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Rational Design Concepts Applied to Stormwater Runoff Management

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by

Marcia Ferreira

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Abstract of the Dissertation

Rational Design Concepts Applied to Stormwater Runoff Management

by

Marcia Ferreira

Doctor of Philosophy in Civil Engineering
University of California, Los Angeles, 2014
Professor Michael K. Stenstrom, Chair

After the success of regulating point-source discharges, the major cause of pollution into waterbodies in the United States is stormwater runoff. Runoff usually runs freely into waterbodies and its capture and treatment are usually challenging and costly. Even though many treatment units currently used in the treatment of stormwater runoff are based on sedimentation principles, there is usually a lack of rational design applied to the study of their performance. Runoff treatment units are usually selected on an empirical estimate of their efficiency as opposed to the theoretical basis of their removal mechanism. The common practice is to measure one parameter (such as total suspended solids) of the influent and effluent of the treatment unit and report percent removal as efficiency measurement. However, this practice may not translate in the good removal of pollutants.

This work reports the concentration of fourteen metals as they appear in the dissolved phase and over four particulate size fractions (0.45-8μm, 8-20μm, 20-100μm, and >100μm). For all the metals, the size fraction 8-20μm had the highest concentration and particle strength. This observation emphasizes the importance the importance of studying the particulate-phase metals as a function of particle size distribution. In addition, total suspended solids (TSS) did not correlate strongly with the particulate-phase metals concentration. Thus, if the objective of the treatment unit is to reduce a particular pollutant, measuring TSS will not be a good proxy for efficiency measurement.

This work also analyzes the performance of a hydrodynamic device and a detention basin in removing particles and pollutants. Particle size distribution affects the removal of particles by sedimentation units and thus simple overall removal efficiency can lead to erroneous conclusions regarding the performance. The two full-scale devices analyzed perform well in removing particles within certain size fractions, consistent with sedimentation theory. Using particle size distribution in evaluating treatment unit performance is a more accurate and precise way of determining the actual performance.

The dissertation of Marcia Ferreira is approved.

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2014

To Mimi

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VITA

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PUBLICATIONS AND PRESENTATIONS

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CHAPTER 1

Regulating Water Pollution in the United States

Stormwater runoff is currently the major contributor of pollutants into waterways in the United States. However, until recently, it was merely seen as a nuisance due to flood risks. Stormwater runoff is formed when precipitation flows over the ground, instead of infiltrating into the soil. In highly urbanized areas, due to the extensive use of concrete and asphalt, the surface coverage is almost entirely impervious, preventing the stormwater from seeping into the ground and thus contributing to the increase of surface runoff flow. In addition, urbanization has spread into floodplains, requiring the design and construction of flood control projects, such as the channelization of the Los Angeles river. Although these projects are beneficial from the point of view of the residents, i.e., they move the water quickly away from properties, they favor the increase of volume and rate of runoff flow. This concentrated runoff flow contributes directly to the transport of contaminants, previously accumulated in the streets and roads. A study of 87 stormwater areas (such as roofs, parking areas, streets, detention ponds, etc) showed that 40% of urban runoff contained compounds of moderate toxicity to extremely toxic (Pitt et al., 1995). Unfortunately, problems related to water quality are harder to identify and resolve in comparison to water quantity issues (USEPA, 1983).

Due in part to the success of controlling the discharge of pollutants from point sources, e.g., industrial or wastewater discharges, the diffuse pollution transported by stormwater runoff represents a challenge for municipalities, public agencies, and others. Over the years, several regulations have been introduced to address the impairment of waterways due to diffuse pollution. A brief narrative of the history of water pollution regulations in the United States, from addressing the blockage to waterways to wastewater discharge permitting (Section 1.1) to diffuse pollution (Section 1.2) should help the reader understand the evolution of environmental regulations.

1.1 Controlling Point Source Pollution

Point source pollution, or simply point sources, are identifiable origins for pollutants present in waterways. For example, a pipe discharging industrial waste directly onto a river is considered a point source. Presently, it is unimaginable that such type of discharge would exist in the United States, but it did happen not too long ago and it is still present in many developing countries.

The oldest piece of legislation that remotely dealt with water pollution is the *Rivers and Harbors Appropriation Act* of 1899 (USCongress, 1899). This legislation was introduced because, after the Civil War, rivers and harbors were being appropriated at a fast pace under the supervision of the US Army Corps of Engineers (Cowdrey, 1975). Besides not being part of the presidential agenda, environmental concerns were seen mainly as a local responsibility (Percival, 2001). Water quality was not a concern by modern standards; however, there was a growing unease with waterways being blocked by bridges and industrial activities such as dredging (Cowdrey, 1975). Most of the conflicts, such as pollution caused by smelters, were resolved by common law, instead of legislation (Percival, 2001). Even though the *Rivers and Harbors Appropriation Act* was created to prevent blockage of waterways, a section commonly known as the "Refuse Act" was successfully used in lawsuits regarding the discharge of refuse matter into a river (e.g. United States versus Pennsylvania Industrial Chemical Corp. 411 U.S.

655 (1973) (Burton, 1974)). Since the legislation was intended to keep waterways open for navigation, there were no set limits for discharge or levels of contamination allowed. The lawsuits were based primarily on the visual observation that a discharge was impairing a river.

For half a century, the "Refuse Act" of 1899 was the only piece of legislation dealing, even if indirectly, with water pollution. The first legislation created specifically to deal with water pollution issues was the *Water Pollution Control Act* of 1948. Even though it was drafted to address water pollution, it only allowed the government to start a lawsuit if the discharge of pollutants was causing problems in another state (Barry, 1970). The resistance to the control of point sources was decreasing and in 1956 Congress allocated grants for local governments to build wastewater treatment plants (Percival, 2001). A veto to this allocation was placed by President Eisenhower but quickly overturned by Congress (Percival, 2001). This Act underwent five amendments from 1956 to 1970, but still no water quality standards were set and the inadequacy of the controls were never resolved (Barry, 1970).

The environmental movement of the 1960s, thanks chiefly to Rachel Carson's Silent Spring (Percival, 2001), led to a change to the way the public expected the government to preserve natural resources, which favored the creation of the Environmental Protection Agency (EPA) in December 1970. With the EPA as a regulatory agency, in 1972 the U.S. Congress enacted the *Federal Water Pollution Control Amendments*. One single law, the PL92-500, changed the course of regulatory policy. The Federal government started to have a greater participation in water pollution control, including financial support for publicly owned treatment works (POTWs). PL92-500 also listed small pollution control activities such as oil spills management and creation of sanitary devices for boats and ships. Eventually, it evolved to what became known as the *Clean Water Act* (CWA). The CWA introduced the National Pollutant Discharge Elimination System (NPDES) permits, which is a required permit for point source discharges. All industrial polluters were awarded permits that provided limits on average and maximum daily limits of pollutants discharged. Guidelines were established by industry type, defining the maximum legal permit level, but EPA and states were allowed to assign lower guideline values.

When the NPDES was established, much less was known regarding stormwater runoff, and point source discharges were a major issue that the public could easily observe. Over time, as point sources, such as from wastewater treatment plants, were regulated, attention turned to non-point sources or diffuse pollution, such as carried by stormwater runoff.

1.2 Controlling Non-Point Source Pollution

Due to numerous uncertainties regarding the problems caused by non-point sources, the EPA sponsored a large-scale project called the National Urban Runoff Program (NURP). Its main objectives were to assess the water quality of urban runoff (USEPA, 1983) and the performance of stormwater best management practices (BMP). The NURP findings were published in 1983 and concluded that heavy metals were the most common pollutants in stormwater runoff (USEPA, 1983). In addition, non-point source pollution caused significant water quality impairment in many parts of the United States (USEPA, 1983).

1.2.1 Challenges to the Control of Non-Point Source Pollution

The NURP report, for being the first to look at water quality, offers a simplistic view of treatment. In its findings, street sweeping was considered inadequate while detention basins were labeled as very effective (USEPA, 1983). In reality, the NURP report does not refer to treatment of stormwater but to BMPs. At the time, only wastewater treatment processes were well established and calling stormwater runoff “treatment” would imply a deeper knowledge of how to treat the highly variable quality of runoff. Nevertheless, numerous treatment units were created such as several types of ponds, wetlands, rain gardens, media filters, among others (Section 1.2.2). The challenge of dealing with the quality of stormwater runoff involves a series of components ranging from institutional measures such as public education, street sweeping, product replacement to structural treatment measures such as sand filters and infiltration basins. A single component is not enough to treat the stormwater runoff; a treatment train is necessary.

The understanding of pollutant transport in stormwater runoff is key to the treatment process selection. Predictive models to describe treatment process performance have not existed in many cases, which results in extensive testing and reliance on empirical procedures. The use of predictive models relying on first principles is needed to improve efficiency and reduce overall costs. For example, often sedimentation units are designed to achieve particle removal efficiency relying on retention time as engineering parameter, as opposed to overflow rate. In addition, particle size distribution (PSD) has not been used as a design criteria for the treatment units (Park et al., 2010). PSD information has not been widely available, even though several studies have indicated that the pollutants are adsorbed to the particles (e.g. (Pitt et al., 1995)). The need for high removal efficiency often competes with the need for remote, unattended operation.

The concept of using more theoretical approaches for characterizing treatment unit performance is called unit operations and processes approach, and occurred in the 1950s with wastewater treatment plants (Rich, 1961). The goal of this research is to develop methodologies based on theoretical principles for several treatment units, formerly characterized only as BMPs, and demonstrate how the new methodologies can be used to more precisely interpret data and define treatment performance.

1.2.2 Complying with Regulatory Requirements - Stormwater Runoff Treatment Units

Wastewater treatment plants usually are centralized locations to where all the sewage flow is directed for treatment. Stormwater runoff treatment units, on the other hand, are usually installed in a decentralized manner without operators. This decentralized nature makes it imperative that the stormwater runoff treatment units have low maintenance and do not require frequent operator intervention. In response to the regulations requiring the treatment of stormwater runoff, numerous structural and non-structural approaches have been proposed. The challenge is how to choose the best procedure or treatment unit to accomplish the task. Due to the highly variable nature of stormwater runoff, no single procedure or technique can be sufficient; a treatment train including non-structural approaches and treatment units is preferred.

Figure 1.1: Generic Example of Treatment Train

A treatment train can be described as a series of subsequent treatments or procedures in which each step has the ability of reducing some pollution (Figure 1.1). In case of direct discharge of stormwater runoff into waterways, educational campaigns highlighting its final destination could help minimize gross solids (e.g., litter, trash and leaves). Even if it is hard to measure the impact of educational campaigns, it is a necessary step. Similar to the treatment train used in wastewater treatment plants, the next step is the minimization of gross solids. Street sweeping and the installation of screens on the stormwater drains can be used to reduce the gross solids. Even though the NURP report (USEPA, 1983) has found that the use of street sweeping may not substantially reduce pollutants in the stormwater runoff, street sweeping can remove litter and debris. Similarly to wastewater treatment plants, the removal of gross solids is beneficial to avoid clogging filters or reducing efficacy of other treatment units.

There are two main groups of unit operations that treat stormwater runoff: the ones that rely on settling of particles and the ones that filter the particles. Wet ponds, dry ponds, and artificial wetlands, are all examples of unit processes that rely on the settling of particles to treat the stormwater runoff. An additional benefit of this type of unit is the infiltration of water, which reduces the volume of runoff. Grass swales, filter strips, and sand filters work by filtering the stormwater runoff.

1.2.3 Assessing the Performance of Treatment Units

In 1996, ASCE and the U.S. EPA started a cooperative project to develop a database of available treatment technologies, available online for public use. Currently, the database (http://www.bmpdatabase.org) is supported by the Water Environment Research Foundation, American Society of Civil Engineers (ASCE) Environmental and Water Resources Institute, U.S. Environmental Protection Agency (EPA), Federal Highway Administration and the American Public Works Association. The maintenance and operation of the database is done by Wright Water Engineers, Inc. and Geosyntec Consultants. This centralized database showed the difficulty in comparing different studies (Strecker et al., 2001). The lack of standard methods for studying stormwater runoff, unlike wastewater protocols, makes the comparison among studies virtually impossible. Major inconsistencies are present from the sampling techniques (grab samples vs. automatic or composite sampling, timing of sampling in relation to the start of the runoff) to the water quality constituents (what to measure, methods used, in dissolved vs. particulate form) (Strecker et al., 2001).

There is no single treatment unit that is appropriate for all stormwater runoff treatment. Parameters such as cost and land requirement are important, but knowing how well a certain treatment unit works for the constituent of interest is fundamental. The difficulty is how to interpret the performance published for each treatment unit. Many reports indicate percent removal as the measure of efficiency of a particular treatment unit. However, this is a poor parameter to report because the percentage can be deceiving. As outlined by Strecker et al. (2001), percent removal is a function of the relationship between influent and effluent measurements and not necessarily indicates the performance of a treatment unit. For example, Table 1.1 shows the influent and effluent concentration for a particular pollutant and also the percentage removal. If only the percentage removal values had been published, one would say that for storms 2 and 3 the treatment unit did not perform well. However, that is not the case: for storms 1 and 2 the treatment unit reduced the pollutant effluent concentration to about 25 mg/L, even though the influent concentration on storm 1 is 10 times higher.

Storm	**Inflow Concentration (mg/L)**	**Outflow Concentration (mg/L)**	**Removal by Storm**
1	352	24	93%
2	30	25	17%
3	99	83	16%

Table 1.1: Comparison of pollutant removal efficiency (from Strecker et al., 2001)

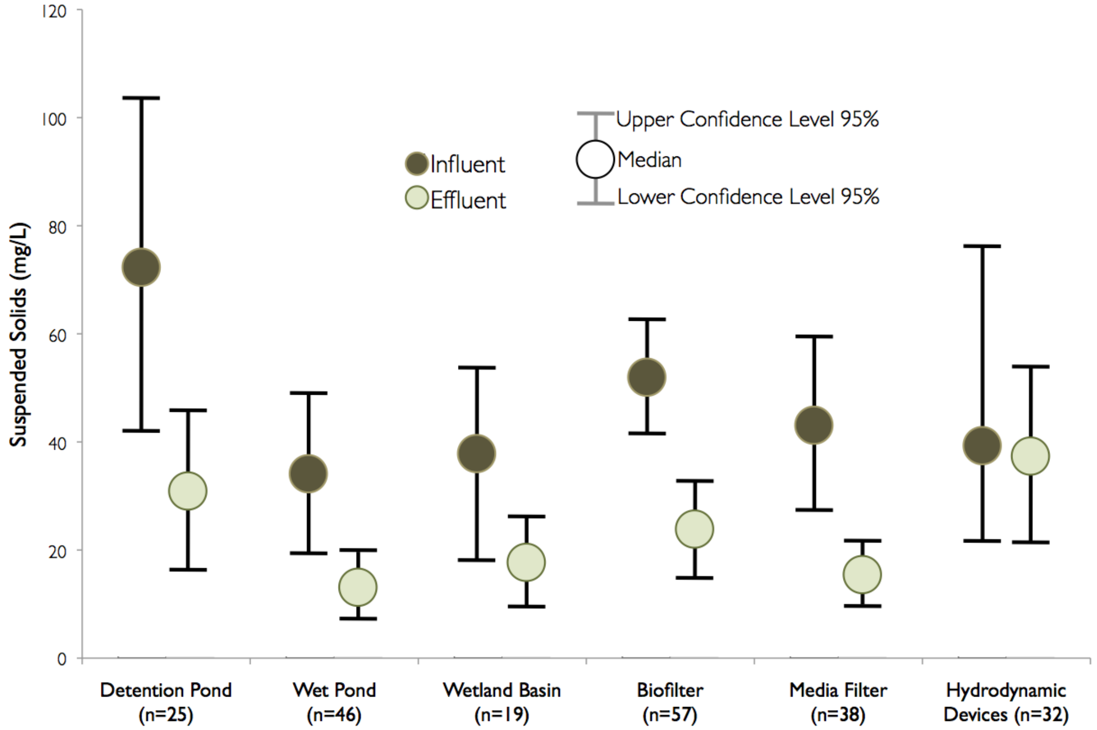

Figure 1.2: Comparison of influent and effluent concentrations for total suspended solids for six categories of treatment units as reported to the International BMP Database ("n" indicates number of samples) (Data source: Geosyntec Consultants, 2008a)

Some of the problems with using percent removal as metric for treatment unit performance are: percent removal calculation is inconsistent among studies; percent removal is strongly influenced by outliers; percent removal does not indicate the total runoff nor the amount of treated runoff. The authors list other 15 reasons (BMPDatabase, 2011). Also, the lack of particle size distribution or size fractionation of samples might indicate that certain treatment units do not work (Figure 1.2). The whiskers on the plot indicate the calculated statistical 95% confidence limits for the data. As indicated by Geosyntec Consultants (2008a), wet ponds, biofilters, and media filters all have statistically significant differences between the median of average influent and effluent. Detention basins and wetland basins do not have strong statistical significant differences, while hydrodynamic devices have no statistical significant differences between the median of average influent and effluent. As highlighted in the study (Geosyntec Consultants, 2008a), the treatment units were combined into the umbrella terms without considering the differences in design for each treatment unit. The authors of the report suggested future work in creating sub-categories that would more adequately combine treatment units. However, the broad classification might not be the only reason for the lack of good performance for the treatment units.

A study describing the 3-year life of five Austin Sand Filters constructed and operated by Caltrans (Barrett, 2003) showed that the effluent total suspended solids (TSS) was usually lower than 10 mg/L even when the influent TSS was 200 mg/L. This way of reporting is better than reporting on a storm-by-storm basis because this would imply that all the storms are similar. Also, for treatment units with a permanent pool, the influent and effluent during a single storm event are not necessarily related (Strecker et al., 2001). Unless the storm is large enough to displace the entire volume of the pool, storm-by-storm analysis should be discouraged (Strecker et al., 2001).

1.3 Aim of the dissertation

Even though most treatment units work on the basis of sedimentation, particle size distribution (PSD) information is not used since it is not commonly part of studies (Park et al., 2010). Rather, the main design criteria are retention time concepts and filtration rates (Park et al., 2010). Several studies have highlighted that pollutants are transported adsorbed on the surface of particles (Pitt et al., 1995, Lau and Stenstrom, 2005), and thus having a clear understanding on how the treatment unit removes the particles is fundamental.

Earlier studies have indicated that most of the mass of particles are concentrated in the larger fractions (i.e. greater than 200μm), while other studies (Lau and Stenstrom, 2005) demonstrate that pollutants are transported on the surface of particles, making the understanding of performance of treatment units based on particle removal more critical.

In 1961, L. G. Rich wrote “Today, (. . .) processes are becoming more complex and there is an increased emphasis on higher efficiencies. Empiricism can no longer be trusted. (. . .) Although empirical design is still the rule in practice, the book has been oriented toward rational design” (Rich, 1961). While he was referring to wastewater treatment, his words are valid today in respect to stormwater runoff treatment. Currently, stormwater runoff treatment units are based on empirical data and very few theoretical, or rational, bases. It is past due that stormwater runoff treatment should be seen as unit operations in the same way water and wastewater treatment are.

Aim of this dissertation: This work uses particle size distribution (PSD) to provide a more accurate estimate of overall treatment unit removal efficiency that can serve as a selection guide.

CHAPTER 2

Highway Runoff: Fourteen Metals in Five Size Fractions

Highway runoff is an important non-point source of pollutants, especially metals (Section 2.1). This chapter reports data from 17 storm events at three highway sites (Section 2.2) for six commonly sampled metals: cadmium, chromium, copper, lead, nickel, and zinc. The study also reports the results of eight additional metals: aluminum, arsenic, cobalt, iron, manganese, selenium, strontium, and vanadium (Section 2.3). For each of the fourteen metals, concentrations in the soluble phase, defined as passing a 0.45 μm filter, and particulate phase concentrations on four size fractions from 0.45 to larger than 100 μm are reported.

In addition to metals concentrations, comparisons between the water quality parameters from this study and other highway runoff studies are included (Section 2.4). One noticeable pattern is that, for all the fourteen metals, the size fraction 8-20μm has the highest concentration and particle strength. This observation emphasizes the importance of studying the particulate-phase metals as a function of particle size distribution (Section 2.5).

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2.1 Introduction

Highways are significant non-point sources due to their extensive impervious areas. Runoff on highways can easily capture and transport contaminated particles deposited on the pavement. The sources of pollutants in highway runoff are numerous. Davis et al.(2001) has shown that atmospheric deposition contributes to lead, copper, and cadmium pollution, vehicle brake wear to copper, and tire wear to zinc. A study in Japan (Osaki et al., 2004) has identified other sources of metal pollution to highways: tire wear containing zinc and cadmium, white road marking paint containing cadmium and arsenic, yellow road marking paint containing lead and chromium, road pavement containing nickel, and gray painting and anti-corrosives used on guardrails containing nickel, zinc, and chromium. Used motor oil can contribute significant amounts of metals to the runoff (Table 2.1), with zinc being the main component of all heavy metals emissions on a mass basis (Boughton and Horvath, 2004).

Table 2.1: Metals present in used motor oil.

	This Study*	**CA Recycled Oil****		**Maryland Recycled Oil*****
	avg (ppm)	avg (ppm)	range	avg (ppm)
Cr	0.53	1.4	<1 to 2	
Ni	1.72	1	<1 to 1.7	
Cu	21.16	40	28 to 64	0.89
Zn	502	822	600 to 877	104.28
As	0.03	-	-	
Cd	0.04	1	<1 to 2	0.023
Pb	3.36	33	18 to 38	0.31

* Analysis of a composite sample of used motor oil from about 50 vehicles.

** (Boughton and Horvath, 2004) *** (Davis et al., 2001)

There are numerous studies reporting the concentration of metals in highway runoff. Most of these studies, including (Sansalone et al., 1996, Characklis and Wiesner, 1997, Helmreich et al., 2010), report metal fractionation between dissolved (as filtered on a 0.45μm filter) and particulate phases. Others, such as (Sansalone and Buchberger, 1997, Roger et al., 1998, Morquecho and Pitt, 2003, Tuccillo, 2006), describe PSD and the associate metal fractionation for size fractions. This study goes beyond the limitations of sieving and reports values for fourteen metals in five size fractions ($< 0.45\mu$m, $0.45-8\mu$m, $8-20\mu$m, $20-100\mu$m, and $> 100\mu$m). Knowledge of concentrations as a function of particle size can be used to predict treatment unit removal efficiency on a rational basis. This work aims to highlight the importance of studying the metals fractionation (beyond dissolved vs particulate) as a basis for the selection of runoff treatment units.

2.2 Methodology

As part of a long-term study sponsored by the California Department of Transportation (Caltrans), three sites in West Los Angeles were chosen for monitoring (Figure 2.1). All sites are almost completely impervious capturing stormwater runoff from the highways 101 or 405; represent very small catchment areas (from 3917 to 16918 m^2), and host heavy traffic load (approximately 300,000 annual average daily traffic). Since southern California has a Mediterranean climate, the rainy season is concentrated during winter (December-February).

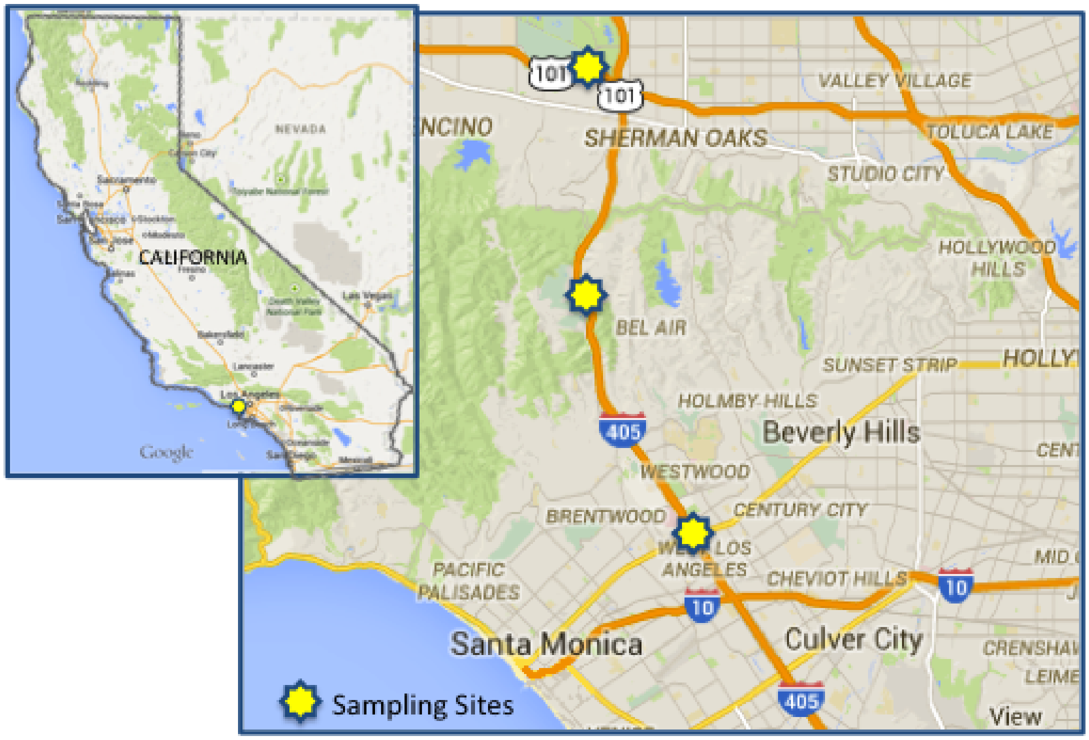


Figure 2.1: Three HighwayRunoff Sampling Sites

2.2.1 Field and Laboratory Procedures

On each of the three sites (Table 2.2), grab samples were collected every 15 minutes during the first hour of detectable runoff, and then hourly during the storm similarly to the sampling protocol described by (Han et al., 2006a). The number of samples depended on the duration of the storm (Table 2.3 and Table 2.4), and the more frequent sampling during the first hour was to capture the first flush of pollutants (Ma et al., 2009). For all three sites, American Sigma Ultrasonic 950 Area Velocity Flow Meters (American Sigma, Loveland, Colorado) were used to record runoff flow and rainfall information was obtained by the use of tipping bucket rain gauges with volume resolution of 0.25mm/tip. Flow-weighted composite samples were obtained by automatic samplers (Sigma 900MAX, American Sigma), and comparisons to grab samples have been presented previously (Han et al., 2006a).

The samples were transported to the laboratory at UCLA within 6 hours of collection in order to initiate the particle size distribution (PSD) analysis. This is the maximum holding time to allow accurate PSD counts for particles between 0.5μm and 500μm (Li et al., 2005). The samples for other analysis were stored at 4^oC.

Table 2.2: Sampling Site Description

Site Name	**Site Location**	**Post (km)**	**ADT (cars/day)**	**Catchment area (ha)**	**Impervious**
Site 1	101 Freeway	29.2	328,000	1.3	100%
Site 2	405 Freeway	53.6	260,000	1.7	95%
Site 3	405 Freeway	49.7	322,000	0.4	100%

Particle size distribution (PSD) was measured with a Nicomp Particle Sizing Systems (Santa Barbara, California) AccuSizer 780 optical particle size analyzer module equipped with an auto-dilution system and a light scattering/extinction sensor (analogous mechanism to Coulter counter) to obtain counts for particles measuring between 0.5μm and 500μm. In this manuscript, the term PSD refers to the actual number of particles in the sample, and not the mass of particles.

Duplicate samples were sequentially filtered into five selected fractions: dissolved ($< 0.45\mu$m), $0.45 - 8\mu$m, $8 - 20\mu$m, $20 - 100\mu$m, and $> 100\mu$m. The suspended solids retained in each filter were digested using nitric acid and microwave extraction following EPA method 3051A, and then diluted to 50 ml. US EPA method 200.8 was used on the Agilent 7500i Inductively Coupled Plasma-Mass Spectrometer (ICP-MS) to analyze the filtrate (for the $< 0.45\mu$m size fraction) and the extraction fluid for the fourteen metals and ultimate detection limits were about 0.001μg/L. The final concentration is a concentration (μg/L) that represents the mass of metal by volume of runoff filtered. Solid phase concentration was not always measurable because the solids mass retained on the filter paper was sometimes less than the detection limit of the balance.

Table 2.3: Number of Grab Samples for Each Pair Site/Storm

	Antecedent Dry (days)	**Site 1**	**Site 2**	**Site 3**
17-Oct-04	215	8	12	-
26-Oct-04	6	12	12	14
5-Dec-04	8	12	12	14
7-Jan-05	2	12	12	12
10-Feb-05	8	12	12	12
18-Mar-05	5	-	12	5
28-Apr-05	31	-	10	7

Eleven water quality parameters were measured in the bulk sample following methods described in the (Methods, 1998). The measured parameters were: Total Suspended Solids (TSS), Volatile Suspended Solids (VSS), Turbidity, Conductivity, Hardness, Chemical Oxygen Demand (COD), Dissolved Organic Carbon (DOC), Oil and Grease, Ammonia, Nitrate, and Nitrite.

2.2.2 Data Analyses

Event mean concentration (EMC) is the flow-weighted concentration over the duration of the storm, which is numerically calculated by integrating the product of concentration and flowrate. Since this study uses a series of grab samples, the integration was substituted by a summation of the product of discrete values of pollutant concentration and flow volumes over each discrete time interval to calculate total pollutant mass and total runoff volume, as shown in Equation 2.1.

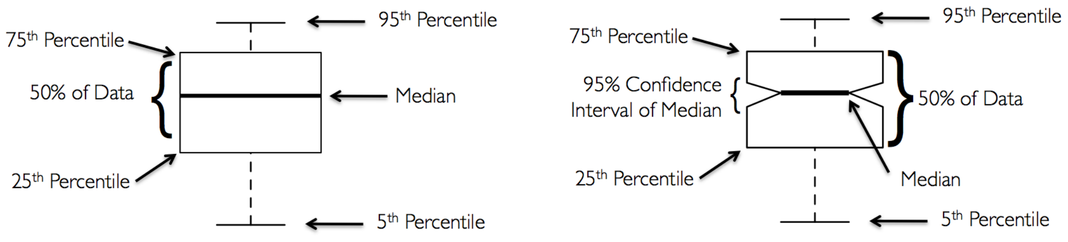
$$EMC = \frac{M}{V} = \frac{\sum M_i}{\sum V_i} = \frac{\sum C_i Q_i \Delta t_i}{\sum Q_i \Delta t_i} \tag{2.1}$$

where M = total pollutant mass (g), V = total flow volume (m^3), M_i = pollutant mass in the i^{th} interval (g), V_i = flow volume in the i^{th} interval (m^3), C_i = pollutant concentration at time i (mg/L), Q_i = flowrate in the i^{th} interval (L/min), t_i = i^{th} time interval (minutes)

Particle strength is defined as the concentration of the metal (μg/L) in a particulate fraction divided by the total suspended solids concentration (mg/L) in the same particulate fraction, giving a mass/mass concentration (mass of the metal by the mass of particles). This is mathematically similar to the concentration for metals obtained by first separating the particles by sieving, thus obtaining a mass of particles on a size fraction, and then measuring the concentration of the metal.

2.2.3 Statistical Analyses

All statistical analyses were performed using “R” statistical software (freely available online at http://www.r-project.org). Most of the data is graphically represented in one of two types of boxplots (Figure 2.2) to illustrate the spread of the distribution of the data and its skewness.



(a) Standard boxplot (b) Notched boxplot

Figure 2.2: Definition of boxplots

Each dataset was first checked for normality by the use of probability plots, and when necessary, a log-transformation was used prior to the other statistical tests as used previously by other authors (e.g., (Strecker et al., 2001, Buren et al., 1997)). ANOVA (Analysis of Variance) with α=0.05 was performed on the log-transformed data to identify statistically significant differences among groups. A calculated p-value of 0.01 or less was taken as evidence of a significant difference in the mean results for each group. Tukey's Honest Significant Difference (THSD) Test with 95% family-wise confidence level (similar to Fisher's Least Significant Test for pair-comparison) was used as a follow-up. The THSD Test highlights the pair-wise comparisons exposing which pairs have significant differences. Correlation analysis among water quality parameters and metals concentration were made using the EMC values for each storm/site combination using the Spearman method. This method was preferred over the Pearsons method for being less sensitive to outliers and for indicating a monotonic increasing or decreasing correlation and not necessarily a linear relationship between the constituents.

2.3 Results

A total of 202 discrete samples were collected at the three monitoring sites during seven storms in the winter of 2004-2005 (Table 2.3). The 2004-2005 winter season was a wetter than average season. According to the National Weather Service Public Information Statement from July 1st, 2005, the 2004-2005 rainy season had 950mm of rainfall in downtown Los Angeles, which was greater than the average of 400mm and only the 1883-1884 year had greatest rainfall of 970mm. Both the precipitation data and the runoff flow (Table 2.4) were measured at each sampling site.

Eleven water quality parameters were measured for all 202 samples and reported as EMCs (Event Mean Concentration) values (Table 2.5). The difference between mean and median for all the parameters measured indicates that the distribution of the parameters is not normal, which has been observed in other stormwater runoff studies (i.e., (Buren et al., 1997, Helmreich et al., 2010)).

Particle size distribution (PSD) was identified for all 202 collected samples. The raw data consisted on particle counts in each diameter (from 0.5μm to 500μm) as detected by the PSD analyzer (Figure 2.3). Statistical comparison using ANOVA analysis and THSD Test of the log-transformed number of particles in each of the four size fractions indicated significant difference between all pairs of size fractions, except between the size fractions 8-20μm and 20-100μm, significant at the 81% confidence level. The smaller size fraction (0.45-8μm) represents 99.79% of all particles measured. First-flush was observed for all storms and sites, but impacted only the total number of particles and not the relative distribution among particles size fractions.

Table 2.4: Storm Event Characteristics

	Rain Start Date	**Event Rain (mm)**	**Maximum Intensity (mm/hr)**	**Total Runoff Flow (L)**	**Peak Flow (L/s)**
Site 1	10/17/2004	11.94	24.38	19,911	7.02
	10/26/2004	61.47	36.58	704,237	96.2
	12/5/2004	14.22	12.19	53,246	8.12
	1/7/2005	155.96	33.53	1,847,605	58.3
	2/10/2005	68.83	27.43	449,613	40.2
Site 2	10/17/2004	21.84	30.48	254,334	110
	10/26/2004	48.26	27.43	710,979	106
	12/5/2004	17.02	12.19	250,631	62.6
	1/7/2005	287.02	33.53	4,392,559	93.8
	2/10/2005	78.23	27.43	1,011,186	98.2
	3/18/2005	5.08	3.05	51,587	8.47
	4/28/2005	32.77	27.43	522,038	109
Site 3	10/26/2004	45.21	30.48	131,656	25.0
	12/5/2004	14.73	12.19	24,850	5.65
	1/7/2005	202.18	51.82	758,139	66.5
	2/10/2005	52.07	24.38	176,821	27.1
	3/18/2005	2.79	3.05	4,102	2.42
	4/28/2005	29.72	42.67	104,863	37.3

Table 2.5: Summary of water quality parameters for combined storms/sites (values are in EMCs)

	Mean	**Median**	**Minimum**	**Maximum**	**Standard Deviation**
TSS (mg/L)	63.5	49.5	9.49	199.8	45.6
VSS (mg/L)	26.5	19.2	5.35	82.0	20.9
Turbidity (NTU)	27.3	19.5	10.6	71.0	17.9
Conductivity (m℧/cm)	255	104	31.2	1575	409
Hardness (mg/L)	107	35.5	11.3	1011	232
COD (mg/L)	159	75.4	36.3	736	190
DOC (mg/L)	27.8	10.9	2.89	176	44.0
Oil and Grease (mg/L)	9.56	4.61	1.32	42.2	11.5
NH3-N (mg N/L)	2.43	1.09	0.431	10.0	2.99
NO2- (mg N/L)	0.398	0.0938	0.0388	4.70	1.08
NO3- (mg N/L)	1.51	0.881	0.222	5.37	1.58

For each of the selected size fractions, the volume occupied by the particles was calculated assuming spherical geometry (Figure 2.4). The values exhibit a skewed distribution, very close to a log-normal distribution. Therefore, the values were log-transformed before other analyses were performed. ANOVA analysis of the calculated volumes in the four fractions indicated that a significant difference ($p \ll 0.01$) existed among at least one pair of size fractions. THSD Test indicated statistically significant difference between the largest size fraction ($> 100\mu$m) and each one of the other size fractions. No statistically significant difference was indicated for the other pairs.

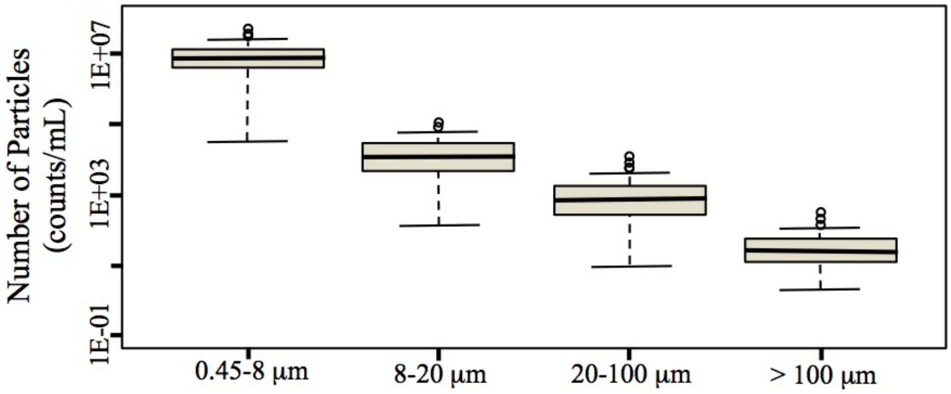


Figure 2.3: Measured number of particles for all 202 samples

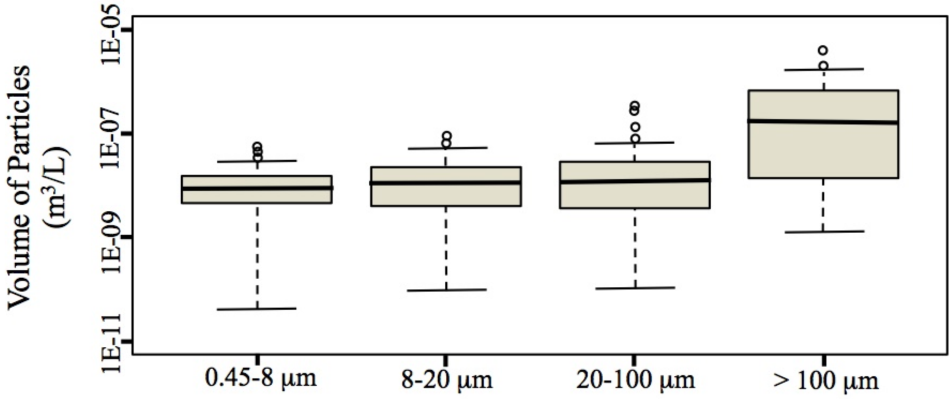


Figure 2.4: Calculated volume of particles for all 202 samples

For each of the selected size fractions, the total surface area of the particles in each sample was calculated assuming spherical geometry (Figure 2.5). Statistical comparison using ANOVA analysis and THSD Test of the log-transformed calculated surface areas of the four size fractions indicated significant difference between all pairs of size fractions, except between the size fractions 20-100μm and greater than 100μm.

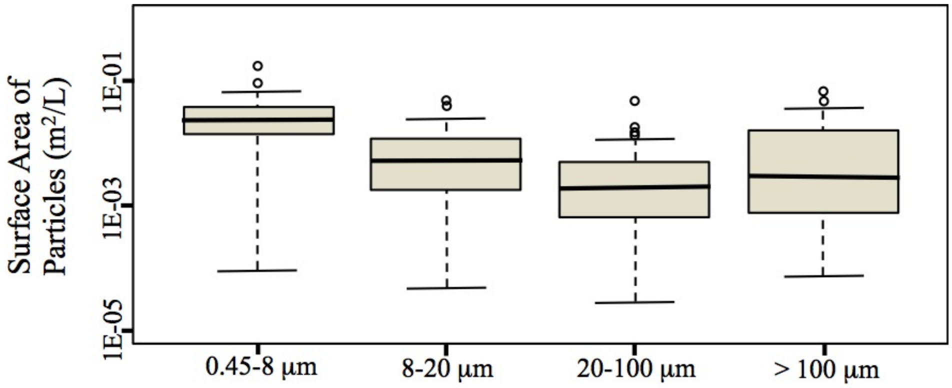


Figure 2.5: Calculated surface area of particles for all 202 samples

The concentrations (mass of metal per volume of filtered runoff) of the six commonly reported metals - cadmium (Cd), chromium (Cr), copper (Cu), lead (Pb), nickel (Ni), and zinc (Zn) - are shown in boxplots in Figures 2.6 and 2.7. For each metal, there are 5 boxplots representing the 5 size fractions. Each boxplot contains data from all 202 samples collected, and the box represents the distribution around the median value. The mean concentration of a metal in the dissolved phase (defined as passing through a 0.45μm filter) is higher than the concentration in the particulate phase for Cd, Cu, Ni, and Zn (Table 2.6). Statistical comparison of the log-transformed data using ANOVA analysis and THSD Test, as indicated on Table 2.6, shows that the mean concentration on all size fractions for each metal are different ($p \leq 0.01$), with the exception of Cd, Cu, Pb, and Zn in the fractions 0.45-8μm and 20-100μm.

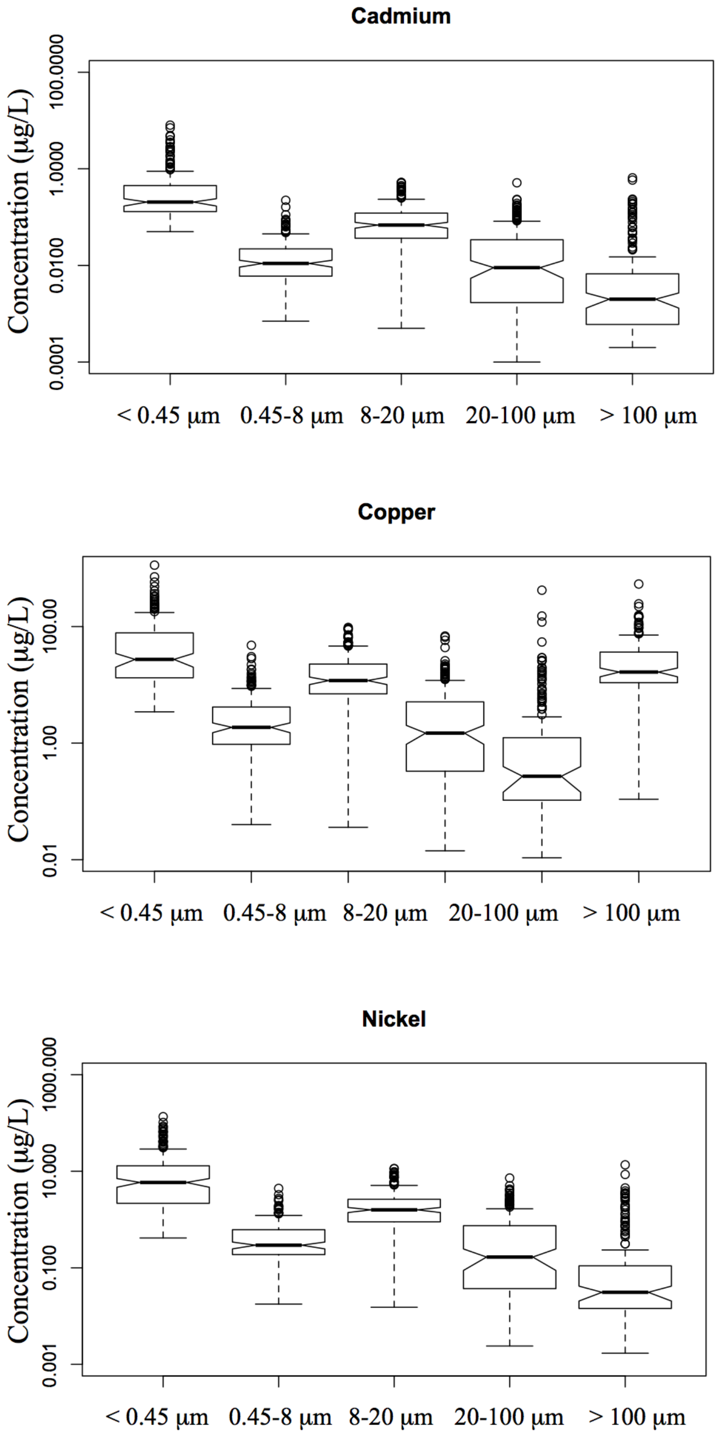


Figure 2.6: Boxplots for the concentrations of cadmium, copper, and nickel in five size fractions

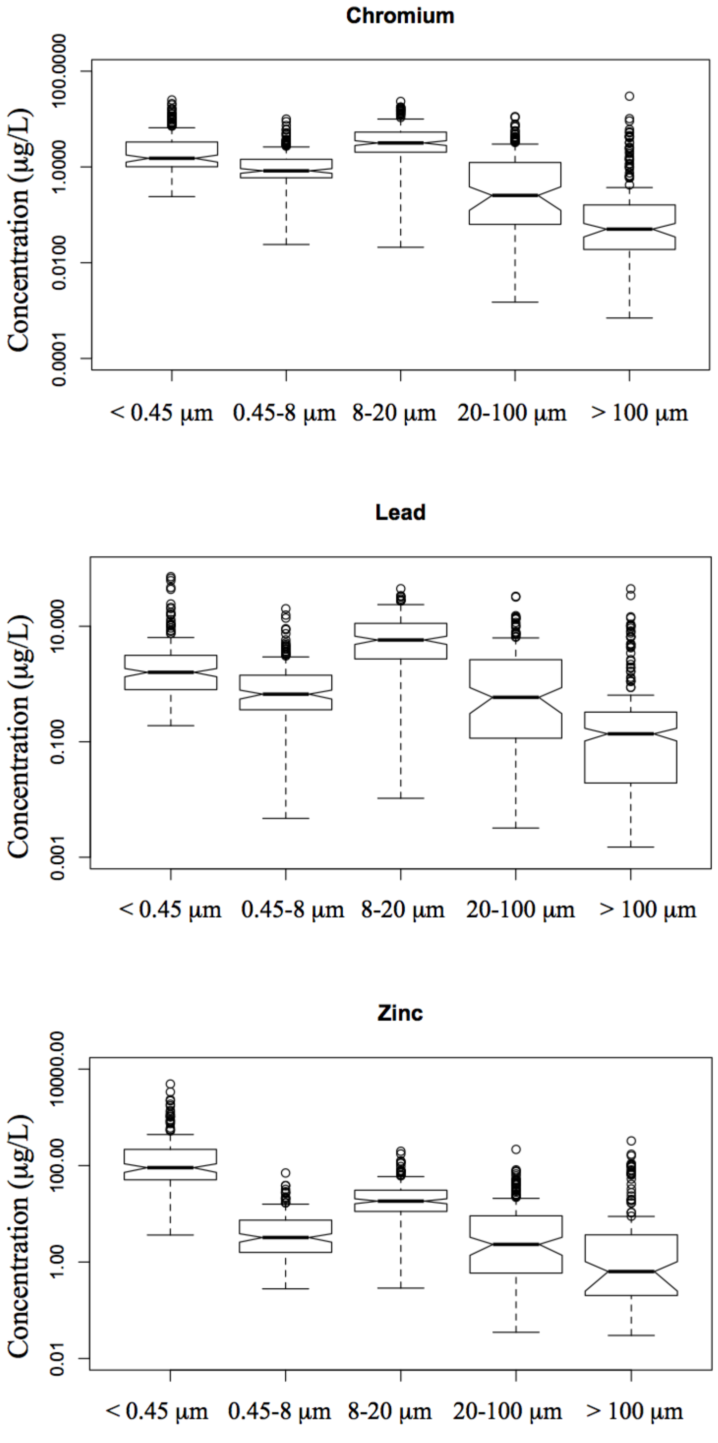


Figure 2.7: Boxplots for the concentrations of chromium, lead, and zinc in five size fractions

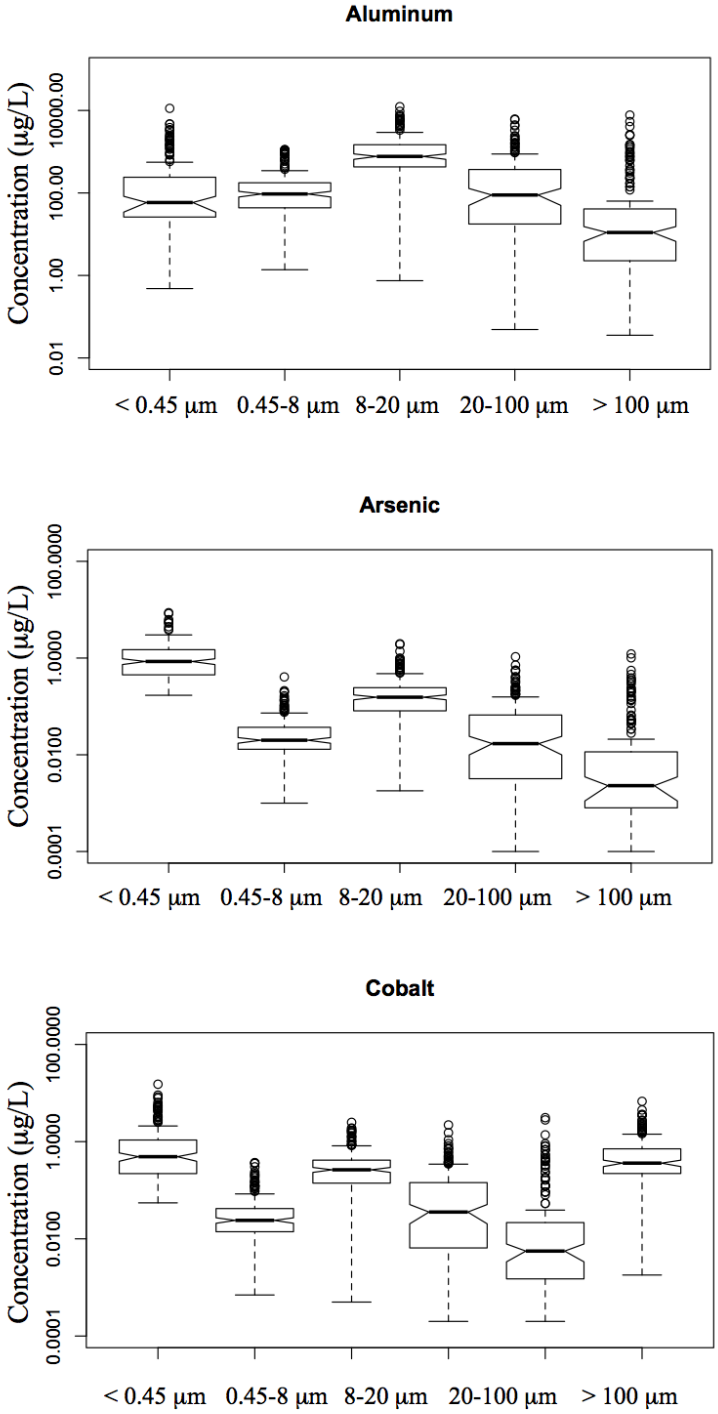


Figure 2.8: Boxplots for the concentrations of aluminum, arsenic, and cobalt in five size fractions

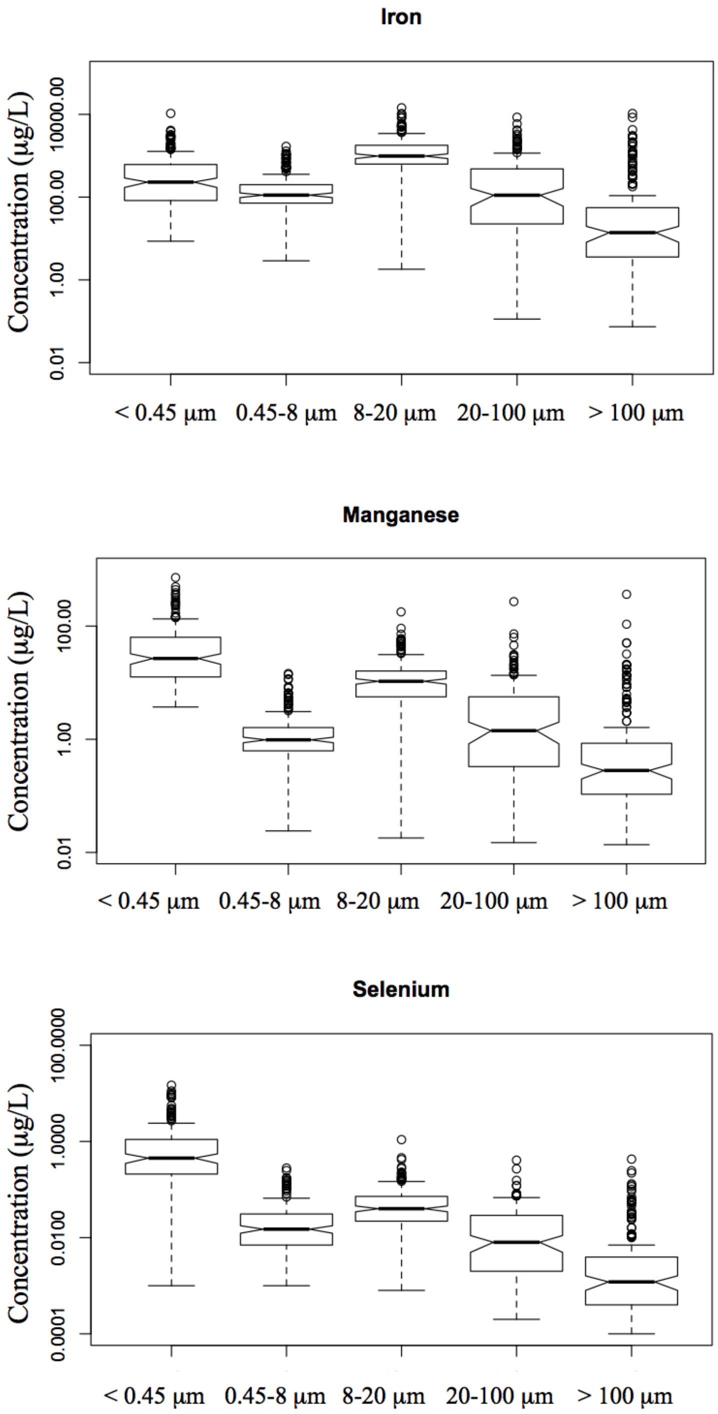


Figure 2.9: Boxplots for the concentrations of iron, manganese, and selenium in five size fractions

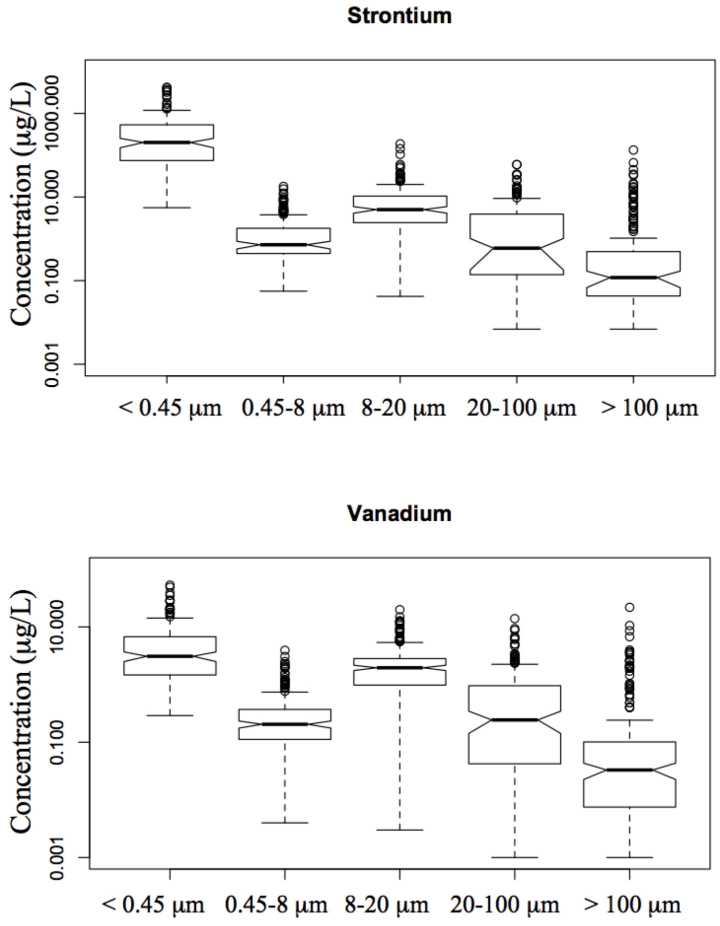


Figure 2.10: Boxplots for the concentrations of strontium and vanadium in five size fractions

Boxplots for the concentration of eight non-traditionally studied metals aluminum (Al), arsenic (As), cobalt (Co), iron (Fe), manganese (Mn), selenium (Se), strontium (Sr), and vanadium (V) are shown in Figures 2.8, 2.9, and 2.10. ANOVA and THSD Test analyses performed on the log-transformed data for each of the size fractions for each of the metals shows that there is a statistically significant difference among the means of each fraction ($p \leq 0.01$). As indicated in Table 2.6, there is no statistical difference for the fractions 0.45-8μm and 20-100μm for all metals except cobalt; also aluminum does not have a statistical difference for the fraction $< 0.45\mu$m and 0.45-8μm and $< 0.45\mu$m and 20-100μm. In addition, aluminum and iron had the highest concentration in the fraction 8-20μm; for all other metals, the dissolved fraction ($< 0.45\mu$m) has the highest mean.

The particle strength calculation requires a TSS measurement for each size fraction. For the dataset in this study, TSS could only be measured for the composite sample. Using the PSD information an estimated particle strength can obtained by calculating the TSS, assuming that the particles are spheres with density 2.6 g/cm^3. Using this calculated TSS (mg of particles/L) and the concentration of the metal (μg of metal/L), the Particle Strength of the pollutants in each particulate size fraction was calculated (Figures 2.11, 2.12, 2.13, 2.14, and 2.15). The group of six commonly reported metals (Figure 2.11 and 2.12) has the highest mean in the 8-20μm size fraction, and all the size fractions are statistically different from the others (ANOVA and THSD Test with $p \leq 0.01$). Similarly, the group of eight non-traditional metals (Figures 2.13, 2.14, and 2.15) has the highest mean in the 8-20μm size fraction, and all the size fractions are statistically different from the others (ANOVA and THSD Test with $p \leq 0.01$), except for vanadium in the fractions 0.45-8μm and 20-100μm.

Table 2.6: Results from THSD test indicating if difference between size fractions is statistically significant (yes) or not (no) for metals

	Cd	**Cr**	**Cu**	**Ni**	**Pb**	**Zn**	**Al**	**As**	**Co**	**Fe**	**Mn**	**Se**	**Sr**	**Va**
F1-F2	yes	yes	yes	yes	yes	yes	**no**	yes	yes	yes	yes	yes	yes	yes
F1-F3	yes	yes	yes	yes	yes	yes	yes	yes	yes	yes	yes	yes	yes	yes
F1-F4	yes	yes	yes	yes	yes	yes	**no**	yes	yes	yes	yes	yes	yes	yes
F1-F5	yes	yes	yes	yes	yes	yes	yes	yes	yes	yes	yes	yes	yes	yes
F2-F3	yes	yes	yes	yes	yes	yes	yes	yes	yes	yes	yes	yes	yes	yes
F2-F4	**no**	yes	**no**	yes	**no**	**no**	**no**	**no**	yes	**no**	**no**	**no**	**no**	**no**
F2-F5	yes	yes	yes	yes	yes	yes	yes	yes	yes	yes	yes	yes	yes	yes
F3-F4	yes	yes	yes	yes	yes	yes	yes	yes	yes	yes	yes	yes	yes	yes
F3-F5	yes	yes	yes	yes	yes	yes	yes	yes	yes	yes	yes	yes	yes	yes
F4-F5	yes	yes	yes	yes	yes	yes	yes	yes	yes	yes	yes	yes	yes	yes
HM	F1	F3	F1	F1	F3	F1	F3	F1	F1	F3	F1	F1	F1	F1
HPM	F3	F3	F3	F3	F3	F3	F3	F3	F3	F3	F3	F3	F3	F3

(size fractions: F1 = $< 0.45\mu$m, F2 = $0.45 - 8\mu$m, F3 = $8 - 20\mu$m, F4 = $20 - 100\mu$m F5 = $> 100\mu$m. HM = Highest mean and HPM = Highest Particulate mean)

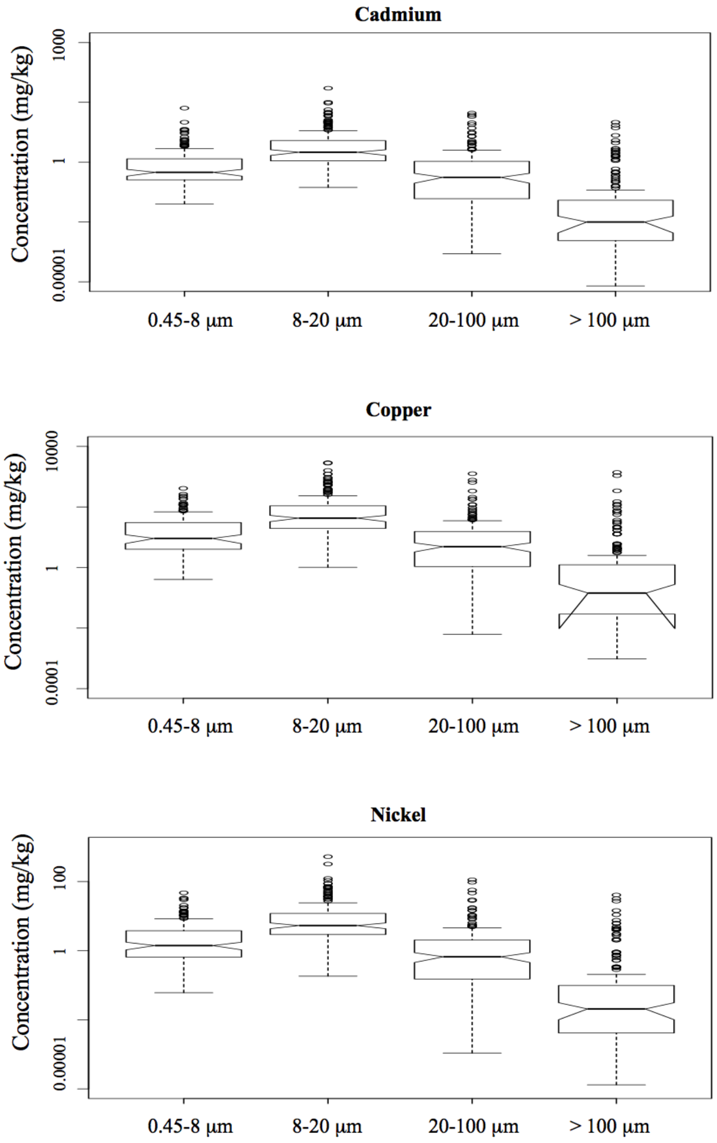


Figure 2.11: Boxplots for the particle strength of cadmium, copper, and nickel in five size fractions

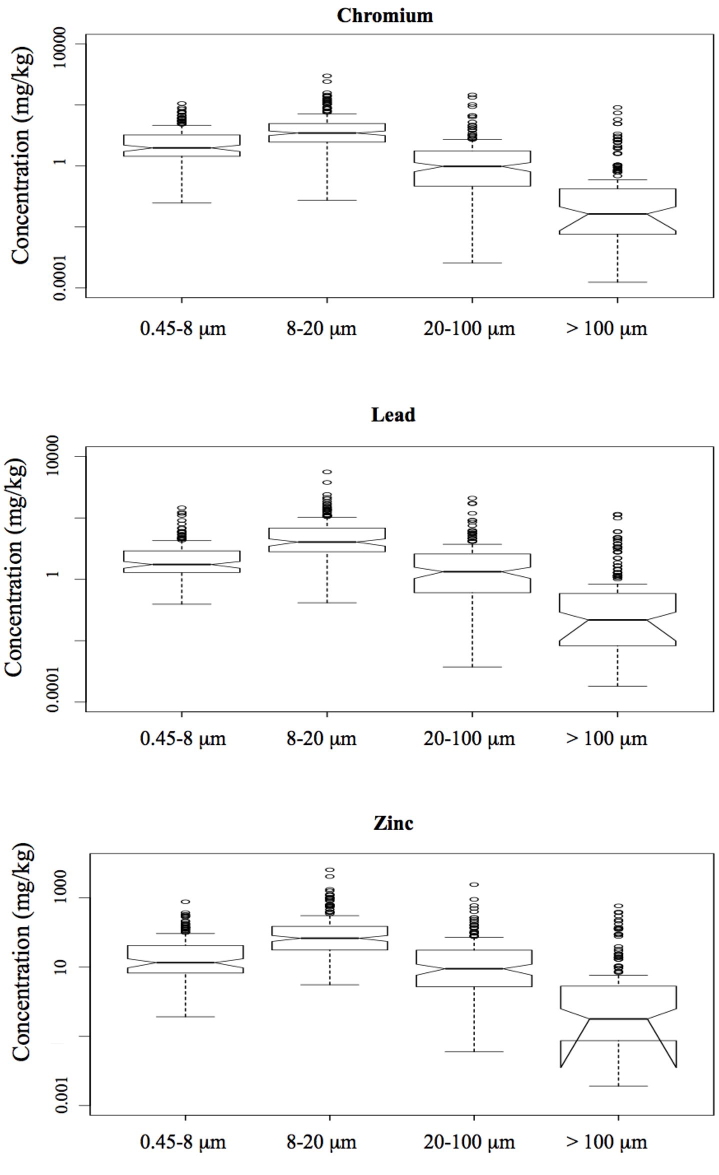


Figure 2.12: Boxplots for the particle strength of chromium, lead, and zinc in five size fractions

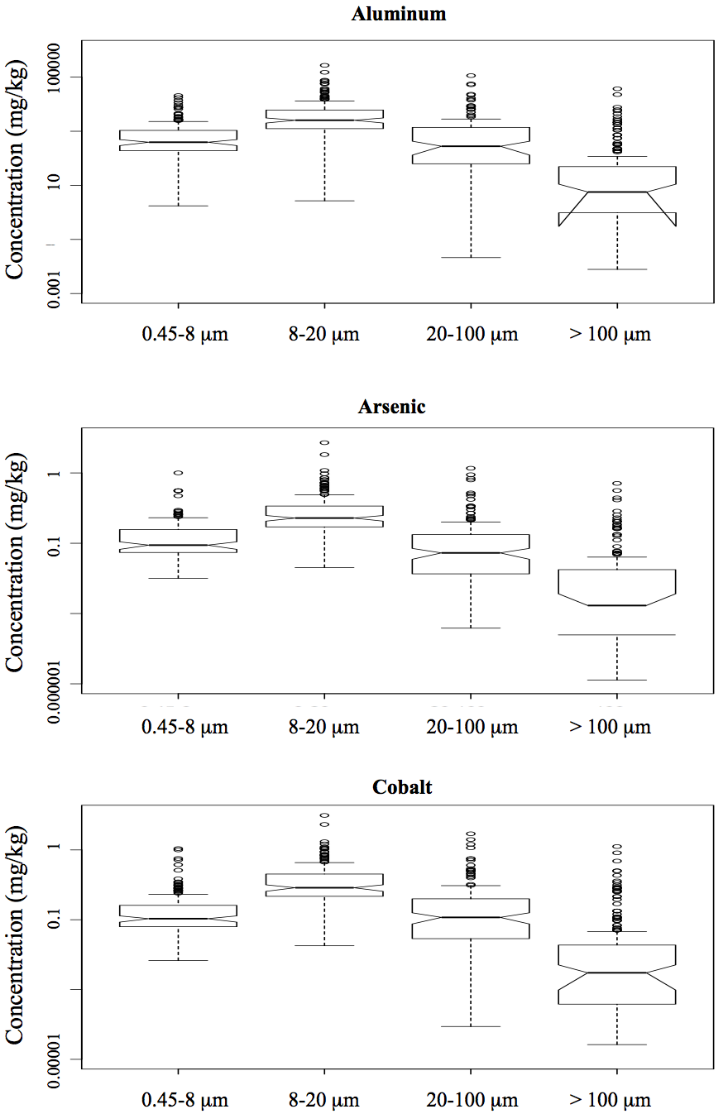


Figure 2.13: Boxplots for the particle strength of aluminum, arsenic, and cobalt in five size fractions

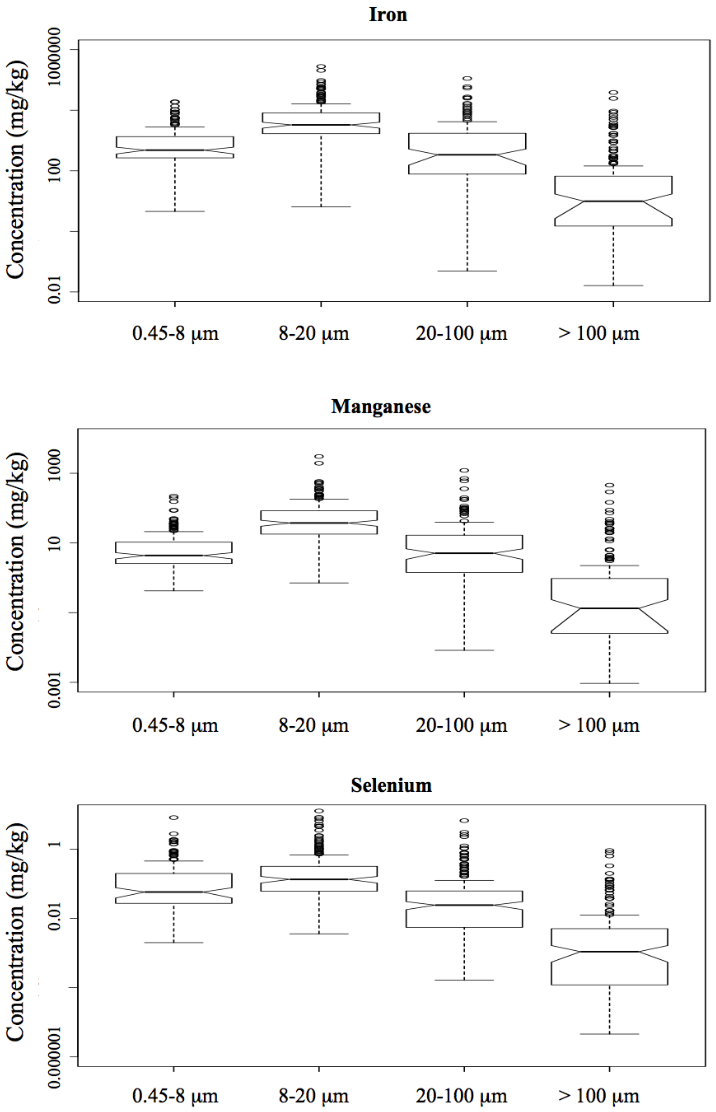


Figure 2.14: Boxplots for the particle strength of iron, manganese, and selenium in five size fractions

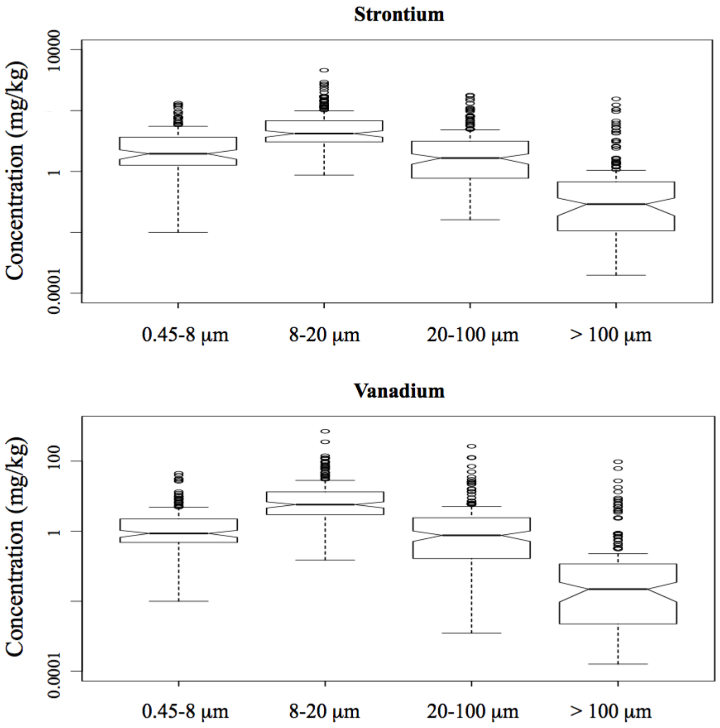


Figure 2.15: Boxplots for the particle strength of strontium and vanadium in five size fractions

2.4 Discussion

The water quality constituents observed in this study are comparable to previous samples from these three sites, which were surveyed during 62 storms between 2000 and 2003 (Han et al., 2006a). Table 2.7 shows a comparison between the 2000-2003 dataset (Han et al., 2006a) and the current study. Even though the 2004-2005 rainy season was wetter than the 2000-2003 seasons, the mean EMCs for TSS of both datasets are similar, which is less than half of the California statewide dataset (monitoring program during 1997-2001 presented by Kayhanian et al. (2003)). This variation could have occurred because the runoff from the highway shoulders in our three sites drains away from the sample sites, which is not typical of all Caltrans sites. Also, the mean for turbidity in 2000-2003 (Han et al., 2006a) is almost twice as much as the reported in this study and the statewide value is about fourteen times as high. This could be attributed to a dilution effect due to the wetter rainy season.

Due to the presence of outliers in the dataset in this study, the Spearman rank-order technique was used to determine correlations among water quality parameters. Table 2.8 shows the correlation analysis results for the water quality parameters shown on Table 2.5. There is a strong correlation ($\rho \geq 0.80$) between the following pairs: TSS-VSS, VSS-Turbidity, Conductivity-Hardness, COD-DOC, COD-OG (Oil and Grease), COD-NH3-N, COD-NO2-, COD-NO3-, DOC-OG, DOC-NH3-N, DOC-NO2-, DOC-NO3-, OG-NH3-N, OG-NO2-, OG-NO3-, and NO2–NO3-. Han et al. (2006b) using Pearson correlation coefficients indicated strong correlation ($\rho \geq 0.80$) between TSS-VSS, COD, DOC, Conductivity-Hardness, COD-OG, and DOC-NH3-N. The pH was not routinely measured for all samples in this study; samples from the same sites in three previous years averaged 6.7 ± 0.6 for all the 62 monitored storms ((Han et al., 2006a)).

Since many treatment units report performance based on removal of TSS, it

Table 2.7: Comparison of water quality event mean concentration with other studies

	Current Study	**Study 1***	**Study 2****	**Study 3*****
TSS (mg/L)	63.5	67.7	175	122
VSS (mg/L)	26.5			40.1
Turbidity (NTU)	27.3	46.8	366	
Conductivity ($\mu\mho$/cm)	255	239	363	
Hardness (mg/L)	107	78.9	50	
COD (mg/L)	159	253		197
DOC (mg/L)	27.8	66.9	19	
Oil and Grease (mg/L)	9.56	14	6.6	
NH3-N (mg N/L)	2.43	4.6	0.83	
NO2- (mg N/L)	0.398	0.3	0.14	
NO3- (mg N/L)	1.51	2.7	0.97	

* (Han et al., 2006a) ** (Kayhanian et al., 2003) *** (Sansalone et al., 1998)

is interesting to see how well TSS correlates with the pollutant concentrations. For this study, correlation tables between TSS and all the size fractions for each of the fourteen metals were created. As an example, TSS does not have a strong correlation with any of the size-fractions for arsenic (Table 2.9). However, there is a very strong correlation between the 8-20μm size fraction and the total concentration for the particulate arsenic and also between the dissolved ($< 0.45\mu$m) arsenic and the total arsenic concentration. Similarly to arsenic, all the other thirteen metals exhibit a strong correlation ($\rho \geq 0.80$) between the 8-20μm size fraction and the total concentration for the particulate phase of the metal (data not shown). This correlation strengthens the observation that the highest mean for particle strength is at the 8-20μm size fraction (Figures 2.11 through 2.15). Table 2.10 shows the correlation between TSS and the particulate fraction for each of the fourteen metals.

Table 2.8: Correlation analysis results among event mean concentration values for water quality parameters

	TSS (mg/L)	**VSS (mg/L)**	**Turbidity (NTU)**	**Cond. (μ℧/cm)**	**Hardness (mg/L)**	**COD (mg/L)**	**DOC (mg/L)**	**OG (mg/L)**	**NH3-N (mg N/L)**	**NO2- (mg N/L)**	**NO3- (mg N/L)**
TSS	*****	**0.905**	0.639	0.267	0.23	0.416	0.389	0.459	0.558	0.104	0.201
VSS	< 0.001	*****	**0.81**	0.521	0.465	0.672	0.672	0.732	0.765	0.426	0.488
Turbidity	0.005	< 0.001	*****	0.453	0.335	0.688	0.664	0.707	0.738	0.598	0.678
Cond.	0.282	0.028	0.061	*****	**0.981**	0.628	0.699	0.783	0.68	0.587	0.703
Hardness	0.357	0.053	0.174	< 0.001	*****	0.556	0.626	0.699	0.602	0.515	0.618
COD	0.087	0.003	0.002	0.006	0.018	*****	**0.967**	**0.934**	**0.924**	**0.843**	**0.827**
DOC	0.111	0.003	0.003	0.002	0.007	< 0.001	*****	**0.963**	**0.895**	**0.895**	**0.862**
OG	0.057	0.001	0.001	< 0.001	0.002	< 0.001	< 0.001	*****	**0.934**	**0.802**	**0.827**
NH3-N	0.018	< 0.001	0.001	0.003	0.01	< 0.001	< 0.001	< 0.001	*****	0.695	0.787
NO2-	0.68	0.079	0.01	0.012	0.031	< 0.001	< 0.001	< 0.001	0.002	*****	**0.866**
NO3-	0.422	0.042	0.003	0.002	0.007	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	*****

(values above diagonal are Spearman rank-order coefficients ”r”; values below diagonal are probability values (p-values);
values in bold show correlation > 0.8)

Table 2.9: Correlation analysis results among event mean concentration values for arsenic concentrations

	TSS	**F1**	**F2**	**F3**	**F4**	**F5**	**Particulate**	**Total**
TSS	*****	-0.073	0.352	0.478	0.531	0.773	0.529	-0.009
F1	0.773	*****	0.418	0.001	-0.441	-0.323	-0.104	**0.948**
F2	0.152	0.086	*****	0.544	-0.024	0.079	0.494	0.523
F3	0.047	>0.999	0.021	*****	0.682	0.556	**0.975**	0.232
F4	0.025	0.069	0.928	0.002	*****	0.713	0.761	-0.276
F5	<0.001	0.191	0.754	0.018	0.001	*****	0.624	-0.195
Particulate	0.026	0.68	0.039	<0.001	<0.001	0.007	*****	0.117
Total	0.974	<0.001	0.028	0.352	0.267	0.436	0.644	*****

(values above diagonal are Spearman rank-order coefficients “r”;
values below diagonal are probability values (p-values); values in bold show correlation > 0.8)
(size fractions: F1 = $< 0.45\mu$m, F2 = $0.45 - 8\mu$m, F3 = $8 - 20\mu$m, F4 = $20 - 100\mu$m, F5 = $> 100\mu$m. Particulate is the sum of F2, F3, F4, and F5)

None of the metals has a strong correlation ($\rho \geq 0.80$) with TSS, opposed to the results reported by Helmreich et al. (2010) for copper, lead, and zinc. However, a previous study of the same sites (Han et al., 2006b) also showed no correlation between TSS and the following metals: cadmium, chromium, copper, nickel, lead, and zinc. TSS showed a good correlation ($\rho \geq 0.70$) with all metals in the $> 100\mu$m size fraction, except for manganese, selenium, and zinc (Table 2.11). In addition, with a few exceptions, all metals in the $> 100\mu$m size fraction show strong correlation ($\rho \geq 0.80$) with one another. Perhaps the discrepancy with the Helmreich et al. (2010) study is due to the fact that their samples contained more of the larger particles ($> 100\mu$m) than the current study. This result highlights the importance of investigating several size fractions and not only particulate versus dissolved fractions.

Due to the limitations of sieving (difficult to separate particles in size fractions smaller than about 40μm), this study uses particle strength to characterize the

Table 2.10: Correlation analysis results among event mean concentration values for TSS and the metals in the particulate fraction

	TSS	**Cr**	**Ni**	**Cu**	**Zn**	**As**	**Cd**	**Pb**	**Al**	**V**	**Mn**	**Fe**	**Co**	**Se**	**Sr**
TSS	*****	0.622	0.474	0.672	0.356	0.529	0.595	0.571	0.761	0.765	0.548	0.773	0.614	0.228	0.451
Cr	0.007	*****	**0.92**	**0.934**	0.738	0.783	**0.839**	0.612	0.676	**0.814**	0.703	0.752	0.787	0.744	**0.814**
Ni	0.049	<0.001	*****	**0.822**	**0.853**	**0.886**	**0.884**	0.707	0.647	0.792	0.759	0.732	**0.858**	**0.825**	0.742
Cu	0.003	<0.001	<0.001	*****	0.674	0.631	0.713	0.486	0.612	0.738	0.626	0.699	0.711	0.655	0.701
Zn	0.147	0.001	<0.001	0.003	*****	0.75	**0.822**	0.622	0.664	0.583	0.678	0.719	0.703	0.767	0.653
As	0.026	<0.001	<0.001	0.006	0.001	*****	**0.909**	**0.853**	0.763	**0.868**	**0.872**	0.798	**0.961**	0.612	0.562
Cd	0.011	<0.001	<0.001	0.001	<0.001	<0.001	*****	**0.856**	0.75	**0.833**	0.777	**0.806**	**0.868**	0.684	0.703
Pb	0.015	0.008	0.001	0.043	0.007	<0.001	<0.001	*****	0.692	**0.833**	0.717	0.732	**0.841**	0.509	0.412
Al	<0.001	0.003	0.005	0.008	0.003	<0.001	0.001	0.002	*****	0.779	**0.818**	**0.975**	0.789	0.321	0.451
V	<0.001	<0.001	<0.001	0.001	0.013	<0.001	<0.001	<0.001	<0.001	*****	**0.872**	**0.806**	**0.911**	0.558	0.608
Mn	0.02	0.002	<0.001	0.007	0.003	<0.001	<0.001	0.001	<0.001	<0.001	*****	**0.806**	**0.911**	0.517	0.507
Fe	<0.001	<0.001	0.001	0.002	0.001	<0.001	<0.001	0.001	<0.001	<0.001	<0.001	*****	**0.835**	0.37	0.536
Co	0.008	<0.001	<0.001	0.001	0.002	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	¡0.001	*****	0.534	0.496
Se	0.361	0.001	<0.001	0.004	<0.001	0.008	0.002	0.033	0.194	0.018	0.03	0.131	0.024	*****	0.728
Sr	0.062	<0.001	0.001	0.002	0.004	0.017	0.002	0.091	0.062	0.009	0.034	0.024	0.038	0.001	*****

(values above diagonal are Spearman rank-order coefficients ”r”; values below diagonal are probability values (p-values);
values in bold show correlation > 0.8)

Table 2.11: Correlation analysis results among event mean concentration values for TSS and the metals in the $> 100\mu m$ size fraction

	TSS	**Cr**	**Ni**	**Cu**	**Zn**	**As**	**Cd**	**Pb**	**Al**	**V**	**Mn**	**Fe**	**Co**	**Se**	**Sr**
TSS	*****	0.74	0.717	0.756	0.676	0.773	0.74	0.719	**0.814**	0.725	0.583	**0.806**	0.763	0.633	0.701
Cr	0.001	*****	**0.971**	**0.95**	**0.802**	**0.955**	**0.967**	**0.942**	**0.955**	**0.961**	**0.891**	**0.967**	**0.973**	**0.86**	**0.913**
Ni	0.001	<0.001	*****	**0.95**	**0.839**	**0.942**	**0.971**	**0.959**	**0.938**	**0.965**	**0.874**	**0.95**	**0.969**	**0.827**	**0.932**
Cu	<0.001	<0.001	<0.001	*****	0.765	**0.932**	**0.95**	**0.928**	**0.95**	**0.946**	**0.831**	**0.942**	**0.946**	**0.804**	**0.92**
Zn	0.003	<0.001	<0.001	<0.001	*****	**0.86**	**0.866**	**0.845**	**0.814**	**0.808**	0.715	**0.843**	**0.829**	0.707	**0.876**
As	<0.001	<0.001	<0.001	<0.001	<0.001	*****	**0.975**	**0.967**	**0.948**	**0.965**	**0.895**	**0.955**	**0.973**	**0.804**	**0.94**
Cd	0.001	<0.001	<0.001	<0.001	<0.001	<0.001	*****	**0.977**	**0.932**	**0.955**	**0.868**	**0.942**	**0.957**	**0.862**	**0.961**
Pb	0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	*****	**0.928**	**0.969**	**0.876**	**0.936**	**0.955**	**0.825**	**0.944**
Al	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	*****	**0.963**	**0.897**	**0.994**	**0.975**	0.738	**0.88**
V	0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	*****	**0.92**	**0.967**	**0.99**	0.779	**0.913**
Mn	0.013	<0.001	<0.001	<0.001	0.001	<0.001	<0.001	<0.001	<0.001	<0.001	*****	**0.905**	**0.926**	0.688	**0.835**
Fe	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	*****	**0.981**	0.783	**0.897**
Co	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	*****	0.789	**0.924**
Se	0.006	<0.001	<0.001	<0.001	0.001	<0.001	<0.001	<0.001	0.001	<0.001	0.002	<0.001	<0.001	*****	**0.864**
Sr	0.002	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	*****

(values above diagonal are Spearman rank-order coefficients "r"; values below diagonal are probability values (p-values); values in bold show correlation > 0.8)

Table 2.12: Correlation analysis results among event mean concentration values for lead in all particulate size fractions

	0.45-20μm	**0.45-100μm**	**>100μm**	**Particulate**
0.45-20μm	*****	**0.988**	0.181	**0.976**
0.45-100μm	<0.001	*****	0.24	**0.992**
>100μm	0.01	0.001	*****	0.295
Particulate	<0.001	<0.001	<0.001	*****

(values above diagonal are Spearman rank-order coefficients "r");

(values below diagonal are probability values (p-values);

values in bold show correlation > 0.8)

concentration of metals by the mass of particles in a certain size fraction. However, the major disadvantage in using particle counts is the lack of particle mass information. A previous study at the same field sites (Li et al., 2006) showed good linear correlation between particle counts and total suspended solids (TSS) for the bulk sample ($r^2 = 0.689$). For the dataset in this study, TSS and number of particles are not linearly correlated ($r^2 = 0.00678$), which could be attributed to the episodic appearance of large particles ($> 100\mu$ m). This lack of correlation forced the estimation of TSS based on spherical particles with density 2.6 g/cm^3. The existence of large particles is important in estimating total solids loading but is of lesser importance for metals loading since the metals are less concentrated on the largest particles. If the largest particle fraction ($> 100\mu$m) is excluded, the sum of the other particulate-phase metals correlates well ($\rho > 0.8$) with the total metals concentration, including the metals in the dissolved phase. The correlation for lead is shown on Table 2.12, and similar correlations are observed for the other metals (data not shown).

Assuming spherical shape for particle geometry is an approximation, since runoff particles are irregularly shaped (Sansalone et al., 1998). In addition, particle density is dependent on the nature of the material carried by the runoff: the more organic the lower the density and the more mineral, the higher the density. This relationship has been shown for runoff by comparing particle density and organic content (Kayhanian et al., 2008) and by comparing particle density and mineral content (Andral et al., 1999). In the literature, densities for stormwater runoff commonly range from 2.1 to 2.9 g/cm^3: 2.4 to 2.86 g/cm^3 for roadway runoff samples (Andral et al., 1999); 2.75 to 2.86 g/cm^3 for coarse fraction particles embedded in snowmelt (Cristina et al., 2002); 2.14 and 2.54 g/cm^3 for particles in a road gutter (Zanders, 2005); 2.1 to 2.7 g/cm^3 for highway runoff (Lin et al., 2009); among others). However, Kayhanian et al. (2008) reported a lower range of densities (1.6 to 1.8 g/cm^3), showing that particle density is an important parameter to be characterized instead of relying on any approximated value. Since particle density was not measured in this study, we used 2.6 g/cm^3 to be consistent with previous studies that also assumed particle density (such as Li et al., 2005), although we note that there is growing evidence indicating that particle density, especially for the smallest particles, may be less (Zanders, 2005, Kayhanian et al., 2008).

One simple way to study metals fractionation is by the use of mass fraction ratio, which is the ratio of dissolved metal element mass to particulate metal element mass (Sansalone et al., 1996). If the mass fraction ratio is greater than 1.0 then the metal is mainly in the dissolved form, and treatment units based on particle removal may not be effective in reducing the pollutant of interest. However, even if the mass fraction ratio is less than 1.0, removal efficiency is still uncertain for sedimentation/filtration-based treatment units because they are based on a specific particle size removal, which needs to be studied. This is the main reason the present study divided the samples into 4 size fractions for the particulate phase. Due to the highly variable nature of stormwater runoff, treatment trains are a preferred option rather than a single treatment unit type. In addition, if the pollutant of interest is mostly on the fine particles, sedimentation-based treatment units may not be recommended (Helmreich et al., 2010).

2.5 Conclusion

This chapter has reported the concentration of fourteen metals as they appear in the dissolved phase (defined as filtered through a 0.45μm filter) and over several size-fractions. The observation that the size fraction 8-20μm has the highest concentration and particle strength emphasizes the importance of studying the particulate-phase metals as a function of particle size distribution. The following specific conclusions are made:

1. For each of the fourteen metals, the concentrations in all five size fractions are, in general, statistically different (Table 2.6);
2. Highest mean metal concentrations occur either in the dissolved fraction or the 8-20μm size fraction (Figures 2.6 through 2.10) and the metals in this fraction strongly correlate with the total particulate phase metals concentration (Table 2.9).
3. Among water quality parameters, TSS is only correlated to VSS (Table 2.8);
4. TSS did not correlate strongly with the particulate-phase metals concentration (Table 2.10);
5. For all fourteen metals, the largest size fraction ($> 100\mu$m) does not correlate with the particulate-phase fraction (Table 2.12).

CHAPTER 3

Highway Runoff: Particulate and Dissolved Mercury

Mercury, a highly toxic and ubiquitous environmental contaminant, is rarely studied in stormwater runoff. Due to their large impervious coverage, highways are ideal sites for the transport of pollutants to either treatment units or direct discharge to waterways. This study provides needed information on mercury levels in highway runoff. Removal of mercury on a dry detention basin was observed in the following size fractions: 0.45-8μm, 8-20μm, and 20-100μm and the highest concentration of mercury for both influent and effluent was observed in the 8-20μm size fraction. Treatment units are usually developed for removing a small suite of contaminants however, greater removal might be obtained in specific size fractions. Therefore, the benefits of treatment units may be larger than originally anticipated. For sedimentation-based treatment units, the removal is dependent on size fraction and when one size fraction is removed but not others, the comparison of the entire sample might indicate less or no removal, biasing the results.

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3.1 Introduction

Mercury is a rarely studied contaminant in stormwater runoff. The International Stormwater BMP Database (http://www.bmpdatabase.org) reports approximately 500 studies, but only two have values for mercury. In addition, neither study makes distinction between concentrations in dissolved and particulate phases, which is necessary when dealing with sedimentation-based treatment units. The absence of mercury studies in stormwater is surprising, since mercury in its inorganic form is present in every ecosystem due to long-range atmospheric transport (Ullrich et al., 2001). The sources of atmospheric mercury range from volcanic eruptions to combustion processes, such as burning of fossil fuels and wildfires (Burke et al., 2010, Pirrone et al., 2010, Biswas et al., 2008, Mason et al., 1995). Because of these widely variable sources, landuses with no obvious mercury source such as highways may have mercury concentrations that are subject to stormwater regulations. The largest problem with inorganic mercury in stormwater runoff occurs when it enters aquatic systems; it may be transformed into methylmercury (MeHg), which is a potent neurotoxin that has a tendency to biomagnify in food chains and has been implicated as a developmental toxicant for both humans and wildlife (Mason et al., 1995, Morel et al., 1998, USEPA, 2001).

Even though volcanic eruptions are responsible for about 20-40% of all the mercury (Hg) released into the atmosphere by natural emissions (Pyle and Mather, 2003), the contribution from natural sources to the global atmospheric Hg pool is decreasing. Until the 1970s, chlor-alkali plants were the largest anthropogenic source of atmospheric Hg but their impact has been reduced due to stricter regulations (Schroeder and Munthe, 1998). Currently, burning of fossil fuels, artisanal gold mining, non-ferrous metals manufacturing, cement production, waste disposal, and caustic soda production are the major sources of atmospheric Hg

(Pirrone et al., 2010).

Locations with a Mediterranean climate, such as Southern California, are prone to wildfires due to their long dry summers and the occurrences of high-speed warm dry winds during the Fall (Mensing et al., 1999). These wildfires release contaminants into the atmosphere, which can either travel across the globe or settle nearby via ash deposition. Rothenberg et al. (2010) has shown that for two relatively close lakes (40 km apart), the accumulation of Hg in the lakes sediment was greater on the lake affected more frequently with wildfires. Thus, besides long-range atmospheric transport, an important source of mercury to watersheds in Southern California might be wildfires (Rothenberg et al., 2010, Burke et al., 2010).

The goal of this study is to provide mercury data in highway runoff and its removal on a dry detention basin in Southern California. Since detention basins remove pollutants based on simple sedimentation principles, the data provided are for five size fractions ($< 0.45\mu$m, 0.45 to 8μm, 8 to 20μm, 20 to 100μm, and $>100\mu$m) allowing for a comparison between theoretical removal and achieved removal in the dry detention basin. In addition, this study aims to reinforce the use of particle size distribution for the pollutant removal efficiency versus overall percent removal of a certain contaminant.

3.2 Materials and Methods

3.2.1 Study Area

The presence of mercury in stormwater and its removal by sedimentation was investigated using data collected from a 100m^2 dry extended detention basin (identified in this study as detention basin) located in Southern California next to the junction of the I-605 and SR-91 highways (Figure 3.1). The two highways host very heavy traffic (approximately 220,000 annual average daily traffic) and transport runoff from a catchment area of 4,000 m^2 into the dry detention basin. This detention basin is 30 m long, 3.3 m inside width, and sides with a slope of 1:2.8 m (approximately 19.6^o), without a permanent pool and the accumulated runoff usually is discharged up to 72h after collection.

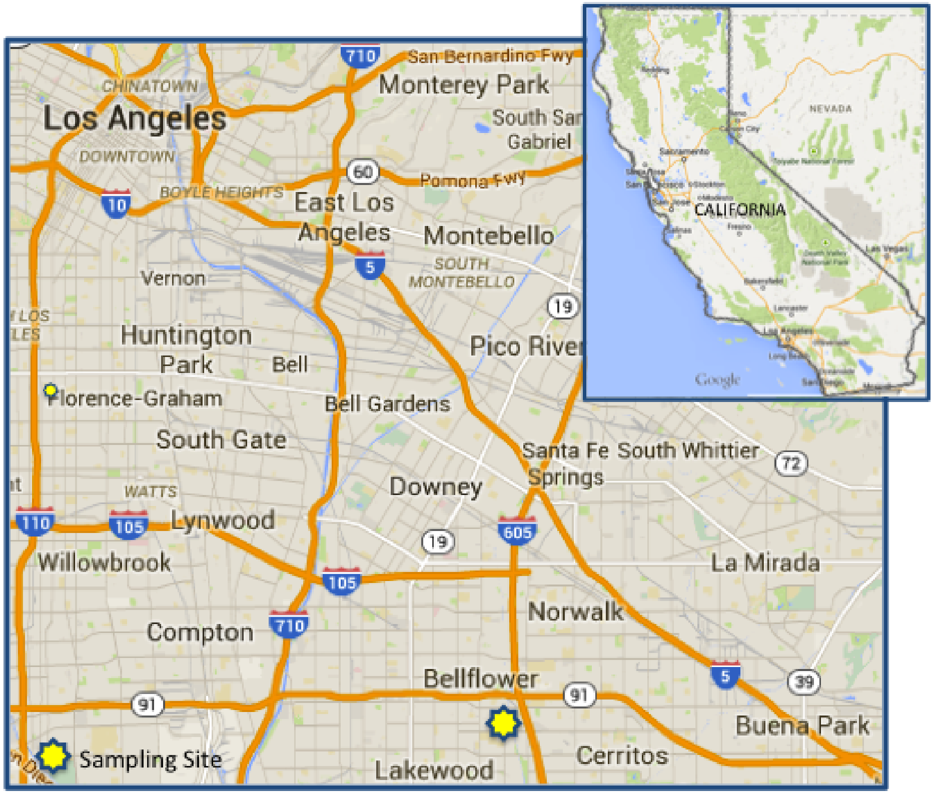

Figure 3.1: Detention Basin Sampling Site

Sampling procedure for the influent involved frequent (every 15 minutes) grab samples during the first hour to capture first flush, and then hourly during the storm. The first effluent grab sample was collected when water started flowing out of the basin, which was generally 1 to 3 hours after the beginning of the rainfall. Subsequent grab samples of the effluent were collected after 3, 6, 12, 24 hours and, if there was still outflow, at 48 hours and 72 hours. The number of samples varied depending on the total duration of the storm (Table 3.1).

3.2.2 Laboratory Analyses

Samples were transported to the laboratory at the University of California, Los Angeles (UCLA) and prepared for analyses within 6 hours of collection. Samples were analyzed for common water quality parameters such as total suspended solids (TSS), chemical oxygen demand (COD), and turbidity, following the Standard Methods (American Public Health Association et al., 1999). Duplicate samples were sequentially filtered into five selected fractions ($<0.45\mu$m, 0.45 to 8μm, 8 to 20μm, 20 to 100μm, and$>100\mu$m). The suspended solids retained in each filter were digested using nitric acid and microwave extraction following EPA method 3051A, and then diluted to 50 ml. The size-fractionated samples (the filtrate for the $<0.45\mu$m fraction and the extraction fluid for the other size fractions) were analyzed for total mercury (THg) using a CETAC Tech. M-6000A Cold Vapor Atomic Absorption Mercury Analyzer with standard Hg solutions prepared immediately prior to analysis. The final concentration is a concentration (ng/L) that represents the mass of THg by volume of runoff filtered.

3.2.3 Statistical Analyses

The datasets were tested for normality using probability plots and log-transformed when necessary prior to the statistical tests using the freely available R statistical software (http://www.r-project.org). Influent and effluent data were plotted as boxplots (Figure 3.2).

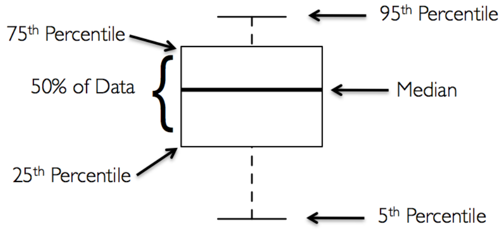

Figure 3.2: Definition of boxplots

The comparison among the several size fractions for either the group of influent or effluent samples was done using ANOVA (Analysis of Variance) with $\alpha = 0.05$. A calculated p-value of 0.01 or less was taken as evidence of a significant difference in the mean results for each group (influent or effluent). In order to determine which size fractions were different with statistical significance, the Tukeys Honest Significant Difference (THSD) Test with 95% family-wise confidence level (similar to Fishers Least Significant Test for pair-comparison) was used as a follow-up. The THSD Test highlights the pair-wise comparisons exposing which pairs in each group have statistically significant differences.

Comparisons between influent and effluent concentrations for each size fraction were done by using Welchs t-test, which is a modification of the traditional Students t-test for groups with different variances. Correlation analysis among water quality parameters and mercury concentration were made using the Spearman method. This method was preferred over the Pearsons method for being less sensitive to outliers and for indicating a monotonic increasing/decreasing correlation and not necessarily a linear relationship between the constituents.

3.3 Results

A total of 67 discrete samples were collected at the detention basin during four storms in the winter of 2005-2006 (Table 3.1). A total of 38 influent grab samples and 29 effluent grab samples were collected at the inlet and the outlet of the detention basin. After 72 hours the detention basin was usually empty.

Table 3.1: Rainfall Characteristics

Storm Date	**Rainfall (mm)**	**Volume of Runoff** (m^3)	**Length of Storm (hour)**	**Influent Samples**	**Effluent Samples**
2/27/06	47.5	190	22	12	12
3/17/06	4.8	19.3	5	5	5
3/28/06	16.8	67.1	16	12	6
4/14/06	10.9	43.7	7	9	6

(Volume calculated assuming drainage area of 4,000 m^2)

Total suspended solids was measured for all 67 samples and the data are shown as histogram on Figure 3.3. None of the effluent samples had a TSS greater than 80 mg/L and 23 out of 29 effluent samples had TSS below 30 mg/L. The calculated mean of influent TSS is 127.25 mg/L while the effluent TSS average is 25.17 mg/L, representing 80% removal of solids. The Welch t-test comparing influent and effluent TSS confirms that there is a statistical significant difference between the two groups ($p < 0.05$).

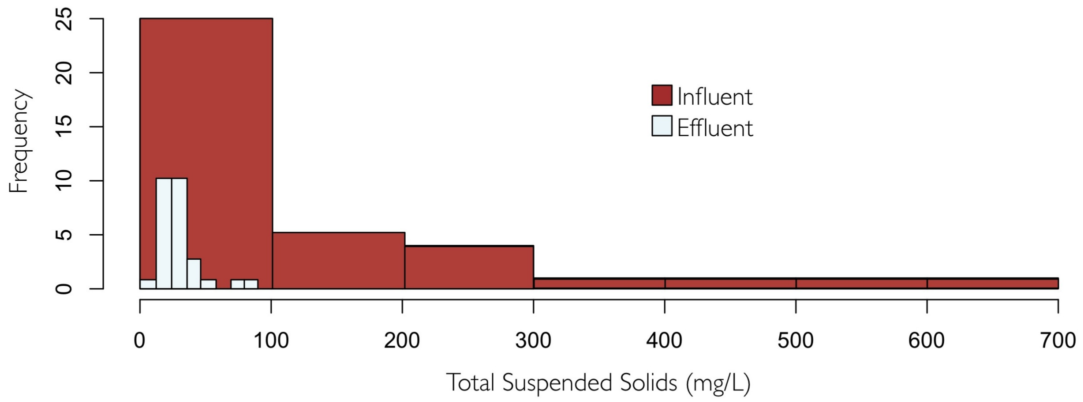

Figure 3.3: Histograms for Total Suspended Solids in the influent (n = 38) and effluent (n = 29) grab samples for the detention basin

In addition to total suspended solids (TSS), seven other water quality parameters were analyzed (Table 3.2). Volatile suspended solids (VSS), chemical oxygen demand (COD), and DOC (dissolved organic carbon) are some of these parameters. Applying the Welch t-test comparing the influent and effluent for each of the seven parameters, the result shows that there is a statistical significant difference between the two groups ($p < 0.05$) for VSS, Turbidity, COD, and Oil-Grease. For conductivity, hardness, and DOC, there is no statistical significant difference between influent and effluent samples.

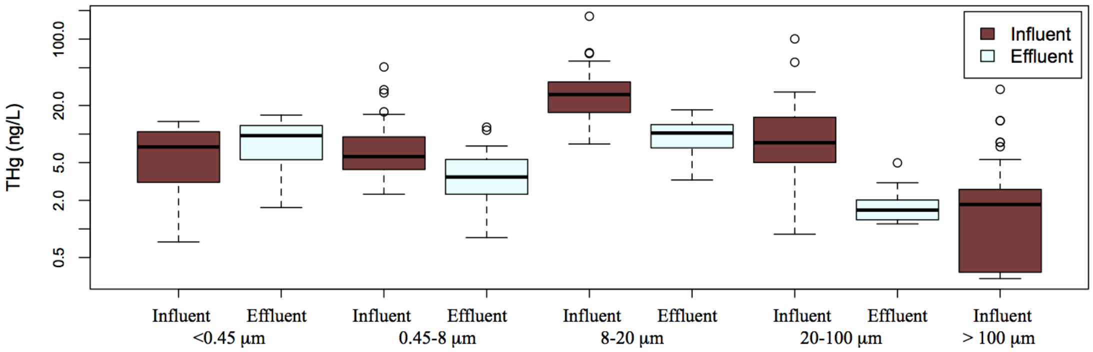

Figure 3.4: Boxplots for Total Mercury concentration in five size fractions for influent and effluent

Figure 3.4 shows boxplots for the concentration of mercury (mass of mercury per volume of filtered runoff) in all size fractions, both for the influent and effluent samples. The darker line in the middle of the rectangles indicates the mean value for that size fraction, the rectangles extend from the 25th percentile to the 75th percentile, and the whiskers show the spread of the distribution beyond the percentiles. There is no boxplot for the effluent in the biggest size fraction ($>100\mu$m) because only 4 samples had enough mass for Hg analyses (Concentrations are: 1.00, 1.31, 1.65, and 5.98 ng/L).

Table 3.2: Summary of water quality parameters for combined storms

		VSS (mg/L)	**Turbidity (NTU)**	**Conductivity ($\mu\mho$/cm)**	**Hardness (mg/L)**	**COD (mg/L)**	**DOC (mg/L)**	**Oil-Grease (mg/L)**
Influent	Min	5.18	27.0	62.0	22.0	6.49	6.60	2.54
	Median	24.5	53.6	157.2	54.0	104.2	13.3	7.00
	Mean	38.1	62.9	163.8	57.3	125.4	17.4	8.33
	Std Dev	41.6	37.3	56.4	18.5	81.9	12.6	5.33
	Max	189.5	230.0	319.0	108.0	289.2	62.3	23.1
Effluent	Min	1.97	9.0	41.0	18.0	17.0	3.16	1.52
	Median	7.79	26.0	163.0	54.0	59.6	13.2	5.27
	Mean	8.57	28.3	167.8	57.3	58.8	13.1	5.06
	Std Dev	4.78	12.5	50.9	19.2	29.5	3.93	1.71
	Max	24.7	70.0	252.2	104.0	127.8	20.5	9.21

3.4 Discussion

In this study, the terms mercury and total mercury (THg) are used interchangeably. Total mercury in this study refers to all the species of mercury present in each size fraction sample, and not particulate plus dissolved phases. Implications for toxicity are not clear from the concentrations of THg, since THg concentrations cannot always predict MeHg concentrations (Kelly et al., 1995). In addition detention basins usually do not exhibit anoxic zones, thus making it unlikely to foster biotic transformation of inorganic Hg into MeHg.

Comparison of the influent samples in all size fractions indicates that the highest mean concentration is on size fraction 8-20μm. ANOVA (Analysis of Variance) with $\alpha = 0.05$ was performed on the log-transformed influent data and showed statistically significant differences among groups (the influent samples were compared against the other influent samples, as well as the effluent samples compared to the other effluent samples). Tukey‘s Honest Significant Difference (THSD) Test with 95% family-wise confidence level was used as a follow-up and showed that the only influent pairs of size fractions that did not have statistically significant difference were <0.45μm and 0.45-8μm, <0.45μm and 20-100μm, and 0.45-8μm and 20-100μm (Table 3.3). For the effluent, the highest mean concentration is also on size fraction 8-20μm. ANOVA testing also showed difference among groups, which is only statistically significant for the effluent pairs: 0.45-8μm and 8-20μm, and 8-20μm and 20-100μm (Table 3.3). No comparison was made using size fraction >100μm due to the low number of measured samples.

Table 3.3: Summary of statistical analyses involving influent and effluent samples in the following size fractions: F1= <0.45 μm, F2= 0.45-8 μm, F3= 8-20 μm, F4= 20-100 μm, F5= >100 μm. "YES" means that there is a statistically significant difference between the fractions compared. "—" means that no comparison was made.

		Influent					Effluent				
		F1	F2	F3	F4	F5	F1	F2	F3	F4	F5
Influent	F1	—	NO	YES	NO	YES	NO	—	—	—	—
	F2	—	—	YES	NO	YES	—	YES	—	—	—
	F3	—	—	—	YES	YES	—	—	YES	—	—
	F4	—	—	—	—	YES	—	—	—	YES	—
	F5	—	—	—	—	—	—	—	—	—	—

Comparisons between influent and effluent concentrations were done by using Welch's t-test and showed that there is statistical significant removal of THg in size fractions 0.45-8μm, 8-20μm, and 20-100μm (Table 3.3). The poor removal of THg in the dissolved fraction was expected, since detention basins are based on settling of particles by gravity. A high removal of THg on the largest size fraction (>100μm) was expected, based on the theoretical removal of particles of that size. However, since 25 out of 29 effluent samples were non-detects (generally less than 1 ng/L), it was not possible to perform a statistical valid comparison between influent and effluent for the >100μm size fraction. However, the high number of non-detects gives an indication that the mercury has been removed.

Figure 3.5 shows a scatterplot of total suspended solids (TSS) for all the influent and effluent samples and the total amount of mercury in the samples, identified as unfiltered samples (numerically equals to the sum of the concentration of THg in all size fractions for a particular sample).

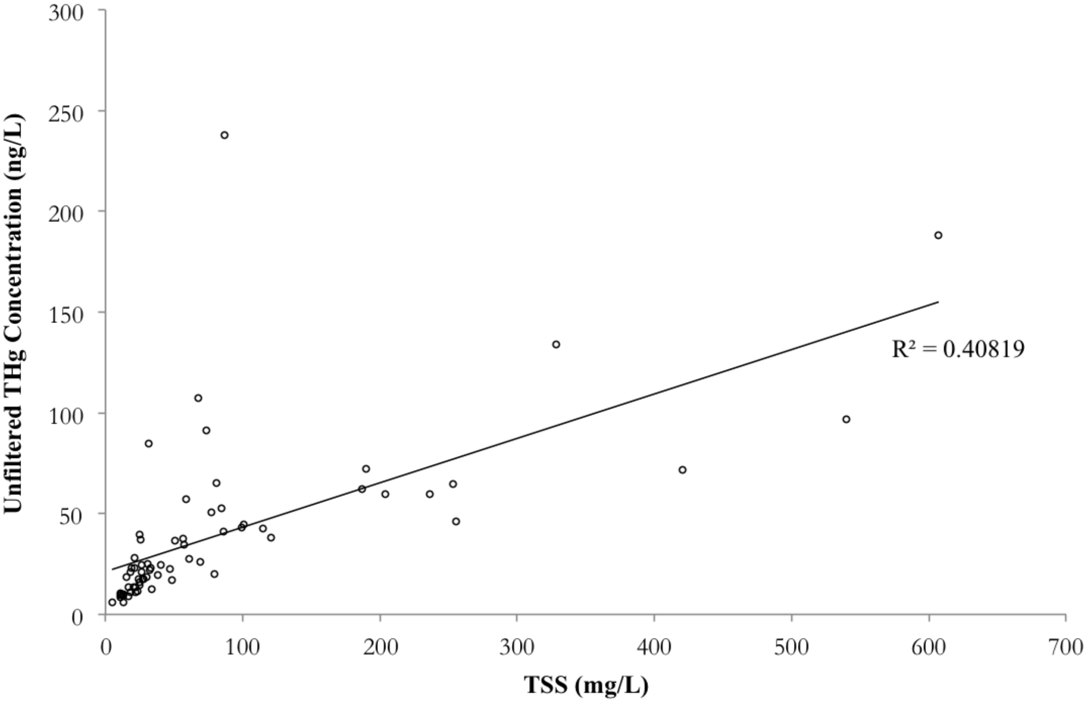

Figure 3.5: Scatterplot of total suspended solids (TSS) versus the total amount of mercury (THg) in the samples (referred to as Unfiltered).

Due to the samples with high values of TSS, the correlation between THg and TSS is poor ($r^2 = 0.41$). All these samples were on the influent, during the first hour of sampling, showing that a first flush of particles is occurring. The extreme outlier with the highest concentration of THg (237 ng/L) is also from an influent sample during the first hour. If the six extreme outliers are removed, the correlation improves to $r^2 = 0.65$, however there is no strong reason to discard these samples. An earlier study (Eckley and Branfireun, 2008) has shown a good agreement between TSS and unfiltered THg samples ($r^2 = 0.77$), which cannot be confirmed by the current study. This lack of correlation is a good indication that, the use of only one parameter such as TSS to estimate the removal of specific pollutants might not be a good estimate. The same poor correlation is observed if TSS is plotted against only particulate THg concentrations (Figure 3.6), because the measured concentration in the dissolved fraction is at least one order of magnitude smaller than the particulate fraction.

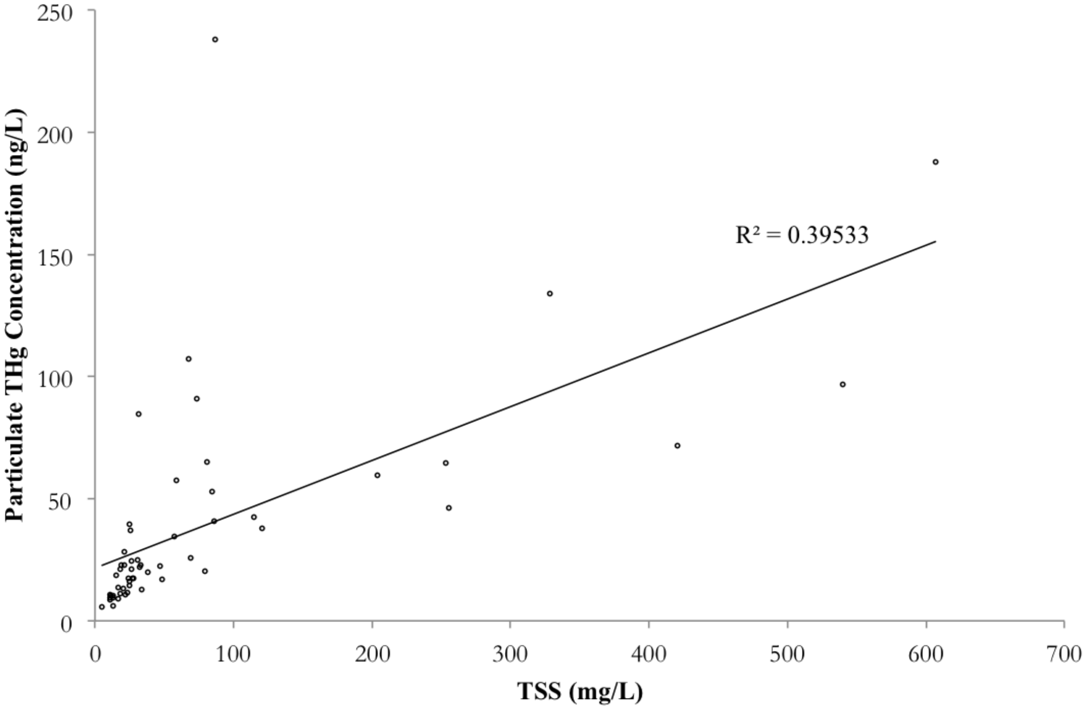

Figure 3.6: Scatterplot of total suspended solids (TSS) versus the particulate in the samples.

As indicated previously, there are several outliers in the dataset, thus the Spearman rank-order technique was used to determine correlations among influent water quality parameters and mercury concentrations (Table 3.4). The analyses results indicate high correlation ($r > 0.8$) for the concentration of Hg in the particulate phase and the unfiltered sample. Also, the correlation between Hg in the particulate phase and TSS is good ($r = 0.7$), as shown previously by other researchers.

Table 3.4: Correlation analysis results among influent concentration values for water quality parameters and Hg concentration (values above diagonal are Spearman rank-order coefficients "r"; values below diagonal are probability values (p-values); values in bold show correlation 0.8).

	Hg Dissolved	**Hg Particulate**	**Hg Total**	**TSS**	**VSS**	**Turbidity**	**Conductivity**	**Hardness**	**COD**	**DOC**	**Oil Grease**
Hg Dissolved	*****	-0.233	-0.067	-0.225	-0.294	-0.231	0.174	0.171	0.163	-0.163	-0.192
Hg Particulate	0.159	*****	**0.975**	0.733	0.764	0.768	0.051	-0.037	0.413	0.436	0.512
Hg Tota	l 0.689	< 0.001	*****	0.691	0.719	0.728	0.063	-0.035	0.44	0.414	0.474
TSS	0.175	< 0.001	< 0.001	*****	**0.97**	**0.826**	-0.168	-0.223	0.437	0.198	0.346
VSS	0.074	< 0.001	< 0.001	< 0.001	*****	**0.81**	-0.087	-0.158	0.505	0.352	0.468
Turbidity	0.163	< 0.001	< 0.001	< 0.001	< 0.001	*****	-0.062	-0.187	0.386	0.284	0.373
Conductivity	0.297	0.759	0.705	0.313	0.602	0.709	*****	**0.939**	0.355	0.655	0.518
Hardness	0.304	**0.827**	**0.837**	0.179	0.344	0.26	< 0.001	*****	0.211	0.52	0.398
COD	0.329	0.01	0.006	0.006	0.001	0.017	0.029	0.204	*****	0.691	0.82
DOC	0.328	0.006	0.01	0.233	0.03	0.084	< 0.001	0.001	< 0.001	*****	**0.899**
Oil - Grease	0.248	0.001	0.003	0.034	0.003	0.021	0.001	0.013	< 0.001	< 0.001	*****

A similar analysis may be performed for the samples in the effluent. The correlation between Hg Part-Hg Total and VSS-TSS both decreased to 0.74, VSS-Turbidity decreased to 0.4, and Oil-Grease-COD and Oil-Grease-DOC decreased to 0.58 and 0.54 respectively. Only conductivity-hardness correlation increased slightly to 0.97.

Samples were filtered within 6 hours of collection, and this was done to preserve particle size characteristics, since our earlier study (Li et al., 2005) noted that a natural aggregation of particles quickly occurs. This natural aggregation of particles will increase the suspended solids fraction of the samples as holding time increases. The brief holding time (less than 6 hours) may be partly responsible for generally lower particulate-phase metals concentrations (Lau and Stenstrom, 2005).

3.5 Conclusion

Treatment units are usually developed for removing a small suite of contaminants based upon Total Maximum Daily Load (TMDL) or other permitting requirements. However, stormwater runoff contains dozens of contaminants and many, if not most, treatment units are capable of removing a large suite of contaminants present in determined size fractions. Mercury (Hg) is just one example. Therefore, the benefits of treatment units may be larger than originally anticipated.

The International BMP Database has many reports that show no significant removal of certain pollutants. However, this should not be interpreted as lack of removal. Removal for sedimentation-based treatment units is dependent on size fraction. When one size fraction is removed but not others, the comparison of the entire sample might indicate no removal, masking the results. Since percent removal is an easy to understand metric, this study advocates its use only in specific size fractions.

CHAPTER 4

Particles in Runoff: Theoretical versus Experimental Removal

Treatment units for stormwater management are being routinely required for new construction and upgrading of older facilities. This chapter shows how particle size distribution affects the removal of sedimentation units and how erroneous results are often obtained if one uses simple overall removal efficiency or if the particle size distribution is not considered. Two full-scale devices are used for demonstration. A hydrodynamic device, which generally has low, overall suspended solids removal efficiency, is used for the first case, and it is shown that it actually removes large particles very well but has virtually no removal of small particles. The second case is for a dry detention basin. It is shown that the removal rates are generally in accord with sedimentation theory, removing larger and medium size particles well. Using particle size distribution in evaluating treatment unit performance is a more accurate and precise way of determining the actual performance.

A version of this chapter has been published as the paper: **Ferreira, M.**, and Stenstrom, M. K. (2013). *The Importance of Particle Characterization in Stormwater Runoff*, Water Environment Research v.85(9), pp. 833-842

4.1 Introduction

The performance of detention basins for the treatment of highway runoff is reported to be highly variable in removing TSS and metals (e.g. (Hossain et al., 2005, Starzec et al., 2005)). There are several reasons for the variability, such as storm intensity, storm duration, highway traffic volume, size of the pond, and metal fractionation. Comings et al. (2000) observed that more efficient ponds had longer detention times, large volumes in relation to the drainage area, and minimal short-circuiting. As indicated in the U.S. Environmental Protection Agency report on the National Urban Runoff Program (NURP), even though dry detention basins are extensively used to control flooding, they usually do not have good removal rates for pollutants (USEPA, 1983). Similarly, hydrodynamic devices have poor reported performance (Birch and Matthai, 2009, Geosyntec, 2008a).

This study uses particle size distribution (PSD) with sedimentation theory to demonstrate the methodology to predict overall treatment unit removal efficiency, and can serve as a guide for the selection of a sedimentation-based treatment unit. A hydrodynamic device is taken as first example of a manufactured device that can achieve good performance within certain PSDs. Simple observations do not detect significant removal rates but a theoretical analysis based on particle size predicts where significant removal can be expected and we provide a dataset to validate this conclusion. In addition, a constructed dry detention basin is used to exemplify the removal of sediments and dozens of constituents.

4.2 Methodology

Data presented were compiled from two separate studies in California: (1) laboratory performance test of a hydrodynamic device and (2) performance test of a detention basin in southern California. Both projects have the data in report format (Woodward Clyde Consultants, 1998 and Kayhanian et al., 2006, respectively).

4.2.1 Theoretical Removal Efficiencies

The removal of particles by sedimentation depends on the size and specific gravity of the particles. Stoke's law (Equation 4.1) quantifies the relationship between settling rate and diameter of particles. On an ideal case, settling rate (V_P) is directly proportional to the square of particle diameter and inversely proportional to the viscosity of water.

$$V_P = \frac{g(\rho - 1)d^2}{18\mu} \tag{4.1}$$

where: V_P is settling rate, g is gravity, ρ is the specific density of the particles, d is the particle diameter, and μ is the viscosity of water.

For discrete particle settling, we can construct removal efficiency charts based on overflow rate. Assuming laminar flow and spherical particles, particle removal efficiency is the ratio between settling rate (V_P) and overflow rate (V_o). Thus, for discrete particle settling, removal efficiency charts can be constructed based on the equation 4.2:

$$\eta = \frac{V_P}{V_o} = \frac{\frac{g(\rho-1)d^2}{18\mu}}{V_o} \tag{4.2}$$

where: V_P is settling rate, V_o is the overflow rate, g is gravity, ρ is the specific density of the particles, d is the particle diameter, and μ is the viscosity of water.

For discrete sedimentation, removal rate is independent on the hydraulic retention time. For a fixed depth, retention time is proportional to overflow rate. If we assume a depth of 3 meters, the retention time can be estimated and curves for six overflow rates (0.01 m/h to 1000 m/h) are plotted on Figure 4.1. Particle density is assumed to be $2.65 g/cm^3$. Curves for other particle densities and overflow rates can be constructed using Equation 4.2, depending on the conditions being studied.

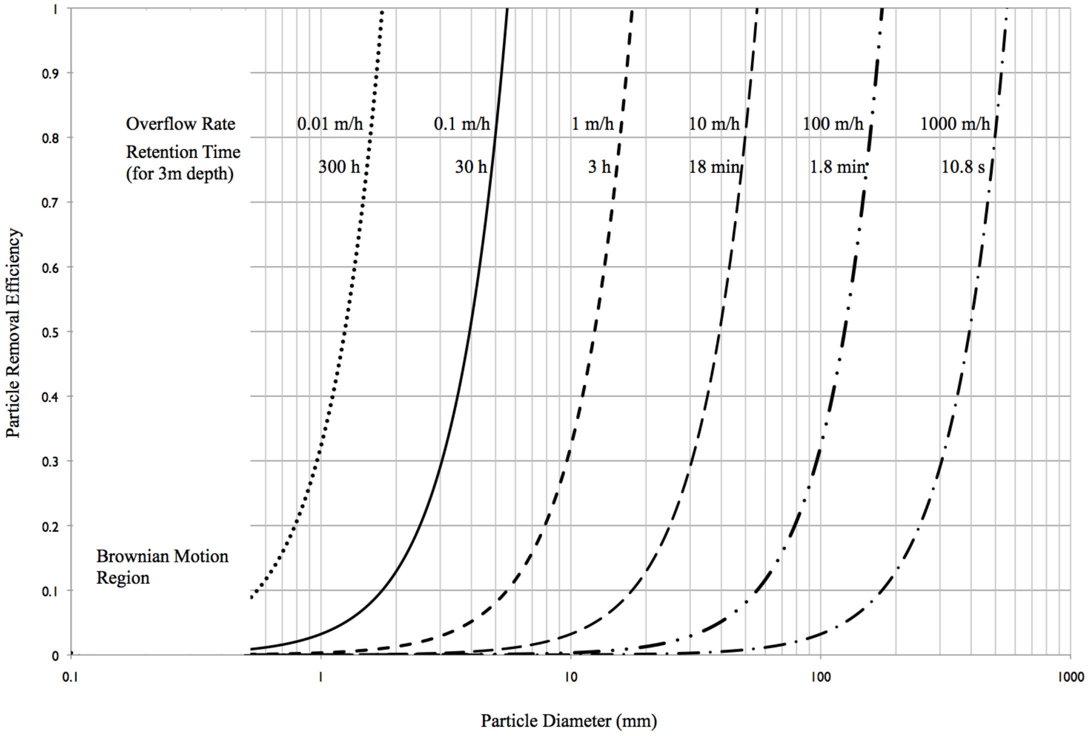

Figure 4.1: Theoretical removal efficiencies for sedimentation-based systems (based on Equation 4.2 for laminar flow, spherical particles with density $2.65 g/cm^3$ and temperature 20^oC

4.2.2 Hydrodynamic Device: Experimental Procedure

Hydrodynamic Device (HD) units are systems placed on large storm drains to capture large debris and sediments. The data presented in this study were collected using a pilot Continuous Deflective Separation (CDS) unit (Contech Engineered Solutions, West Chester, Ohio). Although it appears that these units separate particles by centrifugation or sieving, the removal occurs by settling. The influent water travels inside the unit and has to change direction and pass through a removable screen to exit the unit. The screen only acts as a sieve for gross pollutants such as litter; otherwise, the particles settle in the quiescent region formed by the screen. The typical screen size is much larger than the particles that are removed by the HD unit.

For the test (Woodward Clyde Consultants, 1998), a small HD unit with external and internal diameters of 0.91m and 0.59m respectively, was used with a flow of tap water at 473 L/min spiked with 50 mg/L sand in four size fractions (75-150μm, 150-250μm, 250-425μm, and >425μm). Tests were conducted using three different HD screens (fine, medium, and coarse, respectively 1200, 2400, and 4700μm). An inverted cone was inserted into the bottom of the unit to capture the removed particles (part of the experimental setup; the operation units do not have such cone). The accumulated sand in the cone was removed after the test, dried, weighed, sieved, and weighed again. The comparison of mass of sand in the influent and the effluent for each size fraction was reported as percent removals.

4.2.3 Detention Basin: Field and Laboratory Procedures

In this study, the term detention basin refers to a dry extended detention basin. This type of detention basins does not have a permanent pool and the accumulated runoff usually is discharged up to 72h after collection. Data from a detention basin located in Southern California next to the junction of the I-605 and SR-91 freeways were used for this study (Kayhanian et al., 2006). This detention basin was 30 m long, 3.3 m inside width, and sides with a slope of 1:2.8 m (approximately 19.6^o). The detention basin received runoff from the two highways (catchment area 4,000 m^2) that host very heavy traffic (approximately 220,000 annual average daily traffic). Grab samples of the influent were collected every 15 minutes during the first hour, and then hourly during the storm. The number of samples depended on the duration of the storm, and the more frequent sampling during the first hour was to capture the first flush of pollutants (Ma et al., 2009). The first effluent grab sample was collected when water started flowing out of the basin, which was generally 1 to 3 hours after the beginning of the rainfall. Subsequent grab samples of the effluent were collected after 3, 6, 12, 24 hours and, if there was still outflow, at 48h and 72h.

Following the method described in Li et al. (2005), the samples were transported to the laboratory at the University of California, Los Angeles (UCLA) and analyzed for PSD within 6 hours of collection. The number of particles per volume of sample in each diameter from 0.5μm to 500μm was obtained with a Nicomp Particle Sizing Systems (Santa Barbara, California) AccuSizer 780 optical particle size analyzer module equipped with an auto-dilution system and a light scattering/extinction sensor (analogous mechanism to Coulter counter). TSS was obtained following the method described in the Standard Methods for the Examination of Water and Wastewater.

Duplicate samples were sequentially filtered into five selected fractions ($< 0.45\mu$m, $0.45 - 8\mu$m, $8 - 20\mu$m, $20 - 100\mu$m, and $> 100\mu$m) for metals analyses. The suspended solids retained on each filter were then digested and diluted to the same volume. US EPA method 200.8 was used on the Agilent 7500i Inductively Coupled Plasma-Mass Spectrometer (ICP-MS) to analyze the filtrate (for the $< 0.45\mu$m size fraction) and the extraction fluid for seventeen metals, and detection limits were approximately 0.001μg/L. The final concentration is a concentration (μg/L) that represents the mass of metal by volume of runoff filtered. Solid phase concentration was not always measurable because the solids mass retained on the filter paper was sometimes less than the detection limit of the balance.

4.2.4 Statistical Analyses

The datasets were tested for normality using probability plots and log-transformed when necessary prior to the statistical tests using the freely available R statistical software (http://www.r-project.org). Influent and effluent data were plotted as boxplots (Figure 4.2).

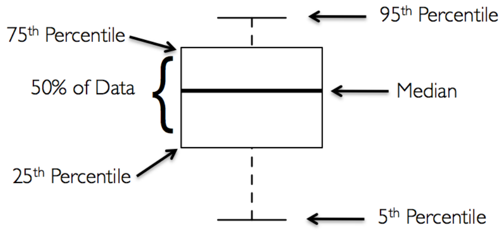

Figure 4.2: Definition of boxplots

ANOVA (Analysis of Variance) with α=0.05 was performed on the log-transformed data to identify statistically significant differences among groups. A calculated p-value of 0.01 or less was taken as evidence of a significant difference in the mean results for each group. Tukeys Honest Significant Difference (THSD) Test with 95% family-wise confidence level (similar to Fishers Least Significant Test for pair-comparison) was used as a follow-up. The THSD Test highlights the pair-wise comparisons exposing which pairs have significant differences. Comparisons between influent and effluent concentrations were done by using Welchs t-test, which is a modification of the traditional Students t-test for groups with different variances.

4.3 Results

4.3.1 Theoretical and Experimental Removal of Particles by a Hydrodynamic Device (HD) unit

For the design parameters of the experiment (flow 437 L/min and internal diameter 0.59 m), the overflow rate is approximately 100 m/h. Table 4.1 shows the theoretical removal of particles for the HD unit calculated using Equation 4.2 and the measured density of $2.65g/cm^3$. The experimental removals obtained during the experiment are also shown on Table 4.1.

Table 4.1: Theoretical and Experimental Removals for the Hydrodynamic Unit

		Experimental Removals		
Particle Size Fractions	**Theoretical Removal**	**Fine Screen**	**Medium Screen**	**Coarse Screen**
75-150μm	18-72%	21%	20%	19%
150-250μm	72-100%	69%	47%	41%
250-425μm	100%	87%	78%	58%
>425μm	100%	100%	95%	95%

Hydrodynamic devices are not expected to have good removal rates for particles between 75 and 150 μm (at most 72%, average removal 45%), and the removals obtained by the three different screens are about 20%. For the largest particles (>425 μm), all three screens performed with good removal (above 95%), matching the theoretical removal of 100%. For the size fraction 150-250 μm, the fine screen performed at the lowest end of the theoretical removal (72%), while the medium and coarse screens performed much worse than the theoretical removal. At the 250-425 μm size fraction the fine screen performance matched the theoretical removal (100%), but the medium and coarse screens had a poor performance removing the sand (78% and 58% respectively).

4.3.2 Theoretical and Experimental Removal of Particles and Pollutants by a Detention Basin

Particle size distribution (PSD) as particle counts per volume is shown on Figure 4.3 for all influent and effluent samples. Each graph shows the PSD for all the grab samples from one storm. In general, the particle counts for the effluent samples are lower than for the influent samples on a given storm and given particle diameter. The particle counts decrease over time for the influent, which explains why some of the effluent curves overlap influent curves. Assuming spherical particles and using particle counts, a total volume of particles in the influent and the effluent can be calculated. Then, a percent removal of the total volume of particles can be estimated by ranges of particles (Table 4.2). Since these values (Table 4.2) are calculated, it is possible to calculate the percent removal by estimated volume for any range of size fraction. For example, the removal for the smallest particles (0.5 to 5 μm) is 48% (ranging from 15 to 62%). Also, the removal for the rest of the size fractions range from 82 to 91% for all storms combined.

Table 4.2: Percent Removal of the Total Volume of Particles for the Storms Surveyed

	27-Feb	**17-Mar**	**28-Mar**	**14-Apr**
0.5-8μm	75%	57%	57%	71%
8-20μm	89%	84%	84%	91%
20-100μm	84%	87%	84%	95%

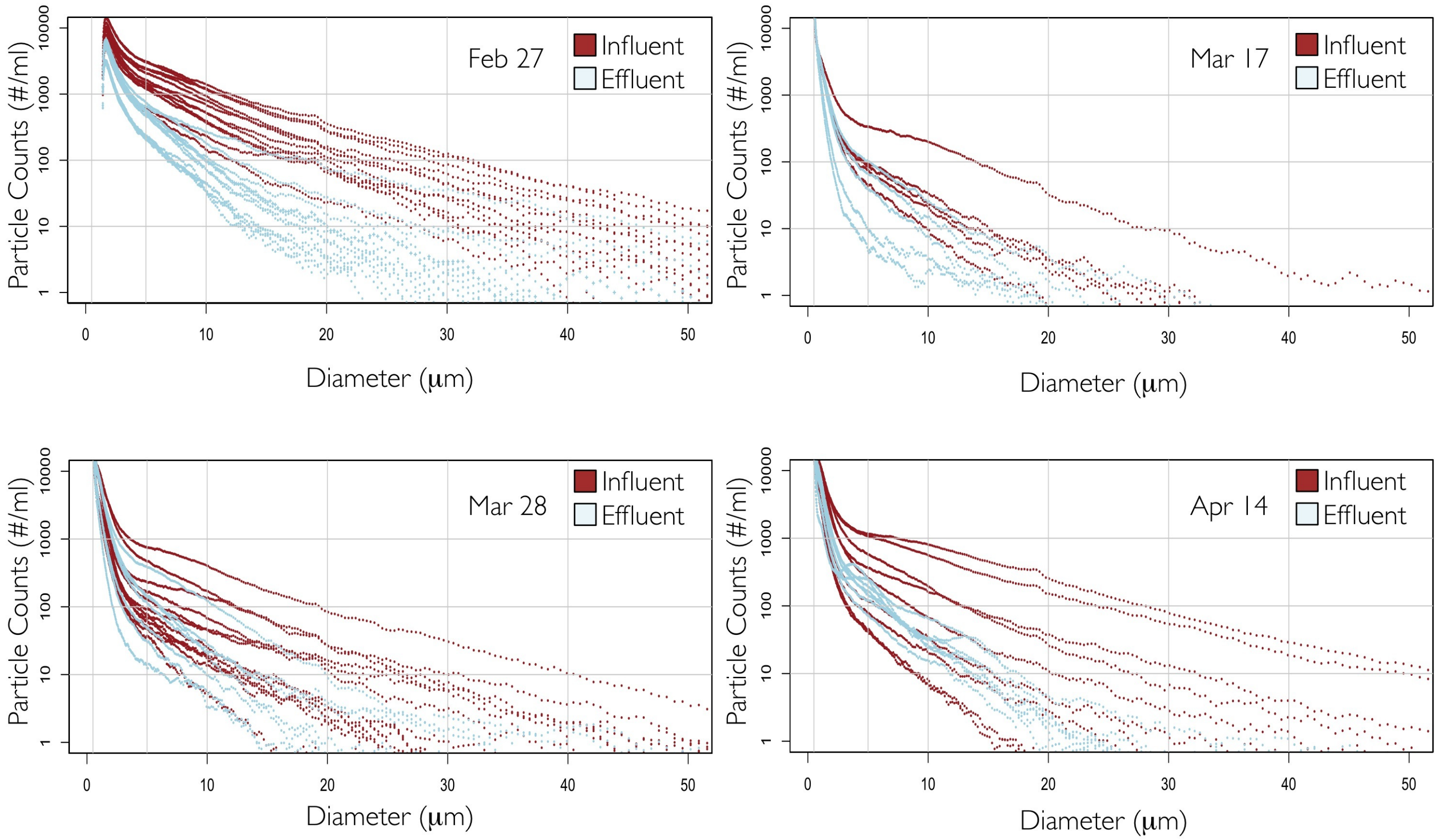

Figure 4.3: Particle Size Distribution for Influent and Effluent Samples

Concentrations (mass of constituent per volume of filtered runoff) for twenty-two constituents are shown on Figures 4.4, 4.5, and 4.6 for the influent and effluent samples. Figure 4.4 shows the commonly reported metals for highway runoff, while Figures 4.5 and 4.6 contain less frequently studied constituents. For each constituent, there are six boxplots representing influent and effluent for three size fractions (<0.45 μm, 0.45-8 μm, and 8-20 μm), and one boxplot representing the influent for the 20-100 μm size fraction, for a total of seven boxplots per constituent. Each box represents the distribution around the median value. The plots have a logarithmic scale, with the exception of cadmium (Figure 4.4), arsenic, cobalt and selenium (Figure 4.5), and uranium (Figure 4.6).

Table 4.3: Estimation of Theoretical Overflow Rate Based on the Flow Calculated by the Rational Formula

						Overflow Rate (m/h)	
Storm Date	**Rainfall (m)**	**Drainage Area (m^2)**	**Volume (m^3)**	**Length of Storm (h)**	**Flow Into Basin (m^3/h)**	**Max Surface Area**	**Min Surface Area**
27-Feb	0.0475	4,000	190.0	22	8.64	0.029	0.087
17-Mar	0.0048	4,000	19.3	5	4.06	0.014	0.041
28-Mar	0.0168	4,000	67.1	16	4.19	0.014	0.042
14-Apr	0.0109	4,000	43.7	7	6.24	0.021	0.063

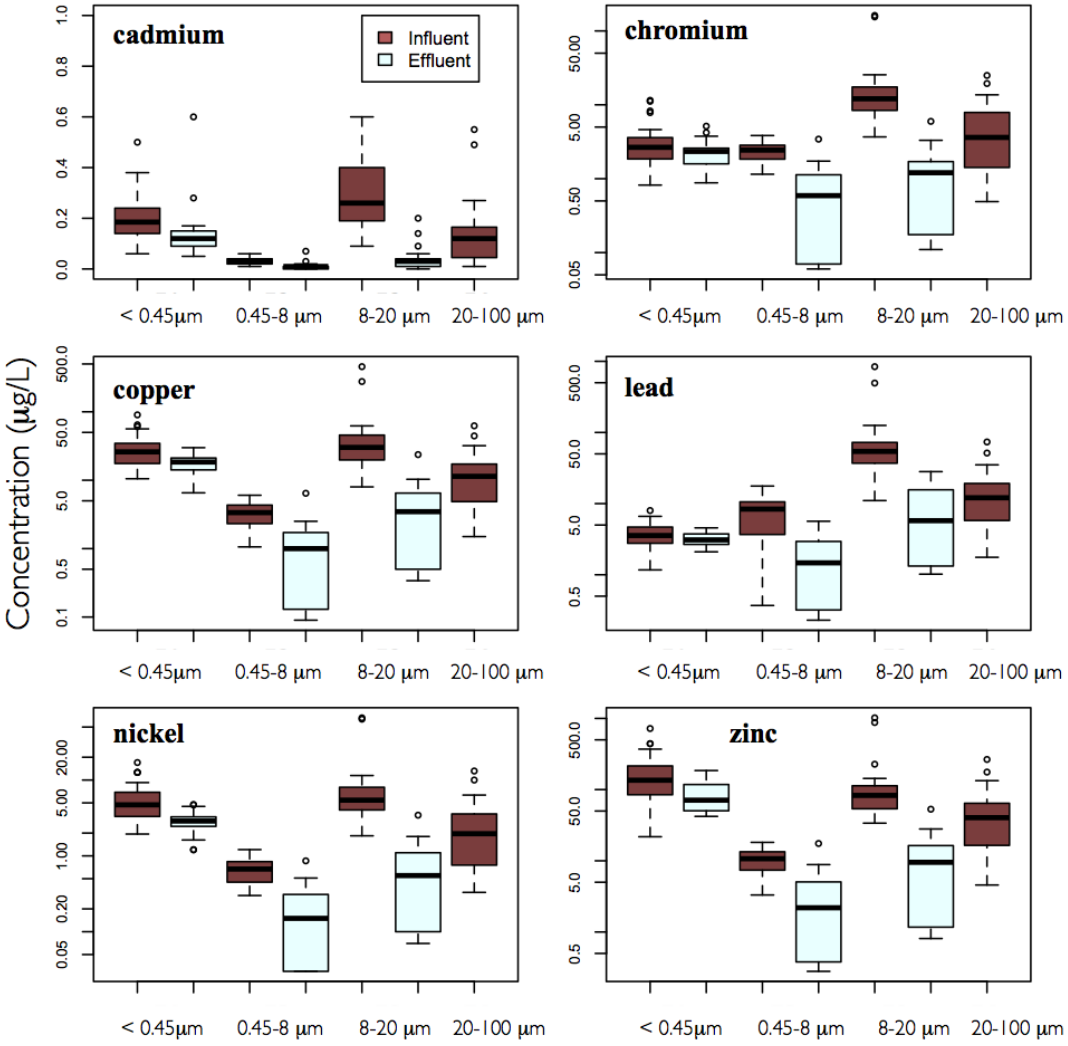

Figure 4.4: Boxplots for the concentration of cadmium, chromium, copper, lead, nickel, and zinc in the influent (dark-colored boxes) and effluent (light-colored boxes) for four size fractions (see text).

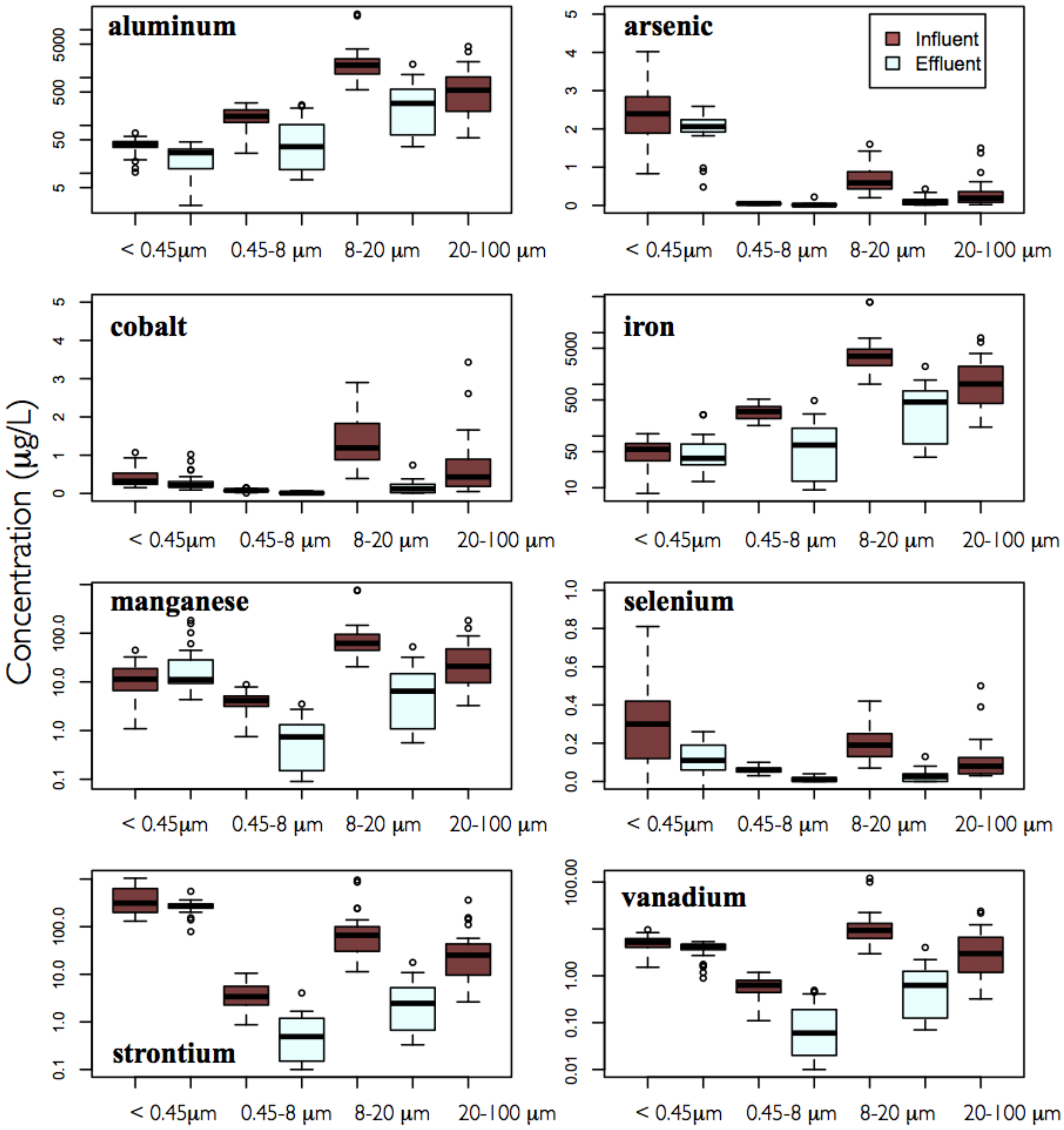

Figure 4.5: Boxplots for the concentration of aluminum, arsenic, cobalt, iron, manganese, selenium, strontium, and vanadium for in the influent (dark-colored boxes) and effluent (light-colored boxes) for four size fractions (see text).

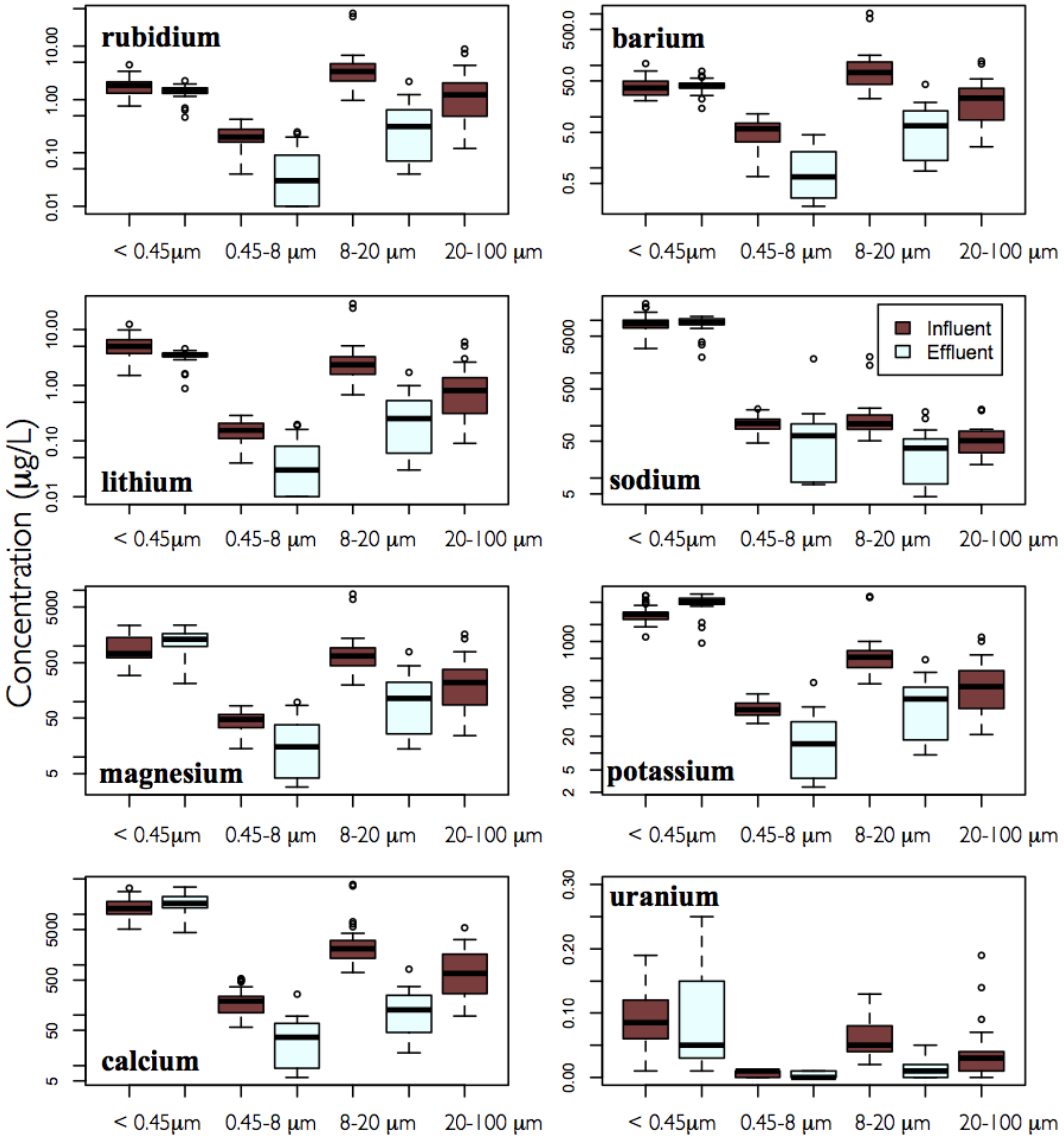

Figure 4.6: Boxplots for the concentration of rubidium, barium, lithium, sodium, magnesium, potassium, calcium, and uranium for in the influent (dark-colored boxes) and effluent (light-colored boxes) for four size fractions (see text).

Statistical comparison of the log-transformed data using ANOVA analysis and THSD Test shows that the mean concentration on all size fractions for the influent in all size fractions for each constituent are different ($p \leq 0.05$), with the few exceptions as shown in Table 4.4. The Welch t-test for the influent and effluent in each size fractions indicates that there is a statistical difference for the concentrations for all the constituents, except sodium, calcium, manganese, iron, barium, and uranium for the dissolved size fraction ($<0.45\mu$m), and sodium for the 0.45-8 μm size fraction (Table 4.4). In addition, manganese and potassium have a statistical significant difference for the dissolved size fraction ($<0.45\mu$m) in which the effluent is higher than the influent (This can be observed in their boxplots on Figure 4.6). Finally, for all the constituents, both in the influent and the effluent, the particulate size fraction with the highest mean concentration is 8-20μm. For seven constituents in the influent (Li, Na, K, Ca, Zn, Sr, and As) the dissolved size fraction ($<0.45\mu$m) has the highest mean concentration while in the effluent, 19 constituents (Li, Na, Mg, K, Ca, V, Cr, Mn, Ni, Cu, Zn, Rb, Sr, Ba, Cd, As, Se, Co, and U) have the highest mean in the dissolved fraction ($<0.45\mu$m).

Table 4.4: Summary of statistical analyses showing the constituents that have no statistically significant difference for the comparisons shown on the left column.

Comparison	**Constituents with no Statistical Significant Difference**
Influent Size Fractions	
<0.45μm and 0.45-8μm	Cr
<0.45μm and 8-20μm	Mg, Ni, Cu, Se, U
<0.45μm and 20-100μm	Cr, Co, U
0.45-8μm and 8-20μm	Na
0.45-8μm and 20-100μm	Se
8-20μm and 20-100μm	U
Influent vs Effluent Size Fractions	
<0.45μm and <0.45μm	Na, Ca, Mn, Fe, Ba, As, U
0.45-8μm and 0.45-8μm	Na

4.4 Discussion

The removal efficiency curves (Figure 4.1) were constructed assuming spherical particles of density 2.65 g/cm^3. As described in Sansalone et al. (1998), when observed under the microscope, particles are irregular in shape and have a greater measured specific surface area than they would if they had spherical shape. In addition, several stormwater runoff studies have reported densities that deviate from 2.65g/cm^3, usually ranging from 2.1 to 2.9g/cm^3 (e.g. (Andral et al., 1999, Cristina et al., 2002, Lin et al., 2009)). The variation in densities suggests that determining the typical particle densities for a particular site should be included in the preliminary studies. Since particle density is dependent on the nature of the material carried by the runoff, the more organic the material the lower the density, and the more mineral the higher the density.

Using basic sedimentation theory is an oversimplification of the processes that happen on a sedimentation-based treatment unit. As discussed in another study (Stanley, 1996), the ideal conditions assumed in the theory described by **?**(**?**) are only approximated in real detention basins. Thus, the actual removal of particles will be smaller than the theoretically predicted. However, selection of treatment units based on the PSD of the stormwater to be treated has rarely been the case, as shown in the case of Ballona creek (Brown et al., 2013).

4.4.1 Hydrodynamic Units

HD design varies among vendors, which may be one of the reasons that these devices have no statistical significant differences between the median of average influent and effluent (Figure 4.7) as reported to the International BMP Database. Lee et al.(2010) performed extensive testing of the performance of a HD unit (different than the one used in this study) and observed that the suspended solids removal was inversely proportional to the surface loading rate (usually called surface overflow rate). This observation is a characteristic of sedimentation devices, and they concluded that gravity was a significant process in the removal of particles in the HD unit. A similar conclusion can be reached for the HD unit in this study.

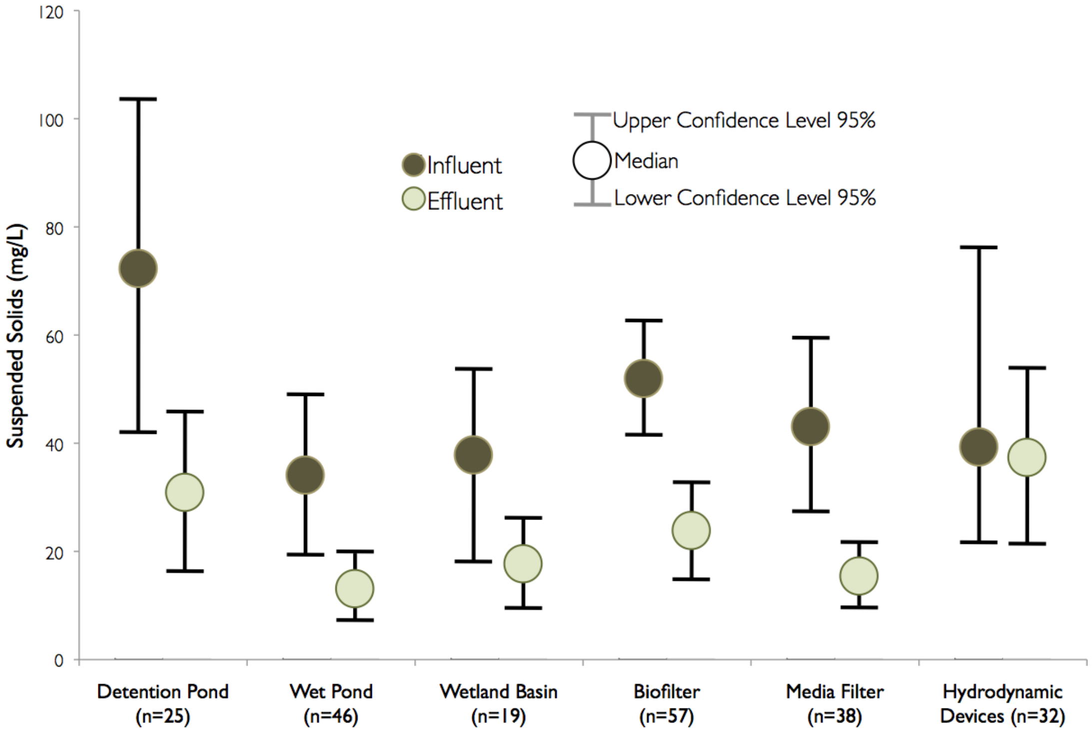

Figure 4.7: Comparison of influent and effluent concentrations for total suspended solids for six categories of treatment units as reported to the International BMP Database ("n" indicates number of samples) (Data source: Geosyntec Consultants, 2008a)

The results summarized on Table 4.1 support the importance of the study of particle size distribution when analyzing performance of treatment units. If TSS had been used as a measure of removal efficiency, then from the initial 200 mg/L of sand of all size fractions entering the HD unit, the effluent using the fine screen would be 56.5 mg/L, resulting on efficiency of 72%. The removal for each size fraction allows the reader to see that, for particles above 200 μm, the HD unit would remove near 100%, but only 20% for particles smaller than 150 μm.

The lack of statistical significant difference for influent and effluent TSS concentrations on Figure 4.7 might be explained not only by design differences but also by the particle size distribution in the influent. If the suspended sediments in the influent were mainly small particles, then the HD unit would have difficulty in removing these small particles, therefore resulting in a worst percent removal. If the user knows which particle size fractions have better removal, the analyses of performance of the HD unit would be more specific and probably yielded precise results. The results obtained by Lee et al.(2010) using computational fluid dynamics (CFD) are very similar to the simple analysis done in this study; particles smaller than 100 μm are poorly removed.

4.4.2 Detention Basins

As outlined in Barrett(2005), some treatment units produce a consistent effluent, regardless of the influent concentration. Figure 4.8 highlights this characteristic for the studied detention basin, in which no effluent TSS was above 30 mg/L, even when the influent TSS was greater than 500 mg/L. This is the reason why overall percent removal is not a good measure of performance (Barrett, 2005) This study advocates the use of percent removal only in size fractions, because this is an easy to understand metric and can be very useful when used appropriately. Using curves similar to Figure 4.1, the theoretical removal of particles greater than 10μm for all storms would be 100%, and the field data show removal ranging from 71% to 96%. However, it is generally accepted that detention basins do not exhibit good removal rates (USEPA, 1983). Perhaps this notion is due to the fact that percent removals of TSS are calculated without concern for the PSD of the influent. Stanley(1996) describes a dry detention basin with good percent removal of TSS (71%) but cannot conclusively explain the reason of the good performance while other detention basins have such poor removals. Scouring of particles near the effluent structure probably accounts for the less than predicted removal rates for larger particles. The better than predicted removal for particles less than 10μm could be explained by aggregation of those particles (Li et al., 2005) in a quiescent situation, although it has been reported that settling does not significantly reduces particles smaller than 20μm (Sansalone and Kim, 2008).

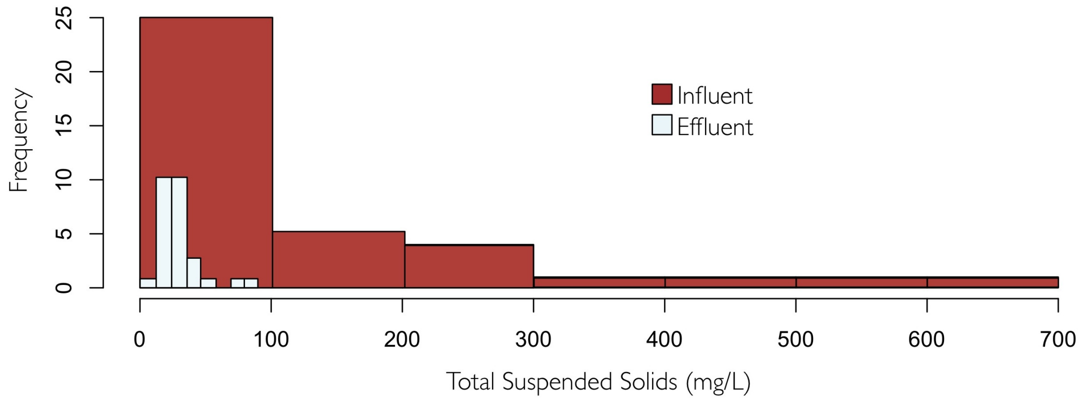

Figure 4.8: Histograms for Total Suspended Solids in the influent (n = 38) and effluent (n = 29) grab samples for the detention basin

The influent PSD dictates the overall efficiency of sedimentation units (Greb and Bannerman, 1997). With the increase of clay-size (defined as smaller than 4 μm) particles in the influent, the pond efficiency decreases significantly (Greb and Bannerman, 1997). PSD in the effluent is more uniform than the influent (Figure 4.3); most of the particles in the effluent are in the smaller size fractions (Greb and Bannerman, 1997). There is a physical limit for the removal of very fine particles by sedimentation alone. This topic is treated extensively in wastewater treatment in which a sequence of treatment units is used to achieve the desired removal. Starting with a large screen, grit chamber, then coagulation and flocculation to force the formation of larger particles that will be most likely removed by sedimentation. Alternatively, after some primary sedimentation without coagulation, a filtration process is necessary to remove the fine particles. Since runoff is generally poorly buffered, overdose of common coagulants such as either ferric chloride or alum exhausts alkalinity and reduces pH (Sansalone and Kim, 2008). Stormwater runoff generally varies not only in water quantity but also water quality, making coagulation a difficult process because it requires an operator on site, similar to wastewater treatment plants, to manage the dosage of coagulant.

Many stormwater treatment units have not been designed for pollutant removal; they were engineered to attenuate runoff flow, and only recently became the subject of investigation for water quality purposes. Unfortunately, sedimentation-based treatment units do not remove small particles and several studies have shown that these are the particles that carry the highest pollutant load. Even if mass loading is greatly reduced by the treatment-unit, the pollutant load might still be high enough to impair downstream lakes and rivers. Sedimentation-based treatment units designed specifically for pollutant removal perform better than other units because there is minimization of short circuiting and extended detention time is part of the design (Comings et al., 2000).

Using removal of sediments as a proxy for removal of pollutants might be misleading. At a minimum, studies should investigate pollutants in particulate and dissolved phases (Barrett, 2005) prior to conclude if a treatment unit is working or not. In addition, since pollutants are generally associated with fine particles, the overall pollutant removal may be less than the overall sediment removal (Greb and Bannerman, 1997). This implies that treatment units relying solely on sedimentation might not achieved the desired removal and additional treatment, such as filtration or coagulation might be needed.

As shown on Figures 4.4, 4.5, and 4.6, the highest influent concentration in the particulate phase is consistently in the 8-20μm size fraction. The implication is that, hydrodynamic devices would not be appropriate to reduce the concentration of these pollutants, given that HD units remove only particles greater than 100 μm. Brown et al. (2013) have made the same observation for urban runoff entering a creek in Southern California. In their study, the highest concentration of pollutants was in the $< 6\mu$m filter fraction, probably due to the pollutants in the dissolved phase being present in this phase. For this study, copper, nickel and zinc (same metals reported by Brown et al. (2013)) have the highest influent concentration in the dissolved phase, which when added to the 0.45 8μm size fraction, gives a concentration higher than the 8-20 μm size fraction.

Of all the size fractions, the dissolved phase was the highest influent concentration for seven constituents, but in the effluent it became important for 19 constituents. This switch just highlights the removal of pollutants in the 8-20 μm size fraction and very little removal of pollutants in the dissolved phase. In addition, for only seven constituents (sodium, calcium, manganese, iron, barium, arsenic, and uranium) there is no statistical significant difference between influent and effluent concentrations in the dissolved phase. Since dissolved phase is used in this study as the filtrate through a 0.45 μm, it could be that the constituents are actually in the colloidal phase and these colloids become aggregate and removed by sedimentation.

4.5 Conclusion

Studies that do not observe statistically significant removal of suspended solids and conclude that no treatment is being provided often miss significant removal of a subset of the suspended solids. This is observed in HD units that only perform well in removing large particles ($\gtrsim$100μm). In order to accurately estimate the removal of particles in sedimentation basins, it is necessary to measure particle size distribution (PSD). Sedimentation rates are not affected by retention time, but by overflow rate and particle characteristics such as size, shape and density. Improved design for treatment units will require better quantification of PSD, particle shape and density, as well as the use of overflow rate as a design parameter, in preference to detention time. Detention time and mixing becomes important for Type II sedimentation, where particle aggregation becomes significant. Improved knowledge of PSD will allow sedimentation units to be designed for specific treatment objectives.

CHAPTER 5

Conclusion

After the success of regulating point-source discharges, the major cause of pollution into water bodies is due to stormwater runoff. The International BMP Database (http://www.bmpdatabase.org) lists almost 500 studies of treatment units in the United States and other countries that were created to mitigate the impact of stormwater runoff to the water quality of receiving bodies.

Even though many treatment units currently used in the treatment of stormwater runoff are based on sedimentation principles, there is usually a lack of rational design applied to the study of their performance. Runoff treatment units are usually selected on an empirical estimate of their efficiency as opposed to the theoretical basis of their removal mechanism. The common practice is to measure one parameter (such as TSS – total suspended solids) of the influent and effluent of the treatment unit and report percent removal as measure of efficiency. Since percent removal is a function of the relationship between influent and effluent measurements, it may not properly indicate the performance of a treatment unit (Strecker et al., 2001). For example, for treatment units that deliver a consistent quality effluent, percent removal will be exclusively a function of the influent and not related to actual pollutant removal (Barrett, 2005). The numerical percent removal would then incorrectly indicate a poor performance if the influent is relatively clean, i.e. when the influent concentration is closer to the achievable effluent concentration.

The use of broad categories for treatment units and the non-use of particle size distribution might lead to erroneous conclusions. As shown on Figure 1.2, detention basins and wetland basins do not have strong statistical significant differences, while hydrodynamic devices have no statistical significant differences between the median of average influent and effluent.

Several factors could impact the efficiency of a sedimentation-based treatment unit, such as particle size distribution (PSD), particle density, overflow rate, detention time, etc. (Clary et al., 2012). The importance of PSD has been suggested by several authors (Greb and Bannerman, 1997, Geosyntec, 2008b, Comings et al., 2000) but remains a parameter seldom measured and reported, especially for the efficiency study of a treatment unit. PSD data have been reported in several studies characterizing contaminants and particles in stormwater (Characklis and Wiesner, 1997, Sansalone et al., 1998, Li et al., 2005), which are specific for certain geographical regions. For example, in regions with severe winters the use of sand to control the snow will result in greater counts of larger particle sizes, versus a region with mild weather that does not require the additional sand. The geology and topography of a region will also affect how particles are transported in stormwater.

When following the performance evaluation recommendations (Strecker et al., 2001), one parameter such as TSS may be used as a measure of efficacy of a treatment unit if excess sediments are of concern. However, using TSS removal as a proxy for removal of other pollutants can lead to incorrect results. While some studies indicate a correlation between TSS and pollutants of interest (Hossain et al., 2005, Helmreich et al., 2010), others indicate a weak correlation or no correlation (Han et al., 2006a). Many of the published studies of stormwater runoff report pollutant fractionation between dissolved (defined as filtered on a 0.45μm filter) and particulate phases (Sansalone et al., 1996, Characklis and Wiesner, 1997, Helmreich et al., 2010), yet pollutants attach preferentially to certain size fractions as reported by other studies (Sansalone and Buchberger, 1997, Roger et al., 1998, Morquecho and Pitt, 2003, Lau and Stenstrom, 2005, Tuccillo, 2006). Thus, pollutant fractionation into particle size fractions is an important parameter to know when considering pollutant removal rates.

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