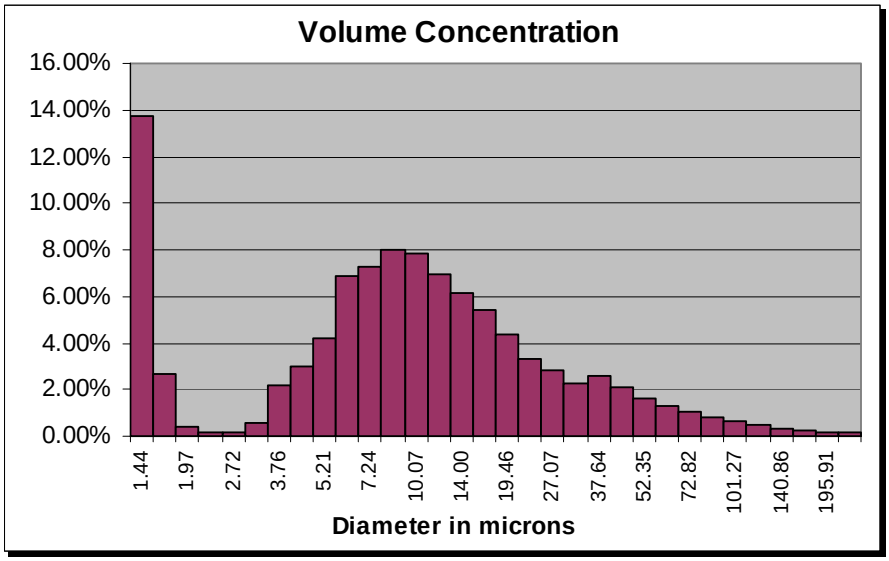


Figure 2-13 A representative distribution of particle size concentration for Kaolinite solution

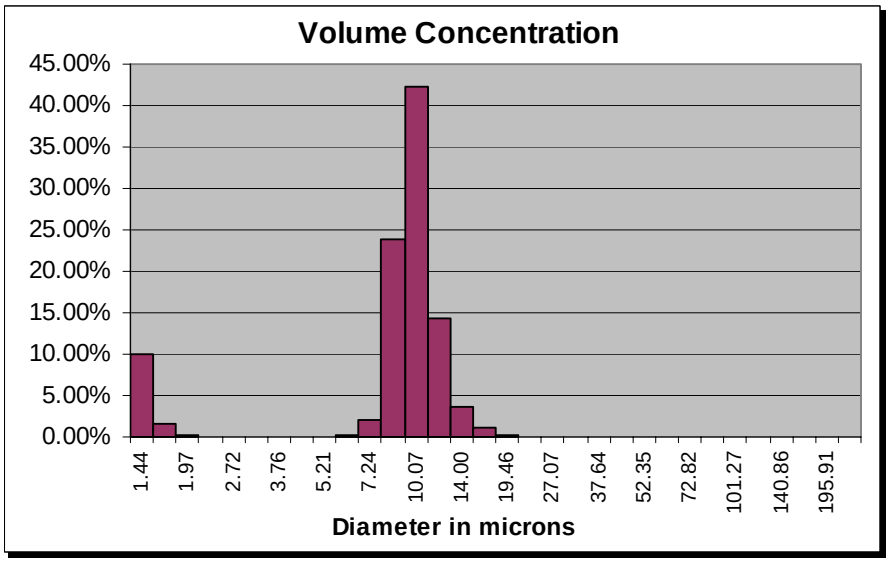


Figure 2-14 A representative distribution of particle concentration using a known 9 μm standard solution

Comparison of measured solids in runoff samples with solids computed from particle size volumetric concentration

Solid count tests were also done on each sample for quality assurance and control of the LISST-100. For each sample, two different methods for obtaining the solids were implemented. The first method obtained the solids by filtering a specific volume

of the sample through membrane filters on a vacuum flask. The second method obtained the solids of each sample by manually calculating it from the results of the particle concentrations measured by the LISST-100. The calculation was obtained using the weighted mean concentrations of each parking lot runoff sample as well as the general density of most runoff particles.

The results from the first Runoff Test show that the filtered solids and the calculated solids do not match. The reason for this difference is because the filter method of obtaining solids implored the use of a 0.45 um membrane filter which caught all suspended particles of sizes 0.45 microns and greater. The LISST-100 can only measure particles of sizes ranging from 1.2 microns to 250 microns. To correct for this discrepancy, we decided to use a 1.2 um membrane filter for the second Parking Lot Runoff Test. The results of the calculated solids and the filtered solids from the second Runoff Test are comparable because of this change in the size of the filter.

Repeatability of continuous PSD measurement

Every sample that was used for Quality Assurance and Control was measured continuously for 1 measurement every 10 seconds for a total of 10 measurements. The LISST-100 analyzer was set to take a total of ten measurements to verify the repeatability of each test result on a continuous basis. The results obtained showed that in nearly all cases the difference between the mean of each test and the overall weighted mean was less than 10 percent.

PARTICLE SIZE FRACTIONATION

Particles in stormwater runoff and synthetic water samples were fractionated using three different methods: (1) serial filtration, (2) settling column (pipette) technique and (3) cell sorter method. The serial filtration was used to fractionate particles in the range of less than 0.45 μm to greater than 100 μm in stormwater runoff, the settling column was used to fractionate particles less than 60 μm in the synthetic runoff samples and the cell sorter was used to sort particles between 0.1 and 1.5 μm for the highway runoff and synthetic water samples. These methods are briefly described below.

Serial Filtration

Runoff samples collected from each storm event at UCLA highway sites were separated into five different fractions according to particles sizes: > 100 μm, 20-100 μm, 8-20 μm, 0.45-8 μm and < 0.45 μm by serial filtration. Nylon net filters (100 μm and 20 μm pore size) and mixed cellulose ester membranes (8 μm and 0.45 μm pore size) from Millipore (Billerica, MA) were used.

One liter (or less, depending on the suspended solids content of the samples) sample was filtered, under vacuum, in series through each filter in the following sequence: 100 μm, 20 μm, 8 μm and 0.45 μm. The filters with retained particles were digested in a microwave unit (CEM Corp., Mathews, NC) according to SW 3051 Method (US EPA, 1998). The digesting fluid was shipped to UC Davis, Dept of Civil and Environmental Engineering for metal analysis by ICP/MS. In some cases, too little solid material was collected in the greater than 100 and greater than 20 μm fractions. For these cases, results from other grab samples were combined. In all cases there was sufficient material for in the two smaller fractions for analysis.

Settling Column (Pipette) Method

The pipette method is a gravimetric method that is outlined in the *Methods of Soil Analysis, Part 1, Physical and Mineralogical Methods*. Settling times were determined by Stokes Law (assuming a spherical density of 2.6 g/mL), ranging from forty-five seconds to six hours. The fractions of <63 μm, <20 μm, <15 μm, <10 μm, <5 μm, and <2 μm were collected in 5 mL aliquots. The <63 μm, <20 μm, <15 μm and <10 μm fractions were collected at 10 cm from the surface and the <5 μm and <2 μm fractions were collected at 5 cm from the surface. For each synthetic water sample, approximately 0.6 g of dry road dust was mixed with 120 mL of synthetic rain. After a twenty-four hour holding time, the 120 mL of synthetic rain was poured into a 100 mL polypropylene graduated cylinder. A 100 mL graduated cylinder was used with 120 mL of synthetic rain because the pipette would not reach the depths required for all the extractions if a 100 mL sample was used. Temperature remained constant around 22 °C, and only fluctuated by a degree throughout the experiment. Samples were inverted 3 times immediately prior to settling using polypropylene

saran wrap to seal the top of the graduated cylinder. After the fractionated particles were collected, the samples were stored at 4°C until further analysis. For each run, a synthetic rain blank was prepared and fractionated in the same manner.

Cell Sorter Method

The DykoCytomation MoFlo Cell Sorter was used sort particles between 0.1 and 1.5 µm in the stormwater runoff and synthetic water samples. Schematic of a cell sorter during the operation is shown in Figure 2-15. The cell sorter uses flow cytometry technology, the process of measuring the physical or chemical characteristics of particles or cells while passing through a fluid stream. Flow cytometry sorts by using the light scattering behavior of particles. The forward and side scattering signals of each particle are plotted on a chart. On this plot, a selection of particles are gated by the operator to restrict the boundaries of each sort. Gating is the process of selecting which particles, based on the forward and side scattering signals, will be included in the count and sort of the desired population. Gates can be drawn to any size or shape on the light scattering plot and reset at the start of each run. Forward scattering is a function of the cross sectional area of the particle and its refractive index. The side scatter signal, also called the orthogonal scatter, is mainly dependent on the granular morphology of the particle.

Storm water samples were transferred directly into the cell sorter. Particle counts per hour varied from 3.8E6 to 2.1E7 depending on the number of particles in the sample. Sorted stormwater samples were transferred from the four wells by the operator to 5 mL propylene sample tubes by a disposable pipette throughout the sort. Saline blanks were taken with each run and subtracted from sample metal concentrations to take into account any metals in the saline solution. The fractionated samples were stored at 4°C until further analysis. In addition to the sample, an additional fluid termed the sheath fluid is pressurized to move through the system and is joined with the sample in the flow chamber. The flow inside the flow chamber past the point of analysis is laminar and minimal mixing occurs. Thus, the resulting stream consists of an inner core of sample and an outer diameter of sheath fluid. (Shapiro 2003) Typically, the ratio of the outer sheath diameter to the

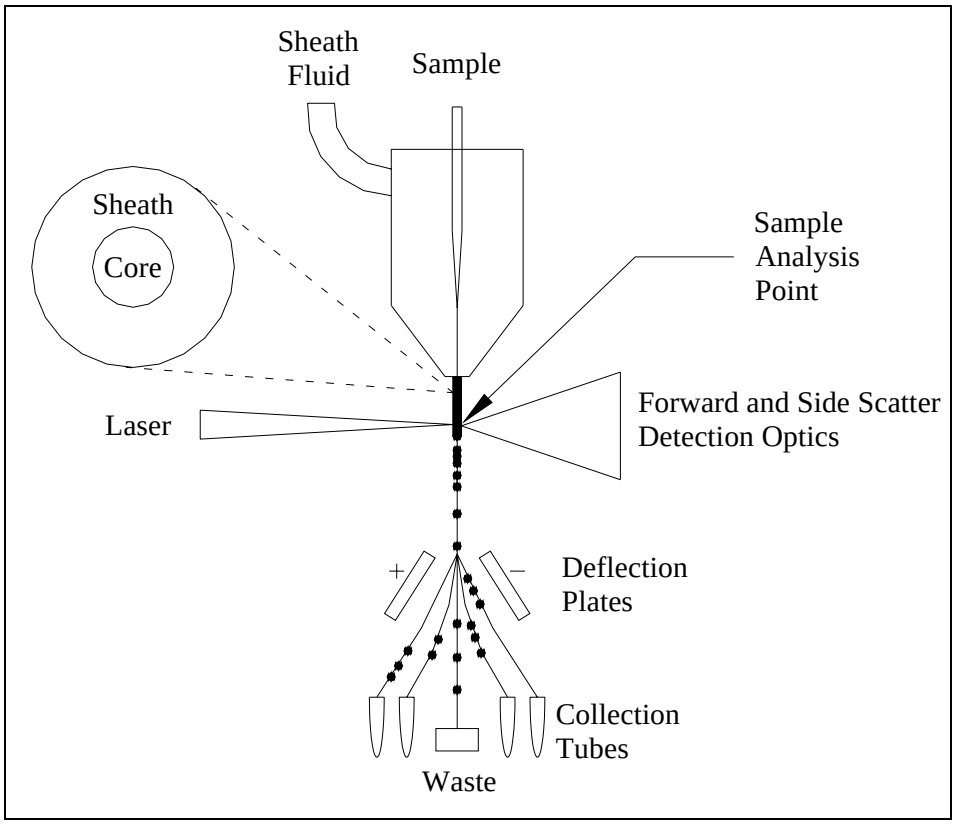


Figure 2-15 Schematic of cell sorter during operation

inner sample diameter is greater than 1:5 promoting a dilution rate of sheath to sample of at least 125. (Durack and Robinson 2000) After the point of analysis, the droplets are charged accordingly by the deflection plates and the sample steams are trajected into the well plates or the waste bin. The sheath fluid serves as the conductive liquid allowing for successful charging and sorting of the particles. The MoFlow cell sorter has the capability of sorting up to four size ranges and also determines a particle count of collected particles in each bin.

Typically, the sheath fluid is a phosphate buffered isotonic saline to satisfy metabolic needs of the cells after the sort. On the first trial of analyzing stormwater samples, a buffered isotonic saline was used to sort our particles but after analyzing the isotonic saline blank without any sorted particles, it was determined that the blank contained a large quantity of metal impurities. Despite the typical usage of buffered saline in cell sorting, sheath fluids down to 10mEq/L should provide enough conductivity for

the sort. (Shapiro 2003) Based on this assumption, 99.999% (metals basis) Puratonic saline was diluted in MilliQ water to 10meq/L and used as the sheath fluid in the subsequent sorts. This saline was cleaner, but still contained a minimal amount of metals. Since 10mEq/L worked sufficiently, 1meq/L of the same Puratonic saline was used for the sheath fluid to further reduce introduction of metal concentration interference with storm sample and proved successful. The 1meq/L saline solution was used throughout the rest of the sorts.

The cell sorter was calibrated using 0.2 μm, 0.4 μm, 0.7 μm, and 1.25μm 1% polystrene microspheres. The microspheres were diluted in MilliQ water to concentrations and size fractions comparable to estimated particle numbers in a highway runoff sample. The percent of the total particle number in the calibration solution for the 0.2 μm, 0.4 μm, 0.7 μm, and 1.25μm sizes were 43.5%, 46.1%, 8.84%, and 1.55% respectively.

After running the microsphere sample through the cell sorter, circular gates were drawn around the four distinct clusters of 0.2 μm, 0.4 μm, 0.7 μm, and 1.25 μm microspheres that resulted on a side scattering v. forward scattering plot. Typical side and scattering plot of microsphere sample is shown in Figure 2-16. The light

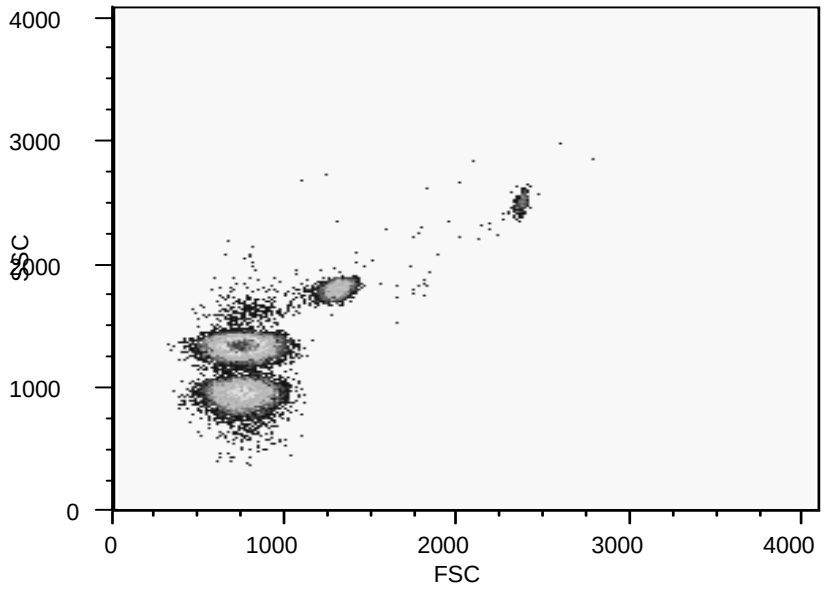


Figure 2-16 A typical cell sorter side and forward scattering plot for polystyrene calibration beads

scattering plots are read like topography plots with the centers of the clusters corresponding to larger concentrations and the outlying areas to lower concentrations. Based on the gates drawn around the four clusters, the particle size distribution in the calibration solution was 35.9%, 49.5%, 10.5%, and 1.78% for 0.2 µm, 0.4 µm, 0.7 µm and 1.25 µm respectively. The good agreement between known and measured number percentages of microspheres in the sample indicate that the cell sorter can accurately sort and count this range of small particles between 0.2 and 1.25 µm. Based on the uncertainty of the gating boundaries in an actual sample, the gate around the 0.2 µm microsphere was estimated to include a size range of 0.1-0.3 µm; corresponding size estimated for the other gates were 0.3-0.5 µm for the 0.4 µm gate, 0.5-1.0 µm for the 0.7 µm gate, and 1.0-1.5 µm for the 1.25 µm gate.

The gates calibrated to the microspheres were used to sort the highway and synthetic runoff samples. Prior to each cell sorter run, the microsphere bead mixture was rerun and the gates were modified as needed to account for instrument variability. All parameters of the cell sorter were monitored by the cell sorter operator throughout the course of the sort. A representative side and forward scattering plot for stormwater runoff sample is shown in Figure 2-17.

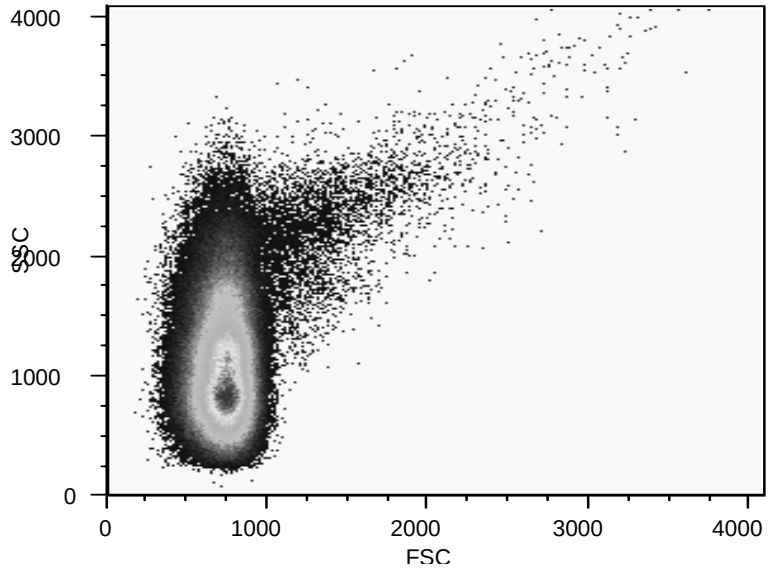


Figure 2-17 A representative side and forward scattering plot prepared by cell sorter for stormwater runoff sample

In comparison to the information presented in Figure 2-16, the scattered data shown in Figure 2-17, yields a single plot of particles across a large range of side and forward scatter signals rather than four distinct clusters. This is expected due to the continuous size distribution and variable composition of stormwater particles. Actual stormwater runoff particles and synthetic water particles are imperfect spheres which may yield different results depending the angle from which the particle is approaching the laser. The nominal sizes of the collected particles 0.1-0.3 µm, 0.3-0.5 µm, 0.5-1.0 µm, and 1.0-1.5 µm represent an approximation of their actual sizes using the microspheres as a reference. Highway particles are more variable in their share and composition than the microspheres and will undoubtedly differ in their refractive index.

CHEMICAL ANALYSIS OF CONSTITUENTS SORBED TO PARTICLES

Analysis of Metal Constituents

Samples for metals analysis are poured into new plug-seal polypropylene centrifuge tubes (Fisher Scientific, Pittsburgh, PA) and acidified with TraceMetalGrade Nitric Acid (Fisher Scientific, Pittsburgh, PA). The Agilent 7500i ICP-MS in the Department of Civil and Environmental Engineering at UCDavis is operating an Argon plasma at 1350W. Sample uptake is 0.4mL/min from a peri-staltic pump with 1.2L/min carrier gas through a Babbington-style nebulizer into a Peltier-cooled double-pass spray-chamber at 2C. 1L/min auxiliary and 12L/min plasma gas are added for a total of 14L/min separated from Ni cones by a sampling depth of 8.5mm. Oxides are tuned to <0.4% CeO/Ce and double ions to 1.5% Ce++/Ce+. Sensitivity (cps/ppb) is 20k for Li, 30k for Y, and 20k for Tl.

Ultimate detection limits are about 1pg (1 part-per-trillion in a <1mL sample) for nearly all metals in the periodic table. Non-metals (such as Si, Cl…) plus those with interferences (such as Fe, Ca, K…) are higher, around 1ng. External calibrations are performed starting as low as 10pg/mL for trace elements, through 100ug/L for minor elements, continuing up to 100mg/L for major elements such as Na, Mg, Al, K, Ca, and Fe. Sequences are run automatically with a Cetac ASX-510 (Omaha, NE)

liquid sampler, which uses a flow-through rinse station for the sampling probe after each sample, followed by a static rinse bottle of dilute nitric acid.

All analysis, quality control and quality assurance were performed according to USEPA method 6020 and other standard method specified in Standard Reference Manual in the NIST 1648 (Gaithersburg, MD) and SLRS-4 (NRC, Ottawa, Ontario, Canada).

Analysis of Organic Compounds

The pre- and post-centrifuge water samples were initially filtered through glass fiber filters (GF/F) to separate the PAHs into the dissolved and particulate phases. Filtered water was then passed through XAD-2 resin column to collect PAHs. Each fraction of sample (50 mL) containing different size of particles, which were collected from the settling column, was also filtered through glass fiber filters (GF/F). XAD-2 resin samples were extracted with acetone and hexane sequentially using Soxhlet. Glass fiber filters containing particles were extracted with acetone and dichloromethane sequentially using Soxhlet. Surrogate standards (naphthalene-d_8, acenanaphthene-d_{10}, phenanthrene-d_{10}, crysene-d_{12}, and perylene-d_{10}) were added before extraction to validate extraction procedures. Moisture in extracts was removed by anhydrous sodium sulfate. Extracts were concentrated to 2 mL of hexane and were cleaned up using Alumina column chromatography, which was eluted with pentane:dichloromethane (1:1) mixture. Internal standards (pyrene-d_{10}) were added before instrumental analysis to calculate surrogate recovery rates. Identification and quantification of PAHs were accomplished using a Hewlett-Packard HP 6890 gas chromatography equipped with a J&W (Folsom, CA, USA) DB-5MS fused-silica capillary column (30 m $\times$ 1.25 mm ID, 0.25 μm film thickness) and a Hewlett-Packard 5973 mass selective detector. The oven temperature started initially at 60 °C, programmed for three temperature ramps, to 150 °C at 15 °C/min, to 220 °C at 5 °C/min, and to 310 °C at 10 °C/min, and held for 10 min. The mass selective detector was operated in the electron ionization and the selected ion monitoring modes.

METHODS TO EVALUATE METAL MOBILIZATION

Distribution of Metals between Particulate and Dissolved Phases

The most common way to express the distribution of metals between highway particles and storm water runoff is by reporting the fraction of the metal present in the dissolved form, f_d (e.g., Sansalone and Buchberger, 1997a,b).

$$f_d = \frac{C_d}{C_t} \qquad (2\text{-}7)$$

where,

C_d = dissolved (filtered) metal concentration (μg/L),

C_t = total (unfiltered) metal concentration (μg/L).

Although this ratio is easy to calculate, it varies widely for a given metal at a given site, in part because it depends heavily on the total suspended solids concentration in the storm water.

An alternative and more fundamental way to quantify the extent to which metals partition between the particulate and dissolved phases is to report a distribution coefficient, K_D as defined by the following equation:

$$K_D = \frac{\left(\frac{C_t - C_d}{TSS}\right)}{C_d} \qquad (2\text{-}8)$$

where,

K_D = partition coefficient between particulate and dissolved phase (L/kg),

TSS = total suspended solids concentration (mg/L).

A large K_D value indicates that most of the metals in the sample are likely to be particle associated, while a smaller K_D value means that a larger fraction of the metal will remain in solution. Unlike f_d, K_D normalizes for the TSS concentration of the runoff sample and is therefore more likely to be constant as long as other characteristics of the particles and solution do not change greatly. The distribution coefficient does, however, typically depend on characteristics of (i) the solution (pH, temperature and chemical composition), (ii) the particles (surface area, surface

charge, chemical composition), and (iii) the metal (valence, association with other constituents in solution).

Humic substances or other organic ligands can affect K_D significantly by promoting the release of particle associated metals into the aqueous phase (Morel and Hering, 1988). Humic substances are major constituents of soils and surface waters comprising various kinds of functional groups exhibiting a range of affinities for metal ions (Kerndorff and Schnitzer, 1980; Lu and Allen, 2002). Carboxylic, phenolic and hydroxyl groups are the humic material components primarily responsible for complexation of metal cations (Davis, 1984). The presence of such metal binding organic ligands in storm water is in part reflected in the TOC or COD fractions, although these broader measures of organic content are likely to include some organic constituents with little or no metal binding capabilities (e.g., nonpolar hydrocarbons such as oil). Ligand promoted metal dissolution from storm water particles is of particular concern because of the greater bioavailablity and mobility of metals in this form (Sansalone et al., 1997). The partitioning of metals between particles and the dissolved phase thus plays a critical role in the distribution, behavior, fate and transport of metals in aquatic environments (Turekian, 1977; Benoit and Rozan, 1999).

The conceptual model outlined above can be expressed in chemical terms by noting that metals in runoff can be present in three different “phases”, freely dissolved, bound to organic ligands, or bound to particles. The total dissolved metal concentration will then be represented by the sum of the freely dissolved and the ligand bound metal fractions. Examples of the chemical reactions, equilibrium expressions and mass balance governing this process for copper are:

$$Cu^{2+} + \equiv X \leftrightarrow \equiv X - Cu^{2+} \qquad K_{\equiv X\text{-}Cu}$$

$$Cu^{2+} + L^{-} \leftrightarrow Cu - L^{+} \qquad K_{Cu\text{-}L}$$

$$K_{\equiv X\text{-}Cu} = \frac{\left[\equiv X - Cu^{2+}\right]}{\left[Cu^{2+}\right]\left[\equiv X\right]}$$

$$K_{Cu\text{-}L} = \frac{\left[Cu - L^{+}\right]}{\left[Cu^{2+}\right]\left[L^{-}\right]}$$

$$Cu_T = \left[Cu^{2+}\right] + \left[Cu - L^{+}\right] + \left[\equiv X - Cu^{2+}\right]$$

$$Cu_T = \left[Cu^{2+}\right]\left(1 + K_{Cu\text{-}L}\left[L^{-}\right] + K_{\equiv X\text{-}Cu}\left[\equiv X\right]\right)$$

where,

Cu^{2+} represents the freely dissolved copper ion,
$\equiv X$ represents binding sites on the particle not occupied by copper ions,
L^{-} represents the freely dissolved organic ligand,
$\equiv X\text{-}Cu^{2+}$ represents the particle bound copper species,
Cu $-L^{+}$ represents the ligand bound copper in solution,
[ ] represents the concentration (mol/L) of any of the above 5 species,
$K_{\equiv X\ Cu2+}$ = Equilibrium constant for the formation of particle bound copper,
$K_{Cu\ -L+}$ = equilibrium constant for the formation of ligand bound dissolved copper.
Cu_T = total molar copper concentration

This model ignores potentially important copper hydroxide complexes (e.g., $CuOH^{+}$, $Cu(OH)_2^{0}$) because at the pH observed in our field and laboratory testing (6-7) such complexes would not be significant. Extending the model to consider these complexes in other situations would be straightforward.

Limited research has been performed to evaluate the significance of metal complexation by dissolved organic carbon on the particle-water distribution of metals in synthetic and natural surface waters (Davis, 1982; Lin et al., 1994; Lu and Allen, 2002). A recent storm water runoff characterization study performed by the UC Davis Department of Civil and Environmental Engineering for the Department (CTR report reference), found a correlation between the measured distribution coefficients of metals and the DOC concentration in highway stormwater runoff. The result of this preliminary investigation is shown in Figure 2-18. As shown, it appears that DOC is a dominant factor influencing the mobility of metals in stormwater runoff, resulting in potential changes in dissolved copper concentrations of nearly a factor of 10 for runoff with the same TSS and total copper concentrations.

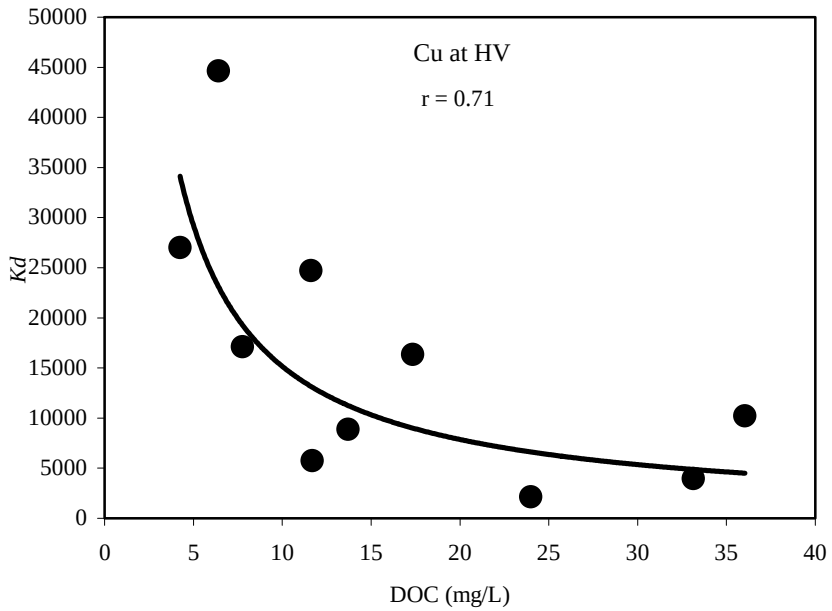


Figure 2-18 Influence of DOC on copper (Cu) desorption

This portion of the study was performed to determine the link between DOC concentration and metal mobility. Specific methods used to develop the link between metals and COD is described below.

Procedures Used to Link Heavy Metal Mobilization to DOC Concentration

Materials and Reagents. All solutions were prepared using deionized, distilled water (Millipore Milli-Q System) with a resistivity of greater than 18.2 MΩ cm. Hydrocholoric acid and sodium hydroxide (ACS Certified grade; Fisher Scientific, Fairlawn, NJ) were used to adjust solution pH. Solvents used included acetonitrile, methanol, diethyl ether, methylene chloride, acetone and water; all were ACS certified or Optima grade (Fisher Scientific, Fairlawn, NJ). Acrylic ester resin Supelite DAX-8 (Sigma Aldrich, St. Louis, MO) and hydrophobic, polyaromatic resin Amberlite XAD-4 (Sigma Aldrich, St. Louis, MO) were used for the humic substances extraction. Millipore Isopore polycarbonate membrane filters (Fisher Scientific, Pittsburgh, PA) were rinsed with MilliQ water prior to sample filtration. All bottles and glassware was cleaned with liquid Alconox, rinsed with hot tap water and then rinsed with copious amounts of MilliQ water prior to use. All internal pieces of the Westfalia Separator were stainless steel and washed, rinsed with MilliQ, and rinsed again with acetone and methylene chloride prior to use. New, sterile Corning

polypropylene 15 mL centrifuge tubes (Fisher Scientific, Pittsburgh, PA) were used in the kinetics and equilibrium experiments. Compressed N_2 gas used for pressure filtration was certified as 99.997% pure. The storm water particles used in this experiment were collected on January 8, 2005 on the third day of a multi-day storm event at the I 80 UC Davis sampling site using procedures described above.

Humic Substances Extraction. A two column array of Supelite DAX-8 resin and Amberlite XAD-4 resin was used to isolate a portion of the humic and fulvic acids from the runoff sample using a procedure adapted from previous studies (Thurman and Malcolm, 1981; Aiken et al., 1992), Prior to use, the resin was cleaned with NaOH and then sequentially soxhlet extracted for one hour each with methanol, diethyl ether, and acetonitrile according to the Thurman and Malcolm protocol. The resin was then packed into 2.5 cm diameter, 45.7 cm length glass columns between glass wool plugs, the columns were fitted with Teflon endcaps and tubing, and the resin was further cleaned with three successive rinses of 0.1 N HCl-0.1 N NaOH immediately prior to use.

Using compressed N_2 and a pressure filtration system described by Datta et al., (2004), 160 L of centrifuged and filtered (0.45 µm, Millipore Isopore polycarbonate membrane filter, Fisher Scientific) storm water runoff was passed through the two column series at a rate of 50-80 mL/min. Each column was separately back eluted with 2 L of 0.1 M NaOH and immediately acidified to pH 2 with HCl to minimize DOC alteration at high pH. Eluates were reconcentrated on a 2.5 cm diameter x 15.2 cm length column of the appropriate resin, and then back eluted with 750 mL of base and acidified to pH 2. The sample was then characterized by TOC analysis to determine the concentration of humic substances in each fraction of the sample.

Equilibrium Study. Dilutions of a 19.2 mg/L DOC stock solution were made to produce concentrations of 0, 3.6, 9.1, 11.8, 14.8 mg/L DOC. The concentrated particle solution (TSS=20,485.7 mg/L) was vigorously mixed and pipetted in 1 mL increments at random into 15 mL sterile, polypropylene centrifuge tubes. 14 mL of each DOC solution (including 0 and the stock) was added to 6 centrifuge tubes. All tubes were equilibrated in the dark at room temperature in an end-over-end tumbler rotating at approximately 20 rpm for a period of 7 days. The time period was

selected based on a prior rate study. At the end of the 7 day period, each tube was removed from the tumbler, filtered and the pH measured. Samples were stored at $4^{o}C$ until analysis for metals and TOC. Duplicate samples were prepared for each sample in this study.

A sample (and duplicate) containing 1 mL of the concentrated particle solution and 14 mL of MilliQ water was strongly acidified and analyzed for dissolved metal concentration using ICP-MS. This last sample provides an estimate of "total extractable metals" concentration, which represents all metals sorbed to the particles available for removal during particle:water interaction. This was the best approach for determining the metals available for partitioning into the dissolved phase; a complete particle digestion would have significantly overestimated the metals available to aqueous solution from the particle fraction of the mixture. Metals concentrations were measured in the samples using procedures described above. All filtered samples were also analyzed for Non-purgable Organic Carbon (NPOC) using a Shimadzu TOC-5050 Analyzer. A calibration curve was prepared prior to processing the samples using known concentrations of potassium hydrogen phthalate: 0, 5, 10, and 20 mg DOC/L. The r-squared value for the calibration curve was 0.9991 for the curve used to analyze the dilutions of DOC solution, and 0.9994 for the DOC measurements of samples containing both DOC and particles from the kinetics and equilibrium studies.

MICROSCOPIC IMAGE ANALYSIS OF PARTICLES

In an effort to better characterize the sizes, shapes and chemical compositions of individual particles in highway runoff, a scanning electron microscope method was employed. Two types of particle samples were analyzed as part of the initial development of this method, (i) particles collected from the UC Davis I 80 highway site using the Westfalia flow through separator, and (ii) particles collected by rinsing brake pads and rotors of cars with a "synthetic rain" solution during visits to an automotive repair facility. The respective particle samples were diluted in methanol and were placed on polycarbonate filters (0.25 µm) using disposable syringes. The scanning electron microscopy (SEM) images were acquired using an XL30-SFEG at an operating voltage of 200 volts. An energy dispersive x-ray spectroscopy (EDS)

system (EDAX Phoenix) was used for elemental analysis. The system automatically scans 100 fields of approximately 500μm x 400μm and records the mass fraction of 15 elements, the largest dimension of the particle and a shape factor. Depending on the initial particle concentration in the sample different dilutions must be prepared to achieve an appropriate average number of particles within each visual field.

3. RESULTS AND DISCUSSION

REPRESENTATIVE PARTICLE NUMBER AND PARTICLE MASS FRACTION IN HIGHWAY RUNOFF

Figure 3-1 shows the number fraction (top) and calculated mass fraction (bottom) of particles in different size ranges, which were calculated for all events for the entire runoff. The horizontal axis indicates the individual particle diameter ranges. The box plots show the number fraction and mass fraction of particles in individual size ranges for all events at three sites in Los Angeles. The

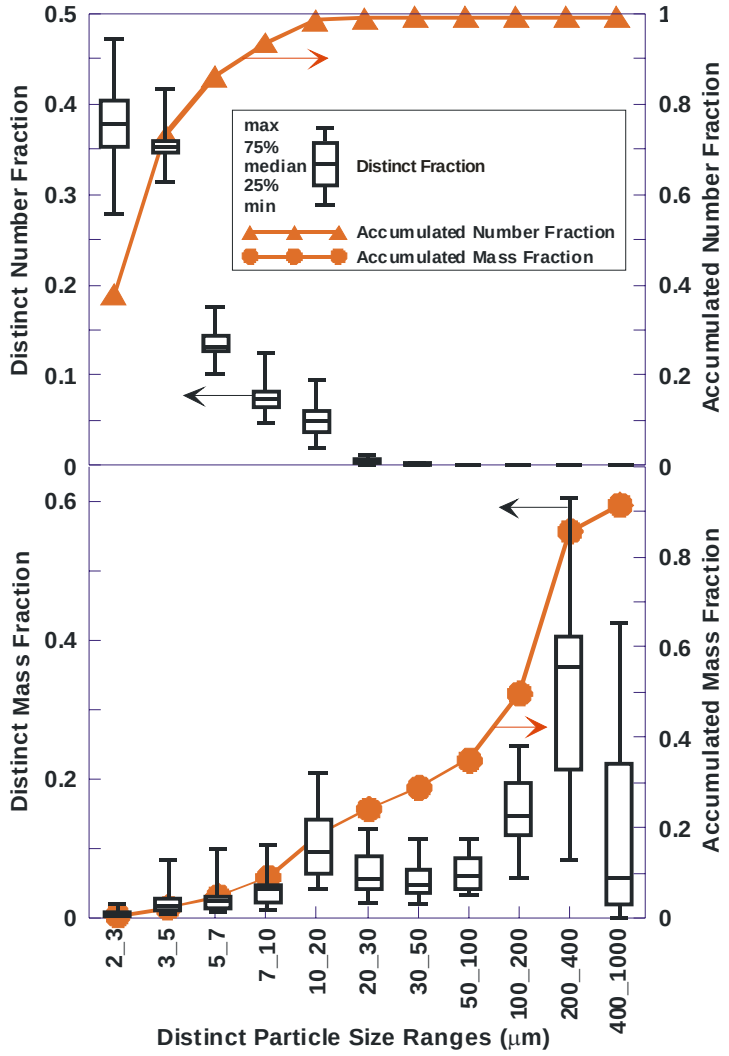


Figure 3-1 Particle number and mass fractions for all storm events captured from three highway sites in Los Angeles during 2002-03 rainy seasons

continuous lines correspond to the secondary y-axis and are the accumulated number fraction (top) and the accumulated mass fraction (bottom) of median values of distinct size ranges.

An additional statistical summary of particles captured from all storm events from the three highway sites in Los Angeles is reported in Table 3-1. Information presented in Figure 3-1 and Table 3-1 demonstrates that small particles are large in number. However, they contribute less to calculated mass. From the accumulative lines, more than 90% of particles in number are less than 10 μm while their mass contribution is less than 10%. Particles larger than 100 μm contribute more than 60% of the calculated mass.

Table 3-1 Statistical summary of particle concentration (#/mL) for different particle size ranges for the three highway sites in Los Angeles during 2004-05 rainy season

Statistical parameter	Particle size ranges (μm)				
	0.5_400	**0.5_8**	**8_20**	**20_100**	**100_400**
Number of cases	200	200	200	200	200
Minimum	31,585	31,440	105	0	0
Maximum	89,669,480	89,074,025	550,990	42,930	1,535
Median	6,591,736	6,581,381	11,742	703	0
Mean	12,214,696	12,186,720	26,132	1,816	28
Std Dev	16,270,320	16,244,764	53,010	4,340	123

Particle concentrations decreased with increasing accumulated rainfall, as shown in Figure 3-2. As can be seen, there is 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 as will be further shown below.

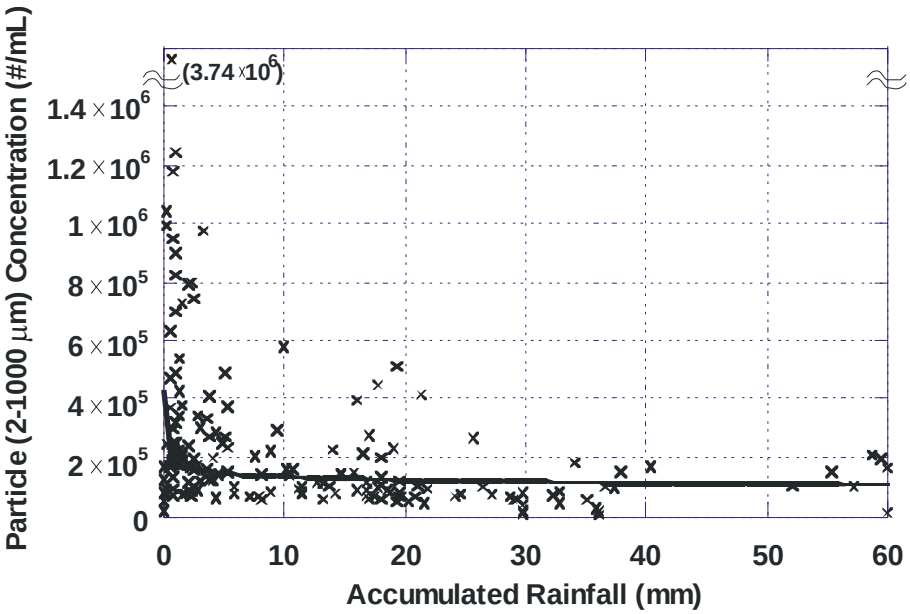


Figure 3-2 Particle number concentration vs. accumulated rainfall for 16 storms from three monitoring sites in Los Angeles during the 2002-2003 rainy season

CORRELATION AMONG PARTICLE CONCENTRATION, TURBIDITY AND TOTAL SUSPENDED SOLIDS

TSS concentration and turbidity increased with increasing particle concentrations, as shown in Figure 3-3. The log of particle concentration was linearly correlated to the log of TSS and turbidity with R^2 values of 0.689 and 0.692 and significance p value of less than 0.001. The log of TSS and turbidity were also correlated with R^2 of 0.485 and p value less than 0.001. The 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.

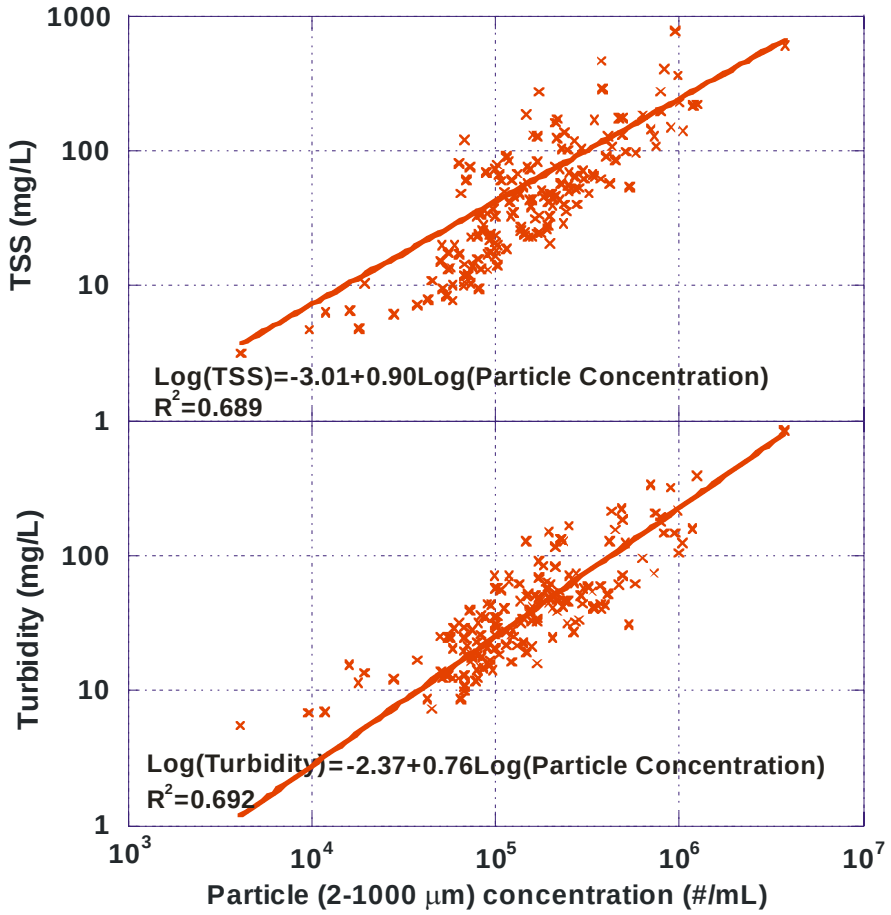


Figure 3-3 Correlation between particle number concentration, turbidity and TSS

Figure 3-4 shows particle median diameter in 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 occurs 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 (please refer to Li et al. 2005 for a discussion of the accuracy of the instrument in measuring concentrations of larger particles). For example, for TSS concentrations greater than 200 mg/L, the contribution of particles larger than 30 microns was more than 60% by mass (assuming spherical particles with uniform density in all size ranges).

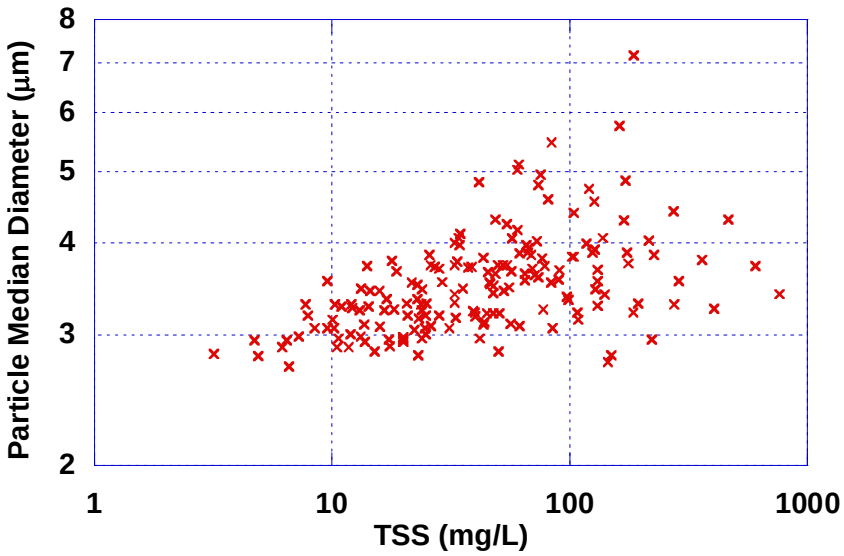


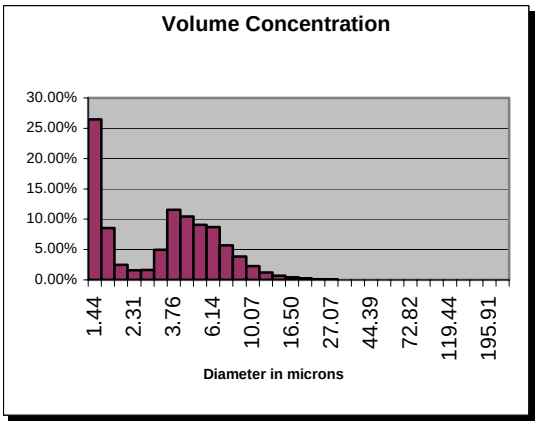
Figure 3-4 Particle median diameters of grab samples vs. total suspended solids concentration

ON-LINE PARTICLE SIZE MEASUREMENT OF RUNOFF

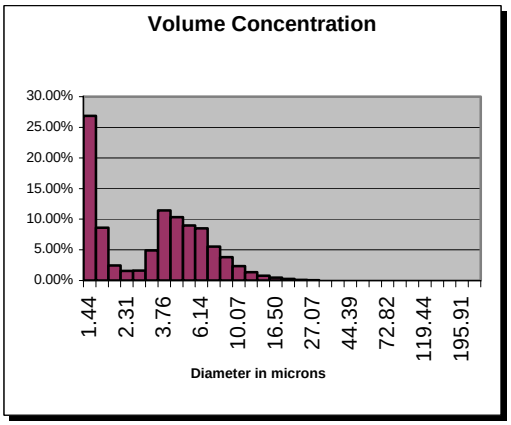
Two synthetic runoff samples were prepared for on-line particle size measurement experiments. For the first experiment, the synthetic runoff sample was allowed to settle for 30 minutes. A sample was taken from the top inch of the solution to avoid the larger settled particles near the bottom. Three dilutions of this sample were prepared for on-line particle size measurement. The runoff was mixed with deionized (Milli-Q) water in 1:3, 1:1 and 3:1 volumetric ratios. Sample was continuously recycled to the sample flask during the experiment to keep the volume constant. One particle size measurement was taken every 10 seconds for a total of 10 measurements. The magnetic mixer constantly mixed each sample so that the particles were evenly distributed throughout the sample flask during measurements. For each on-line particle size analysis, 200mL of the well-mixed solution was taken for solid measurement.

The first parking lot runoff solution was analyzed while the solution was in a settled state, which represented runoff containing only the particle sizes that stay suspended for longer amounts of time. Four separate dilution samples were

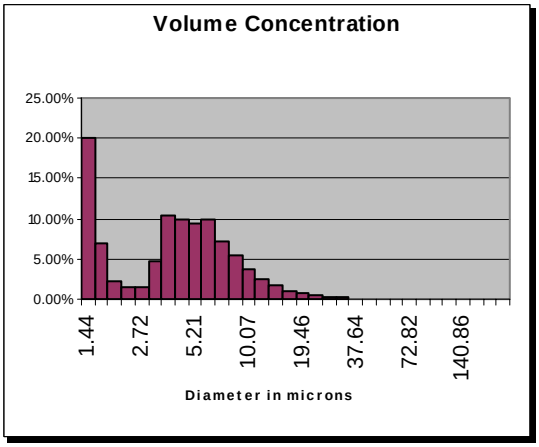
analyzed to find the point of inconsistency between the 10 measurements of each sample. Figures 3-5 show the continuity of two of the measurements of Sample 4 (the pure runoff sample).



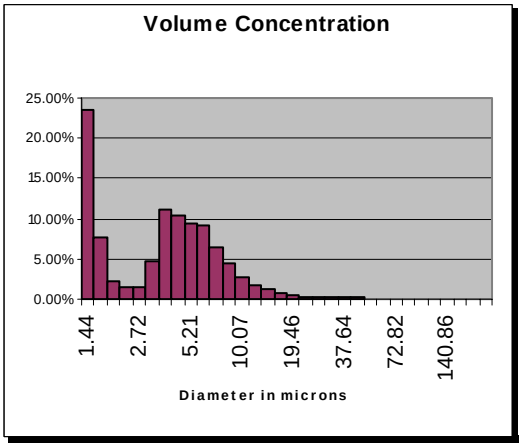
(a) Measurement 6-100% supernatant synthetic runoff



(b) Measurement 8-100% supernatant synthetic runoff



(c) 75% supernatant synthetic runoff and 25% Milli-Q water



(d) 75% supernatant synthetic runoff and 25% Milli-Q water

Figure 3-5 On-line measurement of synthetic runoff particles for experiment 1

According to the results, none of the four samples contained an amount of particles that would hinder the consistency of the measurements. All 10 of the measurements of each of the samples showed continuity, representing the LISST-100's ability to continuously measure even pure and non diluted settled parking lot runoff.

For the second experiment, ten different dilutions of synthetic runoff were prepared. The runoff was first sieved through an 850 μm sieve and a 450 μm sieve to avoid any particles larger than 400 μm from possibly obstructing the flow of the sample since all ten of the samples were taken from the runoff as it was being mixed, meaning that the runoff had no time to settle. The dilution of synthetic runoff was prepared in the order shown in Table 3-2.

Table 3-2 Dilution mix of synthetic runoff with Milli-Q water

% Dilution	Dilution mix
90	200mL synthetic runoff + 1,800mL Milli-Q water
80	400mL synthetic runoff + 1,600mL Milli-Q water
75	500mL synthetic runoff + 1,500mL Milli-Q water
70	600mL synthetic runoff + 1,400mL Milli-Q water
50	1,000mL synthetic runoff + 1000mL Milli-Q water
40	1,200mL synthetic runoff + 600mL Milli-Q water
30	1,500mL synthetic runoff + 500mL Milli-Q water
20	1,600mL synthetic runoff + 400mL Milli-Q water
0	2,000mL of pure synthetic runoff

The second experiment was conducted to determine at which TSS concentration the accuracy of the on-line particle size measurement by LISST-100 would fail because there were too few particles in the sample. To accomplish this objective, different synthetic runoff dilutions prepared as outlined above were analyzed. Partial results of this experiment are shown in Figure 3-6. According to these results, there were none or minor variation in particle size distribution for samples at higher dilutions.

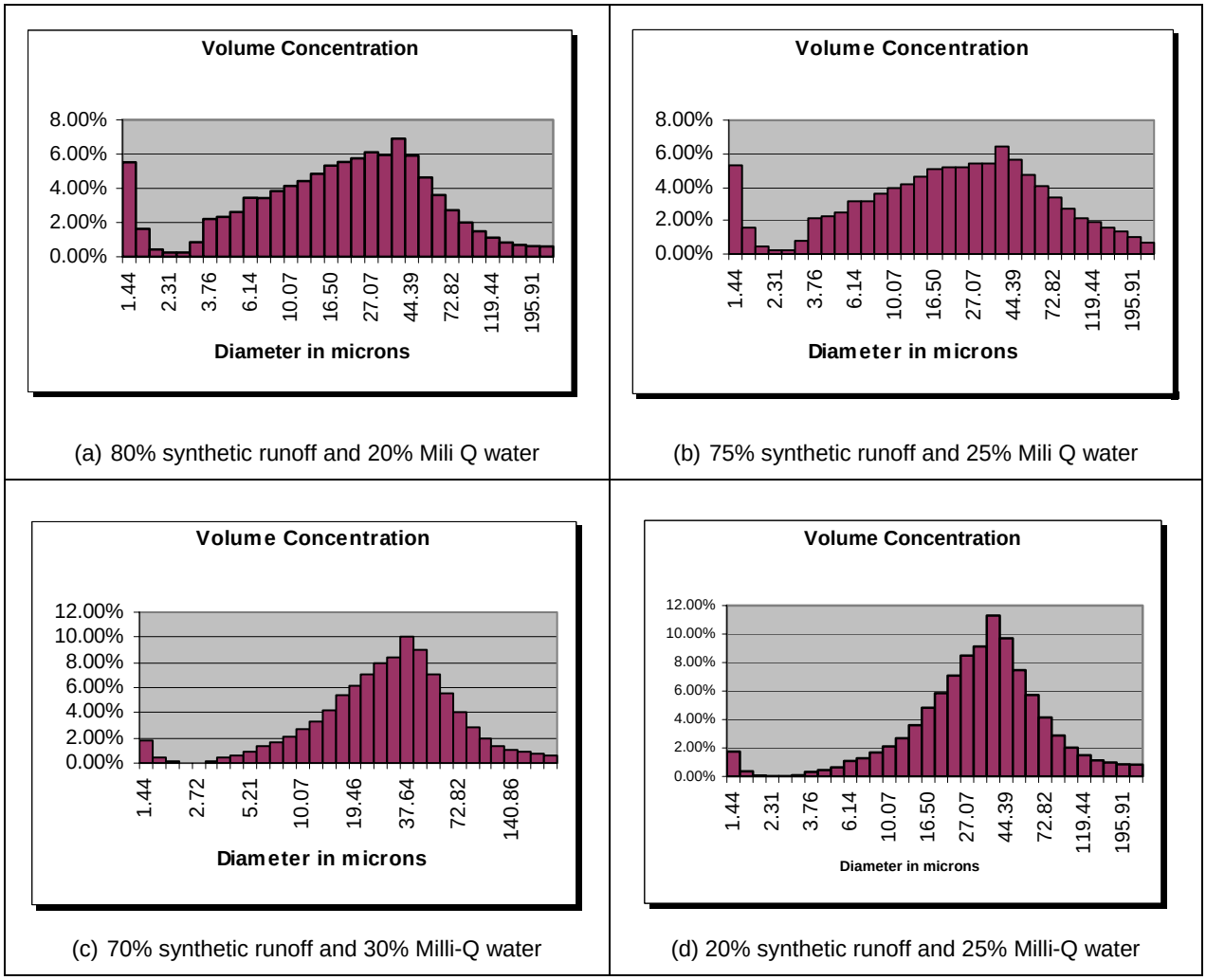


Figure 3-6 On-line measurement of synthetic runoff particles for experiment 2

As shown in Figure 3-6, the results of samples above 75% dilution show a good agreement among particle size distributions. However, the accuracy of the measurements changed dramatically when the runoff dilution reached 70% or below. As shown in Figure 3-6a and 3-6b fair amount of particles in the 1.2-1.44 μm range were present while all of the more diluted samples barely showed any particles in that range. Also, samples above 70% dilution have about the same distribution of particles in the 3-14 micron range while samples below 70% dilution have much lower concentrations of those particles. The corresponding measured and calculated TSS values for various samples that were used for the

on-line particle size measurement are shown in Table 3-2. The measured and calculated TSS concentrations were found to be comparable at values of about 260 mg/L for samples with 75% dilution. A large variation was observed between the measured and calculated TSS when the sample dilution reached 70% or lower. From the above results, it was concluded that the LISST 100 instrument is capable of accurately measuring the amount of particles present in the solution when the TSS concentration is below 260 mg/L.

Table 3-3 Comparison between measured TSS concentrations and those calculated using particle concentration

Sample dilution (%)	Measured TSS (mg/L)	Calculated TSS based on particle concentration (mg/L)
90	95.2	107.7
80	160.4	164.7
75	263.6	257.1
70	320	199.1
50	444.8	188.3
40	634.4	202.5
30	986.6	234.3
20	1008.2	219.2
0	1909.6	235.0

MOBILIZATION OF HEAVY METALS BY DOC

The distribution of metals between highway particulates and the aqueous phase was measured in contact with solutions containing DOC concentrations ranging from 0.5 mg/L to 15 mg/L in laboratory experiments and these results were used to derive the best fit values for K_{D+},$K_{Cu\text{-}L+}$ and the analogous parameters for other metals. The values of these equilibrium constants for copper are 4.22×10^4 and 4.96×10^8. These fitted values were then used to examine how the fraction of metal present in the dissolved form in a runoff event would vary as a function of DOC concentration holding other factors constant. To provide a specific example, the characteristics of the storm water collected on January 8, 2005 at the UC Davis site were used in the simulation (TSS = 71.7 mg/L; Cu_T = 36.4 g/L; ZnT = 64.7 g/L). Results of these simulations are shown in Figures 3-7 and 3-8 for copper and zinc, respectively. For both metals nearly all of the metal

is associated with particles in the absence of dissolved organic carbon. As DOC concentrations increase to 35 mg/L, the fraction of the total metal present in the dissolved phase increases rapidly, ultimately exceeding metal fractions of 0.8 in the DOC complexed metal form. In no case does the freely dissolved form contribute a significant fraction to the total metal concentration. The net effect of DOC binding of copper in this scenario, for example, is to increase the dissolved copper concentration by a factor of 2260 in comparison to the 0 mg/L DOC case. These results suggest the critical importance of DOC in mobilizing metals from highway particles.

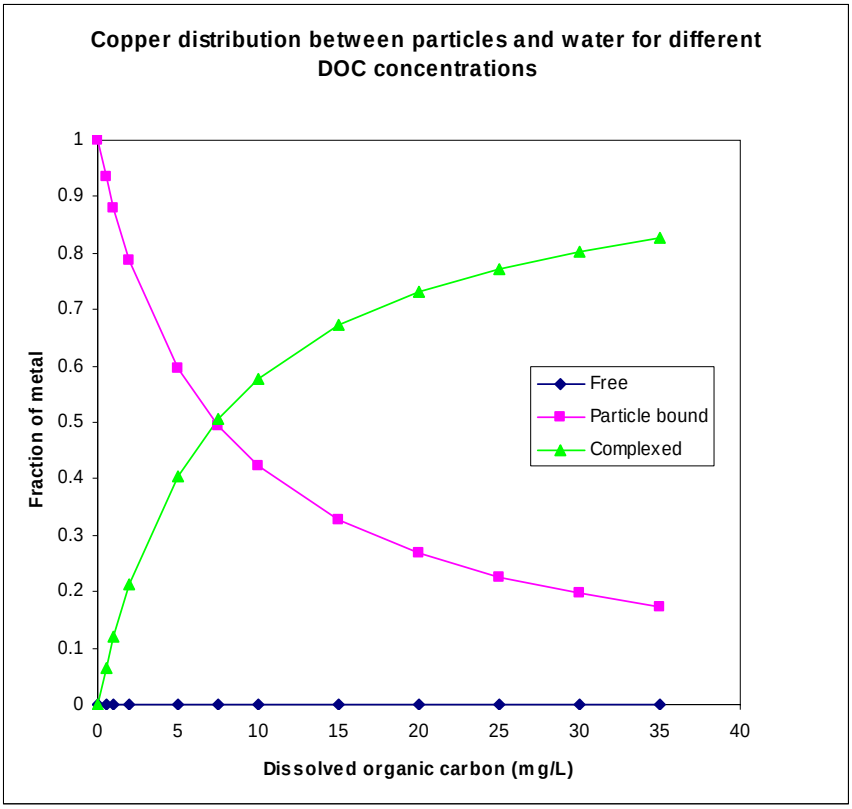


Figure 3-7 Effect of dissolved organic carbon concentration on the mobilization of particle bound copper in highway runoff

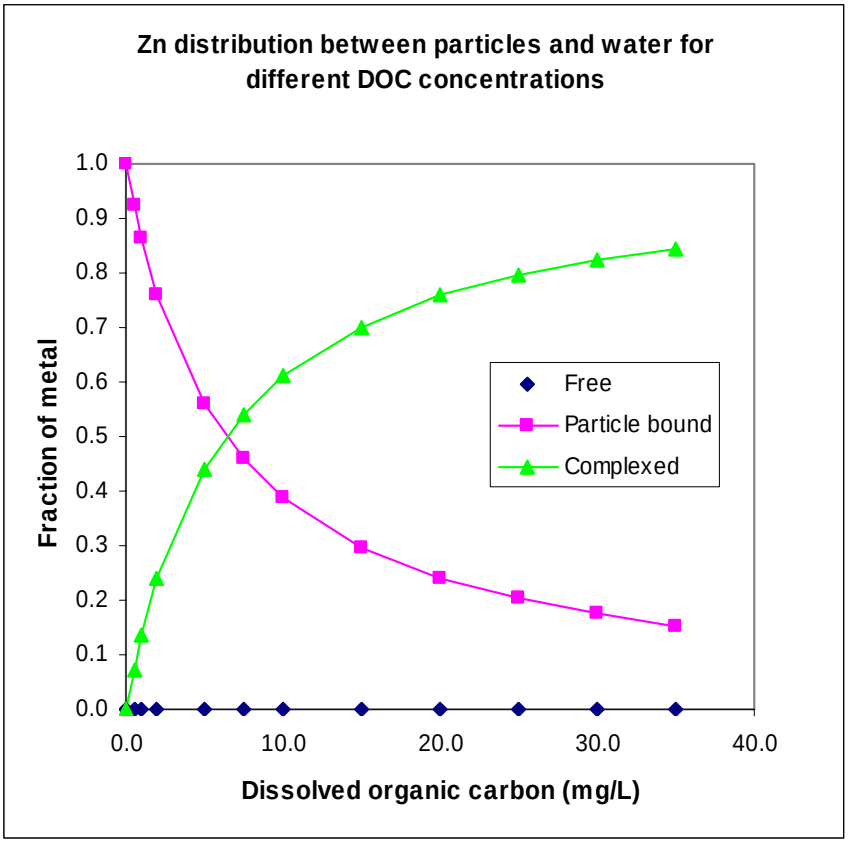


Figure 3-8 Effect of dissolved organic carbon concentration on the mobilization of particle bound zinc in highway runoff

INORGANIC CONSTITUENTS ASSOCIATED WITH SMALL PARTICLES

The concentrations of selected metal constituents in stormwater runoff samples collected from the UC Davis highway site were measured for four very small particle size ranges isolated using the cell sorter method (0.1-1.5 μm). Concentrations of metals associated with these very small particulates are of interest for two reasons. First, these particles may pass filters used to delineate dissolved and particle bound metal fractions, causing them to be erroneously assigned to the dissolved fraction. Second, these types of particles are the most likely to pass through treatment BMPs and enter receiving waters. The measured volumetric metal concentrations within each size fraction (μg metal/volume solution) were transformed to solid phase concentrations (μg metal/mass particle) by assuming that particles are spherical and have a density of 2.3 g/cm^3. To determine whether a metal was "enriched" or "depleted" in a

particular size fraction, the solid phase metal concentration was divided by the average solid phase metal concentration for the entire storm event. The latter value was calculated as:

$$\text{Bulk solid phase concentration } (\mu\text{g/mg}) = \frac{\text{total metals } (\mu\text{g/L}) - \text{dissolved metals } (\mu\text{g/L})}{\text{TSS (mg/L)}}$$

Ratios of solid phase concentrations within individual particle size classes to solid phase concentrations in the bulk sample are shown in Table 3-3. As expected, fewer particles were collected in the larger size bins resulting in the large number of gaps in the data for the larger fractions. In general, the highway runoff samples show that the concentrations of chromium, nickel, copper, zinc and lead on very fine particles are considerably larger than the corresponding concentrations in bulk stormwater particles. In contrast, the fine particle:bulk concentration ratio is closer to unity, ranging from 0.1 to 10, for elements that predominate in the earth's crust such as aluminum, manganese, and iron. the metal fractions vary between storms due to the variation in storm characteristics, but the crustal element ratios remain close. The greater consistency of the concentration ratio for the crustal elements between different particle size classes and storm events is expected because it is assumed that crustal elements associated with fine particles have their origin in larger soil particles with similar elemental composition.

Table 3-4 Ratio of particle bound concentrations of selected metals to their bulk particle bound concentrations in stormwater runoff

Storm Number	Size Range (µm)	Mass of particles (g/L)	Fraction of Metal Relative to Bulk Solution[c]								Total Mass%
			Al	Mn	Fe	Cr	Ni	Cu	Zn	Pb	
3[b]	0.1 - 0.3	1.94E-04	1.2	8.1	1.2	48.1	48.2	92.1	200.5	51.0	22.0
	0.3 - 0.5	6.25E-04	0.3	1.4	0.4	14.9	14.6	27.1	57.8	9.8	6.2
	0.5 - 1.0	9.09E-04	0.3	3.1	0.3	10.2	8.5	18.6	33.1	-	4.4
	1.0 - 1.5	2.70E-04	-	-	-	-	-	-	-	-	-
4[a]	0.1 - 0.3	2.56E-05	4.7	21.8	11.7	865.2	659.3	398.8	994.5	72.7	161.3
	0.3 - 0.5	8.68E-05	2.0	8.6	4.2	271.9	188.0	119.7	293.5	44.3	52.2
	0.5 - 1.0	4.61E-04	-	-	-	-	-	-	-	-	-
	1.0 - 1.5	3.49E-04	-	-	-	-	-	-	-	-	-
5[a]	0.1 - 0.3	1.82E-05	13.3	38.5	22.2	2941.0	2285.2	2738.3	159.7	158.5	226.4
	0.3 - 0.5	9.21E-05	2.1	7.9	4.2	587.8	464.0	622.7	39.2	23.1	48.7
	0.5 - 1.0	5.59E-05	-	-	-	-	-	-	-	-	-
	1.0 - 1.5	8.24E-04	-	-	-	-	-	-	-	-	-
7[b]	0.1 - 0.3	2.36E-05	12.6	-	4.5	1382.5	171.5	210.8	750.4	252.6	92.9
	0.3 - 0.5	9.42E-05	3.1	-	-	360.1	31.3	45.1	170.3	-	20.1
	0.5 - 1.0	7.51E-04	0.7	-	0.3	42.6	6.1	6.4	23.9	-	3.9
	1.0 - 1.5	1.44E-03	-	-	-	-	-	-	-	-	-
8[b]	0.1 - 0.3	1.85E-05	14.6	-	54.6	1422.4	-	65.3	-	4497.9	138.4
	0.3 - 0.5	6.83E-05	7.6	-	3.6	404.8	-	15.9	-	376.0	17.8
	0.5 - 1.0	5.02E-04	-	-	-	-	-	-	-	-	-
	1.0 - 1.5	2.12E-03	0.2	-	0.2	14.6	-	1.5	0.6	5.5	0.6

[a] 10mEq saline sheath fluid used

[b] 100mEq saline sheath fluid used

[c] All - values are either ND or values eliminated due to RSD% values exceeding 60

The very high solid phase metal concentrations observed for the "anthropogenic" elements in very fine particulate matter was anticipated because of the higher specific surface areas associated with smaller particles; adsorption of metals to surfaces is promoted in a high surface area environment. As shown above, however, smaller particles do not contribute a significant amount of the TSS load in most runoff, so it is important to try to assess what fraction of the total metal load in a particular storm event is associated with these very fine particles. An estimate of the fraction of each metal's event mean load (EML) accounted for by particles in the 0.1 to 1.5 μm size range is shown for storm events 3 and 7 in Figures 3-9 and 3-10. These results show that a potentially significant fraction of the EML of these metals leaves the right-of-way associated with very fine particulate matter. Conversely, fine particles are never a significant contributor to EMLs for the crustal elements aluminum, manganese and iron.

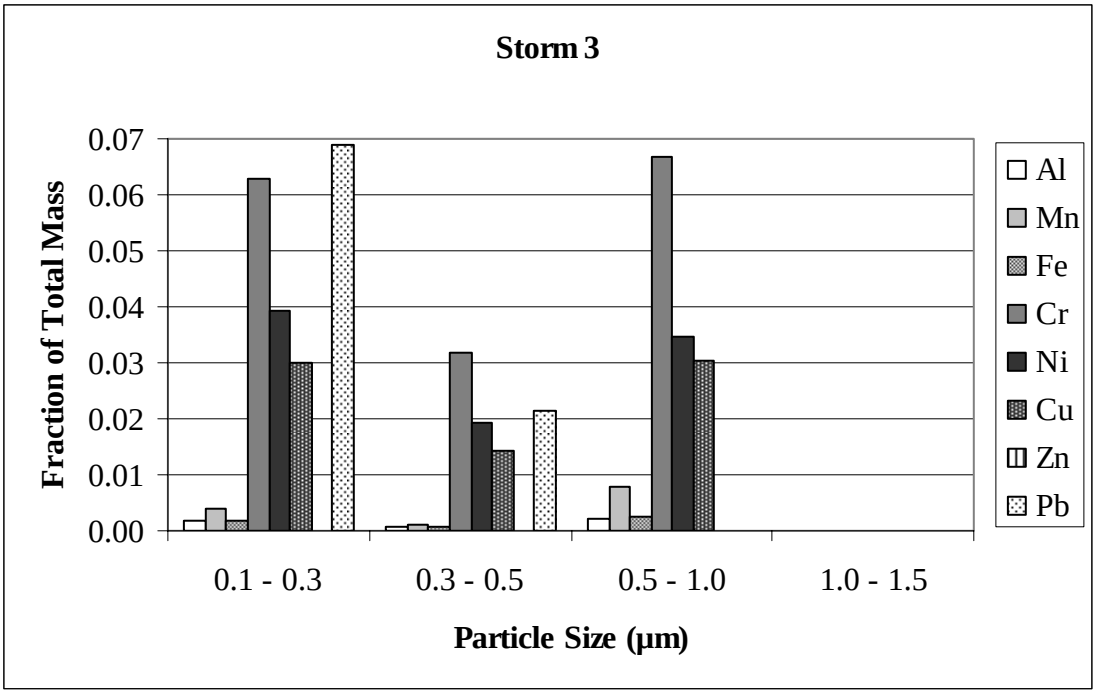


Figure 3-9 Fraction of event mean load (EML) associated with particulate matter of varied sizes for storm event 3

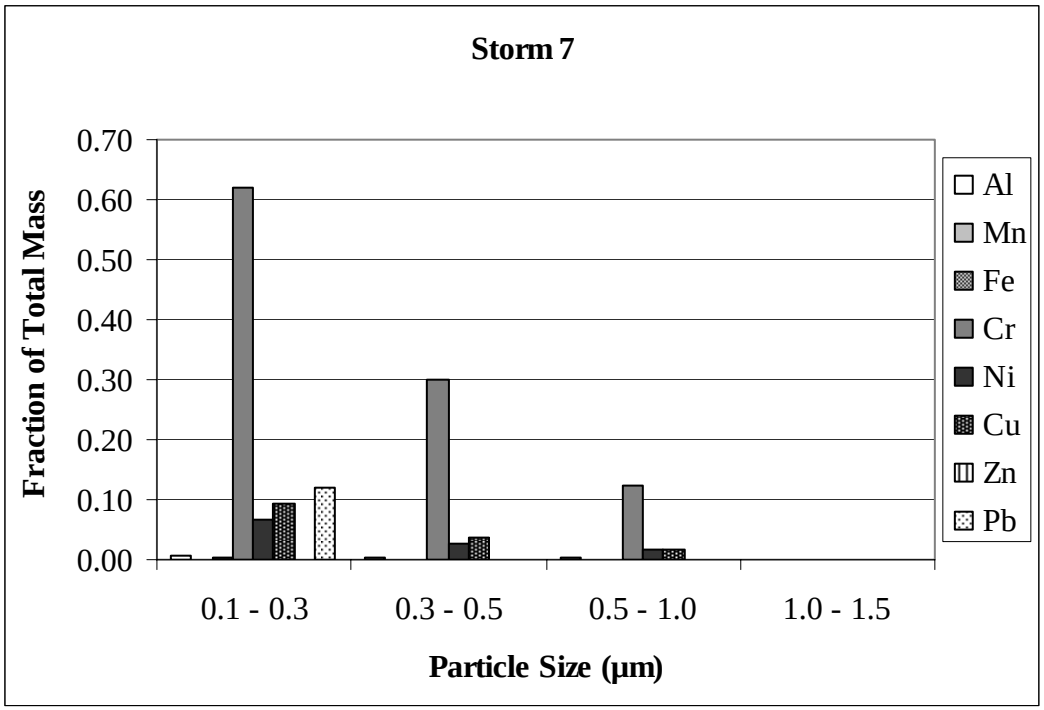


Figure 3-10 Fraction of event mean load (EML) associated with particulate matter of varied sizesfor storm event 7

ORGANIC CONSTITUENTS ASSOCIATED WITH SMALL PARTICLES

Particles were collected from the Davis I-80 site and separated by centrifuge as described elsewhere. Most of the concentrated particles were then re-suspended in filtered stormwater in a graduated cylinder to use Stokes Law gravitational settling for separation into ever smaller size ranges. Trace organic analysis was conducted as for the CTR project (Reference), using solvent extraction, sample clean-up, concentration and quantification by GC-MS.

Figure 3-11 depicts the representative results from the February 13, 2005 storm event. For the 4 smallest PAHs, the largest concentration is found in the dissolved phase – shown in the darkest bars in the column graph. For the next 5 larger PAHs, the dissolved concentration is detectable, but forms a rapidly diminishing fraction of the total. In a few cases, the largest concentration is in the 63um to 20um fraction, but generally, the large PAHs are mostly in the 20um to 10um and 10um to 5um fractions. The 5um to 2um fraction is also detectable, but always at a lower concentration.

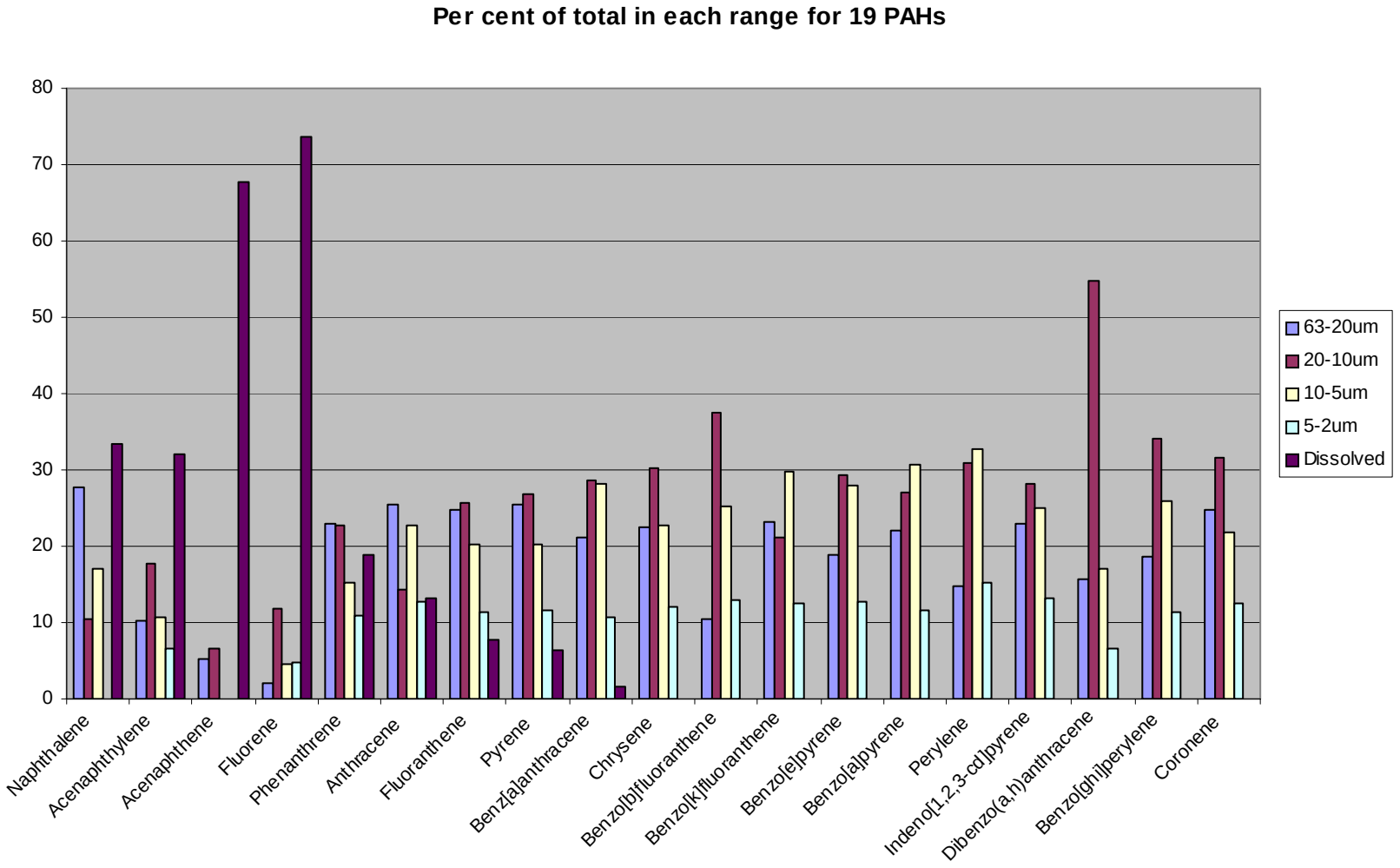


Figure 3-11 Percent PAH concentration relative to various particle size ranges

CORRELATION BETWEEN PARTICLE SIZE AND METAL CONSTITUENTS

The relationship between particle size and metal constituent concentrations for samples collected from the UC Davis highway site discussed above shows that there is a significant mass fraction of metals associated with very small particles and that particle bound metal concentrations are negatively correlated with particle size. Furthermore, the fractionated particles collected from the Davis I-80 site during the February 13, 2005 storm event is analyzed for metals constituents. Metal removal based on fraction of particles removed and particle diameter is shown in Figure 3-12. For each element, the right hand point shows the percent on all particles: from ~95% for Pb down to less than 50% for Cu. Then, as the curve descends to smaller particles, one sees how significantly each size class contributes to the particle-bound fraction. In general, the decline in particle and metal constituent removal occurred moderately until about the 20um range, at which point the removal begin to descend more steeply. A substantial portion of each metal is found on particles smaller than 20 μm. Once the size of 2 μm is reached, only about 10 to 15 percent of these metal constituents remain on particle. Of course, in some cases, a large fraction is dissolved.

Similar trends have been observed for metal constituents over a wider range of particle sizes (0.45 to 100 μm) for samples collected from the three UCLA highway sites. The correlation between Cd, Cr, Cu, Ni, Pb and Zn metal constituents with various particle size ranges for combined sites 7-201, 7-202 and 7-203 are presented as probability plots in Figures 3-13 through 3-15. As shown, large concentrations of these metals are in the dissolved form, and the majority of particle bound metals are associated with particles in the range of 8-20 μm.

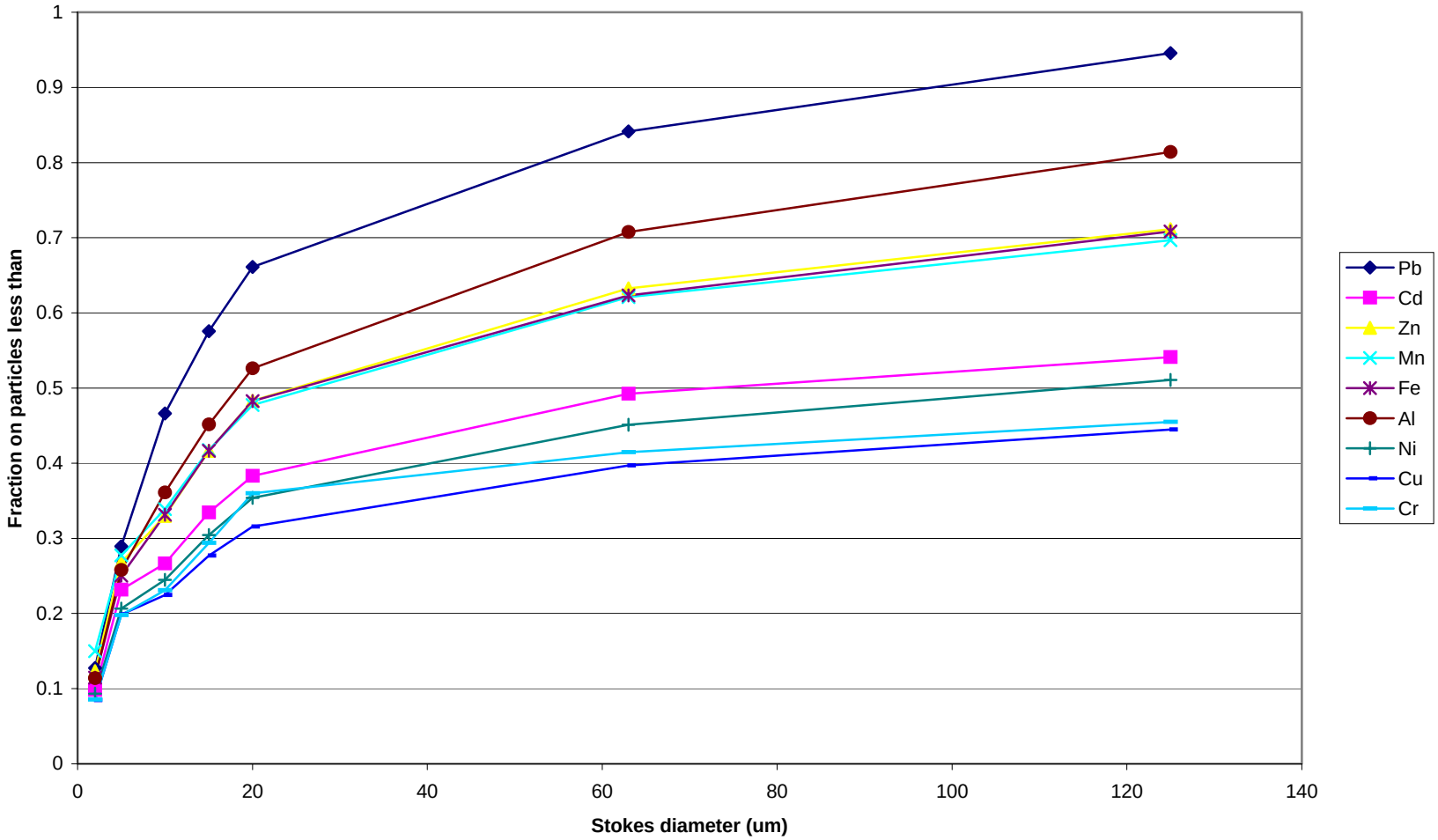


Figure 3-12 Fraction of particle and metal constituents removed vs. particle size

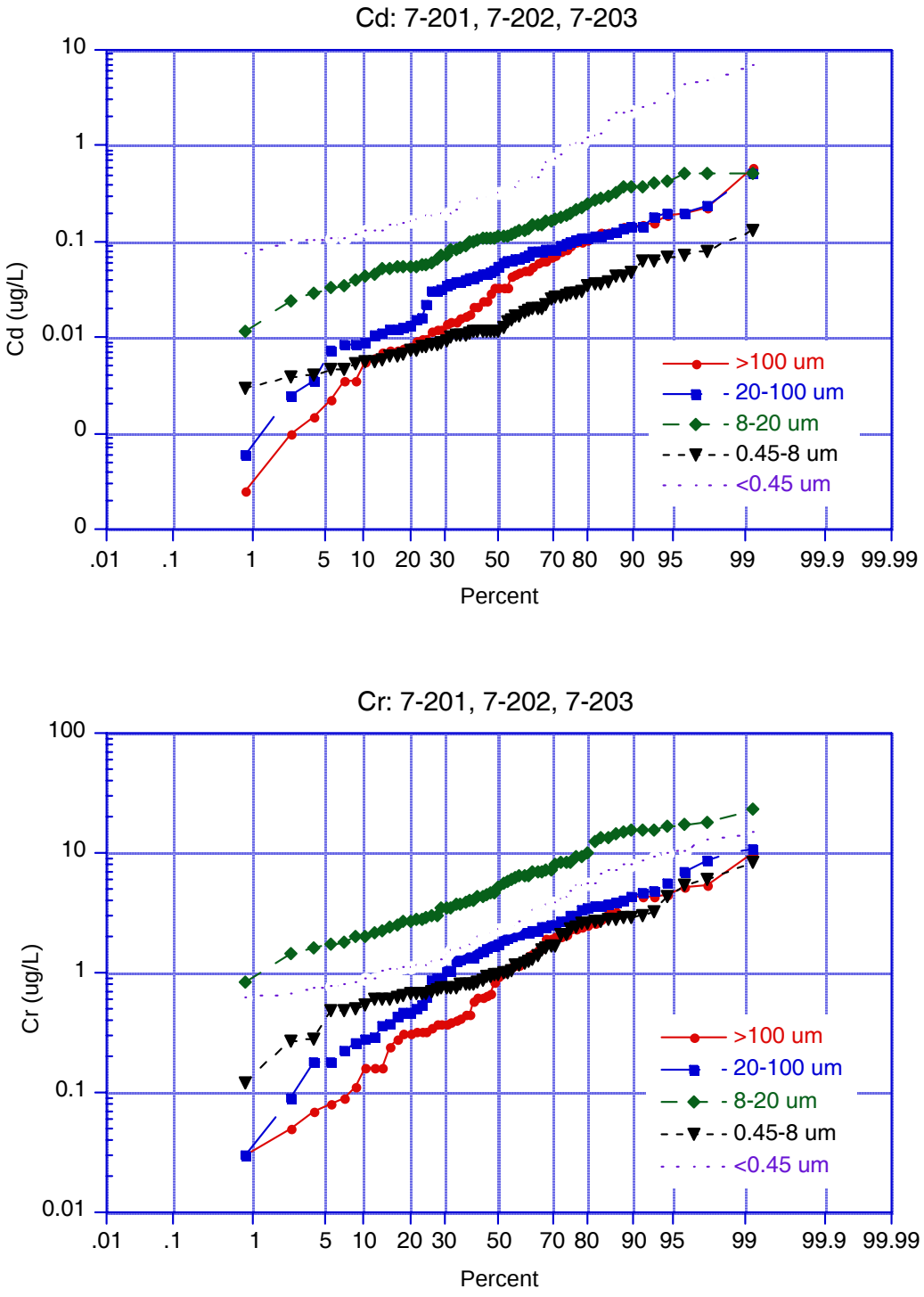


Figure 3-13 Correlation between Cd and Cr and particle size range for the three highway sites in Los Angeles

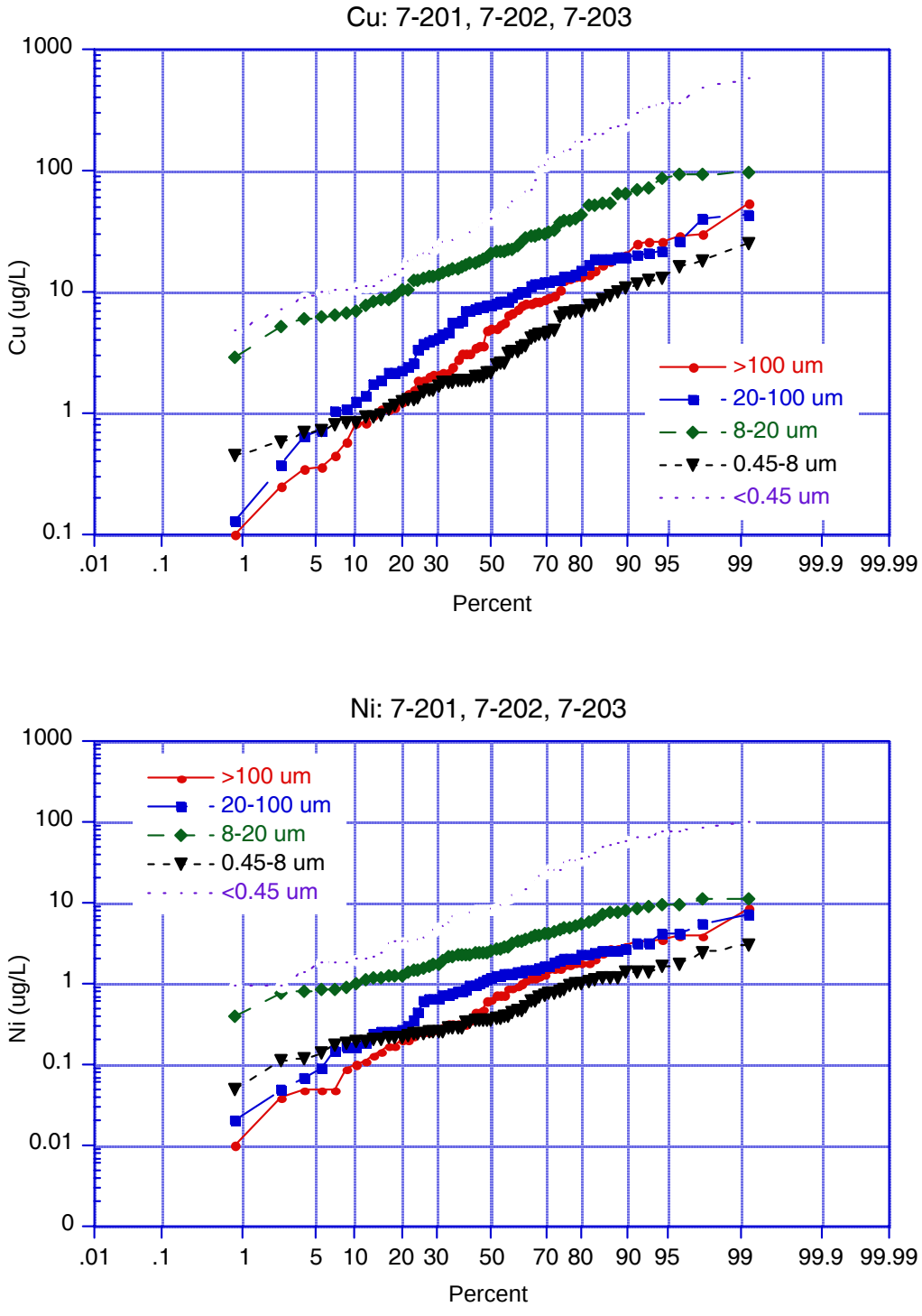


Figure 3-14 Correlation between Cu and Ni and particle size range for the three highway sites in Los Angeles

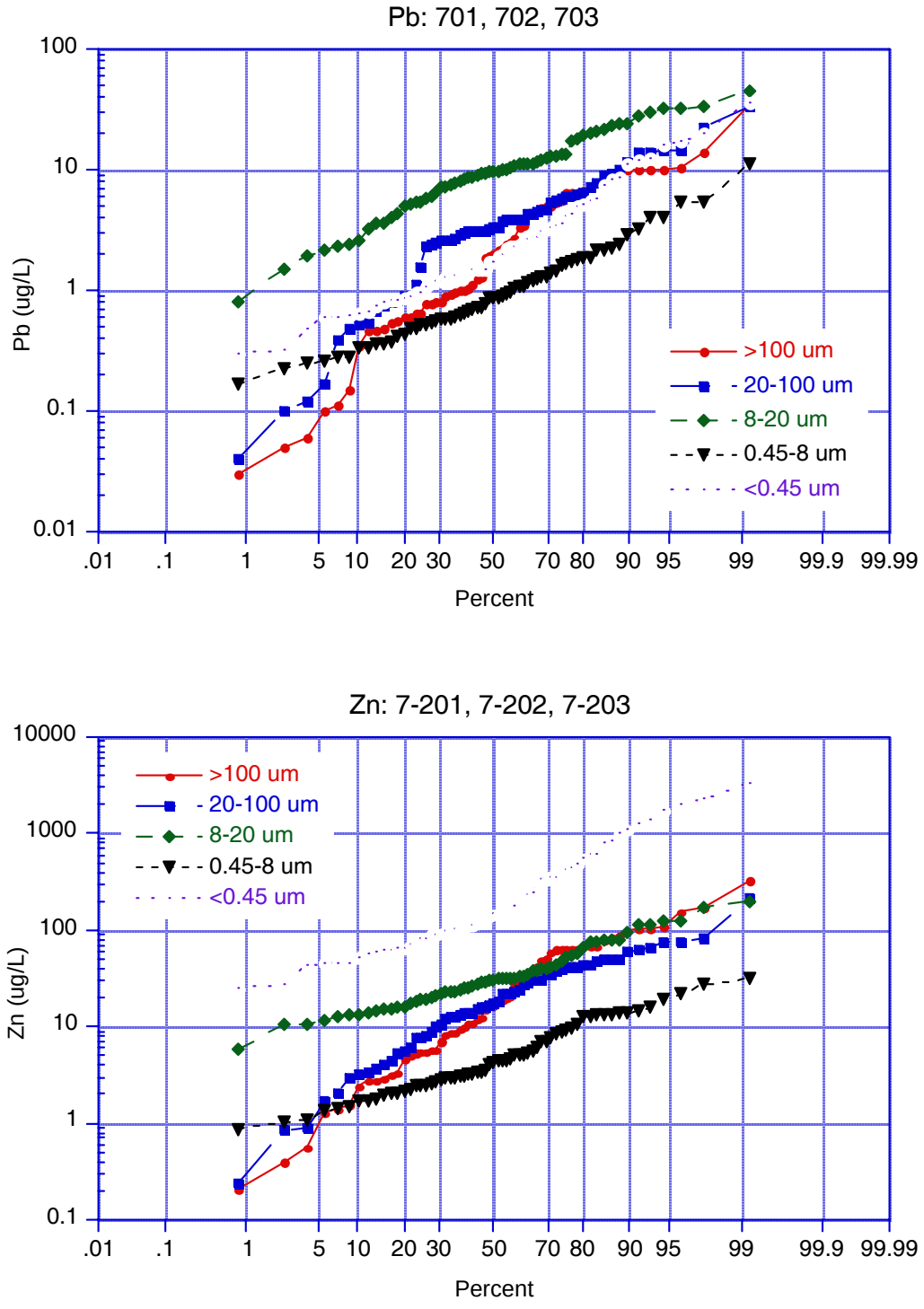


Figure 3-15 Correlation between Pb and Zn and particle size range for the three highway sites in Los Angeles

FIRST FLUSH OF PARTICLES

We extended the mass first flush ratio (MFF) developed for water quality parameters (Ma et al., 2002; Kayhanian and Stenstrom, 2005) to particle first flush and referred to the analogous parameter as particle number first flush, PNFF. The derivation of PNFF ratio was described in Section 2, which defined as the normalized number of particles within a certain range divided by normalized volume fraction at any point of a normalized runoff diagram. The ratio allows convenient characterization of first flush. For example, $PNFF_{20}$ = 3 means that 60% of particle count is contained in the first 20% of the runoff.

Figures 3-16 and 3-17 show the number first flush ratios ($PNFF_{10}$, $PNFF_{20}$, $PNFF_{40}$) for particles in different size ranges for storm events monitored during the 2002-03 and 2004-05 rainy seasons, respectively. The top and bottom of the box marks the limits of ± 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. The $PNFF_{20}$ values are summarized in Table 3-4. The information presented in Figure 3-16 and Table 3-4 illustrate median $PNFF_{10}$, $PNFF_{20}$, $PNFF_{40}$ values generally increase with increasing particle diameter. The PNFF ratio is generally about 25% 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.

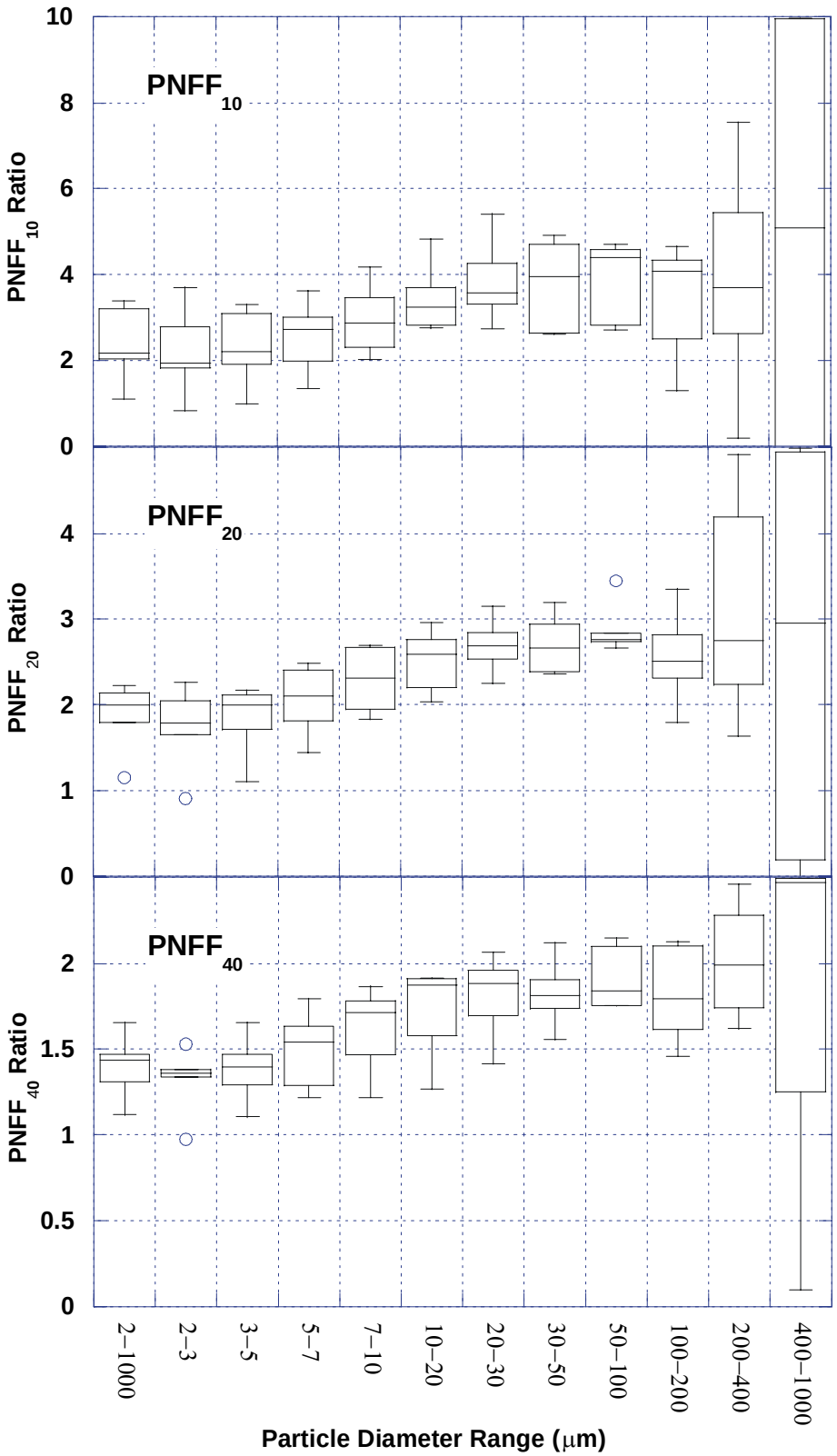


Figure 3-16 Boxplots for PNFF ratios of 10, 20 and 40 at different particle size range for storm events during 2002-03 rainy seasons

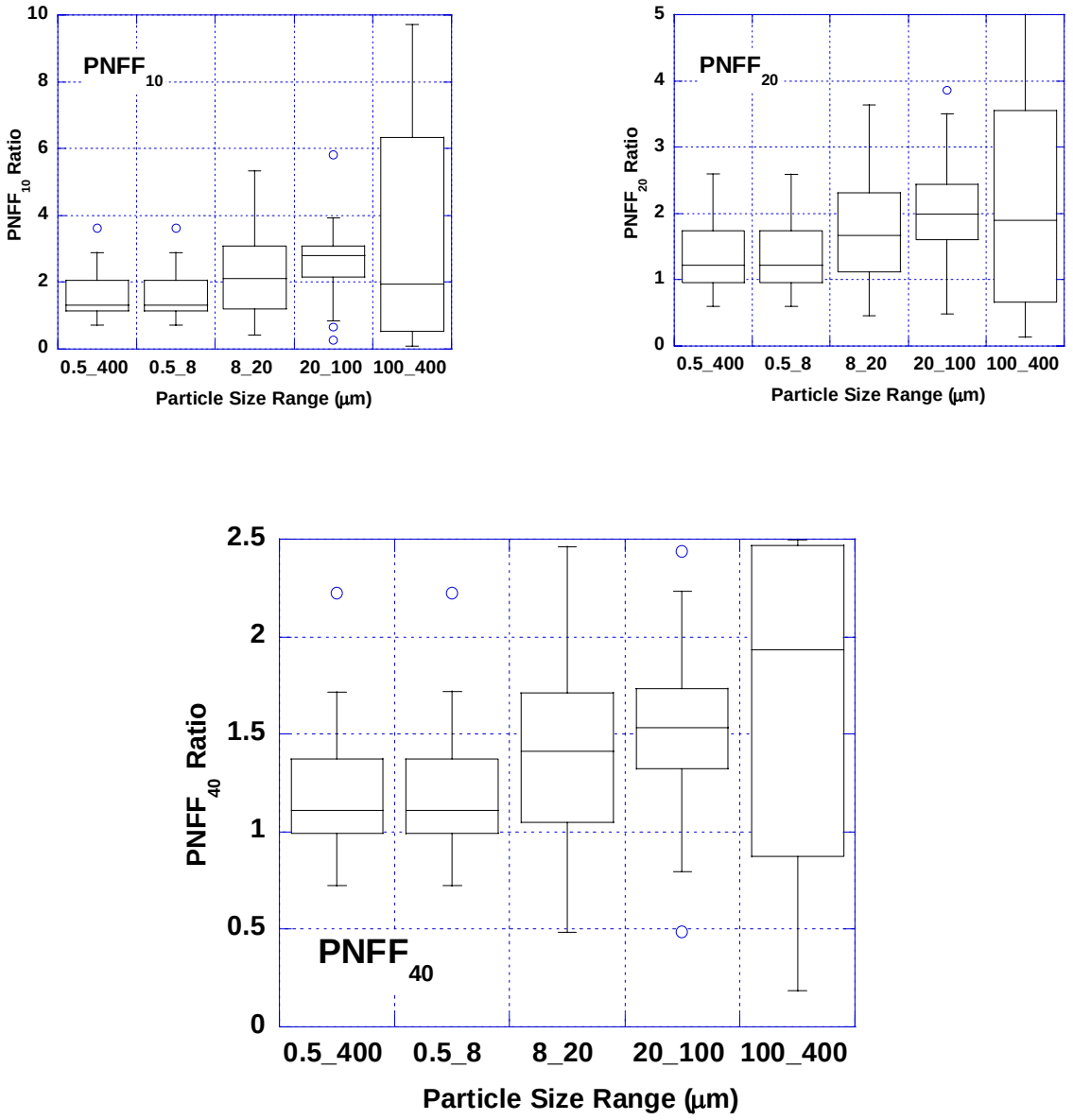


Figure 3-17 Boxplots for PNFF ratios of 10, 20 and 40 at different particle size range for storm events during 2004-05 rainy seasons

Table 3-5 Statistical summary of $PNFF_{20}$ values for different particle size ranges for three highway sites in Los Angeles during 2004-05 rainy seasons

Particle Size Range (μm)	Monitoring Site	Minimum	Maximum	Median	Mean	Std Dev	N>1.1[a]
0.5_400	Combined Sites	0.60	2.59	1.22	1.41	0.60	11/18
	Site 7-201	0.77	1.74	1.74	1.12	0.37	2/5
	Site 7-202	1.05	2.59	2.59	1.77	0.65	6/7
	Site 7-203	0.60	2.15	2.15	1.22	0.55	3/6
0.5_8	Combined Sites	0.60	2.59	1.21	1.41	0.60	11/18
	Site 7-201	0.77	1.74	1.74	1.12	0.37	2/5
	Site 7-202	1.05	2.59	2.59	1.77	0.65	6/7
	Site 7-203	0.60	2.15	2.15	1.22	0.55	3/6
8_20	Combined Sites	0.46	3.64	1.67	1.80	0.92	14/18
	Site 7-201	0.66	3.42	3.42	1.72	1.10	3/5
	Site 7-202	0.64	3.64	3.64	2.13	1.02	6/7
	Site 7-203	0.46	2.13	2.13	1.50	0.64	5/6
20_100	Combined Sites	0.48	3.86	1.99	1.97	0.92	14/18
	Site 7-201	0.55	3.86	3.86	2.08	1.18	4/5
	Site 7-202	0.76	3.51	3.51	2.24	0.88	6/7
	Site 7-203	0.48	2.44	2.44	1.58	0.74	4/6
100_400	Combined Sites	0.14	5.00	1.90	2.28	1.78	10/18
	Site 7-201	3.53	5.00	5.00	4.40	0.79	5/5
	Site 7-202	0.14	4.29	4.29	1.79	1.62	3/7
	Site 7-203	0.44	2.55	2.55	1.10	0.78	2/6

[a] N = $PFFN_{20}$ values greater than 1.1 was observed per total number of events monitored

MICROSCOPIC IMAGE ANALYSIS OF PARTICLES

Particle samples collected from stormwater runoff and two different brake assemblies were the focus of the SEM study; the average diameter, shape and elemental composition of each particle was measured for both types of sample. The results of the particle size analysis are shown in Table 3-5 and Figure 3-18. The median runoff sample particle diameters were slightly greater than for the brake samples. For all of the samples, more than 80 % of the particles were smaller than 5 μm, with the medians being between 2 and 2.65 μm. The maximum diameters were 32.4 to 79.0 μm.

Significant variability in sizes, shapes and elemental compositions from particle to particle in the runoff sample is illustrated in Figure 3-19. Within this one

representative microscope field the particles vary in average diameter by nearly a factor of 10 and in some cases the elemental mass fractions vary by factors greater than 30. Such significant variations suggest different particle origins. One important goal of this portion of the study was to produce a technique that could be used to identify the sources of highway particles and their relative contributions. Comparing the particle by particle analysis of runoff samples to those in samples collected from plausible sources of highway particles such as brakes, tires, auto exhaust and roadside soils should support efforts to estimate what fraction of particles are contributed by each source type. Such information could form a critical part of subsequent source control efforts.

Runoff particle characteristics were compared to those for one plausible particle source category (brakes) to illustrate the potential of this technique. Histograms of the compositions of 15 elements (N, O, Mg, Al, Cd, K, Ca, V, Cr, Mn, Fe, Co, Ni, Cu, Pb) as percents of total elements analyzed are summarized in Figures 3-20 through 3-22 for both types of samples.

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Table 3-6 Average particle diameter distribution (µm)

Sample type	Statistical summary					
	Average	**SD**	**Max**	**Min**	**Median**	**Sample Size**
Stormwater runoff	3.57	2.87	32.4	1.04	2.65	3787
Brake pad (Ford Explorer)	2.47	1.78	50.6	1.04	2.01	5931
Brake pad (Toyota Camry)	2.96	3.24	79.0	1.04	2.20	6975

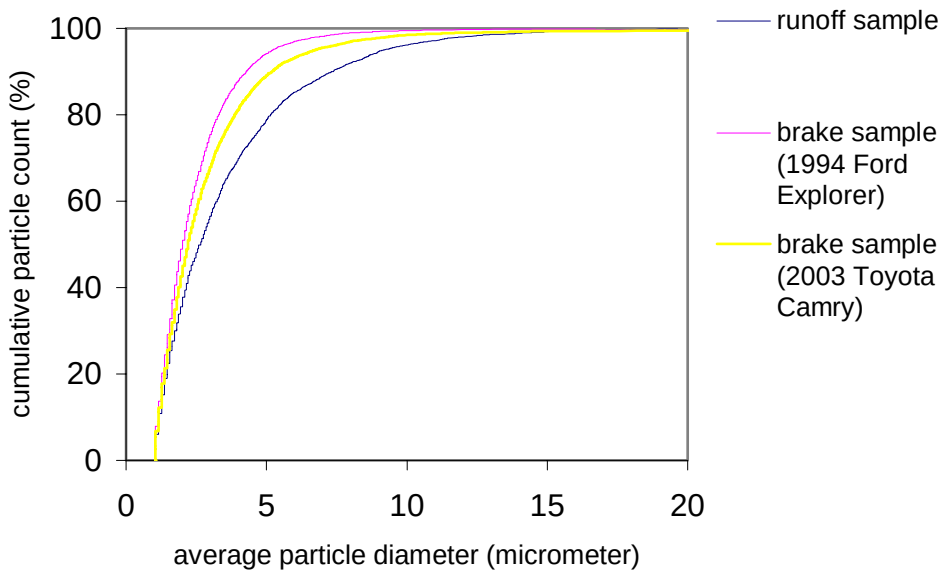


Figure 3-18 Cumulative particle counts of runoff and brake pad samples

It is important to note that there are elements that can be present on particles that were not analyzed such as carbon. It was not possible to analyze carbon because particles were prepared on polycarbonate filters. As a result, the numbers do not represent the complete particle compositions.

Of the 15 elements analyzed, O was the most abundant for all of the samples. The runoff samples contained significant amount of Al and N, and brake samples contained significant amount of Fe and N. The contributions of Cd, K, Ca, V, Cr, Mn, Co, Ni were less significant in all of the samples.

The distributions of these elements were different for different samples especially for N, O, Al, Fe, Cu and Pb. For N and O distribution, the brake sample from the Toyota Camry showed two peaks whereas the runoff and the brake sample from the Ford Explorer showed only one peak. The runoff sample showed a wide Al concentration distribution with the peak at 12.5 to 15 % whereas for both of the brake samples more than 80% of the particles contained less than 5% of Al. Nearly 80% of the particles contain less than 10% of Fe in the runoff sample. The brake sample from

the Ford Explorer shows a wide peak at Fe content of 25 to 35 %, and the brake sample from Toyota Camry shows two peaks at less than 5% Fe content and at 35 to 50%. The runoff sample and the brake sample from Toyota Camry shows the highest peak at less than 1% Cu content, and the brake sample from Ford Explorer shows a wide peak at 2 to 2.5% Cu content. Majority of particles of the runoff sample and the brake sample from Toyota Camry show less than 1% of Pb content, however, there are smaller wide peaks between 2 and 9 % Pb content ,and 3 and 10 % Pb content, respectively. The brake sample from the Ford Explorer shows a wide peak between 3 and 10 % Pb content. Contributions of Cd, K, Ca, V, Cr, Mn, Co, and Ni in most of the particles of all of the samples were not significant. However, the runoff sample showed more particles with higher K and Ca contents, and the brake sample from Toyota Camry showed more particles with higher Cr, Mn, Co, Ni contents. Overall these results show that major elements in soils (Al, Ca, K, Mg) are present in higher concentrations in the runoff and those which are considered anthropogenic are in many cases present in higher concentrations in the source sample (brakes).

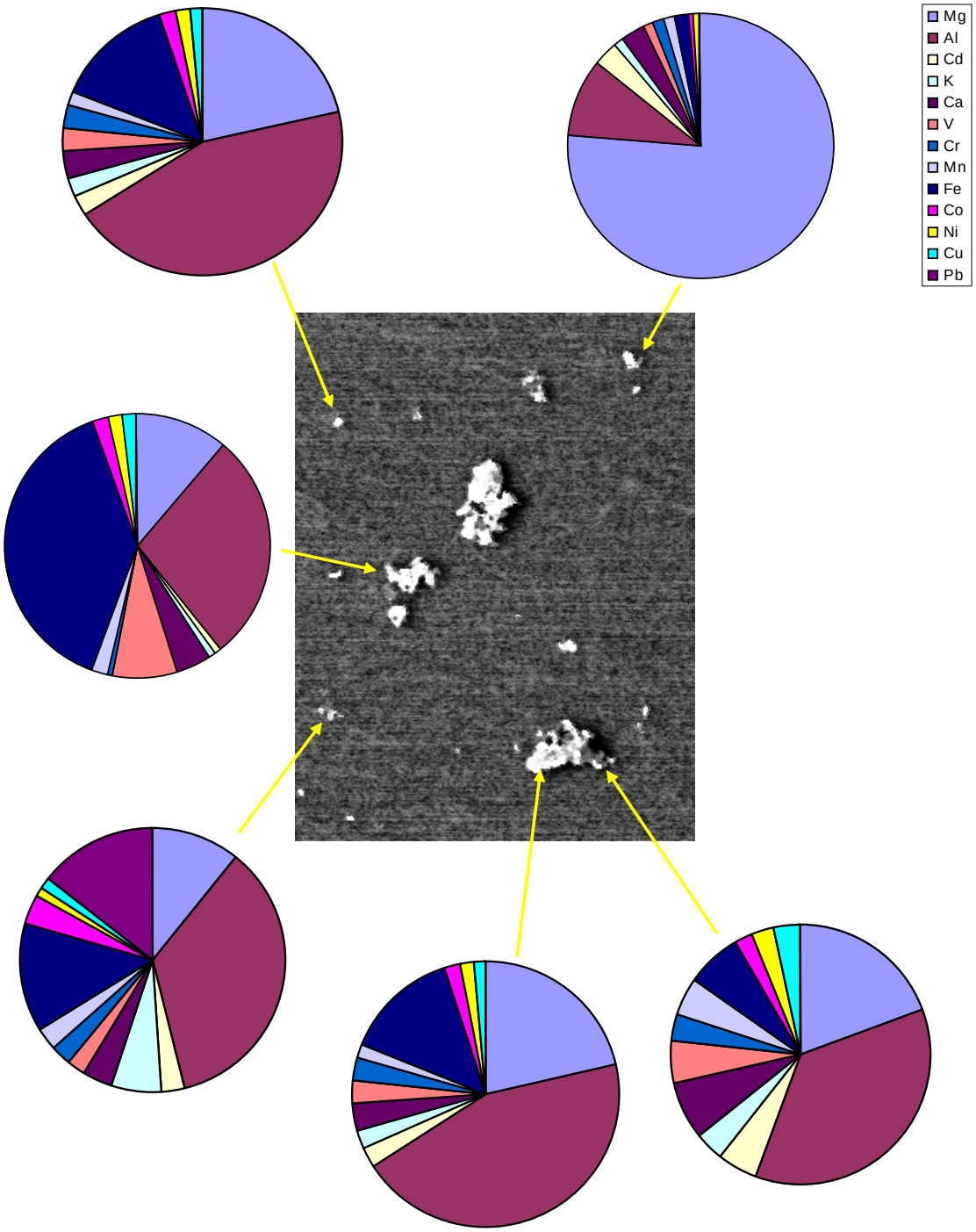


Figure 3-19 Photomicrograph of an individual SEM field and the variation in elemental composition between individual particles. Average particle diameters of the particles represented in this field range from 1.47 to 13.12 μm.

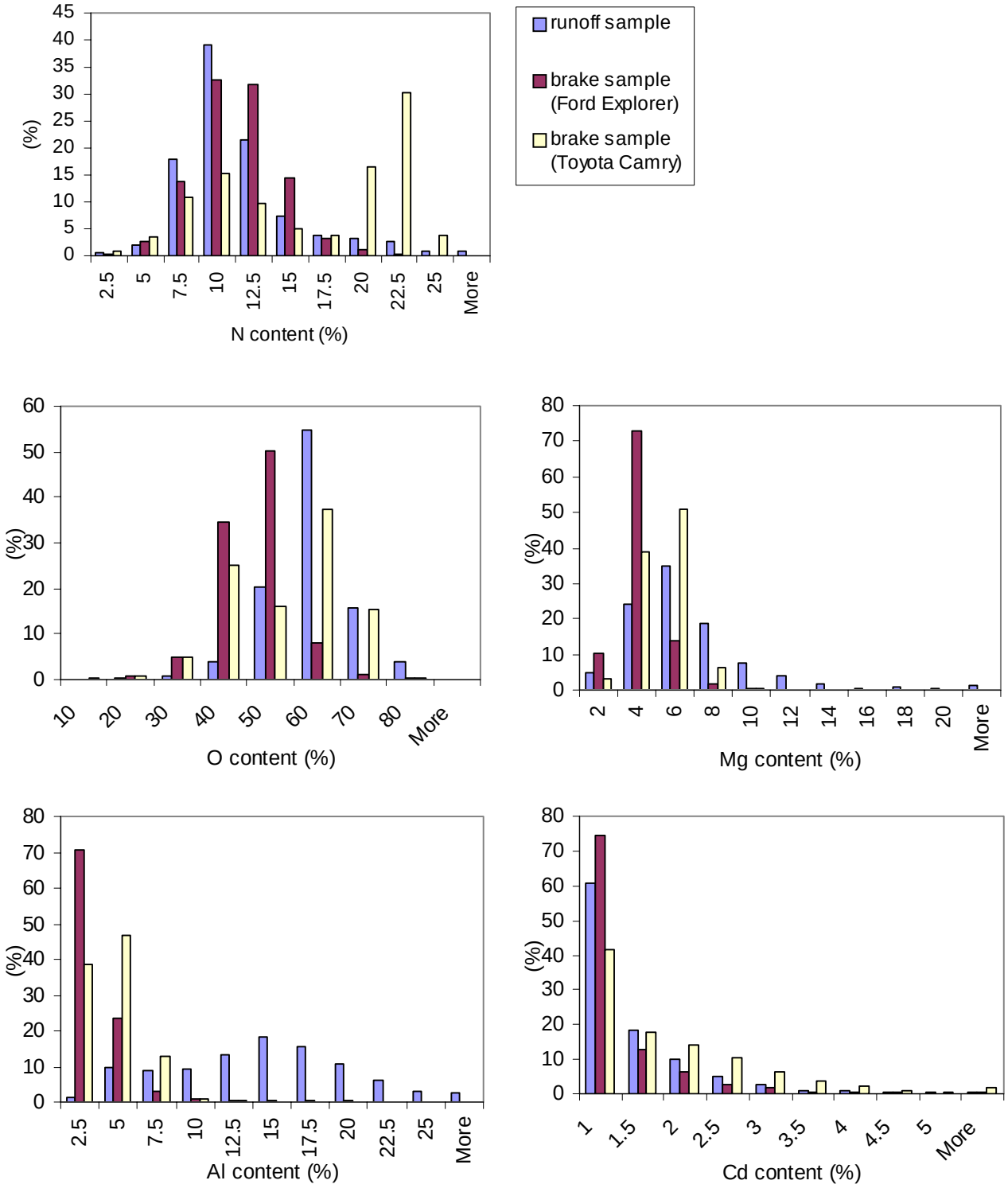


Figure 3-20 Histograms of elemental composition for O, Mg, Al and Cd

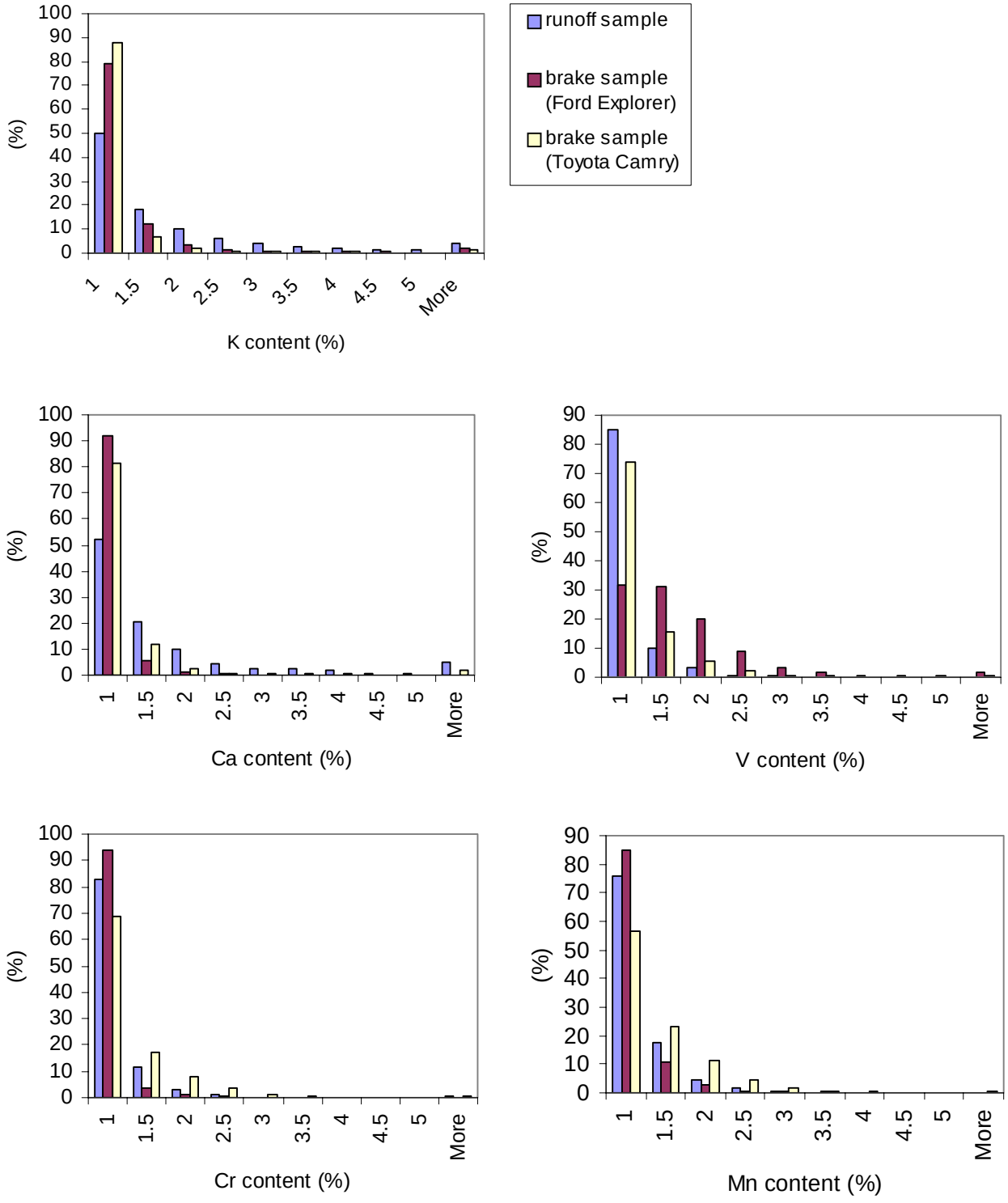


Figure 3-21 Histograms of elemental composition for Ca, V, Cr and Mn

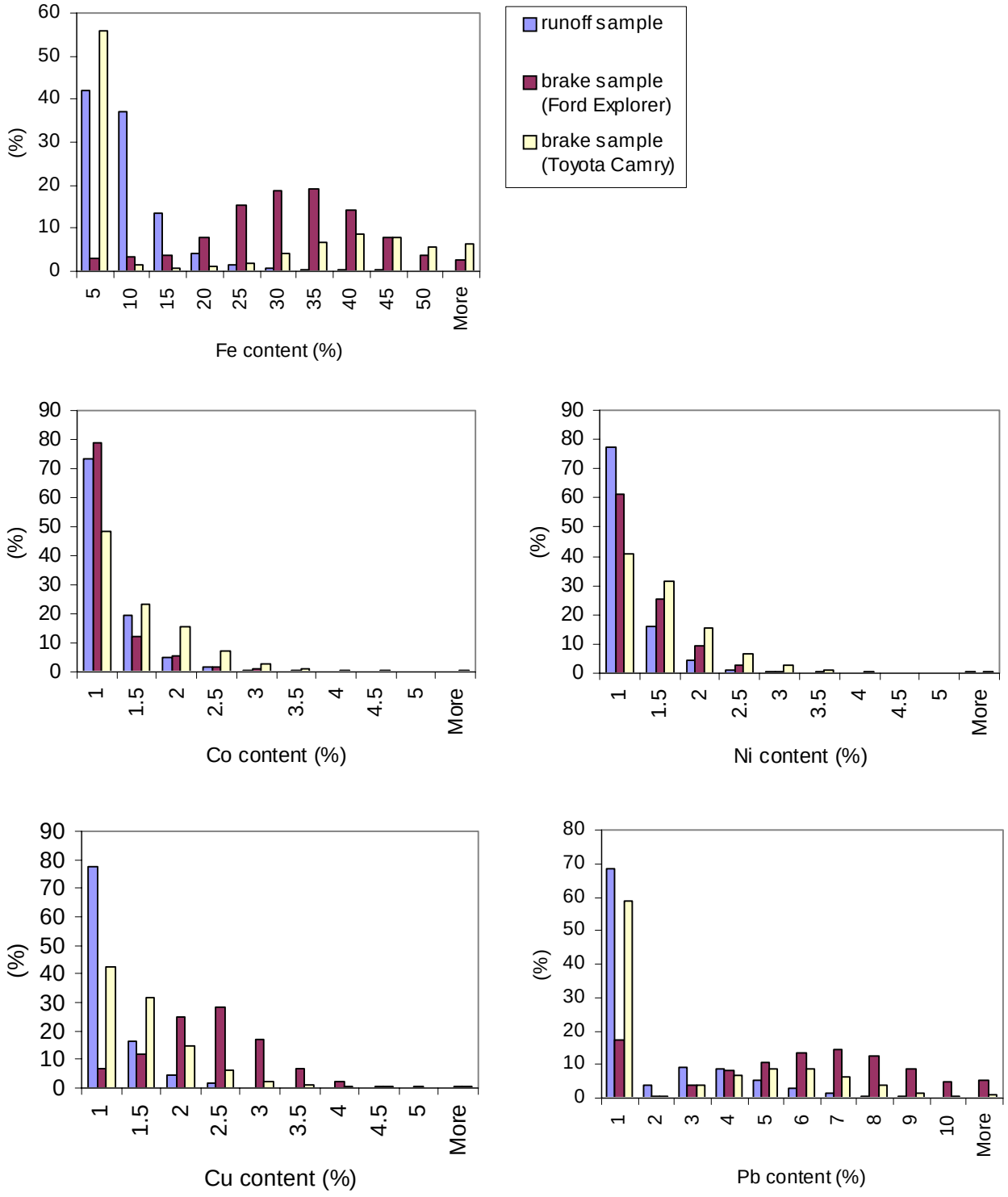


Figure 3-22 Histograms of elemental composition for Co, Ni, Cu and Pb

PRACTICAL IMPLICATION OF THE RESULTS

The results obtained from this study can be used in many different ways to promote more effective storm water runoff management. In particular, the knowledge gained from measuring particle size distributions and the contaminant load associated with particles of various sizes can be applied in BMP design and performance evaluations. Two topics considered to assess the practical application of particle size characterization results include: (1) the use of particle size analysis as a screening tool to select BMPs and (2) the potential for using two compartment settling tanks to optimize particle and contaminant removal.

Particle Size Analysis as a Screening Tool to Select BMPs

The simple concept of classifying the solid particles in runoff (and their associated contaminant load) as particulate and dissolved may not be sufficient to fully assess the quality of water and/or use the information for design and evaluation of BMPs. Using this approach, a specific cutoff size or separation process will delineate the "particulate" and "dissolved" fractions. For instance, the "dissolved" fraction in *Standard Methods for the Examination of Water and Wastewater* (1997) is defined as the solids that pass through a specific filter paper, Whatman 934AH (nominal pore size = 1.5 µm) or its equivalent. Some portion of the solids with sizes smaller than 1.5 µm may be trapped on the filter paper and hence be counted as particulate solids, and the magnitude of this fraction will depend on the type and concentration of particles and the volume of sample filtered. Errors associated with the results will have significant implications for estimates of dissolved and particulate pollutant mass loads. Aside from the error that is associated with particulate phase measurement, unless the mass fraction of contaminants associated with specific particle size range is identified it will be impossible to determine the efficiency of treatment BMPs for effective removal of organic and inorganic constituents. Using the current measurement techniques it has been shown that a large fraction of Cu, Ni, Pb and Zn are found in runoff in particle-associated form (see Figure 3-20).

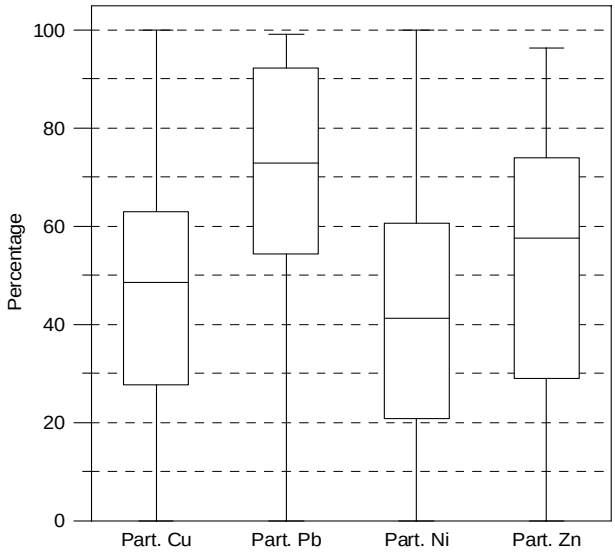


Figure 3-23 Particulate fractions of Cu, Pb, Ni and Zn in stormwater runoff

As previously shown, particles in storm water runoff may range from below 0.1 μm to over 100 μm. Evaluating the constituent mass or concentration that is associated with specific size ranges will enable us to examine the true performance of approved BMPs without more complicated and expensive pilot investigations. For example, Figure 3-24, shows that a large fraction of the total Cu, Pb and Zn for all storm events monitored during 2004-05 at site 7-202 are associated with particles in the range of 8-20 μm. Most existing BMPs are considered to be ineffective in removing particles smaller than 20 μm. In such a case pilot investigations with expensive field monitoring will not provide additional useful information about the efficacy of treatment BMPs. In addition, the results can be useful in recommending the use of chemical treatment (e.g. coagulation) if the intent is to remove a higher mass fraction of particulate phase metal or organic pollutants. Further, if a new contaminant of concern emerges in the future, its removal in a BMP can be immediately assessed without any field testing once the new contaminant's concentrations in varied particle sizes are determined and the effective particle size cutoff of the BMP is known.

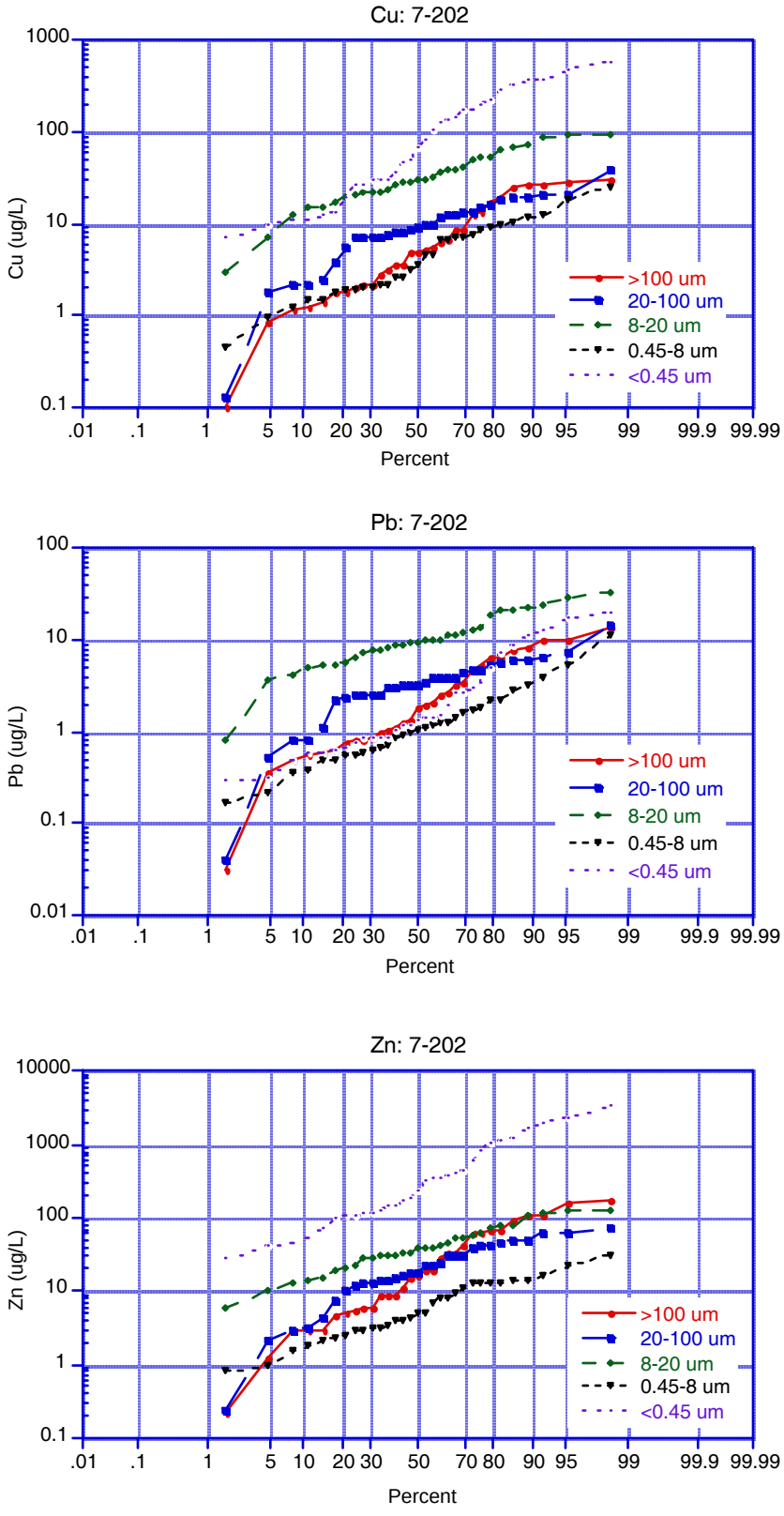


Figure 3-24 Probability relationship for particulate bound Cu, Pb and Zn for highway site 7-202 during storm events of 2004-05 monitoring seasons

Two-Compartment Settling Tank Design

Description of Two-Compartment Settling Tank Design

A flow diagram and the concept used in the two-compartment settling tank design is shown in Figure 3-25. The first compartment captures the initial runoff and then after filling bypasses to a second compartment, which functions as a continuous flow clarifier. The two-compartment design takes advantage of the first flush as well as other factors such as higher initial concentrations. This study demonstrates the application of a two-compartment settling tank using newly acquired particle size information complemented with literature data on solid phase concentrations of metals presented in Table 3-6. Total particle and metal removals are calculated. The calculations show that capturing the first flush in the storage compartment and removing the smaller particles in the captured runoff improves overall removal rates. The results will be useful in designing best management practices (BMPs) to optimize highway stormwater treatment.

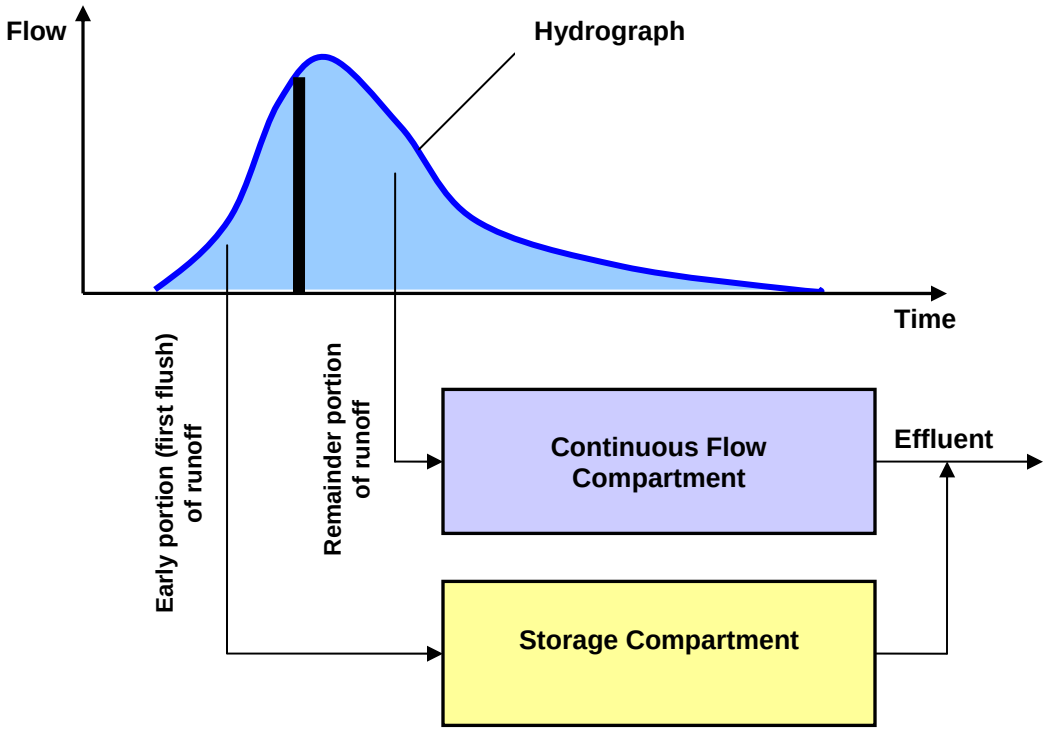


Figure 3-25 Two-compartment sedimentation design

Table 3-7 Concentrations of Metals with Respect to Different Particle Size Ranges

Size ranges (μm)	Heavy metal concentration (μg/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		
<20		0.51	19.7	37.4		17.3	21.2	263	Highway runoff suspension	Caltrans (2002)
20-300		0.6	19.4	33.7		17.3	21.4	311		
300-850		0.41	18.1	30.1		17.4	22.5	231		
850-2000		0.35	10.2	15.2		8.74	16.6	121		
>2000		0.42	12.7	25.7		11.8	19	262		

Particulate metal removal efficiency was calculated based on particle removal efficiency and associated metal concentrations for different particle size ranges. Assuming dissolved metal concentration would not change after the treatment, total metal removal efficiency could be achieved with dissolved metal fraction f_d values. The f_d used in this study are from California Department of Transportation's (Caltrans') statewide highway characterization study (Caltrans 2003).

Wide ranges of settling tank sizes can be used for particle and pollutant removal. In this study we assumed a fixed total tank size with relative size difference between the two compartments. The simplest form of the design is when the size of both compartments are the same. Various other compartment size were used to optimize both particle and pollutant removal efficiency. The optimum particle and pollutant removals are accomplished by introducing a removal efficiency optimization objective function expressed as:

Removal Efficiency = *f(r, V, PSD, v, flow)*

Where,

r = volume ratio between the storage compartment and the continuous flow compartment
V = total volume of both compartments
PSD = grab sample particle size distributions of all events
v = settling velocities of particles
flow = flow data for all events

The optimum removal efficiency was calculated by solving the above equation for r from 0 to 1.0 in small increments. The total volume of the two compartments was fixed for a selected design storm size, represented as millimeters of rainfall. The actual total tank volume for a particular site can be calculated by multiplying the design storm size by the site area and runoff coefficient. Settling velocities were calculated using Stokes or Newton's laws (Li et al. 2005b). Total mass of particles were obtained using grab sample *PSD* and *flow* data. Settling tank depth was assumed to be 3 meters. The effects of different pollutant concentrations were simulated by choosing different values from the literature (Table 3). No special optimization tool was used because the equation can be quickly solved.

Optimum Particle Removal

Figure 2 shows the overall particle removal efficiency of the individual and combined compartments for two different design storm sizes as a function of the relative sizes 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 volume fraction 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 3-26 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 a greater volume is allocated to storage, and most of the particle removal occurs in the continuous flow compartment.

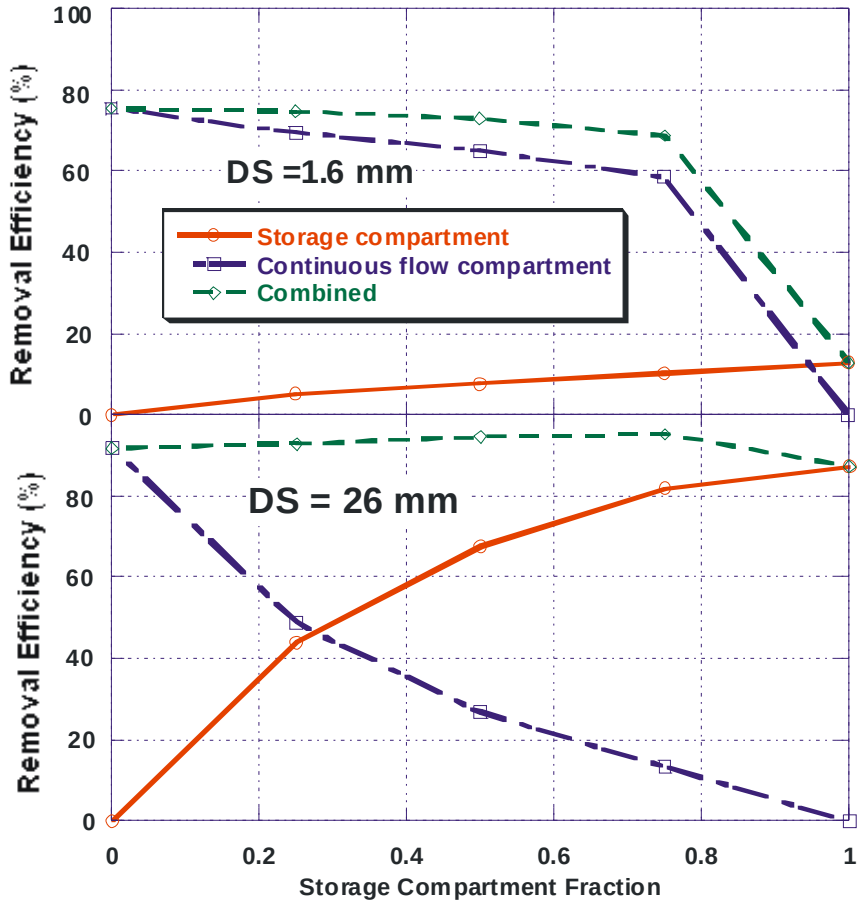


Figure 3-26 Particle Removal Efficiency for Individual Compartments and the Combined System at Design Storm (DS) Sizes of 1.6 mm and 26 mm

This result arises because the volume of the storage compartment is too small and it 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. This large sedimentation tank allows the designer to choose which compartment is (given more volume for treatment) used for treatment. For a large storage compartment volume, the entire flow from smaller storms is captured, and the continuous flow compartment functions only for larger storms. In addition, particle first flush also has an influence on removal efficiency, which is discussed later.

Figure 3-27 shows the overall particle removal efficiency of the 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 a storage fraction of approximately 0.75, the efficiency sharply declines. Although the particle removal efficiency is relatively flat when the storage compartment fraction is less than 0.75, a maximum particle removal efficiency exists at zero storage for low rainfall designs and at approximately 0.75 storage fraction for large rainfall designs.

Figure 3-27 shows the optimized total particle removal rate as a function of design storm sizes. Rainfall probability is also shown. Rainfall probability is calculated from the rainfall data obtained from three highway sites during 1999-2003 monitoring seasons. Although plotted in Figure 3-28 on a linear axis for clarity, the rainfall probability shows a log linear relationship with the total design storm size. Maximum particle removal efficiency increases rapidly with the increase of total design storm up to approximately 13 mm.

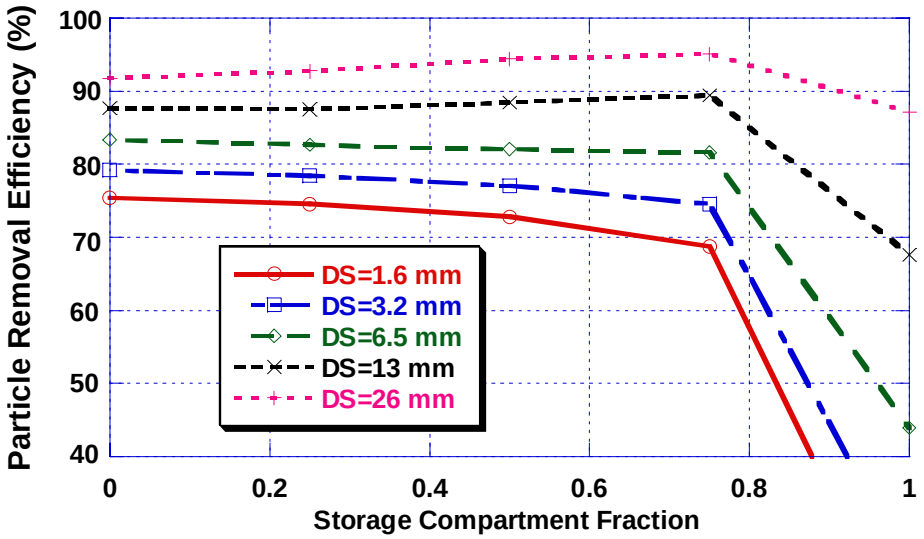


Figure 3-27 Particle Removal Efficiency at Different Design Storm (DS) Sizes

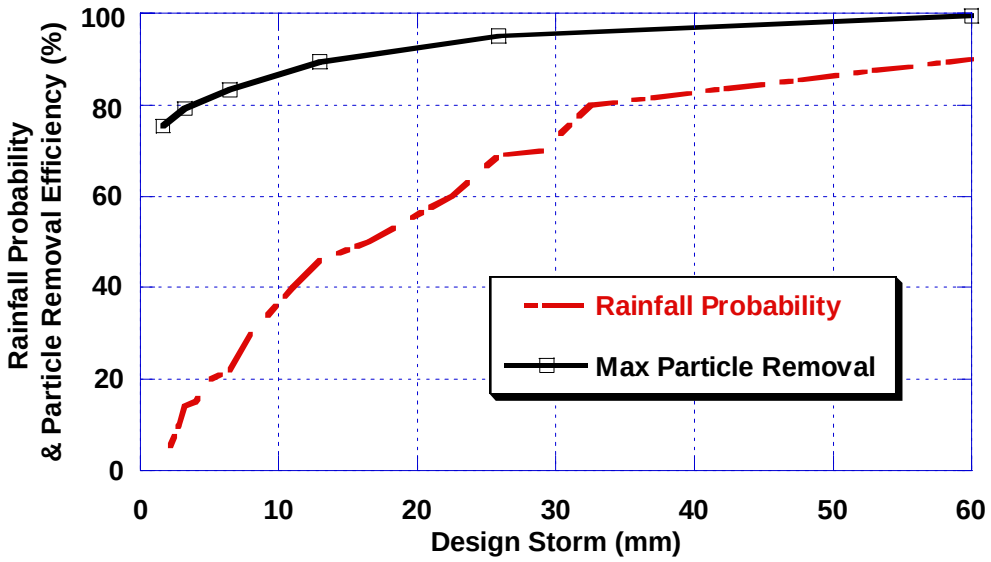


Figure 3-28 Optimized Particle Removal Efficiency and Rainfall Probability vs. Design Storm

When the total design storm is 13 mm, 90% of the particles from the entire season can be removed by the two-compartment tank. If the design storm is doubled, the total particle removal efficiency increases to only 95%.

Total particle removal efficiency does not change drastically with the variation of volume ratio between storage compartment and continuous flow compartment when the storage compartment fraction is less than 0.75 (see Figure 3-29). However, the removal of particles in a specific size range does vary greatly. Figure 5 shows the change in particle removal efficiency for particles in four different size ranges--from 2-10 μm up to 41-104 μm. Large particles with diameters more than 104 μm can be easily removed for any design storm size. This graph illustrates the differential removal of various size particles as a function of design storm size and storage fraction. The removal efficiency of the smallest particles, those with diameters of 2-10 μm, increases with increasing storage fraction for all design storm sizes. Removal efficiency of particles with diameters from 25 to 104 μm decreases with increasing storage tank fraction. It is clear from this figure that storage tank volume primarily benefits removal of the smallest particles. This information is useful for pollutant removal as a function of particle size, which will be discussed below.

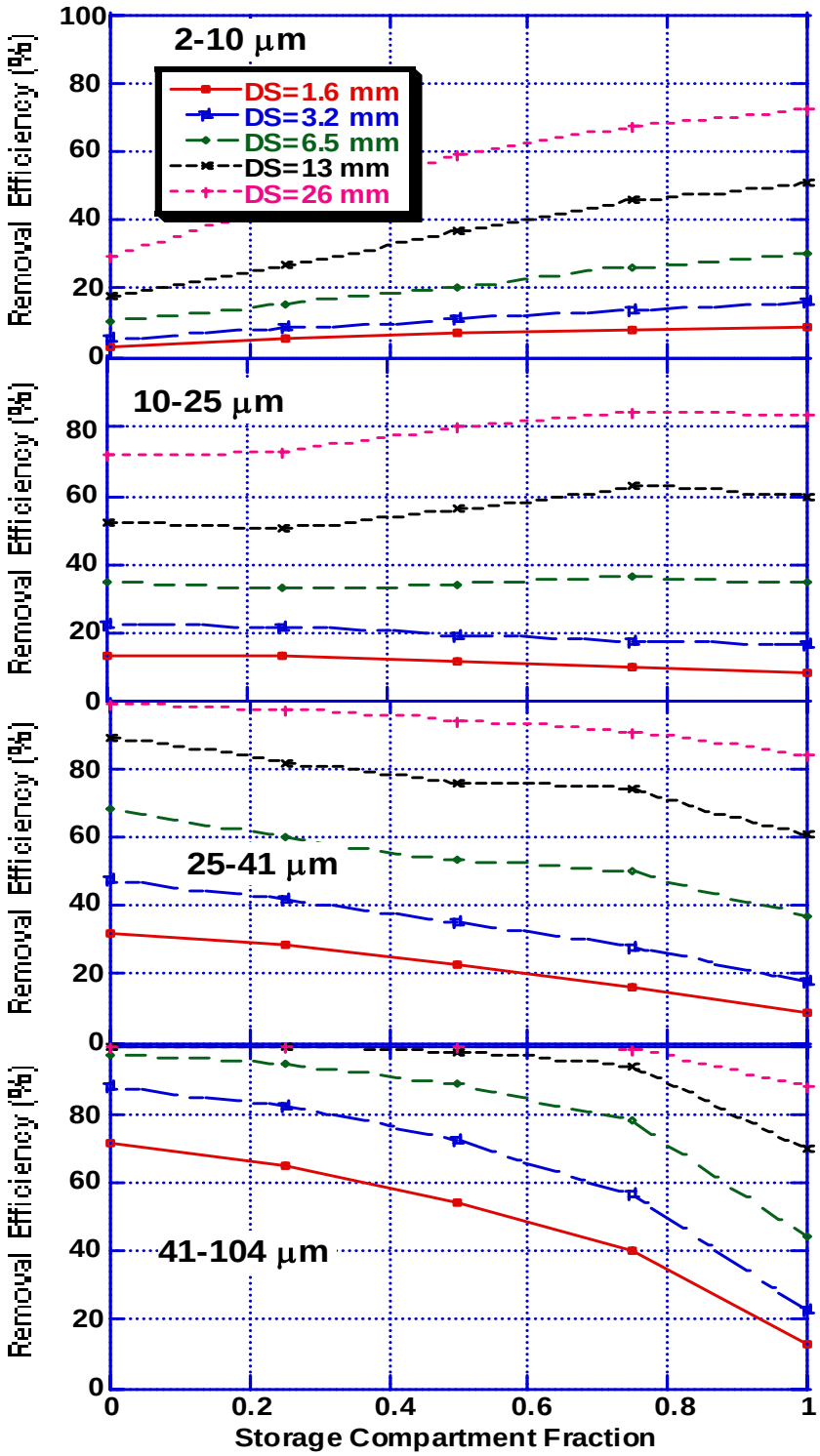


Figure 3-29 Removal Efficiency of Individual Particle Size Ranges at Different Design Storm Sizes

Optimum Contaminant Removal

For pollutants that are sorbed to particles, removal of those particles results in pollutant removal. Pollutant distribution on different size particles is one of the key factors that influence pollutant removal efficiency. Figure 3-27 demonstrates particulate zinc (Zn) removal efficiency for the two-compartment settling tank. For this simulation the Zn concentration distribution as a function of particle size was adapted from Morquecho and Pitt (2003) that is shown in Table 3-6.

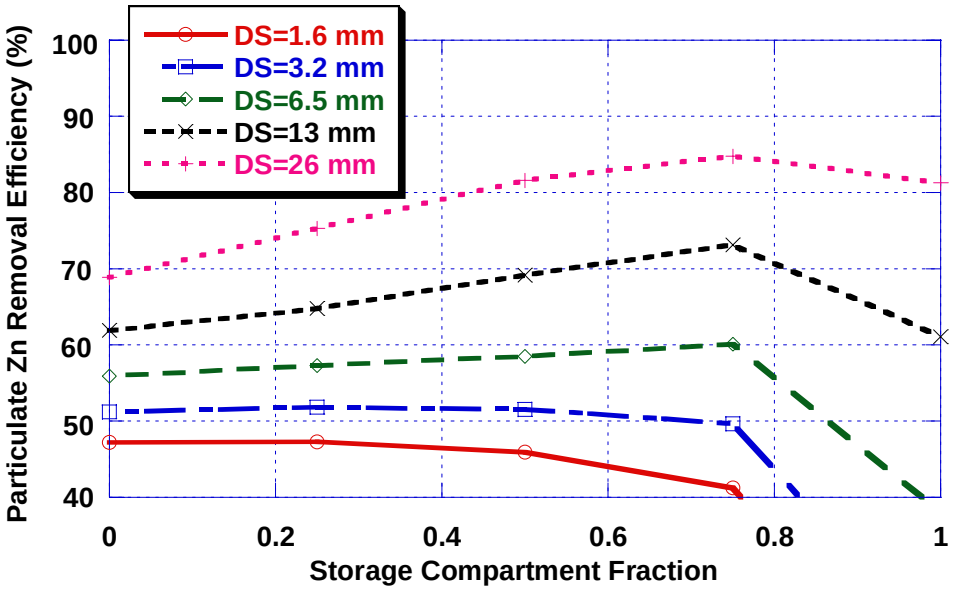


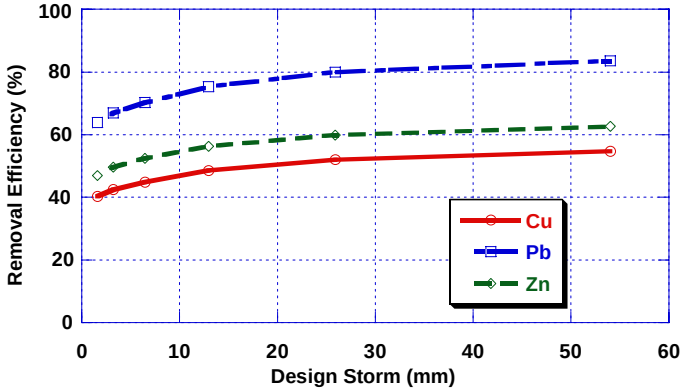
Figure 3-30 Particulate Zinc Removal Efficiency at Different Design Storm (DS) Sizes using Morquecho's Zinc Concentration Distribution on Different particle Size Data

Particulate Zn 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 Figure 3. 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 88% to 89%, 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 particles, e.g. 13,641 μg/g for particles 2-10 μm while 266 μg/g for particles larger than 250 μm in

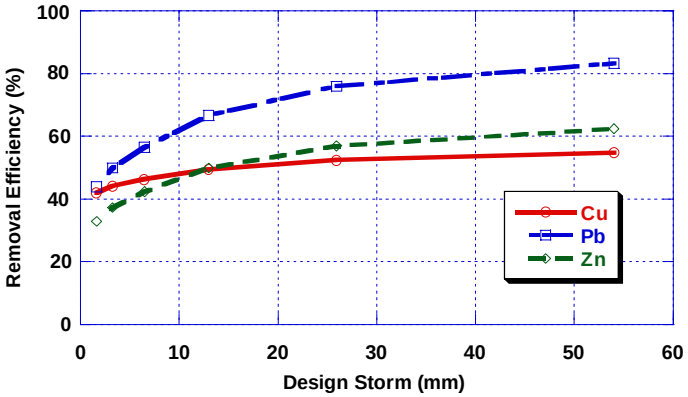
diameter. The higher pollutant concentrations associated with smaller particle sizes shows the importance of their removal and makes increased storage compartment size more important.

Figures 3-31a-c show the maximum metal removal efficiencies for different design storm sizes for metal concentrations data reported by different researchers (Table 3). The optimal storage volume is always used, and is zero for design storms less than 6 to 13 mm, depending on pollutant and particle concentration distributions, and 0.75 for larger design storms. The graphs include 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 dissolved fraction, f_d. Lower values of f_d allow higher metal removal efficiency. For instance, removal efficiencies of Pb are much higher than Cu or Zn due to its low dissolved fraction (f_d values for Pb, Cu and Zn are 0.16, 0.45 and 0.37 respectively).

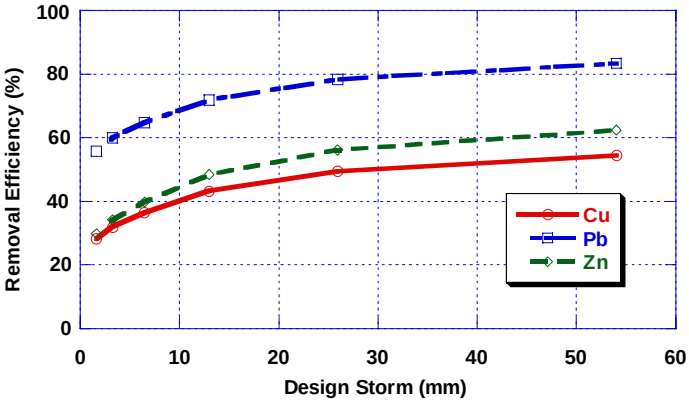
Metal concentration distribution on different size particles also has an obvious influence on removal efficiency. For example, at a design storm of 1.6 mm the removal efficiency of Cu is 0.42 based on the Cu concentration distribution from Lau and Stenstrom 2004 (Figure 8), but it is only 0.28 using data from Roger et al. (1998). This results because there is a large gradient in Cu concentration from small to large particles in Roger et al.'s data while Lau and Stenstrom observed no gradient in Cu concentration with particle size.



(a) Caltrans Data, (2002)



(b) Data of Lau and Stenstrom, (2004)



(c) Data of Roger et al. (1998)

Figure 3-31 The Maximum Removal Efficiency for Individual Pollutants using Different particle size and contaminant data from the literature

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