Characteristics of Highway Stormwater Runoff

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ABSTRACT: Highway stormwater runoff was monitored at three highway sites in Los Angeles, California, during the 2000 to 2003 wet seasons. Event mean concentrations (EMCs), partial event mean concentrations (PEMCs), and mass first flush (MFF) factors were calculated for more than 20 water quality parameters for samples from 20 storm events from each site. The early runoff had higher concentrations, as indicated by the PEMCs at 30 and 60 minutes into the storm, which were 1.9 to 7.4 times higher than the EMCs. A strong first flush was observed for chemical oxygen demand (COD) and other organic pollutants, with 40% of the pollutant mass being discharged in the first 20% of the runoff. A weak first flush was observed for ionic pollutants, such as nitrate and nitrite. Pearson correlation analyses of the EMCs, PEMCs, and MFFs showed strong correlations among dissolved organic carbon, COD, total Kjeldahl nitrogen, oil and grease, and ammonia-nitrogen. Contrary to generally held beliefs, poor correlation between total suspended solids and most other conventional pollutants was observed. In addition, poor correlation between most monitored pollutants and storm characteristics, except for antecedent dry days, was observed. *Water Environ. Res.,* **78,** 2377 (2006).

KEYWORDS: highways, stormwater, correlation, mass first flush, storm characteristics, event mean concentration, partial event mean concentration.

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Introduction

Managing water pollution from the millions of miles of highways throughout the United States is one of the important goals for urban stormwater pollution management. Unfortunately, the magnitude of the potential problem is still not quantified and methods still not developed (Wu et al., 1998). Highways have been identified in some watersheds as one of the leading causes of the degradation of water quality (Barrett et al., 1998; Ellis et al., 1987) and contribute to various other problems, such as the excessive rate of runoff. Highway stormwater runoff is an important source of organic pollutants and micro-pollutants, such as heavy metals, hydrocarbons, and fuel additives (Barrett et al., 1998; Furumai et al., 2002). These are mainly generated from traffic activities, component wear, fluid leakage, pavement degradation, roadway maintenance, and atmospheric deposition (Sansalone and Buchberger, 1997; Shinya et al., 2000). These sources of pollution can be temporary, seasonal, accidental, or chronic (Legret and Pagotto, 1999).

In an effort to manage a watershed, accurate knowledge of the runoff quantity and quality is required to assess the effects of runoff on the environment and to develop appropriate mitigation technologies (Barrett et al., 1998). Maestri and Lord (1987) propose four management measures, including vegetative controls, wet detention basins, infiltration basins, and wetlands, as cost-effective best management practices (BMPs) for highway runoff. In addition, analyzing the correlation among stormwater pollutants may reveal relationships or ways to reduce the costs associated with monitoring and will assist in evaluating BMPs.

Correlations among pollutants can sometimes be used to predict BMP removal rates without collecting additional data. This paper reports a large quantity of highway stormwater runoff data and characteristics collected in West Los Angeles, California, over three wet seasons (2000 to 2003). A variety of correlations among pollutants, event mean concentrations (EMCs), storm and site characteristics, and mass first flush (MFF) ratios were examined. This paper describes conventional pollutants and a following paper will describe metals and polycyclic aromatic hydrocarbons. The information gained from this correlation analyses may assist transportation agencies to reduce the number of pollutants that are they are required to monitor and may be used to evaluate or predict the performance of BMPs.

Methods

Site Description. The three sites in West Los Angeles had catchment areas ranging from 3917 to 16 918 m^2 and annual average daily traffic (AADT) of over 260 000 cars per day. These three sites were chosen as typical small catchment sites with heavy traffic load. All sites were equipped with American Sigma Ultrasonic 950 Area-Velocity Flow Meters (American Sigma, Loveland, Colorado), which can record flow and rainfall in 1-minute intervals, tipping bucket rain gauges with volume resolution of 0.25 mm/tip, and composite auto samplers (Sigma 900MAX, American Sigma). Samples were collected by analyzing a series of grab samples and by using automatic samplers. Table 1 summarizes the three sites. The sites are highly impervious, and the runoff coefficients were typically 0.9 to 0.95.

Sample Collection and Analysis Procedure. Grab and composite runoff samples were collected during each storm event. Runoff flow and rainfall were continuously monitored. Grab samples were manually collected from a free waterfall, using a polypropylene scoop that received the entire flow, and were then transferred to 4-L amber glass bottles. Sampling was typically triggered after the start of detectable runoff, and 5 grab samples were collected every 15 minutes until the end of the first hour. After the first hour, samples were taken at 1-hour intervals for the next 7 hours. One or two additional grab samples were collected for events lasting longer than 8 hours. The number of samples collected depended on the storm duration. In addition, a flow-weighted composite sample was collected by the autosamplers, which covered the duration of each storm. The automatically collected samples were used as a comparison to the grab samples. Unless specifically noted as being collected using the automatic samplers, the EMCs reported in this paper are all calculated from the grab samples and flow data.

Table 1—Site description summary.

Site number	Location	AADT (vehicles/d)	Catchment area (m^2)	Number of lanes (each direction)	Approximate impervious area (%)
1 (7-201)	Hwy 101, Van Nuys	328 000	12 800	6	100
2 (7-202)	Hwy 405, Getty Center Exit	260 000	16 920	5	95
3 (7-203)	Hwy 405, Santa Monica Blvd.	322 000	3920	5	100

All samples were transported back to the laboratory at the University of California, Los Angeles (UCLA) after collection and refrigerated at 4°C until analyzed. To facilitate certain analysis (for particle size distribution and metals [not shown in this paper], see Han et al. [2006] and Li et al. [2005]), which must be performed very soon after sample collection, the samples were transported back to UCLA after the first hour and two more times during the next 7 hours. The composite sample was retrieved after the event. All analyses were performed within the U.S. Environmental Protection Agency (U.S. EPA) maximum recommended holding time. All analytical methods conform to U.S. EPA methods or *Standard Methods* (APHA et al., 1998) protocols, except for oil and grease, which used the protocol described by Lau and Stenstrom (1997).

Event Mean Concentrations, Partial Event Mean Concentrations, and Mass First Flush Ratio Calculation. Storm characteristics and first flush have been previously quantified by using several criteria (Bertrand-Krajewski et al., 1998; Gupta and Saul, 1996; Lee et al., 2003, 2004; Ma et al., 2002). In this paper, we will use EMC, partial event mean concentrations (PEMC), and MFF to quantify the concentration of a pollutant during a storm event and determine how its concentration or mass discharge changes during the event.

The EMC is the flow-weighted concentration over the duration of the storm and can be calculated by integrating the flowrate and product of concentration and flowrate. The EMC can be calculated from a series of grab samples if the flowrates are simultaneously measured. Instead of integration, approximations created by discrete measurements of flowrate and concentration must be used. If we assume we measured the concentration and the flowrate based on equal time intervals in a storm event, the EMC can be estimated as follows:

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

Where

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

The PEMC can also be calculated using eq 1, except that the integration or summation ends at a point in the storm, such as after a specific amount of time (e.g., 30 minutes or 1 hour) or after a defined fraction of the runoff volume.

The concept of the first flush phenomenon was first advanced in the early 1970s, and various definitions have been proposed. First flushes can be based on the concentration or mass of the constituent. The PEMC can be used to show the decline in concentration as the storm progresses, and the ratio of the PEMC at a defined point in the storm to the EMC can be used. A concentration-based first flush may be more important than a MFF for constituents that have toxicity or strict limits established by regulatory agencies.

Bertrand-Krajewski et al. (1998) defined a significant MFF if at least 80% of the total pollutant mass was transported in the first 30% of the volume discharged during rainfall events. However, such instances are extremely rare and found in only 1% of the events (Lee et al., 2003). Ma et al. (2002) generalized the Bertrand-Krajewski et al. (1998) definition to the MFF ratio, which describes the fractional mass of pollutants emitted as a function of storm duration. It is defined mathematically, as follows, and can also be calculated using discrete samples:

$$MFF_n = \frac{\frac{\int_0^{t_1} C(t)Q(t)dt}{M}}{\frac{\int_0^{t_1} Q(t)dt}{V}} \quad (2)$$

Where

MFF_n = mass first flush ratio at a cumulative flow volume corresponding to n% of total flow volume (dimensionless),
t_1 = lapsed flow time corresponding to n% of total flow volume (minutes),
$C(t)$ = concentration of pollutant at time t (mg/L), and
$Q(t)$ = runoff flowrate at time t, with M and V as defined in eq 1 (L/min).

For an MFF to exist (e.g., $MFF_n > 1$), the concentration must not only be greater during the early part of the storm than during the later part of the storm, but the mass emission rate must also be greater. The ratio allows convenient characterization of the first flush and allows the first flush to be analyzed statistically. Figure 1 graphically shows the MFF ratio. For example, $MFF_{20} = 2.5$ means that 50% of mass load is contained in the first 20% of the runoff. The 80% of the mass in the first 30% of the runoff volume defined by Bertrand-Krajewski et al. (1998) can be defined as $MFF_{30} = 2.66$.

Both mass- and concentration-based first flushes are described in this paper. The ratio of PEMCs to EMCs is used to quantify the concentration-based first flush, and MFF ratios are used for MFFs. Generally, the concentration-based first flushes have higher ratios, because of the flow rate, and therefore mass emission rate at the beginning a storm is less. This results because of a portion of the first part of the rainfall, even for highly impervious sites, wets the site and fills the depression storage.

Correlation Analysis. Correlations were performed on data from individual sites and for the combined data. First, correlations among 23 water quality parameters were analyzed using data sets collected over three wet seasons for 18, 21, and 23 storm events

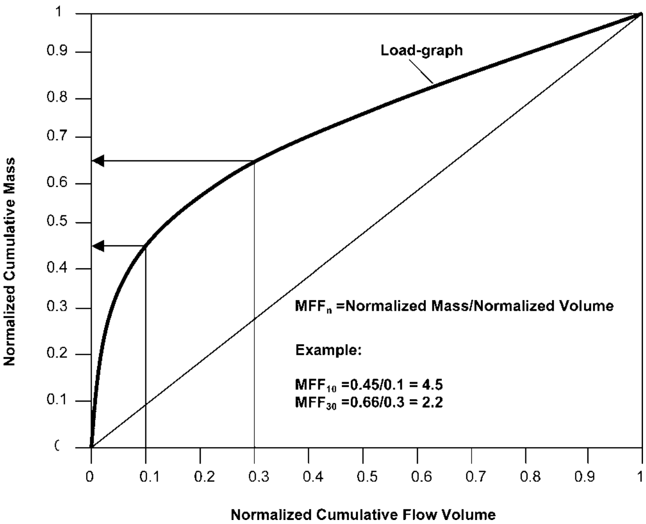

Figure 1—Example of the normalized load-graph for MFF_n calculation.

monitored for sites 7-201 to 7-203, respectively. In addition, correlations among storm characteristics and EMCs were conducted to determine if there was a significant storm characteristic that could contribute to the pollutant loading rate.

Statistical and graphical correlation analysis of the MFF ratios with storm characteristics was developed to determine if the first flush was related to site or storm characteristics. Thirteen parameters were selected—seven storm characteristics and MFF ratio analyzed at five points (10 to 50%, by 10% increments). The MFF ratios were also ranked by parameter and median value.

Results and Discussion

Storm Characteristics. Figure 2a shows the rainfall that occurred during the three wet seasons and compares the total and monthly rainfall for each wet season with the average of the past 43 years. The vertical bars, which show the monthly rainfall clearly, illustrate that the majority of rainfall occurred in January and February and almost no rainfall occured between May and October. This rainfall pattern is associated with Mediterranean climates and will be important in considering the seasonal first flush because pollutants may build up during the dry season (Lee et al., 2004). Based on the average rainfall of the past 43 years, the 2000 to 2001 season was much wetter than normal, the 2001 to 2002 season was qualified as a drought, and the 2002 to 2003 season was approximately average. Figures 2b and c show the rainfall and storm duration arranged in probability plots. The 50% probability storm rainfall for the sites was 18 mm and 7.2 hours for the storm duration.

In general, all storms producing measurable runoff at each site were monitored. Measurable runoff was produced after 3 to 5 mm of rainfall, depending on the rate. Storms that followed an earlier storm within 24 to 36 hours were generally not monitored. A special effort was made to ensure that the first storm of each rainy season was monitored. The number of storms monitored at each site varies because of spatial differences in the rainfall, which may have produced runoff at one site but not all sites. Table 2 lists basic statistics of all the events monitored between October 2000 and April 2003 for each site and combined sites. The largest single storm rainfall and maximum 5-minute intensity were 156 mm and 61 mm/h, respectively, and the longest antecedent dry day (ADD) period was 192 days, corresponding to the first storm of the 2001 to 2002 wet season at sites 7-202 and 7-203.

Water Quality Data and Event Mean Concentrations. The large amount of data collected over the three wet seasons is useful in characterizing highway runoff and first flush phenomena. In addition, the aggregated or combined data from the three sites form a large dataset to characterize highway runoff from a single area for very high AADT and is the largest dataset in the inventory of highway data known to the authors. The average number of observations for each parameter or pollutant was approximately 175 per site and 530 for the combined sites. A total of 23 water quality parameters, including conventional parameters, nutrients, fecal and total coliform, and oil and grease, were measured.

Table 3 shows the basic statistics of EMCs calculated and the ratio to the simple mean and median concentration of the grab samples for principal pollutants analyzed during the three years of study. There were generally 62 EMCs calculated from grab samples. The number of EMCs measured from automated composite samplers was 45. This is less than the number of calculated EMCs because the automatic samplers were deployed later in the study, and, in some cases, equipment failed. The maximum values for some pollutants were startlingly high. For example, the maximum values of COD and conductivity were 2280 mg/L and 1992 μmho/cm, respectively. These high values occurred during the first rainfall event of the 2001 to 2002 wet season at site 7-202 with 192 ADD. These data and others support the existence of a seasonal first flush (Lee et al., 2004).

Figure 3 compares the EMCs obtained from the automatic samplers with the EMCs calculated from the grab samples. In theory, the two groups of EMCs should be equal, but they are not because of various types of experimental errors. The correlation between the two EMCs ranged from 0.90 for TKN to 1.17 for total suspended solids (TSS). The *r* values for four of the parameters were greater than 0.9, while TSS and turbidity were lower (0.81 and 0.89, respectively). Two outliers were removed from the correlations for COD, TKN, and ammonia-nitrogen (NH_3-N), and three outliers were removed for dissolved organic carbon (DOC). The COD, DOC, TKN, and NH_3-N were removed from the October 30, 2001, event at site 7-202. This was the first rainfall of the 2001 to 2002 wet season with 192 ADD and a very short storm duration of 1.6 hours. The COD, DOC, TKN, and NH_3-N for site 7-203 and DOC for site 7-202 were removed from the March 6, 2002, event. Because there was not sufficient runoff volume to be sampled in the first part of flow, it was not a representative sample. The relationships shown in Figure 3 show good agreement between sampling methods and confirm the suitability of either method for controlled and well-managed conditions and where the parameters are suitable for automatic sampling (i.e., not oil and grease). Stenstrom et al. (2004) have discussed some of the pitfalls of using a series of grab samples, including the timing of sample collection and the number of samples needed to reduce error.

The California Department of Transportation (Caltrans) performed an extensive, multi-year monitoring study of highway runoff throughout California. The sampling sites were equipped with flow-weighted composite samplers, and the results were all analyzed by certified laboratories. The program included 138 highway runoff sites in 12 Caltrans districts for six years (1997 to 2003). The Los Angeles District, in close proximity of this study area, had the most sites (41). In this large Caltrans study, EMCs monitored from 1997 to 2003 were analyzed and compared for each

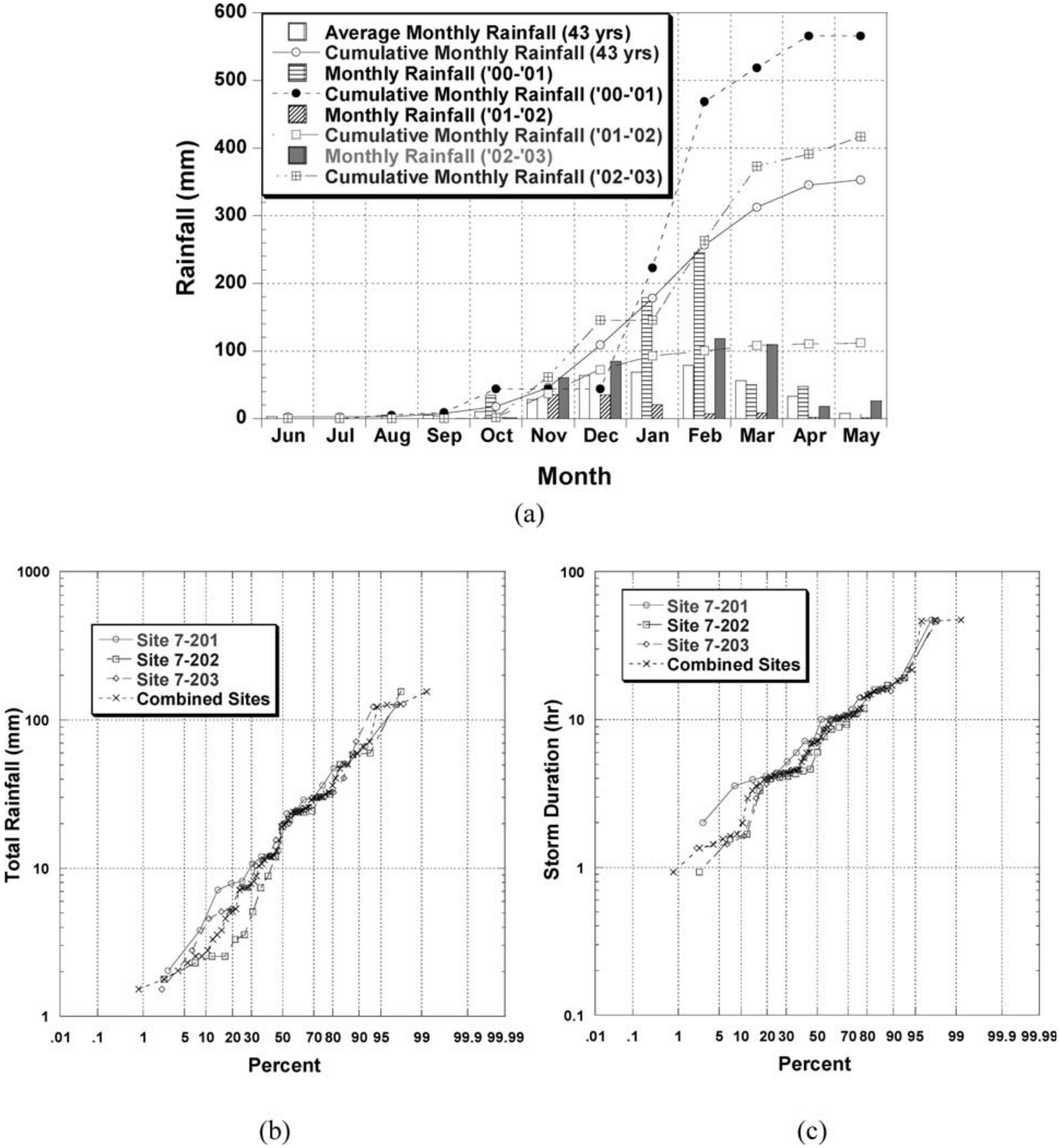

Figure 2—Rainfall characteristics during the study: (a) annual rainfall, (b) probability plot of total rainfall, and (c) probability plot of storm duration.

district. Results from the first 4 years of the monitoring program were presented by Kayhanian et al. (2003). The results were reanalyzed with the additional 2 years of data and are presented as comparisons with the first flush sites.

Table 4 compares the mean EMCs of this study, the larger Caltrans monitoring dataset, and results from other researchers. There are some major differences in the mean EMCs for specific parameters. The mean EMCs for TSS and turbidity of this study were approximately one-half or less than those reported by Caltrans, Barrett et al. (1998), and Wu et al. (1996, 1998). This may have occurred because the three sites in this study were entirely paved, including the shoulders. Unpaved and/or unvegetated areas are a primary source for TSS and turbidity (MacDonald et al., 1997). The EMCs for the study sites for COD, DOC, oil and grease, and nutrients were generally higher than those observed by others.

Correlation Analysis Between Pollutants. Analyzing correlations among water quality parameters and storm characteristics can be important to establish BMP strategies. For example, prediction of BMP removal rate for some pollutants can sometimes be made for other pollutants if they are correlated and have similar

Table 2—Basic statistics of storm events.

Site number	Total rainfall (mm)	Maximum intensity (mm/h)	Antecedent dry day	Storm duration (hours)	Average rainfall intensity (mm/h)
1 (7-201)					
Minimum/maximum	2.0/127.0	3.0/51.8	2.0/69	2.0/47.5	0.6/10.7
Median/mean	18.3/28.3	15.2/20.3	14/20	8.6/10.7	1.9/3.0
Standard deviation	30.5	17.8	18	10.3	2.7
2 (7-202)					
Minimum/maximum	1.8/156.0	3.0/61.0	1.0/192	0.9/46.5	0.2/11.3
Median/mean	19.1/26.1	12.2/17.3	20/29	6.0/9.3	2.0/3.2
Standard deviation	34.9	16.3	41	10.0	3.3
3 (7-203)					
Minimum/maximum	1.5/128.5	6.1/39.6	0.3/192	1.4/47.1	0.2/8.9
Median/mean	19.8/28.5	21.3/21.1	14/26	6.9/9.9	2.5/3.3
Standard deviation	34.5	11.2	40	9.7	2.6
Combined sites					
Minimum/maximum	1.5/156.0	3.0/61.0	0.3/192	0.9/47.5	0.2/11.3
Median/mean	19.4/27.6	15.2/19.6	16/25	7.2/9.9	2.2/3.2
Standard deviation	33.0	15.0	35	9.8	2.8

characteristics and behavior. Strong correlations may also occur if the sources are similar or if the analytical method measures related properties (i.e., COD and total organic carbon [TOC]).

Pearson correlation analyses for the grab sample results for 23 water quality parameters including DOC, TKN, COD, and TSS were calculated. The Pearson correlation coefficient (*r*) is defined as the sum of the products of the standard scores of two variables divided by the degrees of freedom and shows how well a linear equation describes the relation between two variables. The probability value (*P*) is a measure associated with obtaining a random result with the same value of *r* (lower numbers indicate less likelihood of a random or artifactual finding). Generally, *P* values less than 0.05 are considered significant results.

The correlations were performed for each site and the pooled data. Very strong, significant correlations ($r \geq 0.90$, $P < 0.01$) existed between TSS and volatile suspended solids (VSS), COD and DOC, total phosphorus and dissolved phosphorus, and conductivity and sulfate (SO_4). Strong, significant correlations ($r \geq 0.80$, $P < 0.01$) existed between conductivity and hardness, COD and oil and grease, DOC and oil and grease, COD and TKN, DOC and TKN, oil and grease and TKN, DOC and NH_3-N, oil and grease and NH_3-N, TKN and NH_3-N, conductivity and chlorine, hardness and chlorine, TKN and chlorine, and hardness and SO_4. The TSS was poorly correlated ($r = -0.20$ for pH to 0.57 for turbidity) with the other parameters, except for VSS. The TSS was not well correlated, even with turbidity ($r = 0.57$), which is sometimes used as

Table 3—Basic statistics of EMCs and simple means calculated from grab samples.

Parameters	Number of cases[a]	Mean	EMC/grab[b] (mean, %)	Median	EMC/grab[c] (median, %)	Minimum	Maximum	Standard deviation
TSS (mg/L)	62/569	67.7	95.0	57.6	125.4	8.8	466	63.0
Turbidity (NTU)	62/569	46.8	89.9	33.1	103.7	10.9	171	39.2
Conductivity (μmho/cm)	62/569	239.0	75.9	135.0	86.0	23.4	1992	302.7
Hardness (mg/L)	62/569	78.9	75.2	50.7	104.7	10.8	598	95.4
pH	62/569	6.7	99.5	6.6	99.0	5.5	9.0	0.6
COD (mg/L)	62/569	252.5	78.6	119.8	86.5	19.1	2280	372.8
DOC (mg/L)	62/569	66.9	82.8	28.9	97.4	2.9	849	127.0
Oil and grease (mg/L)	62/569	14.0	77.3	8.8	83.4	1.5	80	14.6
TKN (mg/L)	62/569	9.6	82.8	4.1	87.4	0.8	111	16.4
NH_3-N (mg/L)	62/569	4.6	84.0	1.4	105.4	0.0	65.0	9.7
NO_2-N (mg/L)	62/569	0.3	62.4	0.2	82.1	0.0	3.0	0.4
NO_3-N (mg/L)	62/569	2.7	84.6	1.3	89.1	0.3	34.7	5.3
Total phosphorus (mg/L)	62/566	0.9	94.1	0.4	89.9	0.1	8.2	1.3
Orthophosphate (PO_4^{3}-P) (mg/L)	45/409	0.2	90.6	0.1	218.0	0.1	2.7	0.4
Dissolved phosphorus (mg/L)	62/568	0.7	95.5	0.2	84.1	0.1	7.3	1.3
Particulate phosphorus (mg/L)	62/565	0.2	87.8	0.1	100.0	0.0	0.9	0.2

[a] Number of 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.

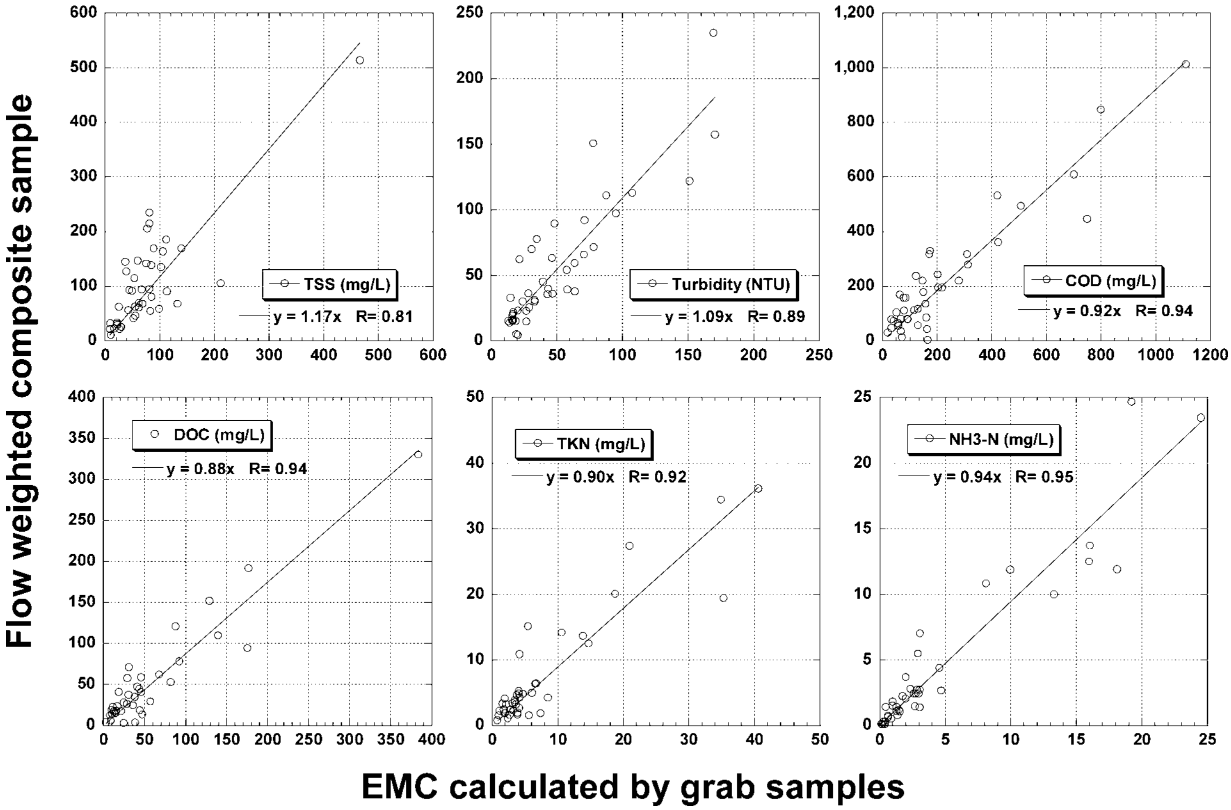

Figure 3—Comparison of EMC calculated by grab samples with composite sample.

a surrogate for suspended solids (Deletic and Maksimovic, 1998). Kayhanian et al. (2003) developed models based on logarithmic transformations of observations from a subset of the Caltrans statewide dataset shown in Table 4, but we have not performed similar analysis for the first flush dataset.

The correlation between organic or oxygen-demanding pollutants are particularly important. The COD and DOC are highly correlated, suggesting that the COD is primarily composed of organic compounds. The high correlations suggest one of two things—either the two correlated pollutants are measuring the same material, or the sources of pollutants are similar or release the pollutants in similar ways. In the case of COD and DOC, the two parameters are measuring similar properties. The two are related depending on the form or oxidation state of the carbon. The high correlation between COD and DOC suggests that the oxygen-consuming pollutants are organic and have a relatively consistent oxidation state. The low oil and grease concentrations cannot account for the high COD and DOC. This implies the existence of organic pollutants that are not hydrocarbons and are too polar or too volatile to be extracted in oil and grease analysis and that are produced or released in the same way as COD- or DOC-containing pollutants. Analysis of volatile organic compounds (not reported here) does not reveal the presence of contaminants that might account for the high COD, but may be lost in the oil and grease extraction.

Correlation Analysis Among Storm Characteristics and Event Mean Concentrations. Correlation analysis among storm characteristics and EMCs were conducted to determine if there is a significant storm characteristic that can contribute to pollutant loading rate. Seven parameters were selected as storm characteristics—total event rainfall, three rainfall intensities (maximum 5 and 15 minutes and average intensity), ADD, antecedent rainfall, and rainfall duration.

Only ADD had modest correlations ($r \approx 0.7$, $P < 0.01$) with EMCs, while other storm characteristics were less well-correlated. Total rainfall was negatively correlated with EMCs and had coefficients between 0.19 and 0.43 for combined sites, and probability values were between 0.00 and 0.14. This suggests that EMCs decrease with total rainfall (Kim et al., 2004) and implies that additional water volume dilutes the pollutants.

Table 5 shows correlations between ADD and EMCs for the principal pollutants. The numbers above the diagonal are the Pearson correlation coefficients (r). The probabilities associated with obtaining a random result with the same value of r are shown below the diagonal line. Each cell has four values of correlation coefficients corresponding to the three sites and a combined coefficient for the pooled data from all three sites, arranged as shown in the footnote at the bottom of Table 5. The probabilities or P-values are arranged in the same fashion, but below the diagonal line. Deletic and Maksimovic (1998) found no correlation with TSS and ADD, but found a weak correlation with conductivity. In this study, ADD was comparatively well-correlated to conductivity, hardness, COD, DOC, and TKN. The correlation with TSS is among the lowest in the table, especially for site 7-203, which has the smallest catchment area and shortest retention time. The trends in correlations among pollutants, as discussed in the previous section using grab sample results, are similar, but greater among the EMCs of those same pollutants.

Mass First Flush, Partial Event Mean Concentrations, and Correlation Analysis. To assess the runoff characteristics and first flush for each pollutant, the MFF_n and ratios of PEMC to

Table 4—Comparison of mean EMCs with other studies.

Parameters	Current study 303 000[a]	Caltrans' state-wide data (1997 to 2003) State wide	Nonurban $<$30 000[a]	Urban $>$30 000[a]	Barrett et al. (1998) 33 465[a]	Wu et al. (1996) 17 300[a]	Wu et al. (1998) 17 300[a]	Shinya et al. (2000) 75 000[a]	Shinya et al. (2003) 62 000[a]	Others
TSS (mg/L)	68	175	233	152	176	135	135	62	54	46[b], 9[c], 65[d]
Turbidity (NTU)	47	366	460	202						
Total dissolved solids (mg/L)		257	425	160			154			
Conductivity (μmho/cm)	239	363	730	211						
Hardness (mg/L)	79	50	42	53						68[e]
pH	6.68	7.11	6.85	7.22						
COD (mg/L)	253				73		34			80[b], 80[c]
BOD (mg/L)		16.6	10.3	25.1	7.5					
TOC (mg/L)								40.5	48.3	
DOC (mg/L)	66.9	19	14	22.4						
Oil and grease (mg/L)	14	6.6	4	6.4			2.7			
Total nitrogen (mg/L)									8.18	
TKN (mg/L)	9.6	2.15	1.68	2.36		0.88	1.2			2.10[b], 1.20[c]
NH_3-N (mg/L)	4.62	0.83	0.42	1.03		0.22	0.7			1.00[b], 1.27[c]
NO_2-N (mg/L)	0.32	0.14	0.08	0.17						
NO_3-N (mg/L)	2.75	0.97	0.47	1.17	1.07					6.70[b], 2.10[c]
NO_{3+2}-N (mg/L)[f]							0.87			
Total phosphorus (mg/L)	0.86	0.54	0.85	0.42	0.22	0.14	0.47		0.16	
PO_4^{3}-P (mg/L)	0.24	0.11	0.08	0.13		0.1	0.21			
Dissolved phosphorus (mg/L)	0.71	0.14	0.08	0.16						
Particulate phosphorus (mg/L)	0.16									
Sulfate (mg/L)	45.1	9.7		9.7						26.0[b], 20.0[c]
Calcium (mg/L)		12.63	5.55	12.97						
Magnesium (mg/L)		3.44	1.05	3.64						
Sodium (mg/L)		11.02	1.53	15.76						
Manganese (mg/L)								0.07	0.1	0.32[e]

[a] AADT (vehicles/d).
[b] Conventional pavement; Pagotto et al. (2000, AADT:12 000).
[c] Porous pavement highway; Pagotto et al. (2000, AADT: 12 000).
[d] Roadway, Westerlund et al. (2003, AADT: 7400).
[e] Urban roadway, Sansalone and Buchberger (1997, AADT: 150 000).
[f] NO_{3+2}-N = NO_2-N + NO_3-N.

EMC were compared by mean and ranked by median values for principal 14 pollutants. Table 6 shows the mean MFF_n and $PEMC_n$ ratios and 30- and 60-minute PEMC ratios for all three and combined sites. These results show that MFF_n is similar to $PEMC_n$ ratios in the tendency and magnitude of values. The 30- and 60-minute PEMC ratios were higher than those of MFF_{10}. These high ratios suggest that the initial variation of runoff volume and concentration and MFF ratio should be considered together for more effective BMP design for first flush.

Although the magnitudes were less than the magnitude (80% mass in 30% runoff) proposed by Bertrand-Krajewski et al. (1998), the ratios are sufficiently high to evaluate treatment strategies that favor the first part of the storm. As shown in the Table 6, MFF ratios were higher at site 7-203. The magnitude of the first flush generally increased with smaller, more impervious sites (Bertrand-Krajewski et al., 1998; Gupta and Saul, 1996). Site 7-201 had lower MFF ratios than site 7-202, although site 7-202 had a larger catchment area. Site 7-201 had a low slope and the longest retention time for runoff. Site 7-202 was on an uphill grade and typically produced runoff quicker after the beginning rainfall than site 7-201. In general, COD, DOC, TKN, and NH_3-N had high MFF ratios, whereas nitrite-nitrogen (NO_2-N), nitrate-nitrogen (NO_3-N), and turbidity had low ratios. This tendency was also shown in overall MFF_n ranking results from MFF_{10} to MFF_{50}.

Figure 4 shows the range of ratios for the combined sites as notched bar plots. The notched bar plots are defined at the bottom of Figure 4, and the definition applies to the following figures also. In Figure 4, generally, the oxygen-demanding (COD) or organics-indicating pollutants (DOC, TKN, and oil and grease) had the highest MFF ratios, whereas the ionic pollutants, such as NO_2-N, NO_3-N, conductivity, and hardness showed the lowest ratios.

Table 7 and Figure 5 show the ranking results of PEMC ratios by mean. The ratios are provided based on the timing and volume of the runoff. The 30- and 60-minute ratios correspond to the ratios after the first 30 or 60 minutes, irrespective of the volume of runoff. The volume ratios correspond to ratios after 10 or 20% of the runoff volume, irrespective of the time. The results show a similar tendency to the MFF_n ranking results. The PEMC ratios for DOC and COD were 7.38 and 6.00 for 30 minutes and 4.95 and 4.04 for 60 minutes, respectively. The PEMC ratios for DOC and COD

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

	ADD		TSS		Cond.		Hard.		COD		DOC		O & G		TKN		PO_4-P	
ADD		1	0.58	0.82	0.56	0.86	0.53	0.88	0.80	0.86	0.76	0.88	0.91	0.70	0.83	0.89	0.48	0.87
	0		0.15	0.56	0.72	0.71	0.58	0.71	0.55	0.73	0.60	0.74	0.60	0.65	0.60	0.76	0.66	0.67
TSS	0.01	0.00		1	0.80	0.95	0.77	0.92	0.84	0.90	0.81	0.92	0.68	0.76	0.79	0.93	0.81	0.91
	0.50	0.00	0		0.43	0.75	0.39	0.70	0.49	0.77	0.42	0.79	0.52	0.72	0.50	0.83	0.27	0.87
Conductivity	0.02	0.00	0.00	0.00		1	0.99	0.97	0.78	0.96	0.87	0.97	0.75	0.82	0.72	0.97	0.98	0.95
	0.00	0.00	0.04	0.00	0		0.91	0.93	0.95	0.88	0.96	0.87	0.94	0.80	0.97	0.90	0.79	0.85
Hardness	0.02	0.00	0.00	0.00	0.00	0.00		1	0.74	0.94	0.84	0.96	0.70	0.78	0.68	0.96	0.97	0.95
	0.00	0.00	0.06	0.00	0.00	0.00	0		0.94	0.91	0.95	0.91	0.84	0.77	0.87	0.89	0.81	0.81
COD	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00		1	0.93	0.98	0.92	0.93	0.98	0.99	0.73	0.97
	0.01	0.00	0.02	0.00	0.00	0.00	0.00	0.00	0		0.99	0.97	0.91	0.92	0.97	0.97	0.77	0.85
DOC	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00		1	0.89	0.86	0.88	0.98	0.81	0.94
	0.00	0.00	0.05	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0		0.88	0.86	0.94	0.96	0.84	0.87
Oil and grease	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00		1	0.93	0.89	0.71	0.88
	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0		0.96	0.91	0.61	0.82
TKN	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00		1	0.68	0.98
	0.00	0.00	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0		0.68	0.90
PO_4-P	0.10	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.01	0.00	0.01	0.00		1
	0.01	0.00	0.32	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0	

*Notes: Correlation coefficient "r" is the Pearson's product moment correlation and appears above the diagonal.
Probability values (*P*-value) appear below the diagonal. A *P*-value of 0.00 means less than 0.005.
The values in individual cells are aranged as follows:

1 (7-201)	2 (7-302)
3 (-203)	Combined

based on volume were 2.89 and 2.77 for 10% of the volume ($PEMC_{10}$) and 2.05 and 2.01 for 20% of the volume ($PEMC_{20}$). The graphs show that the early runoff, measured either by time or volume, is much more contaminated that the runoff later in the storm and the average runoff. The various pollutants are ranked from highest to lowest, with COD and DOC having the greatest decline during the storm, while inorganic pollutants, such as nitrite (NO_2^-), nitrate (NO_3^-), PO_4-P and TSS and turbidity, had the least decline. Figure 5 shows that all measured pollutants exhibited a first flush based on concentration, and ensuring treatment of the early runoff is important.

The range or statistical variability of the MFF ratios is also important. Figure 6 shows notched bar plots of the MFF ratios for TSS, COD, DOC, oil and grease, TKN, and PO_4-P for the combined sites. With the exception of TSS, the MFF_{10} to MFF_{30} median values from vary from 2.4 to 1.5, which indicates that the first 10 to 30% of the runoff contains 24 to 45% of the pollutant masses. The figure documents the higher masses discharged during the first part of the storm, which can be used to estimate the relative benefits of treating the early runoff over treating a portion of the entire runoff. The TSS had lower ratios, ranging from 1.7 and 1.6 for MFF_{10} to MFF_{30}, respectively. The lower ratio may be produced by varying rainfall rates. During some storms, it was noted that bursts of rainfall late in the storm could mobilize TSS, creating high temporary mass emission rates. The TSS discharge rate may not only be dependent on initial washing effect, but other storm characteristics also.

Correlation Analysis Among Storm Characteristics and MFF_n. Previous researchers have noted interactions between storm characteristics and first flush. Furumai et al. (2002) found a stepwise wash-off phenomenon, and the wash-off process did not appear to be linear with the runoff rate and the mass of pol-

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

Parameter	1 (7-201)	2 (7-202)	3 (7-203)	Combined sites
MFF_{10}	1.89	2.43	2.57	2.32
MFF_{20}	1.53	1.85	1.95	1.80
MFF_{30}	1.35	1.53	1.63	1.52
MFF_{40}	1.22	1.35	1.42	1.34
MFF_{50}	1.14	1.23	1.30	1.23
Ratios of 30- and 60-minute PEMCs to EMCs				
30-minute PEMC/EMC	2.87	3.80	6.06	4.39
60-minute PEMC/EMC	2.19	3.12	3.88	3.14
Ratios of $PEMC_n$ to EMCs				
$PEMC_{10}$/EMC	1.80	2.36	2.50	2.26
$PEMC_{20}$/EMC	1.48	1.77	1.88	1.73
$PEMC_{30}$/EMC	1.32	1.50	1.60	1.48
$PEMC_{40}$/EMC	1.21	1.33	1.41	1.32
$PEMC_{50}$/EMC	1.13	1.21	1.29	1.22

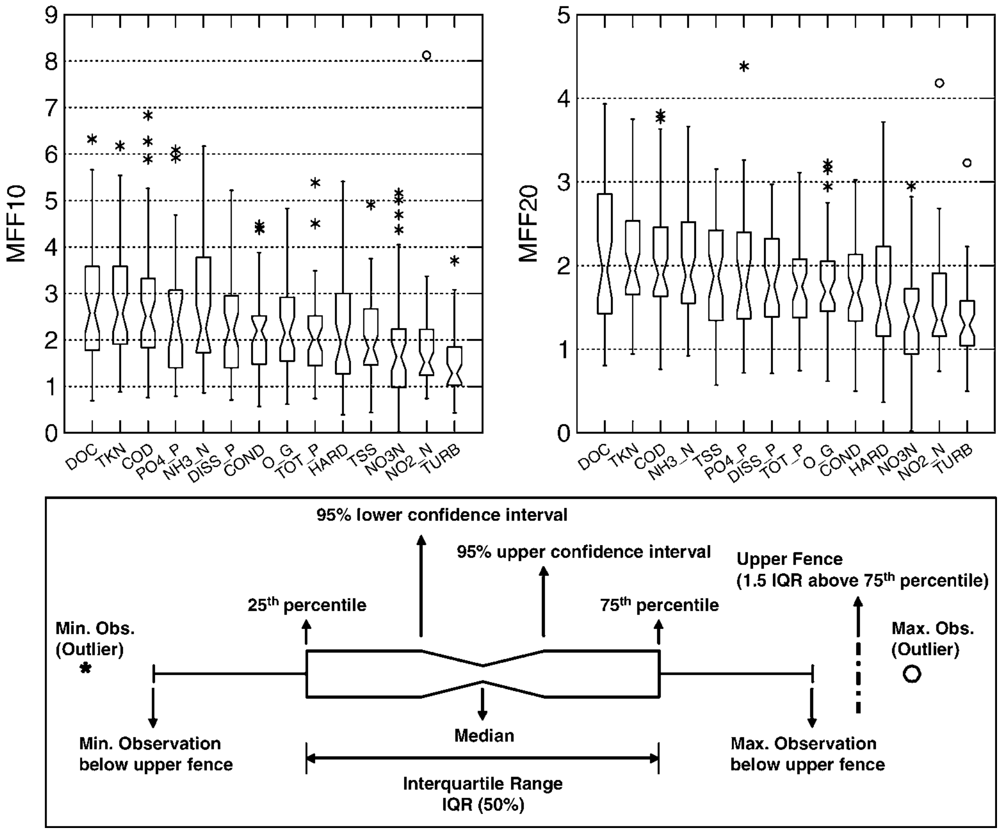

Figure 4—Ranking plots of MFF_{10} and MFF_{20} for combined sites.

lutant. Gupta and Saul (1996) noted that the maximum rainfall intensity, maximum inflow, rainfall duration, and the antecedent dry weather period were the most important parameters influencing first flush.

To determine the influence of storm and site characteristics on first flush, statistical and graphical correlation analyses of the MFF_n with storm characteristics and other pollutants were made. Unfortunately, almost no correlations existed between MFF_n and storm

Table 7—Ranking results of PEMC to EMC ratios for combined sites.

	Mean PEMC to EMC ratios													
Rank	30 minutes		60 minutes		$PEMC_{10}$		$PEMC_{20}$		$PEMC_{30}$		$PEMC_{40}$		$PEMC_{50}$	
1	DOC	7.38	DOC	4.95	DOC	2.89	DOC	2.05	TKN	1.70	TKN	1.48	TKN	1.33
2	COD	6.00	COD	4.04	TKN	2.79	TKN	2.04	DOC	1.69	NH_3-N	1.46	NH_3-N	1.32
3	TKN	5.95	TKN	3.96	COD	2.77	COD	2.01	NH_3-N	1.67	DOC	1.46	TSS	1.32
4	NH_3-N	5.67	NH_3-N	3.89	NH_3-N	2.73	NH_3-N	2.00	COD	1.66	TSS	1.45	DOC	1.31
5	Conductivity	4.72	NO_2-N	3.43	Dissolved phosphorus	2.29	TSS	1.81	TSS	1.61	COD	1.44	COD	1.30
6	Hardness	4.48	PO_4^{3-}	3.42	Oil and grease	2.28	Dissolved phosphorus	1.76	Dissolved phosphorus	1.52	Dissolved phosphorus	1.36	Dissolved phosphorus	1.24
7	NO_2-N	4.32	Conductivity	3.02	Hardness	2.25	Oil and grease	1.73	Total phosphorus	1.49	Total phosphorus	1.34	Total phosphorus	1.24
8	Oil and grease	4.08	Oil and grease	2.95	Conductivity	2.22	Total phosphorus	1.69	Oil and grease	1.48	Oil and grease	1.32	Oil and grease	1.21
9	Dissolved phosphorus	3.99	Dissolved phosphorus	2.83	Total phosphorus	2.10	Hardness	1.64	PO_4^{3-}	1.42	PO_4^{3-}	1.28	PO_4^{3-}	1.19
10	PO_4^{3-}	3.93	Hardness	2.72	PO_4^{3-}	2.05	Conductivity	1.64	Conductivity	1.39	Conductivity	1.24	Conductivity	1.15
11	NO_3-N	3.33	Total phosphorus	2.46	TSS	2.01	PO_4^{3-}	1.63	Hardness	1.38	Hardness	1.23	Hardness	1.14
12	Total phosphorus	3.33	NO_3-N	2.34	NO_3-N	1.86	NO_2-N	1.46	NO_2-N	1.29	NO_2-N	1.18	Turbidity	1.12
13	TSS	2.31	TSS	2.07	NO_2-N	1.84	NO_3-N	1.40	Turbidity	1.24	Turbidity	1.17	NO_2-N	1.11
14	Turbidity	1.94	Turbidity	1.87	Turbidity	1.48	Turbidity	1.33	NO_3-N	1.22	NO_3-N	1.13	NO_3-N	1.07

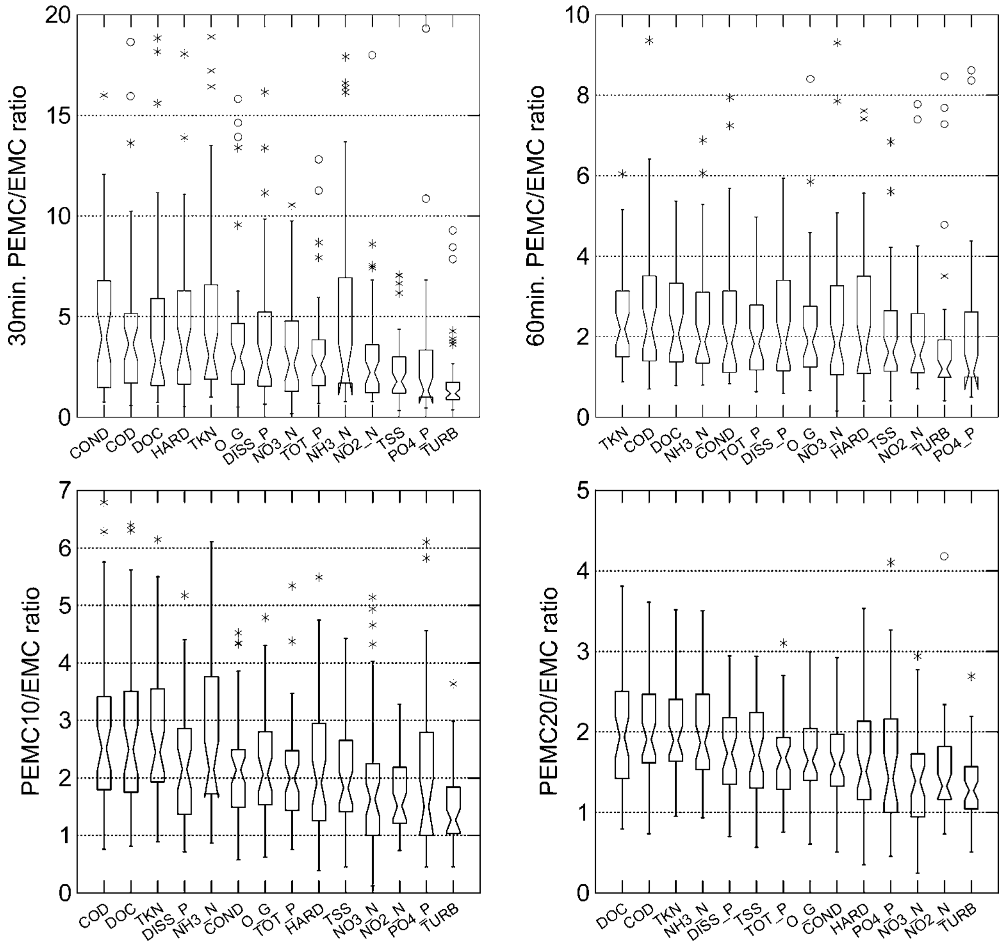

Figure 5—Ranking plots of the ratio of PEMC to EMC for combined sites.

characteristics, with the largest values of r being approximately 0.5. The MFF_{20} ratios between the principal 14 pollutants were highly correlated, which might be expected because the concentrations and EMCs were also correlated. The MFF_{20} ratios for COD and DOC, DOC and TKN, DOC and NH_3-N, and TKN and NH_3-N showed a very strong correlation ($r > 0.87$). This suggests that BMPs that can capture or treat the first flush should be evaluated for their ability to also remove the correlated pollutants because they will be present in the first flush.

Conclusions

A large quantity of highway runoff data collected during three wet seasons (2000 to 2003) at the three sites was examined to describe the constituents' runoff characteristics and were correlated through statistical and graphical procedures to quantify the first flush to determine if it was related to the site or storm characteristics. The conclusions are as follows:

(1) The mean EMCs of the COD and DOC of the runoff were 253 and 66.9 mg/L, respectively. The TKN was 9.6 mg/L, and the sum of NO_3^- and NO_2^- was approximately 3 mg/L. Total phosphorus was less than 1 mg/L. The TSS was only 68 mg/L. Except for TSS, concentrations from these sites with high AADT (>260 000 vehicles/day) were generally higher than reported in previous highway runoff studies at lower average daily traffic. The data reported can be used to estimate highway contributions to watersheds.

(2) Strong correlations were observed for DOC, COD, TKN, oil and grease, and NH_3-N. The TSS was poorly correlated with most other conventional pollutants. The correlation results for combined sites are summarized as follows: very strong correlations ($r \geq 0.90$, $P < 0.01$) for TSS and VSS, COD and DOC, total phosphorus and dissolved phosphorus, and conductivity and SO_4, and strong correlations ($r \geq 0.80$, $P < 0.01$) for conductivity and hardness, COD and oil and grease, DOC and oil and grease, COD and TKN, DOC and TKN, oil and grease and TKN, DOC and NH_3-N, oil and grease and NH_3-N, TKN and NH_3-N, conductivity and chlorine, hardness and chlorine, TKN and chlorine, and hardness and SO_4. Both EMCs and the individual grab sample results were correlated.

(3) Among seven storm characteristics and EMCs, only ADD was reasonably well-correlated with the EMCs of conductivity, hardness, COD, DOC, and TKN. The ADD was poorly correlated with TSS. Total rainfall was negatively correlated with most pollutants.

(4) 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. The oxygen-demanding (COD) or organics-indicating pollutants (DOC, TKN, and oil and grease)

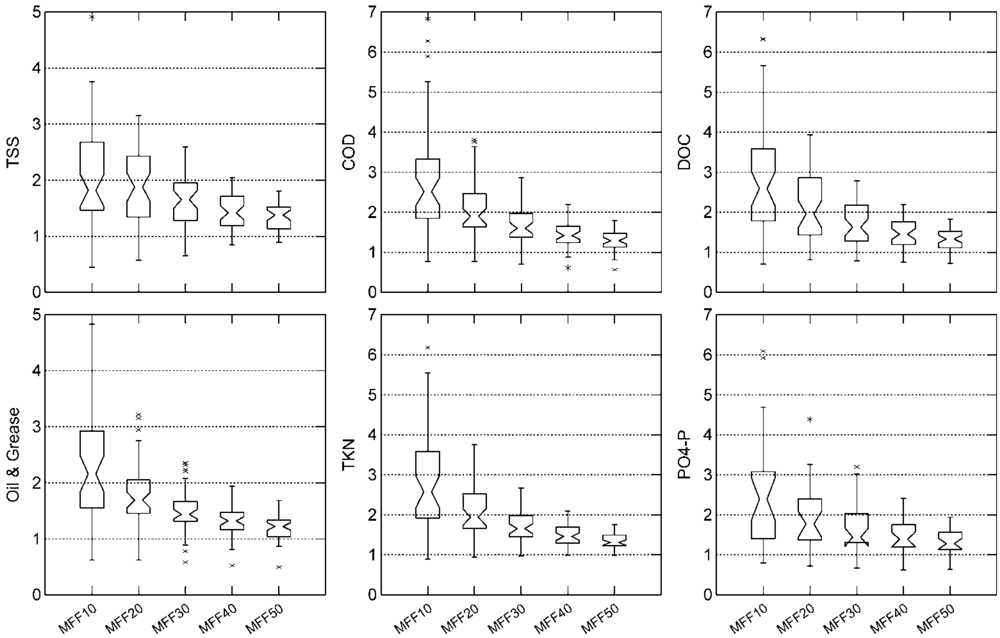

Figure 6—Notched bar plots of MFFs for combined sites.

had the highest MFF ratios ($MFF_{20} \sim 2.0$), whereas the ionic pollutants, such as NO_2-N, NO_3-N, conductivity, and hardness showed the lowest ratios ($MFF_{20} \sim 1.5$).

(5) The $PEMC_n$ ratios were similar to MFF_n in the tendency and magnitude of values. The PEMCs at 30 and 60 minutes were much higher than the EMCs, suggesting that the initial variation of runoff volume and concentration and MFF ratio should be considered together for more effective BMP design to take advantage of the first flush.

(6) The MFF ratios for the different pollutants were highly correlated, with COD and DOC, DOC and TKN, DOC and NH_3-N, and TKN and NH_3-N having the strongest correlations.

These results will be helpful in quantifying the effect of highways in watersheds and in evaluating potential BMP performance.

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