

Characteristics of Highway Stormwater Runoff in Los Angeles: Metals and Polycyclic Aromatic Hydrocarbons

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ABSTRACT: Stormwater runoff from three highway sites in Los Angeles, California, was monitored, during the 2000 to 2003 wet seasons. Correlations among heavy metals, polycyclic aromatic hydrocarbons (PAHs), and storm characteristics were performed using datasets collected for 62 storm events. Statistical correlation analyses of the event mean concentrations (EMCs) and mass first-flush ratios (MFFs) with storm characteristics were conducted to determine if the first flush is related to site or storm characteristics. This study agreed with other highway runoff characterization studies, in that strong correlations were observed among the heavy metals and between heavy metals and total PAHs, and total suspended solids were well correlated with most heavy metals. Only antecedent dry days among storm characteristics were reasonably well-correlated with the EMCs of heavy metals and total PAHs, and dissolved and total metals exhibited similar MFFs, with approximately 30 to 35% of the mass being discharged in the first 20% of the runoff volume. *Water Environ. Res.*, **81**, 308 (2009).

KEYWORDS: highways, stormwater, correlation, mass first flush, storm characteristics, heavy metals, polycyclic aromatic hydrocarbons.

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Introduction

Evidence of pollutants in stormwater runoff, including sediments, nutrients, heavy metals, and polycyclic aromatic hydrocarbons (PAHs) from the highway environment, has been documented (Barrett et al., 1998; Furumai et al., 2002; Kayhanian et al., 2003, 2007; Li et al., 2005, 2006). Among the variety of pollutants in highway stormwater runoff, heavy metals have been of greater concern, because they are found in elevated concentrations, possibly threatening aquatic organisms and human health. Primary sources of heavy metals in highway runoff are reported to be auto parts, auto engine exhaust, tire wear, lubrication oils, and pavement degradation (U.S. EPA, 1995). The particulate form of PAH is another pollutant of concern that is detected from highway runoff; sources of PAHs may include asphalt pavement leachate, tire wear, auto

engine exhaust, lubrication oils, antifreeze, and atmospheric deposition (Herrick, 1995; Latimer et al., 1990; Ngabe et al., 2000; Takada et al., 1991). Although a small quantity of the heavy metals and PAHs occur in nature, short- and long-term exposure to excessive concentrations may cause adverse environmental effects on aquatic organisms in receiving waters.

To assess the potential effect of highway runoff on the environment and develop appropriate mitigation technologies, it is essential to obtain accurate knowledge on the characteristics of pollutant discharge. Extensive statewide highway runoff characterization has recently been performed in the State of California, where the event mean concentration (EMC) of wide ranges of chemical constituents was assessed through automated flow-weighted composite samples monitoring (Kayhanian et al., 2007). In a separate specialized first-flush highway runoff characterization study, the variability of pollutants in highway runoff during a storm was monitored from three highly urbanized highway sites in west Los Angeles during the 2000 to 2003 wet seasons (Stenstrom and Kayhanian, 2005). A large suite of data, including rainfall, runoff, and water quality parameters was collected, and correlations were analyzed among EMCs and mass first-flush (MFF) ratios for conventional pollutants and storm characteristics (Han et al., 2006b). It was shown that there was a strong first flush in chemical oxygen demand (COD) and other organic pollutants, and a weak first flush for ionic pollutants, such as nitrate and nitrite. Using Pearson correlation analyses, strong correlations were found among dissolved organic carbon, COD, total Kjeldahl nitrogen, oil and grease, and ammonium-nitrogen. However, most conventional pollutants were weakly correlated to total suspended solids (TSS). Among seven storm characteristics in the study, only antecedent dry days (ADD) were correlated with monitored pollutants. More detailed results are described in our previous papers (Han et al., 2006a, 2006b).

The focus of this paper is to extend the previous work and present the characteristics and correlation results for 6 heavy metals and 16 PAHs from the three highly urbanized highway sites using the same storm events.

Methods

Site Description. The three monitoring sites (7-201, 7-202, and 7-203) were described previously by Han et al. (2006a); thus, only a brief summary is provided. The sites were located in west Los Angeles, California, and the catchment areas ranged from 3917 to 16 918 m², with runoff coefficients ranging from 0.90 to 0.95. The annual average daily traffic (AADT) of the sites was over 260 000 vehicles per day. All three monitoring sites were equipped with tipping bucket rain gauges and ultrasonic 950 area-velocity flow

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Table 1—Summary description of the monitoring sites.

| Site number | Location | Freeway/ post miles | Area (m ²) | AADT (vehicles/day) | Imperviousness (%) |
|-------------|---|------------------------|---------------------------|------------------------|--------------------|
| 1 (7-201) | Eastbound US 101 | HWY 101 PM 17 | 12 800 | 328 000 | 100 |
| 2 (7-202) | I-405 Freeway and Sepulveda Blvd. | FW 405 PM 34 | 16 900 | 269 000 | 95 |
| 3 (7-203) | Santa Monica Blvd. N. Bound Exit on I-405 | FW 405 PM 30.8 | 3 900 | 322 000 | 100 |

meters (American Sigma, Loveland, Colorado) to record rainfall and flow in 1-minute intervals. Automatic samplers were also installed in conjunction with the flow meters to collect flow-weighted composite samples. A summary description of the monitoring sites is provided in Table 1.

Most of the rainfall events occur in winter months (November to March), which is typical of Mediterranean climates (Lee et al., 2004). The average annual precipitation over the past 43 years was approximately 350 mm. Based on the 43 years' average precipitation, the three wet seasons monitored for this study were wetter than normal, drought, and average for the 2000 to 2001, 2001 to 2002, and 2002 to 2003 wet seasons, respectively (Han et al., 2006a). The 50% probability rainfall amount and duration for the combined site were 18 mm and 7.2 hours, respectively. Total precipitation, duration, and intensity of the monitored storm events ranged from 1.5 to 156 mm, 0.9 to 47.5 hours, and 0.2 to 11.2 mm/h, respectively. The probability plots and basic statistics of the monitored storms were presented by Han et al. (2006a).

Sample Collection and Handling. For each site and storm event, discrete grab samples and a flow-weighted composite sample were collected with continuous measurements of runoff flow and rainfall. Five grab samples were taken during the first 1 hour of runoff at 15-minute intervals, followed by up to 7 grab samples taken at 1-hour intervals for the next 7 hours. If a storm lasted more than 8 hours, 1 or 2 additional grab samples were collected at 1-hour intervals. The grab samples were collected using a polypropylene scoop from a free waterfall at the end of a storm-drain pipe at each monitoring site (Han et al., 2006a) and were then transferred to 4-L amber glass bottles. The automatic samplers were kept in operation until the end of a storm, so that the flow-weighted composite samples covered the whole duration of the storm. The automatically flow-weighted composite samples were compared with the EMCs that were calculated using the individual grab sample concentrations and measured runoff flowrates.

To ensure the quality of a certain analysis (filtration to identify dissolved and particulate phase metals), which must be performed very soon after sample collection, the samples were transported back to the campus laboratory after the first hour and two more times during the next 7 hours. All samples transported back to the laboratory were refrigerated at 4°C until analyzed. The composite samples were retrieved after the event. All analyses were performed within the U.S. Environmental Protection Agency (Washington, D.C.) (U.S. EPA) maximum recommended holding time (APHA et al., 1998). Runoff pH was initially measured in the field and did not change during the following 24 hours; it was subsequently measured in the laboratory.

Analytical Methods for Polycyclic Aromatic Hydrocarbons and Metals. Both dissolved and particulate bounded PAHs were analyzed according to U.S. EPA methods (SW-846, U.S. EPA, 1999). Samples were filtered using a 47-mm GF/B (1- μ m pore size, Whatman, Florham Park, New Jersey) glass fiber filter paper. The

dissolved PAHs were extracted using solid-phase extraction (C18) according to U.S. EPA method 3535 (U.S. EPA, 1999). Particulate PAHs on the filter paper were extracted using a MarsX microwave oven (CEM, Matthews, North Carolina), according to U.S. EPA method 3546 (U.S. EPA, 1999).

Both fractions were analyzed using a Finnigan 4000 Quadrapole mass-spectrometer (Sunnyvale, California) with a Varian 3400 gas chromatograph (Palo Alto, California). A splitless injector (at 290°C) was used for sample injection to a 30 m \times 0.25 mm internal diameter DB-5ms capillary column (Agilent-J&W Scientific, Santa Clara, California). The gas chromatograph temperature program was as follows: initial hold of 30°C for 4 minutes, increase from 30°C to 300°C at 6°C/minute, and 300°C for 30 minutes. Mass spectral data were collected by using a scan range of 35 to 500 AMU and a scan rate of 1 scan/s. The following 16 commonly reported PAHs in the literature were analyzed using this method: naphthalene (NAP), acenaphthylene (ACN), acenaphthene (ACT), fluorene (FLE), phenanthrene (PHEN), anthracene (ANT), fluoranthene (FLT), pyrene (PYR), benz[a]anthracene (BaA), chrysene (CHRY), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), indeno[1,2,3,cd]pyrene (INP), dibenzo (ah)anthracene (DBA), and benz[g,h,i]perylene (BghiP). Identification was confirmed by comparing mass spectra with a reference library and commercially available standards.

Both dissolved and particulate metals were analyzed according to U.S. EPA method 200.8 (U.S. EPA, 1994) for the following six metals: cadmium (Cd), chromium (Cr), copper (Cu), nickel (Ni), lead (Pb), and zinc (Zn). Samples were filtered using a 47-mm membrane filter (0.45- μ m pore size, Osmonic, Minnetonka, Minnesota) as soon as the samples were delivered to the laboratory. The dissolved phase metals were preserved with nitric acid (HNO₃) until analysis. The particulate-bounded metals on the membrane filters were digested using nitric acid according to U.S. EPA method 3051 (U.S. EPA, 1999), using MarsX microwave (CEM). Both fractions were analyzed using a Perkin-Elmer inductively coupled plasma atomic emission spectroscopy (ICP-AES) (Perkin-Elmer, Waltham, Massachusetts) at Castaic Lake Laboratory (Castaic, California).

Event Mean Concentration, Partial Event Mean Concentration, and Mass First-Flush Ratio Calculation. The EMC represents a flow-weighted average concentration of a particular pollutant in runoff from a storm event and can be used to calculate the total amount of a pollutant generated from the storm event. The EMC is mathematically defined as the integration of the products of concentration and flowrate over the whole storm duration (i.e., total pollutant mass) divided by the total runoff volume. Many stormwater monitoring programs measure a series of grab samples instead of a continuous profile of pollutant concentration. If this is the case, the EMC can be calculated from a series of grab samples, with flowrates that are simultaneously measured. Instead of integration, a summation of discrete values of pollutant concentration and flow volume are used at each discrete time interval to

Table 2—Basic statistics of EMCs calculated for combined sites.

| Parameters | Number of cases ^a | Mean of EMCs | EMC/grab ^b (mean, %) | Median of EMCs | EMC/grab ^c (median, %) | Minimum | Maximum | EMC standard deviation |
|-------------|------------------------------|--------------|------------------------------------|----------------|--------------------------------------|---------|---------|------------------------|
| TSS (mg/L) | 62/569 | 67.7 | 95.0 | 57.6 | 125 | 8.8 | 466 | 63.0 |
| PAHs (ng/L) | 62/551 | 360 | 94.0 | 280 | 280 | 28 | 1880 | 370 |
| tCd (μg/L) | 43/362 | 1.8 | 87.7 | 1.1 | 102 | 0.5 | 20.2 | 3.1 |
| tCr (μg/L) | 58/564 | 10.1 | 96.5 | 8.8 | 107 | 2.4 | 40.1 | 6.3 |
| tCu (μg/L) | 62/564 | 93.1 | 83.7 | 55.7 | 88.1 | 16.2 | 921 | 125 |
| tNi (μg/L) | 62/563 | 20.0 | 86.1 | 11.2 | 87.7 | 2.3 | 254 | 33.9 |
| tPb (μg/L) | 47/562 | 33.0 | 135 | 25.0 | 132 | 4.6 | 239 | 38.1 |
| tZn (μg/L) | 62/564 | 507 | 90.2 | 268 | 100 | 83.4 | 8880 | 1140 |
| dCd (μg/L) | 43/363 | 1.3 | 85.5 | 0.5 | 78.0 | 0.5 | 17.8 | 2.7 |
| dCr (μg/L) | 58/566 | 2.8 | 90.1 | 2.0 | 96.9 | 0.5 | 19.3 | 2.8 |
| dCu (μg/L) | 62/566 | 66.0 | 79.0 | 35.4 | 91.9 | 5.3 | 735 | 104 |
| dNi (μg/L) | 62/565 | 15.7 | 83.5 | 7.9 | 91.0 | 0.5 | 229 | 31.3 |
| dPb (μg/L) | 47/564 | 4.9 | 111 | 3.6 | 146 | 0.5 | 43.5 | 6.5 |
| dZn (μg/L) | 62/566 | 416 | 89.5 | 178 | 96.9 | 42.4 | 8150 | 1060 |

^a Number of storm events over total number of grab samples.

^b Arithmetic mean of EMCs divided by mean concentration of grab samples.

^c Arithmetic median of EMCs divided by median concentration of grab samples.

calculate total pollutant mass and total runoff volume. The partial EMC (PEMC) can be calculated in the same manner as the calculation of the EMC, except that the integration or summation ends at a point in the storm, such as after a specific amount of time (i.e., 30 minutes or 1 hour) or after a defined fraction of the runoff volume. A PEMC represents an average pollutant concentration of an initial runoff volume and is generally used to quantify the degree of concentration-based first flush. The ratio of PEMC at a defined point to EMC (i.e., $PEMC_t/EMC$ at time t , or $PEMC_n/EMC$ at $n\%$ of the total runoff volume) can be used to show the change in concentration as the storm progresses. In this study, the values of EMCs for reporting and statistical analyses were based on the calculated EMCs using grab samples. When the measured grab samples were below the detection limit (1 ng/L for both metals and PAHs), half the detection limit (0.5 ng/L) was used for EMC calculation and statistical analyses.

The application of the MFF ratio to estimate the magnitude of the mass-based first flush during various phases of the storm has previously been reported (Kayhanian and Stenstrom, 2005; Kim et al., 2005). For example, the MFF ratio is termed MFF_n , which is defined as the percent pollutant mass discharge at $n\%$ of total runoff volume. This is similar to the Bertrand-Krajewski et al. (1998) method of assuming a specific mass discharged during an event in a specific volume of runoff (80% of the pollutant mass in the first 30% of the runoff volume, $MFF_{30} = 2.66$), except that a parameter is created that can describe any arbitrary length and magnitude of the first flush. In this paper, both concentration- and mass-based first flush are investigated using $PEMC_t/EMC$ (or $PEMC_n/EMC$) and MFF_n . Additional detailed calculation methods for the EMC, PEMC, and MFF ratio are described in our previous paper (Han et al., 2006a).

Correlation Analysis. Data sets for 18, 21, and 23 storm events collected from sites 7-201, 7-202, and 7-203, respectively, over the three wet seasons were used for the correlation analyses. Data sets for individual sites and the pooled data sets from all sites (combined sites) were analyzed. The correlation analyses were performed among the EMCs of 12 heavy metals (6 metals in dissolved and total forms), TSS, and total PAHs, and among storm

characteristics and EMCs of metals and PAHs. Seven storm characteristics were selected for this study—total event rainfall, three different rainfall intensities (5-minute maximum, 15-minute maximum, and average storm duration), ADD, antecedent rainfall, and rainfall duration. Pearson correlation analyses between the MFF ratios and storm characteristics were performed to determine if the first flush was related to site or storm characteristics. Seven storm characteristics and first-flush descriptors, such as MFF_n s and $PEMC/EMC$ s for five points (10 to 50% by 10% increments), were used in the correlation.

Results

Event Mean Concentrations for Metals and Polycyclic Aromatic Hydrocarbons. Table 2 shows the basic statistics of the EMCs calculated from grab samples for total PAHs and total and dissolved metals (prefixed “t” and “d”, respectively). The ratios of the mean and median of EMCs to mean and median of the grab samples from all monitored storms are also shown in columns 4 and 6 of the table, respectively. There were generally 62 EMCs calculated from grab samples, whereas the number of EMCs measured from automated composite samplers was only 45, because the samplers were deployed after the first year of the study, and some samples were lost as a result of equipment failures. There are large variations in the EMCs among different storm events (for most cases, the coefficients of variation [CV] range from 1.0 up to 2.5), suggesting that the pollutant concentrations are strongly influenced by event-specific conditions. As revealed in this study, the EMCs were correlated with ADD ($r = 0.56$ to 0.72 with $p < 0.005$ for combined site data). These data and others support the existence of a seasonal first flush (Lee et al., 2004). The PAHs exhibited a seasonal first flush for the first and third years of the study, but not for the second year, which is likely a result of the low rainfall (drought conditions).

Figure 1 compares the EMCs obtained from the automatic samplers and the EMCs calculated from grab samples for total metals. As with other water quality parameters (Han et al., 2006a), the data points are scattered around the linearly regressed lines, resulting primarily from experimental errors from both grab and automatic

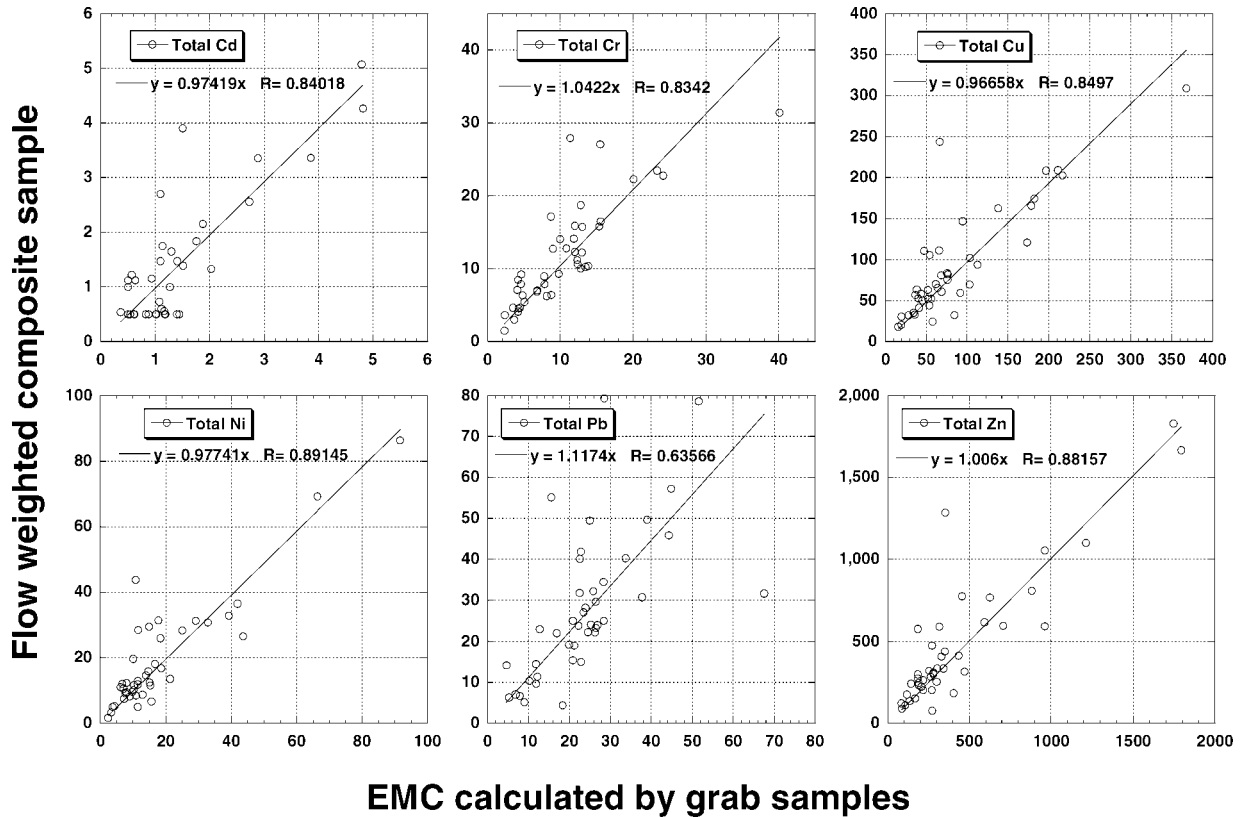


Figure 1—Comparison of EMC calculated by grab samples with composite sample.

sampling methods. Grab samples are taken at individual points of time; therefore, the dynamically varying feature of pollutant concentrations within each sampling interval cannot be considered into the EMC calculation. An automatic sampler may sometimes encounter a problem in capturing an ideal flow-weighted water sample when the flowrate is below the detection limit of the flow sensor. The Pearson's correlation between the two EMCs ranged from 0.96 for total copper (tCu) to 1.17 for total lead (tPb). The values of R for five of the metals ranged from 0.8 to 0.9, while the value of R for tPb was only 0.63. One outlier for the October 30, 2001, event at site 7-202 was identified and removed from the correlations for cadmium, copper, nickel, lead, and zinc (Cook's distance > 10 for all metals except for chromium). This event was the first rainfall of the 2001 to 2002 wet season with ADD = 192 and a very short storm duration of 1.6 hours. In this outlier event, composite sample concentrations were significantly less than calculated EMCs. This is probably because the automatic sampler did not effectively capture the very first part of the storm, which contains significantly high pollutant concentrations resulting from an exceptionally long ADD.

Figure 1 shows good agreement between sampling methods, confirming that either method is suitable for measuring the EMCs of metals if it is properly controlled and well-managed. The 95% confidence intervals of the regression coefficients for cadmium, chromium, copper, nickel, lead, and zinc are 0.862 to 1.096, 0.940 to 1.150, 0.855 to 1.078, 0.870 to 1.084, 0.947 to 1.287, and 0.895 to 1.117, respectively. All confidence intervals include 1.000, suggesting that there is little difference between the two sampling methods in estimating the EMCs. In addition, the grab sampling

strategy that increases sampling frequency at the initial part of a storm generates a reliable estimate of the EMC and MFF ratios (Stenstrom et al., 2004).

Table 3 shows the basic statistics of the EMCs for the 16 PAHs. The PYR was the most abundant, with a mean concentration of 96.4 ng/L and a maximum concentration of 531 ng/L, followed by CHRY and BghiP. These three species account for approximately 60% of the total mass of PAHs and were detected in every sample. Generally, the PAHs between 200 and 250 molecular weight (MW) corresponding to 4 to 5 rings were dominant. The low-molecular-weight PAHs (MW < 200, 2 or 3 rings compounds), such as NAP, ACN, ACT, FLE, and ANT, and some high-molecular-weight PAHs (MW > 270, 5 or 6 rings compounds), such as INP and DBA, were minor species, accounting for only 3% of the total mass of PAHs. Like other water quality parameters, there exists a significant variation in the EMCs among different storm events.

Despite large variations in the EMCs among storm events, the composition of the PAH congeners showed a similar pattern. Figure 2 compares the relative abundance of individual PAHs from different sources. Only the 12 major species of PAHs were selected to compare with existing literature because of data availability. The y-axis is the ratio of individual PAHs to the sum of the 12 PAHs that are shown in the x-axis. The figure includes 8 different sources—diesel engine exhaust, traffic tunnel air, gasoline engine exhaust, urban runoff, fresh and weathered used motor oils (measured in our laboratory), and 2 highway runoff studies (one from our study). By comparing distributions of PAHs for different sources, the possible source of PAHs in highway runoff can be inferred. As shown, there are measurable differences between the

Table 3—Summary of PAHs (ng/L) in EMCs for combined sites.

| Congener | Number of cases | Mean | Median | Minimum | Maximum | Standard deviation |
|-------------|-----------------|------|--------|---------|---------|--------------------|
| Nap | 62 | 2.1 | <1 | <1 | 28.2 | 4.6 |
| ACN | 62 | 0.3 | <1 | <1 | 4.4 | 0.7 |
| ACT | 62 | <1 | <1 | <1 | 0.8 | 0.1 |
| FLU | 62 | <1 | <1 | <1 | 0.9 | 0.2 |
| PHE | 62 | 17.5 | 15.0 | <1 | 82.5 | 15.2 |
| ANT | 62 | 2.0 | 1.2 | <1 | 14.3 | 2.8 |
| FLT | 62 | 41.9 | 27.5 | <1 | 277 | 49.9 |
| PYR | 62 | 96.4 | 67.8 | 5.4 | 531 | 104.0 |
| BaA | 62 | 19.4 | 15.6 | <1 | 102.3 | 19.4 |
| CHRY | 62 | 69.2 | 46.7 | 5.6 | 332 | 70.3 |
| BbF | 62 | 19.6 | 15.6 | <1 | 124.4 | 20.6 |
| BkF | 62 | 9.6 | 7.1 | <1 | 59.6 | 11.2 |
| BaP | 62 | 24.3 | 14.8 | <1 | 147 | 29.4 |
| INP | 62 | 4.2 | <1 | <1 | 64.6 | 10.3 |
| DBA | 62 | 0.5 | <1 | <1 | 15.7 | 2.5 |
| BghiP | 62 | 50.7 | 38.2 | 2.5 | 296 | 52.5 |
| Total PAHs* | 62 | 357 | 281 | 23.6 | 1880 | 371 |

* The statistics for the total PAHs are not equal to the sums of the individual PAHs, because the maximum, minimum, and standard deviations do not all occur in the same sample.

distributions of PAHs for different sources. The patterns of PAHs congeners in the highway runoff of this study are generally typical of gasoline engine exhaust, containing large fractions of FLT, PYP, CHRY, BghiP, and small fractions of PHEN, ANT, and BbA. It is

not unreasonable to assume that motor oil may be a major source of PAHs in highway runoff. Figure 2 also includes two samples of used motor oil measured in our laboratory for different conditions. Used motor oil was collected from a commercial vehicle

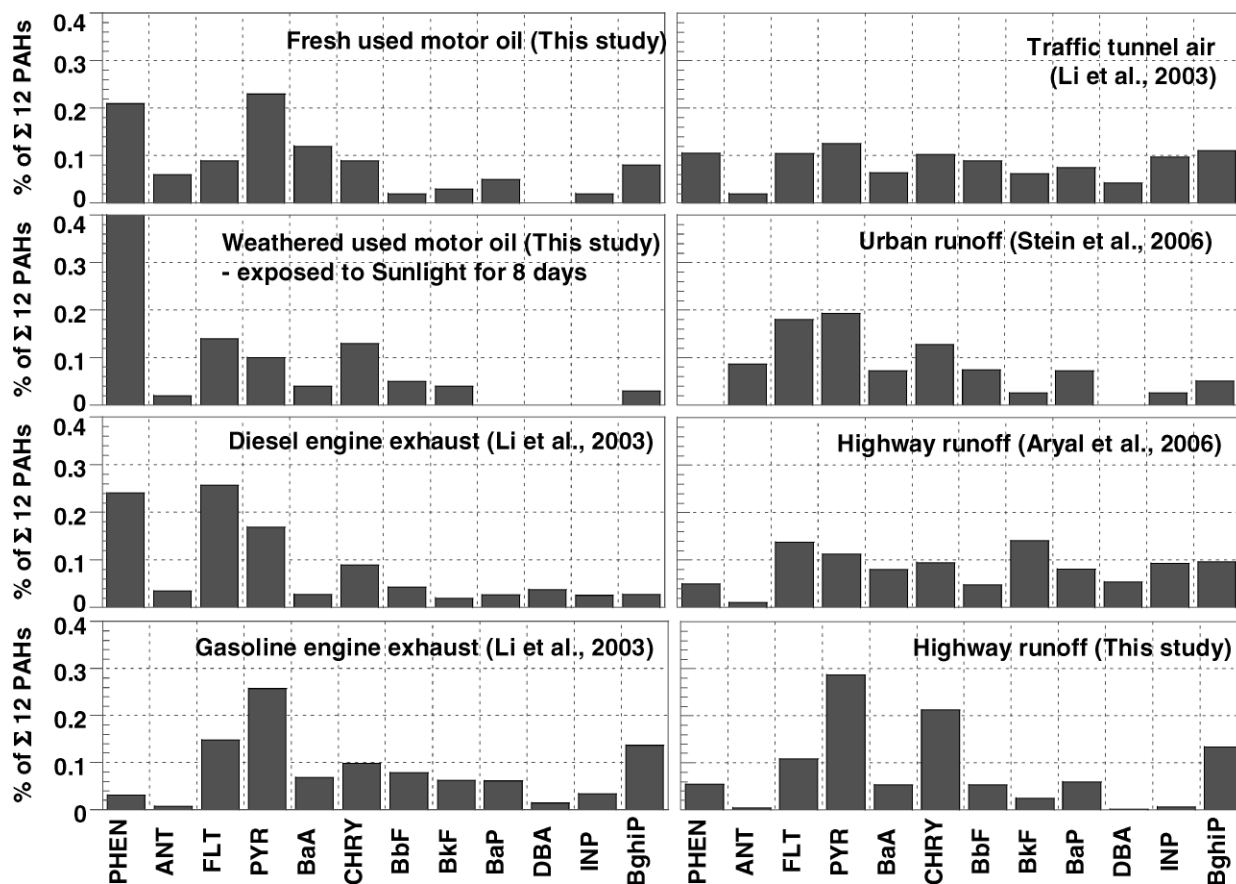


Figure 2—Relative abundance of 12 PAHs for different sources (average values of multiple measurements).

Table 4—Comparison of mean EMCs with other studies.

| Parameters ^a | This study 260 000 | Caltrans' statewide data (1997 to 2003) ^b | | | Pagotto et al.* (2000), 12 000 | | Shinya et al. | | Sansalone and Buchberger (1997) 150 000 ^b , roadway | Westerlund et al. (2003) 7400 ^b , roadway | Others |
|-------------------------|-----------------------|---|---------------------|------------------|-----------------------------------|--------------------|-------------------------------|-------------------------------|--|---|--|
| | | Statewide | Nonurban <30 000 | Urban >30 000 | Conv. ^c | Poro. ^d | (2000) 75 000 ^b | (2003) 62 000 ^b | | | |
| TSS (mg/L) | 68 | 175 | 232 | 152 | 46 | 9 | 63 | 54 | | 65 | 176 ^e , 135 ^f , 135 ^g |
| pPAHs (ng/L) | 360 | | | | | | 1280 | 690 | | | |
| tCd (µg/L) | 1.8 | 0.8 | 0.5 | 0.9 | 0.9 | 0.3 | 1.8 | | 7.0 | 0.1 | 2.5 ^g |
| tCr (µg/L) | 10.1 | 9.1 | 8.5 | 9.4 | | | 6.5 | | 21.2 | | 4.7 ^g |
| tCu (µg/L) | 93.1 | 40.9 | 18.5 | 50.1 | 30.0 | 20.0 | 66.0 | 68.3 | 135 | 12.5 | 24.0 ^e , 13.4 ^g |
| tNi (µg/L) | 20.0 | 10.6 | 10.7 | 10.5 | | | 5.5 | | 43.4 | 3.8 | 4.7 ^g |
| tPb (µg/L) | 33.0 | 54.8 | 18.1 | 70.3 | 40.0 | 8.7 | 33.5 | 30.5 | 64.4 | 5.5 | 52.5 ^e , 13.8 ^g |
| tZn (µg/L) | 506 | 190 | 117 | 221 | 228 | 77.0 | 648 | 718 | 4470 | 49.7 | 138.5 ^e |
| dCd (µg/L) | 1.3 | 0.3 | 0.2 | 0.3 | 0.3 | 0.1 | | | 4.0 | 0.0 | |
| dCr (µg/L) | 2.8 | 2.9 | 2.5 | 3.1 | | | | | 11.9 | | |
| dCu (µg/L) | 66.0 | 13.8 | 6.5 | 16.6 | 19.0 | 16.0 | | | 92.8 | 2.7 | |
| dNi (µg/L) | 15.7 | 4.2 | 3.6 | 4.4 | | | | | 28.8 | 0.5 | |
| dPb (µg/L) | 4.9 | 5.4 | 2.2 | 6.8 | 3.3 | 2.2 | | | 16.0 | 0.1 | |
| dZn (µg/L) | 415 | 69.9 | 40.5 | 81.8 | 140.0 | 54.0 | | | 4050 | 13.9 | |

^a AADT.

^b <http://www.dot.ca.gov/hq/env/stormwater/>.

^c Conventional pavement highway, Pagotto et al. (2000, AADT = 12 000).

^d Porous pavement highway, Pagotto et al. (2000, AADT = 12 000).

^e Highway, Barrett et al. (1998, AADT = 33 465).

^f Highway, Wu et al. (1996, 1998, AADT = 17 300).

maintenance facility, which represents motor oil from hundreds of vehicles. One sample was analyzed directly (fresh used motor oil), and a second sample was analyzed after being exposed outdoors for 8 days to undergo photo-oxidation and volatilization (weathered used motor oil). The fresh used motor oil contained four lower-molecular-weight PAHs (NAP, ACN, ACT, and FLE; 2- or 3- ring compounds), which accounted for 54% of the total PAH mass (these four PAHs are not included in the calculations for Figure 2). The abundance of these lower-molecular-weight PAHs in fresh used motor oil is also supported by other studies (Pruell and Quinn, 1988; Wang et al., 2000). These species were all lost in the weathering process when the PAHs were exposed to sunlight and the atmosphere. The motor oil sample placed outdoors showed rapid reduction in PAHs concentrations, and only 48% of the originally measured PAH mass (12 PAHs shown in Figure 2 plus the 4 lower-molecular-weight PAHs) remained after 8 days. The individual PAHs have different decomposition kinetics and fugacity, resulting in different relative abundance of PAHs between the sources and the weather conditions.

Among the 12 PAHs considered in Figure 2, PHEN and PYR are primary species, accounting for 44% of the mass in the fresh used motor oil. The PHEN was the dominant species in the fresh and weathered motor oil samples, possibly because PHEN is very stable in the liquid phase compared with other PAH species (PHEN concentrations changed little throughout 28 days of the motor oil weathering experiments). In the urban runoff samples, PYR is always more abundant than PHEN, which indicates that motor oil may not be the major contributor to the PAHs washoff from highways; additional sources with greater relative amounts of PYR are suggested. As shown in Figure 2, traffic-related sources, such as highway runoff, generally contain high-molecular-weight PAHs (compounds made up of 4 benzene rings or more). The high-

molecular-weight PAHs are mainly from combustion residuals of fossil fuels by vehicle engines rather than motor oil, which contains low-molecular-weight PAHs as major compounds (Eganhouse and Gossett, 1991; Ngabe et al., 2000).

Comparison with Other Highway Runoff Studies. As performed for the conventional water quality parameters in our previous paper, we compared our data with data from other highway runoff characterization studies, and the mean EMCs are summarized in Table 4. The AADT is shown in the headings, which can be used to compare the traffic loads. There are differences in the mean EMCs for specific parameters. Our monitoring sites, which have the highest AADTs of those sampled by Caltrans (Sacramento, California), have greater mean EMCs for metals than observed in the statewide study, with the exception of tPb, dPb, and dCr. Unequal variance *t*-tests were performed for metals, to assess statistical difference between our measurements and the results from the Caltrans' statewide study (<http://www.dot.ca.gov/hq/env/stormwater/>). Log-transformed EMCs (ln[EMC]s) were used as variables for the *t*-tests, because individual EMC data sets followed a log-normal distribution. The *t*-test results showed that metal concentrations measured from our monitoring sites were greater than the statewide values (*t*-statistic ranging from 3 to 11, with degrees of freedom ranging from 50 to 107, $p < 0.002$), except for dCr. The difference in dCr concentrations between the two datasets was not statistically significant. The differences in tPb and dPb concentrations from the two studies are difficult to interpret because of the large differences in variability of the mean EMCs. The coefficients of variation of the EMCs of tPb and dPb from the statewide data set are 2.7 and 4.3, respectively, and are only 0.8 and 1.6, respectively, in this study. The large statewide dataset variability makes it difficult to observe significant differences, even if they were present. Further analysis of the statewide dataset, which

Table 5—Correlation analysis results between ADD and EMCs for combined site.*

| | ADD | TSS | PAHs | Total Cd | Total Cr | Total Cu | Total Ni | Total Pb | Total Zn |
|----------|------|------|------|----------|----------|----------|----------|----------|----------|
| ADD | | 0.56 | 0.46 | 0.72 | 0.53 | 0.71 | 0.80 | 0.51 | 0.72 |
| TSS | 0.00 | | 0.72 | 0.88 | 0.83 | 0.88 | 0.86 | 0.86 | 0.87 |
| PAHs | 0.00 | 0.00 | | 0.68 | 0.80 | 0.70 | 0.67 | 0.64 | 0.64 |
| Total Cd | 0.00 | 0.00 | 0.00 | | 0.81 | 0.96 | 0.98 | 0.80 | 0.99 |
| Total Cr | 0.00 | 0.00 | 0.00 | 0.00 | | 0.86 | 0.81 | 0.67 | 0.77 |
| Total Cu | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | | 0.97 | 0.72 | 0.96 |
| Total Ni | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | | 0.75 | 0.98 |
| Total Pb | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | | 0.77 |
| Total Zn | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | |

* Notes: Correlation coefficient r is the Pearson's product moment correlation and appears above the diagonal. Probability values (p -value) appear below the diagonal. The p -values less than 0.005 are listed as 0.00 and are statistically significant.

is beyond the scope of this study, is needed to better understand potential differences.

The metals concentrations in this study are generally higher than those reported by Pagotto et al. (2000) and Westerlund et al. (2003), lower than those reported by Sansalone and Buchberger (1997), and similar to those reported by Shinya et al. (2000, 2003). Only Shinya et al. (2000, 2003) reported particulate phase PAHs and, despite lower AADT values, their results are generally 2 to 4 times higher than our results. This may be partly the result of different duration and intensity of daylight between the two study sites, resulting in different decomposition kinetics of PAHs, and partly the result of a different amount of atmospheric deposition or regional air pollution emission (Herricks, 1995). Meanwhile, little relationship existed between TSS and AADT. The TSS concentrations are more influenced by surrounding land uses than by traffic volume (Kayhanian et al., 2003). A recent reanalysis of the statewide database, excluding samples containing large amounts of snow melt, found similar concentrations for most parameters, except for TSS for low AADT sites, which was approximately 50% of the value reported in Table 3 (Kayhanian et al. 2007).

Correlation Analysis Between Pollutants and Storm Characteristics. Table 5 is a Pearson correlation analyses for the grab sample results for six total metals concentrations, TSS, and ADD. The correlations were performed for each site and the pooled or combined data (only the results from the combined site are shown in Table 4). Values above the diagonal are the correlation coefficient, r , and values below the diagonal are the significance, p . Correlations with other storm characteristics, such as total rainfall, were performed, but are not reported in Table 5, because they were not significant. In all cases, for the pooled data, correlations between total metals and TSS were significant ($r > 0.83$ and $p < 0.005$). The existence of a strong relationship between TSS and metals is also supported by other highway runoff characterization studies (Desta et al., 2007; Sansalone and Buchberger, 1997; Shinya et al., 2000). The only case when nonsignificant correlations between total metals and TSS were observed was for site 7-203, for tCd, tNi, tPb, and tZn. The significant correlations for total metals had r values ranging from 0.6 to 0.9. The dissolved metals are less correlated with TSS with r values generally less than 0.4.

The TSS was better correlated for total metals than for other water quality parameters reported in the previous paper (Han et al., 2006a); therefore, it is a better surrogate parameter for metals than conventional pollutants. Han et al. (2006a) suggested that TSS

was a poor surrogate for most conventional water quality parameters.

The only storm characteristic that was significantly correlated was ADD, which showed significant correlations with all six total metals, with the exception of tCd for site 7-201, tCr for site 7-203, and tPb for sites 7-201 and 7-203. The ADD was significantly correlated with TSS for sites 7-201 and 7-202. Total PAHs were significantly correlated with ADD and TSS and with many total metals. Correlation between AADT and water quality parameters was not evaluated, because all three sites had high, similar AADTs. However, in a separate study, Kayhanian et al. (2003) used the California statewide highway runoff characterization data and investigated the effect of AADT on water quality. The results of this study indicate that, while AADT is a major contributing parameter affecting water quality, no direct correlation between AADT and most chemical constituents was found.

The correlations among metals are likely the result of similar sources—automobiles and tires. Automobiles are known sources for many metals (U.S. EPA, 1995). Metals, per se, should not be correlated, because the analyses are independent and do not measure similar properties or tendencies (i.e., dissolved organic carbon and chemical oxygen demand). Possible exceptions are zinc and cadmium, because cadmium is a common impurity in zinc and is typically not removed during zinc refining (Krone et al., 2001).

The correlations among metals, TSS, and PAHs suggest that selecting best management practices (BMPs) that remove TSS will generally be a good strategy for removing metals and PAHs. Also, the positive correlation between PAHs, TSS, and most total metals may suggest that buildup is occurring and that BMPs that can be selectively applied after long dry periods, such as street sweeping or washing and catch basin cleaning, may be used as an alternative BMP or be considered as a pre-BMP treatment option.

First-Flush Analysis. To determine the existence of a first flush of metals and PAHs, the MFF ratios were compared by means and ranked by medians for the total and dissolved phase metals and total PAHs. Table 6 shows the mean MFF ratios for all 14 pollutants for the individual and combined sites from 10 to 50% and PEMC/EMC ratios for 30 and 60 minutes and 10 to 50% of the storm duration. Although the magnitudes of the MFF were less than the MFF criterion ($MFF_{30} > 2.66$) suggested by Bertrand-Krajewski et al. (1998), there is still a first flush, with approximately 32% of the pollutant mass being discharged in the first 20% of the runoff volume. As shown in Table 6, MFF ratios were slightly lower at site 7-201 than the other two sites. This is likely because site 7-201 has

Table 6—Mean MFF_n and PEMC/EMC for the 14 analyzed constituents.

| Parameter | Highway sites | | | Combined sites |
|--|---------------|-----------|-----------|----------------|
| | 1 (7-201) | 2 (7-202) | 3 (7-203) | |
| MFF ratios (MFF _n) | | | | |
| MFF ₁₀ | 1.55 | 2.27 | 2.10 | 2.02 |
| MFF ₂₀ | 1.42 | 1.74 | 1.70 | 1.64 |
| MFF ₃₀ | 1.31 | 1.45 | 1.47 | 1.42 |
| MFF ₄₀ | 1.21 | 1.30 | 1.32 | 1.28 |
| MFF ₅₀ | 1.13 | 1.21 | 1.23 | 1.20 |
| PEMC _i to EMC ratios (PEMC _i /EMC) | | | | |
| PEMC _{30 min} /EMC | 1.92 | 3.23 | 4.25 | 3.23 |
| PEMC _{60 min} /EMC | 1.68 | 2.45 | 2.44 | 2.22 |
| PEMC _n to EMC ratios (PEMC _n /EMC) | | | | |
| PEMC ₁₀ /EMC | 1.55 | 2.25 | 2.07 | 1.98 |
| PEMC ₂₀ /EMC | 1.40 | 1.70 | 1.65 | 1.59 |
| PEMC ₃₀ /EMC | 1.29 | 1.45 | 1.45 | 1.40 |
| PEMC ₄₀ /EMC | 1.21 | 1.30 | 1.32 | 1.28 |
| PEMC ₅₀ /EMC | 1.14 | 1.20 | 1.23 | 1.19 |

the lowest bed slope (0.17 and 1.5% in longitudinal and transverse directions, respectively) and larger catchment area than site 7-203. Site 7-203 did not have greater magnitude of first flush than site 7-202, which has approximately three times the catchment area. This can be explained by the combined effect of bed slope and catchment area. The longitudinal and transverse slopes of site 7-202 are 2.7 and 7%, respectively, which are much higher than 2.5 and 2% of site 7-203. The effect of higher bed slope may compromise the effect of a larger catchment area. The magnitude of first flush is generally proportional to the site slope, but inversely proportional to the site area and infiltration rate (Bertrand-Krajewski et al., 1998; Gupta and Saul, 1996; Kang et al., 2006).

Figure 3 shows the MFF₁₀ and MFF₂₀ ratios for each pollutant for the combined sites using notched box plots. In general, TSS and total and dissolved nickel, copper, and zinc had higher MFF ratios, while total and dissolved lead, cadmium, and chromium had lower MFF ratios. There were a number of outliers, and no discernable pattern among the outliers was observed.

Figure 4 shows the notched box plots of the PEMC/EMC ratios ranked by the median values of individual pollutants for the combined sites. The PEMC/EMC ratios at 30 and 60 minutes generally are earlier in the storm than the ratios and 10 and 20% runoff volume. In general, the metals in which the dissolved fraction is dominant (nickel, copper, and zinc) have larger PEMC/EMC ratios than the metals in which the particulate fraction is dominant (lead and chromium). This is likely because the dissolved fraction can be easily washed out, even with low-flow energy, because particulates need a minimum flow to mobilize them from the catchment surface.

Figures 3 and 4 show that MFF₁₀s and PEMC₁₀/EMCs for nickel, copper, and zinc are greater than those for TSS. As the storm develops, the trend reverses, and the MFF₂₀s and PEMC₂₀/EMCs for these metals are smaller than those of TSS. This is probably because of different flow energy requirements to mobilize the dissolved and particulate metal fractions. The metals that are predominately in the dissolved phase are more likely to be washed out early in the storm, before the flow has fully developed. In the initial part of a storm, perhaps the first 10% of the runoff (*n* = 10%) dissolved fractions are mobilized, while the particulate fractions are not, resulting in greater values of MFF_{s10} and PEMC₁₀/EMCs, particularly for those metals that are primarily dissolved. The metals that are predominately associated with TSS, such as lead and chromium, do not have this early first flush.

The PEMC at 30 minutes can be 10 times higher than the EMC for the most pollutants. This confirms that the early runoff is much more contaminated than the average or later runoff and also shows that first-flush samplers, which capture the first runoff and bypass the remaining runoff, can drastically overestimate the mass loading and should not be used for loading analyses.

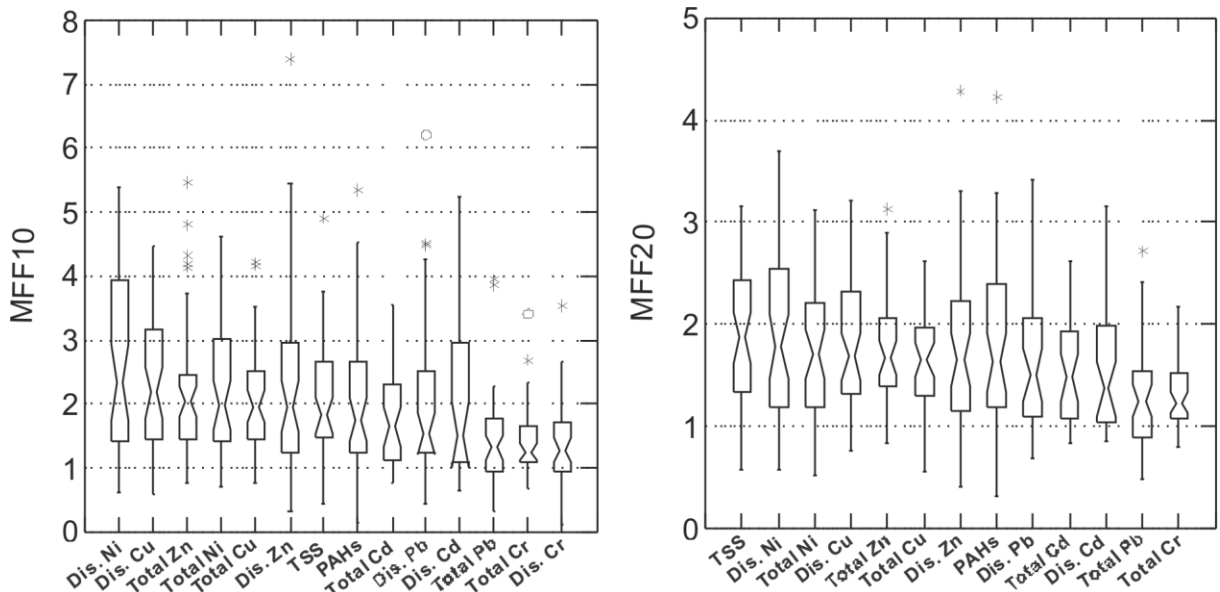


Figure 3—Ranking plots of MFF₁₀ and MFF₂₀ for combined sites (individual plots are notched box plots with outliers).

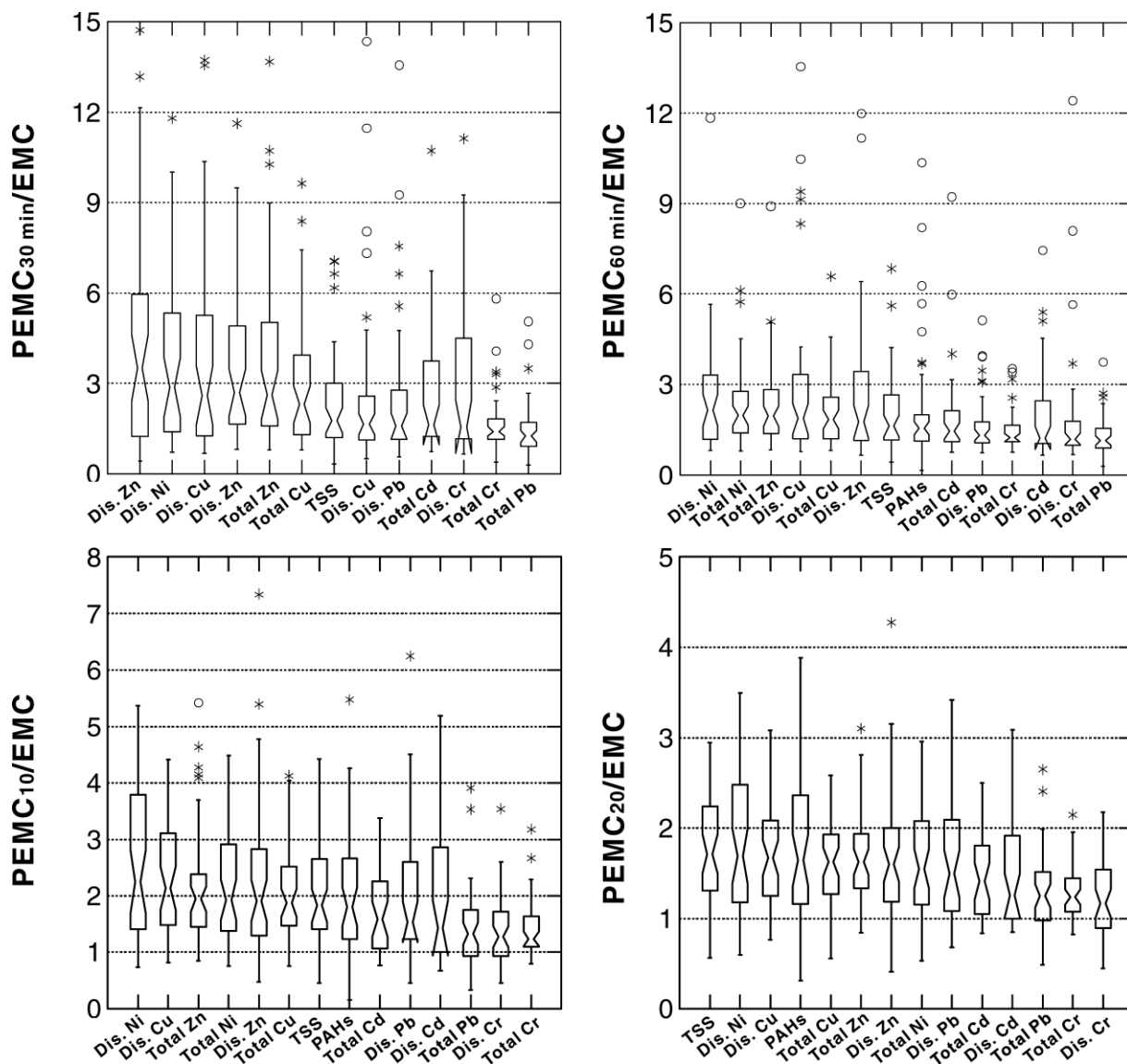


Figure 4—Ranking plots of the ratio of PEMC to EMC for combined sites.

Figure 5 shows the MFF ratios, from $n = 10$ to 50%, for the six total metals as notched bar plots. Similar to the concentration first flush observed in Figure 4, larger MFF ratios exist in nickel, copper, and zinc among the six metals. In addition, variations in the MFF ratios at smaller n values are greater than those at larger n values, which means pollutant washoff in earlier runoff is more susceptible to the event-specific conditions (i.e., shape of hydrograph and ADD).

Pearson correlation analyses were performed to ascertain relationships between storm characteristics and first-flush parameters, but no significant correlations among those parameters were seen. Our previously published work (Kang et al., 2006) showed that the relationship between the mass first flush and storm characteristics was not straightforward, with the magnitude of the first flush being affected differently over ranges of the same storm characteristics or watershed dimensions. Therefore, it will be necessary to classify the data into events or regions where the relationships are linear, to detect them with Pearson analysis.

Conclusions

The results presented here complement our previous paper (Han et al., 2006a), by adding total and dissolved metals (cadmium, chromium, copper, nickel, lead, and zinc) and 16 individual PAHs to the large suite of previously reported highway runoff water quality data. The conclusions drawn from this study are as follows:

- (1) The mean EMCs of the total (dissolved and particulate phase) metals ranged from 1.8 $\mu\text{g/L}$ for cadmium to 507 $\mu\text{g/L}$ for zinc. The EMCs for this study, which is for a highly urbanized highway (>260 000 vehicles/day), were generally greater than observed in a California-wide study and within the mid-range of reported concentrations in the other national highway runoff characteristics reported in the literature.
- (2) Dissolved-phase PAHs were low—generally below detection limits (1 ng/L). The particulate phase PAHs averaged 360 ng/L, which is lower than the other reported highway runoff PAH concentrations of 1280 and 690 ng/L. The lower PAH

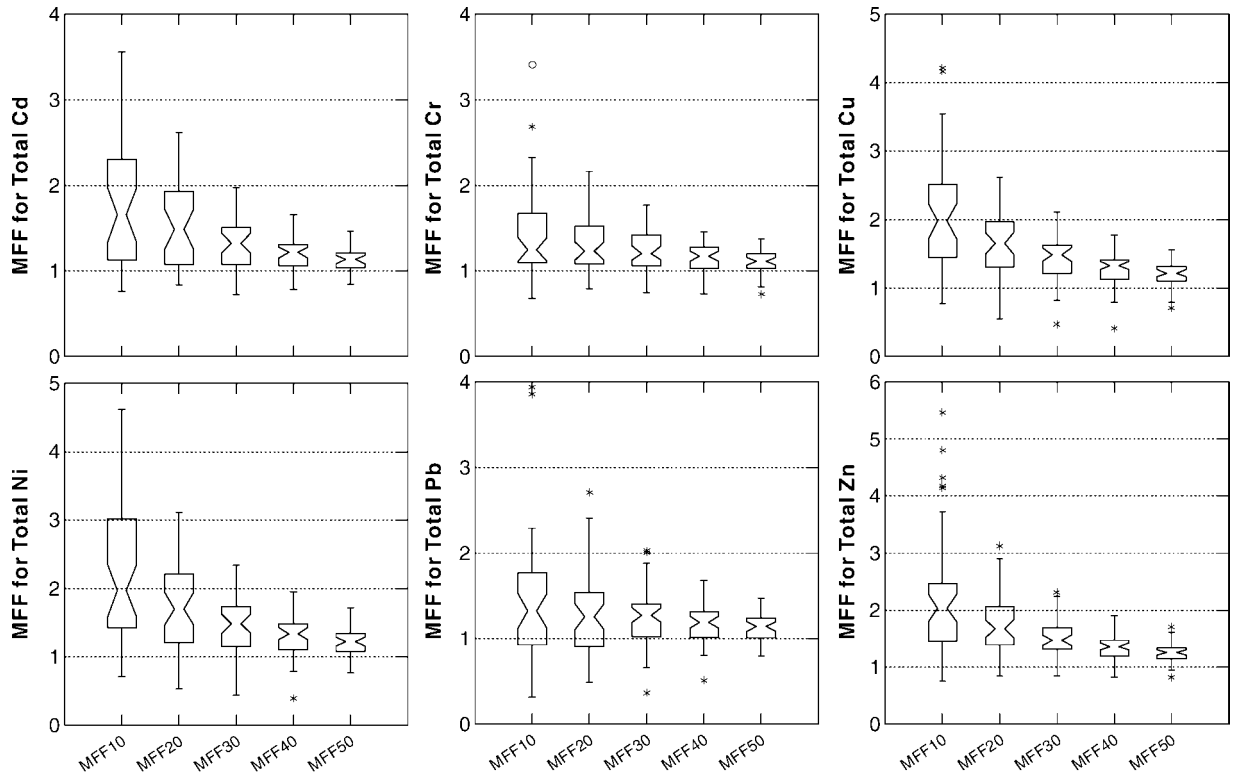


Figure 5—Notched bar plots of MFFs for six heavy metals for combined sites.

concentrations, despite higher traffic volumes, is likely the result of site-specific conditions, such as higher ambient temperature and sunlight.

- (3) The relative abundance of PAHs in highway runoff was similar to that of gasoline engine exhaust, suggesting that the main source of highway runoff PAHs is the combustion residual of fossil fuel by automobile engines. Motor oil is a possible source, but may not be a significant contributor.
- (4) Total metals concentrations were all correlated with each other and correlated with the TSS concentration, which was not true for the conventional pollutants (Han et al., 2006a). Total PAHs were also correlated with TSS. This suggests that BMPs that remove TSS will be good candidates for removing metals and PAHs.
- (5) Among seven storm characteristics, only ADD was significantly correlated with the EMCs of total metals and PAHs.
- (6) The average first flush for 14 different water quality constituents was modest, with 30 to 35% of the mass contained in the first 20% of the runoff. Cadmium, copper, and nickel had higher first-flush ratios, while chromium, lead, and zinc had lower ratios. The order was not related to the particulate-phase metal fractions.

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