Size Fractionation of Metals Present in Highway Runoff: Beyond the Six Commonly Reported Species

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ABSTRACT: Highway runoff is an important non-point source of pollutants, especially metals. This study reports monitoring results from 17 storm events at three highway sites 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. 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. The greatest metal masses were typically observed in the 8 to 20 μm fraction. The size distribution shows that sedimentation as a treatment process typically found in stormwater management can remove only 65% of the mass of most particulate phase metal species. Additional processes, such as coagulation or filtration, are needed to obtain greater removal rates. The results indicate the need to study particle size distribution (PSD) in order to better select treatment alternatives or assess environmental impacts. *Water Environ. Res.*, **85,** 793 (2013).

KEYWORDS: particle size distribution, runoff treatment units, best management practices, stormwater runoff, highway runoff.

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Introduction

For many years, stormwater runoff was seen merely as a nuisance because of flood risks. In past decades, however, stormwater runoff pollution is now recognized as the cause of significant water quality impairments (U.S. EPA, 1983; Ellis, 1991). Urbanization increases the impervious cover which reduces infiltration of stormwater and contributes to the increase of surface runoff flow. Urbanization allied to the success of point source management has resulted in the increased relative contribution of non-point sources. Many studies have been conducted to better understand stormwater problems and how to mitigate their effects showing that in urban areas, runoff carries particles contaminated with metals and hydrocarbons, mainly from roofs and paved surfaces (Gromaire-Mertz et al., 1999; Davis et al., 2001). Impervious areas, such as parking lots and commercial properties, contribute 10 times the oil and grease pollution of open areas or residential areas (Fam et al., 1987). Metals are of great concern because they do not degrade in the environment and can be toxic. A study of 87 urban sites including roofs, parking areas, and streets showed that 40% of the urban runoff contained compounds of moderate to high toxicity (Pitt et al., 1995).

Highways are significant non-point sources, having large impervious areas that create runoff to transport pollutants attached to particles deposited on the concrete or asphalt roads. 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 also contribute significant amounts of heavy metals to air emissions and runoff, with zinc being the main component of all heavy metals emissions on a mass basis (Boughton and Horvath, 2004).

The understanding of pollutant transport in stormwater runoff is key to the treatment unit selection. Predictive models to describe treatment process performance have not existed in many cases, which resulted in extensive testing and reliance on empirical procedures. The International Stormwater BMP (Best Management Practices) Database contains approximately 500 studies on several types of treatment units for stormwater runoff. Overall pollutant removal efficiencies are often reported, irrespective of the mechanisms of removal. Sedimentation and filtration treatment units are selected for their ability to achieve overall particle removal efficiency, which does not always translate into pollutant removal efficiency. As discussed in several studies such as Strecker et al. (2001) and Barrett (2003), the use of percent removal of pollutants as a metric for the efficacy of a treatment unit is flawed. This is because the percent removal calculation does not take into account the particle size distribution (PSD), and tends to numerically favor "dirty" sites with better percent removals than "clean" sites. Several studies, including Pitt et al. (1995) and Gromaire-Mertz et al. (1999), have shown that pollutants are transported on the surface of particles, implying that knowing the pollutants' fractionation across different particle sizes is an important parameter in the selection of runoff treatment units. PSD data is reported in several studies related to metals, such as Characklis and Wiesner (1997), Sansalone et al. (1998), and Li et al. (2005), however, there is no standard PSD method for stormwater runoff samples.

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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), and Helmreich et al. (2010), report metal fractionation between dissolved (as filtered on a 0.45 μm filter) and particulate phases. Others, such as Sansalone and Buchberger (1997), Roger et al. (1998), Morquecho and Pitt (2003), and Tuccillo (2006), describe PSD and the associate metal fractionation for size fractions. This study goes beyond the six commonly reported metals (cadmium, chromium, copper, nickel, lead, and zinc) and adds eight additional metals (aluminum, arsenic, cobalt, iron, manganese, selenium, strontium, and vanadium) in five size fractions (<0.45 μm, 0.45 to 8 μm, 8 to 20 μm, 20 to 100 μm, and >100 μm). 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.

Methodology

As part of a long-term study sponsored by the California Department of Transportation (Caltrans), three monitoring sites were selected in west Los Angeles. As described previously (Han et al., 2006a), all sites are almost completely impervious, represent very small catchment areas (from 3917 to 16 918 m^2), and host heavy traffic loads (approximately 300 000 annual average daily traffic). In addition, there are no anthropogenic inputs of sand or salt to the highway, because there is no snow at the monitoring sites. Because southern California has a mediterranean climate, the rainy season is concentrated during winter (December to February).

Grab samples were collected every 15 minutes during the first hour, and then hourly during the storm similar to the sampling protocol described by Han et al. (2006a). The number of samples depended on the duration of the storm. More frequent sampling occurred during the first hour 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. Rainfall information was obtained by the use of tipping bucket rain gauges with a volume resolution of 0.25 mm/tip. Flow-weighted composite samples were obtained by Sigma 900MAX automatic samplers (American Sigma); comparisons to grab samples have been presented previously by Han et al. (2006a).

PSD was measured with a Nicomp AccuSizer 780 optical particle size analyzer module (Particle Sizing Systems, Santa Barbara, California) equipped with an auto-dilution system and a light scattering/extinction sensor—a mechanism analogous to a Coulter counter—to obtain counts for particles measuring between 0.5 μm and 500 μm. In this study, PSD refers to the actual number of particles in the sample, and not the mass of particles. 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 six hours of collection. The samples for the other parameters were refrigerated at 4 °C until analyzed.

Duplicate samples were sequentially filtered into five selected fractions (<0.45 μm, 0.45 to 8 μm, 8 to 20 μm, 20 to 100 μm, and >100 μm) for metals analyses. The suspended solids retained in each filter were then digested and diluted to the same volume. U.S. EPA method 200.8 (U.S. EPA, 1994) was used on the Agilent 7500i Inductively Coupled Plasma-Mass Spectrometer (Agilent Technologies, Santa Clara, California) to analyze the filtrate for the <0.45 μm size fraction and the extraction fluid for the 14 metals. Ultimate detection limits were approximately 0.001 μg/L. The final concentration measured in μg/L represents the mass of metal by volume of filtered runoff. 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. Several water quality parameters were also obtained following methods described in the Standard Methods (American Public Health Association et al., 1999).

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 flow rate (Han et al., 2006a). Because 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 the following equation (1):

$$EMC = \frac{M}{V} = \frac{\sum M_i}{\sum V_i} = \frac{\sum C_i Q_i \Delta t_i}{\sum Q_i \Delta t_i} \quad (1)$$

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

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 mass of the particles). This is mathematically similar to the concentration for metals obtained by first separating the particles by sieving to obtain the mass of particles on a size fraction, and then measuring the concentration of the metal.

All statistical analyses were performed using "R" statistical software (freely available online at http://www.r-project.org). Each dataset was first checked for normality by the use of probability plots; when necessary, a log–transformation was used before the other statistical tests as used previously by other authors such as Strecker et al. (2001) and Van Buren et al. (1997). Analysis of Variance (ANOVA) 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 a 95% family-wise confidence level (similar to Fisher's Least Significant Difference test for pair-comparison) was used as a follow-up. The THSD test highlights pair-wise comparisons exposing which pairs have significant differences. Correlation analyses among water quality parameters and metals concentration were made using the EMC values for each storm and site combination using the Spearman method. This method was preferred over the Pearson 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.

Table 1—Storm events characteristics.

Monitoring site ID	Rain start date	Event rain (mm)	Maximum intensity (mm/hr)	Antecedent dry (days)	Total runoff flow volume (L)	Peak flow (L/s)	Length of storm
7–201	10/17/2004	11.94	24.38	215	19900	7.02	7h43
	10/26/2004	61.47	36.58	6	704200	96.2	21h29
	12/05/2004	14.22	12.19	8	53200	8.12	19h02
	01/07/2005	156.0	33.53	2	1847600	58.3	81h19
	02/10/2005	68.83	27.43	8	449600	40.2	36h45
7–202	10/17/2004	21.84	30.48	215	254300	110	13h09
	10/26/2004	48.26	27.43	6	710900	106	21h29
	12/05/2004	17.02	12.19	8	250600	62.6	17h23
	01/07/2005	287.0	33.53	2	4392500	93.8	80h59
	02/10/2005	78.23	27.43	8	1011100	98.2	38h54
	03/18/2005	5.080	3.048	5	51500	8.47	19h53
	04/28/2005	32.77	27.43	31	522000	109	6h14
7–203	10/26/2004	45.21	30.48	6	131600	25.0	21h07
	12/05/2004	14.73	12.19	8	24800	5.65	16h13
	01/07/2005	202.2	51.82	2	758100	66.5	80h05
	02/10/2005	52.07	24.38	8	176800	27.1	30h11
	03/18/2005	2.794	3.048	5	4100	2.42	14h01
	04/28/2005	29.72	42.67	31	104800	37.3	3h23

Results

A total of 202 discrete samples were collected at the three monitoring sites during seven storms in the winter of 2004–2005 (Table 1). The 2004–2005 winter 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 950 mm of rainfall in downtown Los Angeles, greater than the city's average of 400 mm; the 1883–1884 season had the greatest rainfall of 970 mm. Both the precipitation data and the runoff flow shown in Table 1 were measured at each of the sampling sites.

Eleven water quality parameters were measured for all 202 samples and are shown in Table 2 as EMC values. Total suspended solids (TSS), volatile suspended solids (VSS), chemical oxygen demand (COD), and dissolved organic carbon (DOC) are some of the parameters measured. 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 including Van Buren et al. (1997) and Helmreich et al. (2010).

Figure 1 shows the PSD for all 202 collected samples. The raw data consisted of particle counts for each diameter (from 0.5 μm to 500 μm) as detected by the PSD analyzer. Figure 1a shows the calculated volume occupied by the particles, assuming spherical geometry, in each of the selected size fractions. 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 ($p < 0.01$) existed among at least one pair of size fractions. The THSD test indicated a statistically significant difference between the largest size fraction (>100

Table 2—Summary of water quality parameters for combined storms/sites (values are in event mean concentrations).

Parameters	Mean	Median	Minimum	Maximum	Standard deviation
TSS[a] (mg/L)	63.5	49.5	9.49	199.8	45.6
VSS[b] (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 (μmho/mm)	25.5	10.4	3.12	157.5	40.9
Hardness (mg/L)	107	35.5	11.3	1011	232
COD[c] (mg/L)	159	75.4	36.3	736	190
DOC[d] (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
NH_3-N[e] (mg N/L)	2.43	1.09	0.431	10.0	2.99
NO_2^-[f] (mg N/L)	0.398	0.0938	0.0388	4.70	1.08
NO_3^-[g] (mg N/L)	1.51	0.881	0.222	5.37	1.58

[a] Total suspended solids.
[b] Volatile suspended solids.
[c] Chemical oxygen demand.
[d] Dissolved organic carbon.
[e] Ammoniacal nitrogen.
[f] Nitrite.
[g] Nitrate.

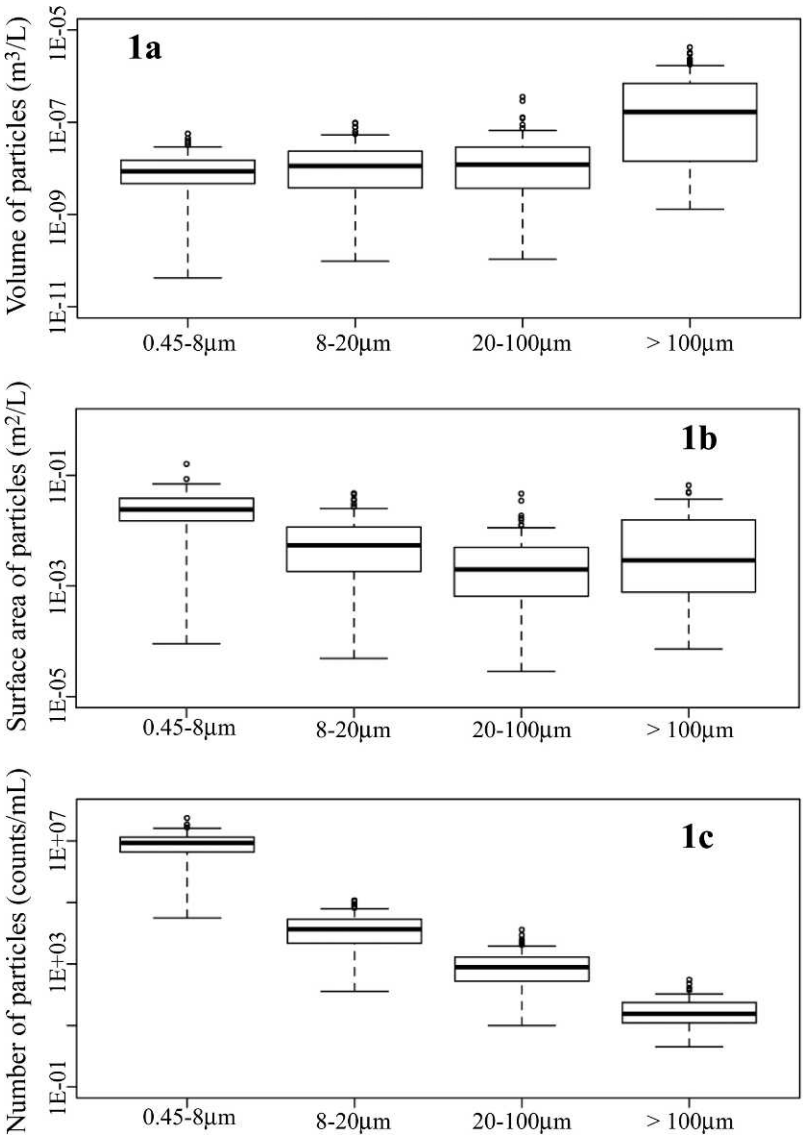

Figure 1—Calculated volume of particles separated by size fraction (a); calculated surface area of particles separated by size fraction (b); measured number of particles (c).

µm) and each of the other size fractions. No statistically significant difference was indicated for the other pairs. Figure 1b shows the calculated surface area of the particles. Statistical comparison using ANOVA analysis and the THSD test of the log–transformed calculated surface areas of the four size fractions indicated a significant difference between all pairs of size fractions, except between the size fractions of 20 to 100 µm and >100 µm. Figure 1c shows the actual number of particles measured in the 202 collected samples. Statistical comparisons using ANOVA analysis and the THSD test of the log–transformed number of particles in each of the four size fractions indicated a significant difference between all pairs of size fractions, except between the size fractions of 8 to 20 µm and 20 to 100 µm, significant at the 81% confidence level. The smaller size fraction (0.45 to 8 µm) represents 99.79% of all particles measured. First-flush was observed for all storms and sites, but effected only the total number of particles and not the relative distribution among particle size fractions.

The concentrations (mass of metal per volume of filtered runoff) of the six commonly reported metals—cadmium, chromium, copper, lead, nickel, and zinc—are shown in boxplots in Figure 2. For each metal, there are five boxplots that illustrate the five 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 0.45 µm filter) is higher than the concentration in the particulate phase for cadmium, copper, nickel, and zinc (Table 3). Statistical comparison of the log–transformed data using ANOVA analysis and the THSD test as indicated on Table 3 shows that the mean concentration on all size fractions for each metal are different ($p \leq 0.01$), with the exception of cadmium, copper, lead, and zinc in the fractions 0.45 to 8 µm and 20 to 100 µm.

Figure 3 shows boxplots for the concentration of eight non-traditionally studied metals: aluminum, arsenic, cobalt, iron, manganese, selenium, strontium, and vanadium. ANOVA and

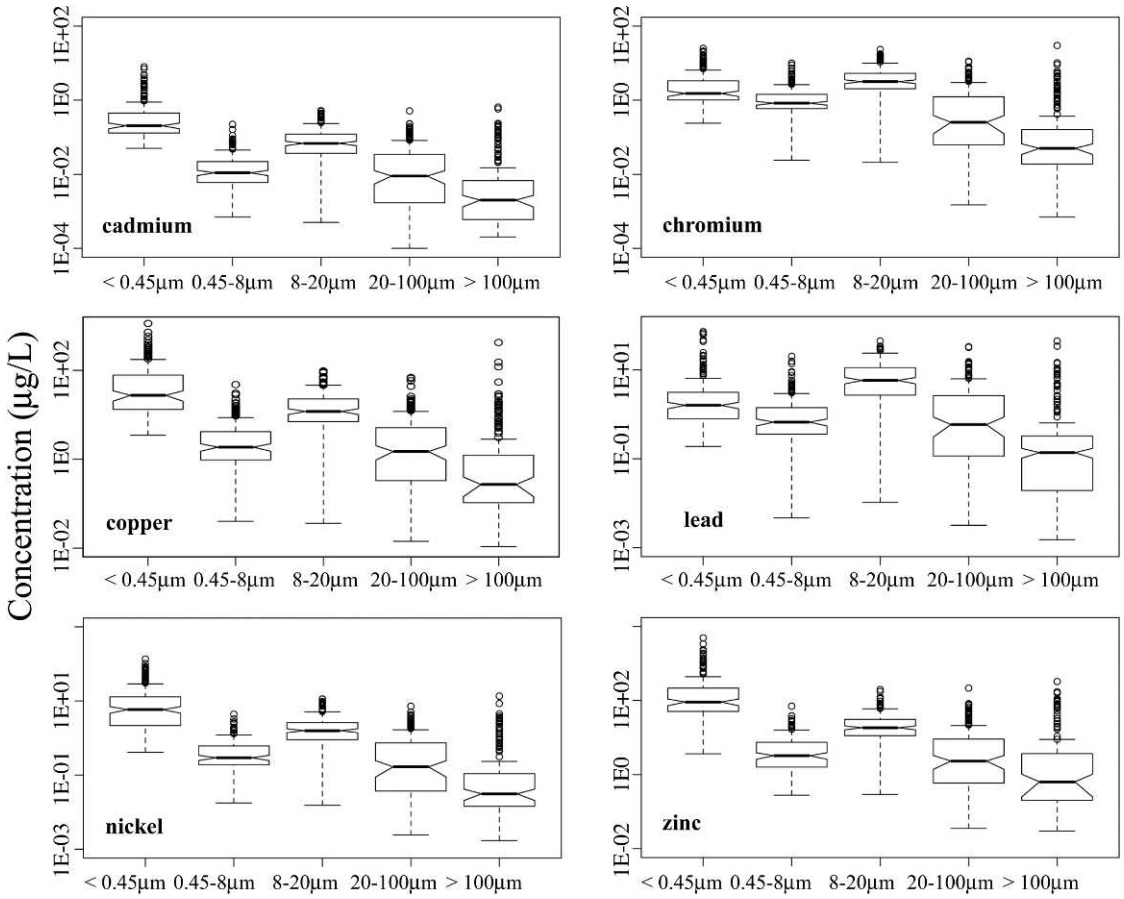

Figure 2—Boxplots for the concentration of cadmium, chromium, copper, lead, nickel, and zinc in five size fractions.

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 shown in Table 3, there is no statistical difference for the fractions 0.45 to 8 µm and 20 to 100 µm for all metals except cobalt; aluminum also does not have a statistical difference for the fractions <0.45 µm and 0.45 to 8 µm, and <0.45 µm and 20 to 100 µm. In addition, aluminum and iron had the highest concentration in the fraction 8 to 20 µm; for all other metals, the dissolved fraction (<0.45 µm) had the highest mean.

Table 3—Results from THSD test indicating if difference between size fractions is statistically significant (yes) or not (no) for six commonly reported metals (a); eight additional metals (b) (size fractions: F1 = <0.45 µm, F2 = 0.45 to 8 µm, F3 = 8 to 20 µm, F4 = 20 to 100 µm, F5 = >100 µm).

	(a) Six commonly reported metals						(b) Eight additional metals							
	Cadmium	Chromium	Copper	Nickel	Lead	Zinc	Aluminum	Arsenic	Cobalt	Iron	Manganese	Selenium	Stronium	Vanadium
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
Highest mean	F1	F3	F1	F1	F3	F1	F3	F1	F1	F3	F1	F1	F1	F1
Highest particulate mean	F3	F3	F3	F3	F3	F3	F3	F3	F3	F3	F3	F3	F3	F3

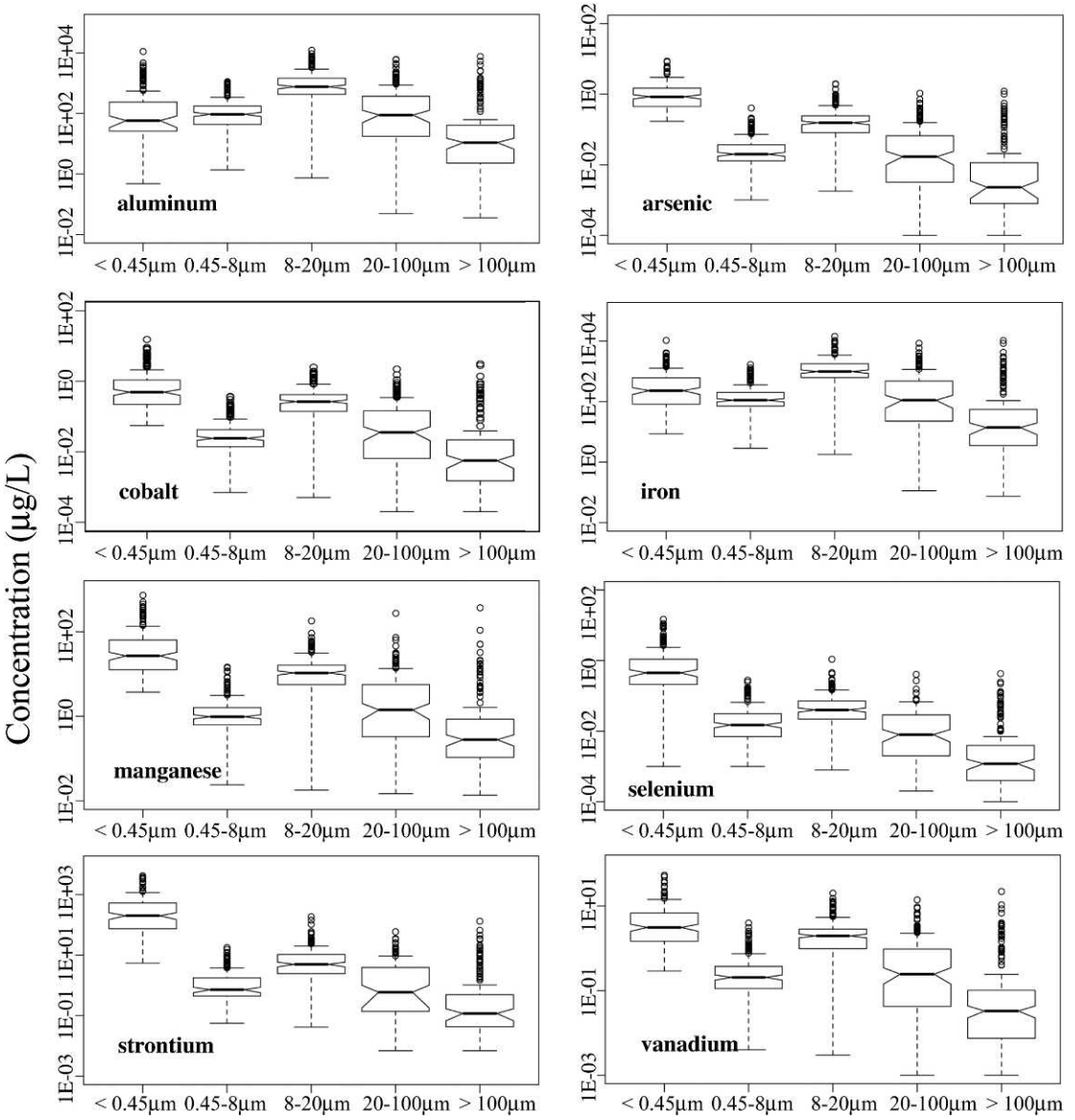

Figure 3—Boxplots for the concentration of aluminum, arsenic, cobalt, iron, manganese, selenium, strontium, and vanadium in five size fractions.

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 be obtained by calculating the TSS assuming that the particles are spheres with a density of 2.6 kg/m^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 4 and 5). The group of six commonly reported metals (Figure 4) has the highest mean in the 8 to 20 µm 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 (Figure 5) had the highest mean in the 8 to 20 µm 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 to 8 µm and 20 to 100 µm.

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 4 shows a comparison between the 2000 to 2003 dataset (Han et al., 2006a) and the current study. Even though the 2004–2005 rainy season was wetter than the 2000 to 2003 seasons, the mean EMCs for TSS of both datasets are similar, which is less than half of the California statewide dataset derived from a monitoring program conducted from 1997 to 2001 (Kayhanian et al., 2003). This variation could have occurred because the runoff from the highway shoulders in the three sites

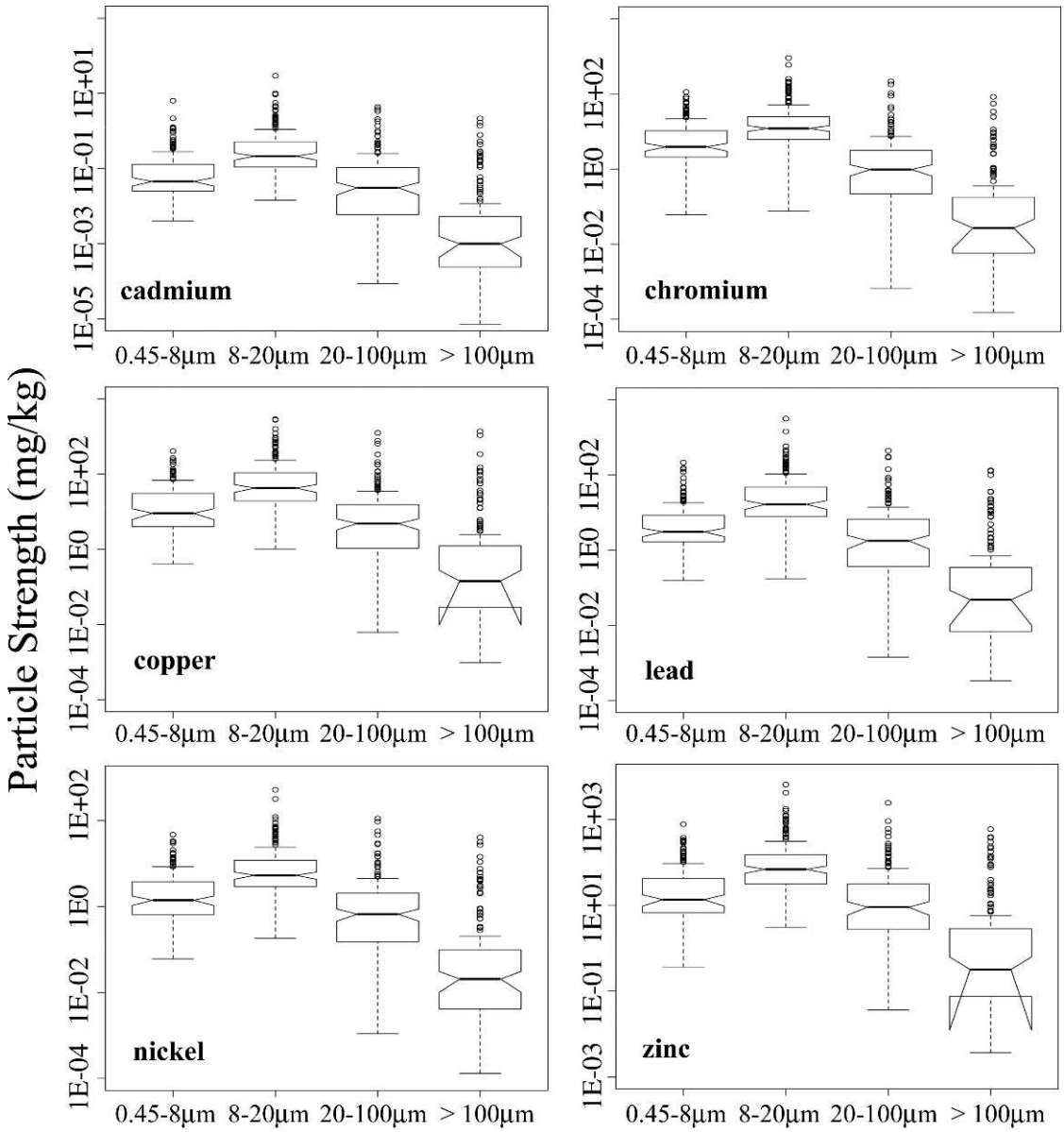

Figure 4—Boxplots for the particle strength concentration of cadmium, chromium, copper, lead, nickel, and zinc in four size fractions.

drains away from the sample sites, which is not typical of all Caltrans sites. Additionally, the mean for turbidity in the 2000 to 2003 dataset (Han et al., 2006a) is almost twice the value reported in this study, and the statewide value is approximately 14 times as high. This could be attributed to a dilution effect as a result of the wetter rainy season.

Because of 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 5 shows the correlation analysis results for the water quality parameters shown on Table 2. 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-NH_3-N (ammoniacal nitrogen), COD-NO_2^- (nitrite), COD-NO_3^- (nitrate), DOC-OG, DOC-NH_3-N, DOC-NO_2^-, DOC-NO_3^-, OG-NH_3-N, OG-NO_2^-, OG-NO_3^-, and NO_2^--NO_3^-. Using Pearson correlation coefficients, Han et al. (2006b) indicated a strong correlation ($\rho \geq 0.80$) between TSS-VSS, COD, DOC, conductivity-hardness, COD-OG, and DOC-NH_3-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 $\pm$ 0.6 for all 62 monitored storms (Han et al., 2006a).

Because many treatment units report performance based on removal of TSS, this study aimed to determine how well TSS correlates with the pollutant concentrations. Therefore, correlation tables between TSS and all the size fractions for each of the 14 metals were created. As an example, TSS does not have a strong correlation with any of the size-fractions for arsenic (Table 6). However, there is a very strong correlation between the 8 to 20 µm size fraction and the total concentration for the particulate arsenic, and also between the dissolved (<0.45 µm)

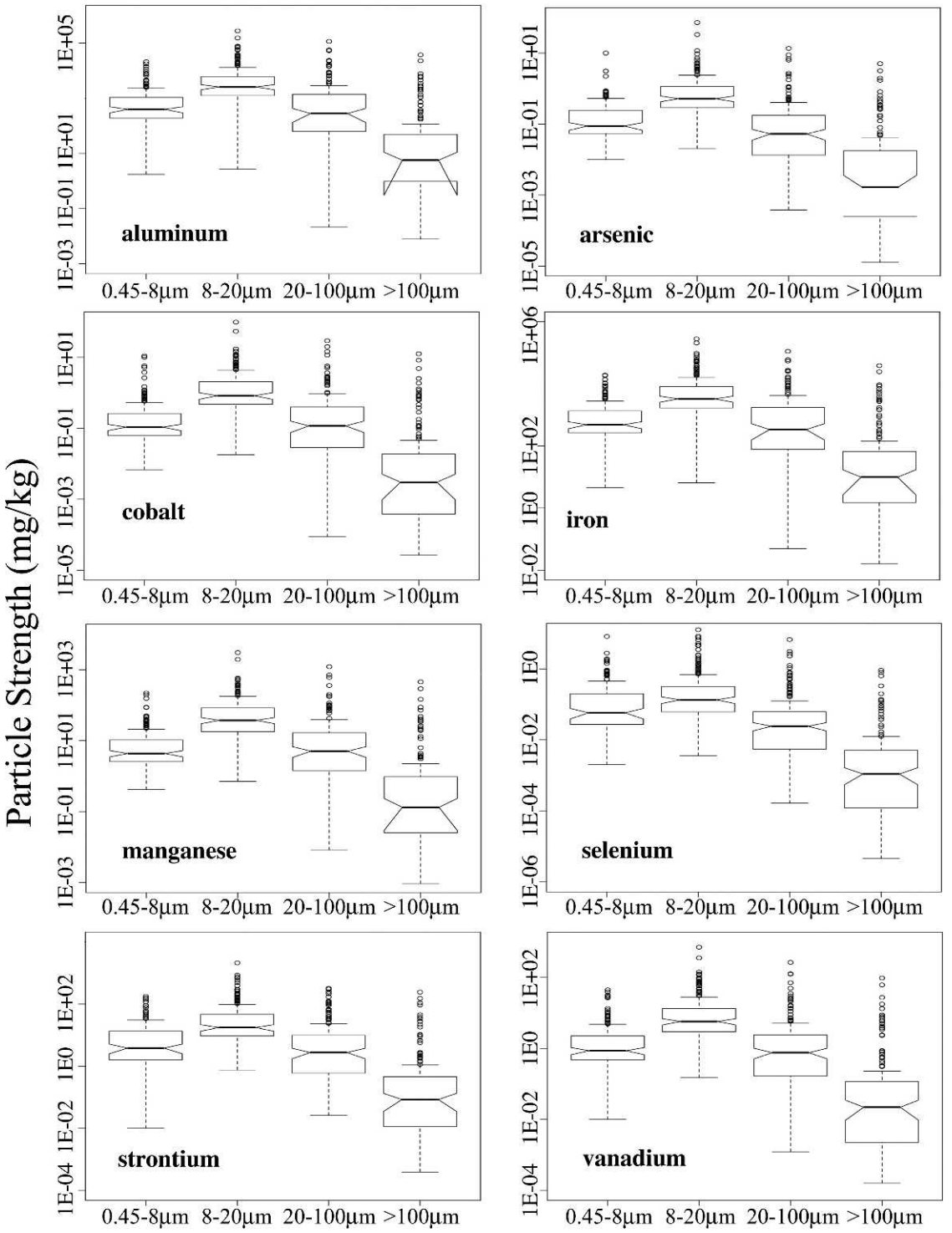

Figure 5—Boxplots for the aqueous concentration for aluminum, arsenic, cobalt, iron, manganese, selenium, strontium, and vanadium in four size fractions.

and total arsenic concentrations. Similar to arsenic, the other 13 metals exhibited a strong correlation ($\rho \geq 0.80$) between the 8 to 20 µm size fraction and the total concentration for the particulate phase of the metal (data not shown). This correlation supports the observation that the highest mean for particle strength is at the 8 to 20 µm size fraction (Figures 4 and 5). Table 7 shows the correlation between TSS and the particulate fraction for each of the 14 metals. None of the metals had a strong correlation ($\rho \geq 0.80$) with TSS, as 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

Table 4—Comparison of water quality event mean concentration with other studies.

Parameters	Current study	Han et al. (2006)	Kayhanian et al. (2003)	Sansalone et al. (1998)
TSS[a] (mg/L)	63.5	67.7	175	122
VSS[b] (mg/L)	26.5			40.1
Turbidity (NTU)	27.3	46.8	366	
Conductivity (μmho/mm)	25.5	23.9	36.3	
Hardness (mg/L)	107	78.9	50	
COD[c] (mg/L)	159	253		197
DOC[d] (mg/L)	27.8	66.9	19	
Oil and Grease (mg/L)	9.56	14	6.6	
NH_3-N[e] (mg N/L)	2.43	4.6	0.83	
NO_2^{-}[f] (mg N/L)	0.398	0.3	0.14	
NO_3^{-}[g] (mg N/L)	1.51	2.7	0.97	

[a] Total suspended solids.
[b] Volatile suspended solids.
[c] Chemical oxygen demand.
[d] Dissolved organic carbon.
[e] Ammoniacal nitrogen.
[f] Nitrite.
[g] Nitrate.

metals: cadmium, chromium, copper, nickel, lead, and zinc. TSS showed a good correlation ($\rho \geq 0.70$) with all metals in the >100 μm size fraction, except for manganese, selenium, and zinc (Table 8). In addition, with a few exceptions, all metals in the >100 μm size fraction showed a strong correlation ($\rho \geq 0.80$) with one another. Perhaps the discrepancy with the Helmreich et al. (2010) study can be attributed to their samples having contained more of the larger particles (>100 μm) than the current study. This result highlights the importance of investigating several size fractions beyond particulate versus dissolved fractions.

Because of the limitations of sieving (difficult to separate particles in size fractions smaller than approximately 40 μm), this study uses particle strength to characterize the concentration of metals by the mass of particles in a certain size fraction. However, the significant disadvantage of using particle counts is the lack of particle mass information. A previous study of the same field sites (Li et al., 2006) showed good linear correlation between particle counts and 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 μm). This lack of correlation forced the estimation of TSS based on spherical particles with a density of 2.6 kg/m^3. The existence of large particles is important in estimating total solids loading but is of lesser importance for metals loading because the metals are less concentrated on the largest particles. If the largest particle fraction (>100 μm) 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. Table 9 shows the correlation for lead, and similar correlations are observed for the other metals (data not shown).

The authors recognize that assuming a spherical shape for particle geometry is an approximation, because 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). Some examples from the literature are as follows: densities for stormwater runoff commonly range from 2.1 to 2.9 kg/m^3 and densities for roadway runoff samples range from 2.4 to 2.86 kg/m^3 (Andral et al., 1999); coarse fraction particles embedded in snowmelt range from 2.75 to 2.86 kg/m^3 (Cristina et al., 2002); particles in a road gutter range from 2.14 to 2.54 kg/m^3

Table 5—Correlation analysis results among event mean concentration values for water quality parameters (values above diagonal are Spearman rank-order coefficients "r"; values below diagonal are probability values (p-values); values in bold show correlation >0.8).

	TSS[a] (mg/L)	VSS[b] (mg/L)	Turbidity (NTU)	Conductivity (μmho/mm)	Hardness (mg/L)	COD[c] (mg/L)	DOC[d] (mg/L)	Oil and grease (mg/L)	NH_3-N[e] (mg N/L)	NO_2^{-}[f] (mg N/L)	NO_3^{-}[g] (mg N/L)
TSS (mg/L)	*****[h]	**0.905**	0.639	0.267	0.23	0.416	0.389	0.459	0.558	0.104	0.201
VSS (mg/L)	<0.001	*****	**0.81**	0.521	0.465	0.672	0.672	0.732	0.765	0.426	0.488
Turbidity (NTU)	0.005	<0.001	*****	0.453	0.335	0.688	0.664	0.707	0.738	0.598	0.678
Conductivity (μmho/mm)	0.282	0.028	0.061	*****	**0.981**	0.628	0.699	0.783	0.68	0.587	0.703
Hardness (mg/L)	0.357	0.053	0.174	<0.001	*****	0.556	0.626	0.699	0.602	0.515	0.618
COD (mg/L)	0.087	0.003	0.002	0.006	0.018	*****	**0.967**	**0.934**	**0.924**	**0.843**	**0.827**
DOC (mg/L)	0.111	0.003	0.003	0.002	0.007	<0.001	*****	**0.963**	**0.895**	**0.895**	**0.862**
Oil and Grease (mg/L)	0.057	0.001	0.001	<0.001	0.002	<0.001	<0.001	*****	**0.934**	**0.802**	**0.827**
NH_3-N (mg N/L)	0.018	<0.001	0.001	0.003	0.01	<0.001	<0.001	<0.001	*****	0.695	0.787
NO_2^{-} (mg N/L)	0.68	0.079	0.01	0.012	0.031	<0.001	<0.001	<0.001	0.002	*****	**0.866**
NO_3^{-} (mgN/L)	0.422	0.042	0.003	0.002	0.007	<0.001	<0.001	<0.001	<0.001	<0.001	*****

[a] Total suspended solids.
[b] Volatile suspended solids.
[c] Chemical oxygen demand.
[d] Dissolved organic carbon.
[e] Ammoniacal nitrogen.
[f] Nitrite.
[g] Nitrate.
[h] ***** = correlation is 1 and p-value zero for values at the diagonal.

Table 6—Correlation analysis results among event mean concentration values for arsenic 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) (size fractions: F1 = <0.45 μm, F2 = 0.45 to 8 μm, F3 = 8 to 20 μm, F4 = 20 to 100 μm, F5 = >100 μm).

	TSS[a]	F1	F2	F3	F4	F5	Particulate	Total
TSS	*****[b]	−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	*****

[a] Total suspended solids.
[b] ***** = correlation is 1 and p-value zero for values at the diagonal.

Table 7—Correlation analysis results among event mean concentration values for total suspended solids (TSS) and all fourteen metals in the particulate fractions (values above diagonal are Spearman rank-order coefficients "r"; values below diagonal are probability values (p-values); values in bold show correlation >0.8).

	TSS	Chromium	Nickel	Copper	Zinc	Arsenic	Cadmium	Lead	Aluminum	Vanadium	Manganese	Iron	Cobalt	Selenium	Strontium
TSS	*****[a]	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
Chromium	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**
Nickel	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
Copper	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
Zinc	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
Arsenic	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
Cadmium	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
Lead	0.015	0.008	0.001	0.043	0.007	<0.001	<0.001	*****[a]	0.692	**0.833**	0.717	0.732	**0.841**	0.509	0.412
Aluminum	<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
Vanadium	<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
Manganese	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
Iron	<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
Cobalt	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
Selenium	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
Strontium	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	*****

[a] ***** = correlation is 1 and p-value zero for values at the diagonal.

Table 8—Correlation analysis results among event mean concentration values for total suspended solids (TSS) and all fourteen metals in the >100 μm size fractions (values above diagonal are Spearman rank-order coefficients "r"; values below diagonal are probability values (p-values); values in bold show correlation >0.8).

	TSS	Chromium	Nickel	Copper	Zinc	Arsenic	Cadmium	Lead	Aluminum	Vanadium	Manganese	Iron	Cobalt	Selenium	Strontium
TSS	*****[a]	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
Cromium	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**
Nickel	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**
Copper	<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**
Zinc	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**
Arsenic	<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**
Cadmium	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**
Lead	0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	*****[a]	**0.928**	**0.969**	**0.876**	**0.936**	**0.955**	**0.825**	**0.944**
Aluminum	<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**
Vanadium	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**
Manganese	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**
Iron	<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**
Cobalt	<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**
Selenium	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**
Strontium	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	*****

[a] ***** = correlation is 1 and p-value zero for values at the diagonal.

Table 9—Correlation analysis results among event mean concentration values for lead in all particulate size fractions (values above diagonal are Spearman rank-order coefficients "r"; values below diagonal are probability values (p-values); values in bold show correlation >0.8).

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

(Zanders, 2005); and particles from highway runoff range from 2.1 to 2.7 kg/m^3 (Lin et al., 2009). However, Kayhanian et al. (2008) reported a lower range of densities (1.6 to 1.8 kg/m^3), showing that particle density is an important parameter to be characterized instead of relying on any approximated value. Because particle density was not measured in this study, 2.6 kg/m^3 was used to be consistent with previous studies that also assumed particle density, such as Li et al. (2005). Although, this study acknowledges that there is growing evidence indicating that particle density, especially for the smallest particles, may be less than 2.6 kg/m3 (Zanders, 2005; Kayhanian et al., 2008).

A simple way to study metals fractionation is by the use of mass fraction ratio (Sansalone et al., 1996), which is the ratio of dissolved metal element mass to particulate metal element mass. 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 it is based on a specific particle size removal, and needs to be studied. This is the primary reason that the present study divided the samples into four size fractions for the particulate phase. Because of the highly variable nature of stormwater runoff, treatment trains are a preferred approach rather than a single treatment unit type. In addition, if the primary pollutant of interest is fine particles, sedimentation-based treatment units may not be recommended (Helmreich et al., 2010).

Ordinary sedimentation of runoff (1 m/h overflow rate which corresponds to a retention time of 3 h for a 3 m deep basin, as shown in Figure 6) will remove no more than 65% of the particulate-phase metals observed in this study; either coagulation or filtration will be needed to obtain greater removals. Treatment units such as hydrodynamic devices sometimes appear to have no statistically significant TSS removal efficiency, but it can be shown theoretically that they are effective in removing particles in the size fraction greater than 250 μm (based on Figure 6 curve for 100 m/h overflow rate and 1.8 min retention time). This highlights the need for studying the pollutants of concern in several size fractions to determine which treatment unit or treatment train would be appropriate.

When choosing among treatment units, such as between sedimentation or filtration, the minimum particle size that can be removed is being selected. Typically, it is assumed that the smallest particle size has the greatest metal mass as a result of the high surface area. This was not true in this study; the 8 to 20 μm size fraction predominantly had the greatest metal mass. A study of swept street particles (Lau and Stenstrom, 2005) showed that the 100 to 250 μm size particles typically had the greatest metal mass. Both the particulate-phase concentration and the number (or mass) of particles in a size range determine the metal mass as a function of particle size. Previous studies and the varying results shown here demonstrate the need to analyze removal rates as a function of PSD when performing stormwater research or treatment studies. Measuring only soluble or particulate-phase metals concentration is not adequate to choose treatment units on a rational basis.

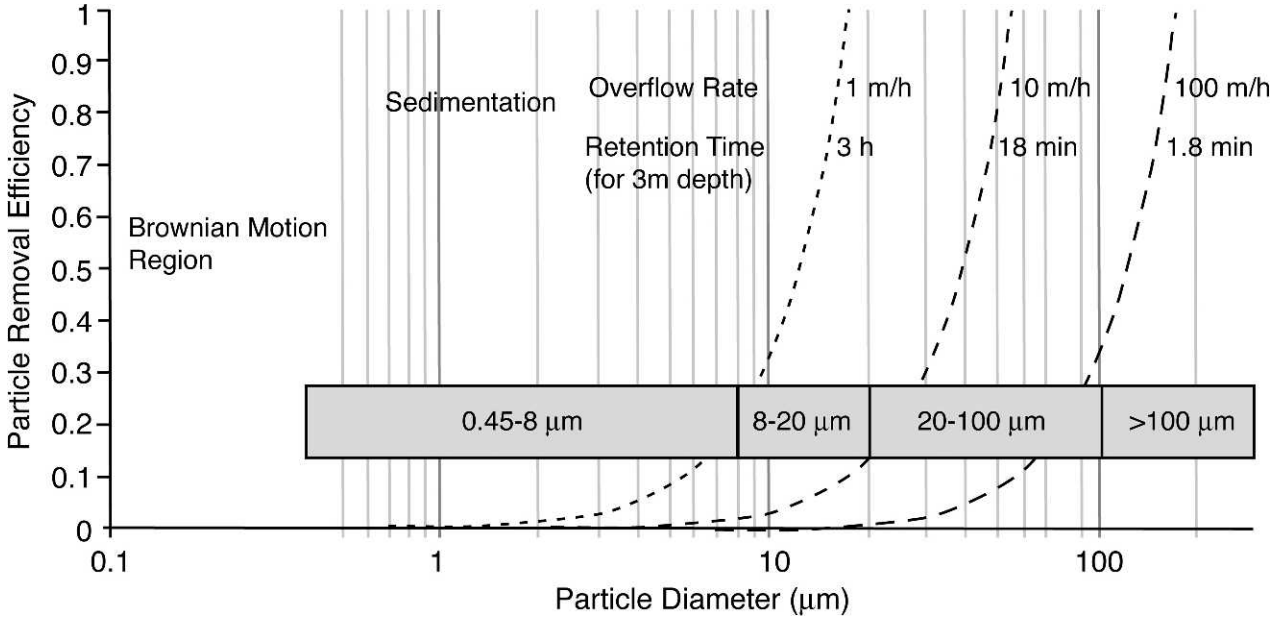

Figure 6—Theoretical removal efficiencies for sedimentation

Conclusions

This paper has reported the concentration of 14 metals as they appear in the dissolved phase (defined as filtered through a 0.45 μm filter) over several size fractions. The observation that the size fraction 8 to 20 μm has the highest concentration and particle strength emphasizes the importance of studying the particulate-phase metals as a function of PSD. The following specific conclusions are made:

(1) For each of the fourteen metals, the concentrations in all five size fractions are, typically, statistically different (Table 3).
(2) Highest mean metal concentrations occur either in the dissolved fraction or the 8 to 20 μm size fraction (Figures 3 and 4) and the metals in this fraction strongly correlate with the total particulate phase metals concentration (Table 6).
(3) Among water quality parameters, TSS is only correlated to VSS (Table 5).
(4) TSS did not correlate strongly with the particulate-phase metals concentration (Table 7).
(5) For all 14 metals, the largest size fraction (>100 μm) does not correlate with the particulate-phase fraction (Table 9).

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