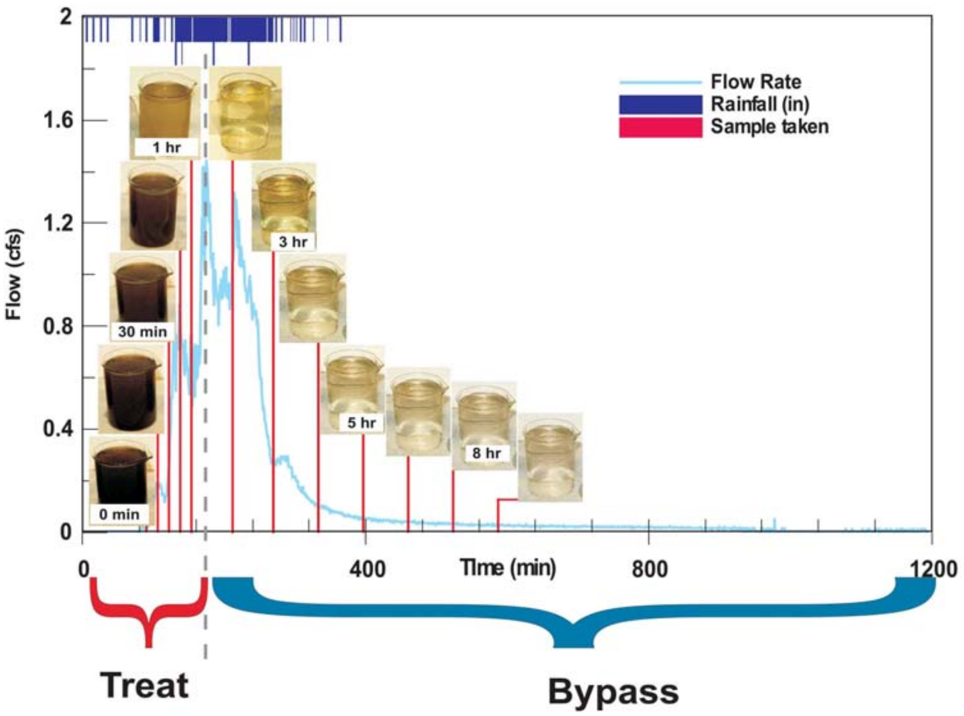
First Flush Phenomenon Characterization



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GLOSSARY

ADD	Antecedent Dry Days
ADT	Average Daily Traffic
AADT	Annual Average Daily Traffic
ASCE	American Society of Civil Engineers
BMP	Best Management Practice
COD	Chemical Oxygen Demand
Department	California Department of Transportation
DOC	Dissolved Organic Carbon (see also Total Organic Carbon)
DOT	Department of Transportation
EMC	Event Mean Concentration
EPA	US Environmental Protection Agency
FF	"First Flush" refers to pollutant concentration or mass that is associated with initial portion of the runoff (usually, less than 50 percent of the total runoff volume) within a storm event. First flush can be applied to a single constituent such as DOC, particle, or litter, and is referred to as "first flush of DOC", "first flush of particles" or "first flush of litter". First flush can also be used for group of constituents such as PAHs that will be referred as "first flush of PAHs". Also see the term seasonal first flush
GC	Gas Chromatography
ICP	Inductively Coupled Plasma
LARWQCB	Los Angeles Regional Water Quality Control Board
LACDPW	Los Angeles County Department of Public Works
MFF	Mass First Flush Ratio
MFF_n	Ratio of the discharged pollutant mass to the runoff volume in the first n% of the runoff. For instance, MFF_{10} = 3 means 30 percent of the discharged mass occurs over the first 10 percent of the initial runoff volume.
MPN	Most Probable Number

NPDES	National Pollutant Discharge Elimination System
O & G	Oil and Grease
PAHs	Polynuclear Aromatic Hydrocarbons
PEMC	Partial Event Mean Concentration
PFF	Particle First Flush Ratio
PNFF	Particle Number First Flush Ratio
$PNFF_n$	Ratio of the number of discharged particle to the runoff volume in the first n% of the runoff. For instance, $PNFF_{20} = 2.5$ means 50 percent of the discharged particles is associated with 20 percent of the initial runoff volume.
PSD	Particle Size Distribution
RMS Error	Root Mean Square Error
Seasonal FF	First flush of pollutant concentration of mass that is associated with the first storm of the season compared with the pollutant concentration or mass in the remaining storm events
TEF	Treatment Effectiveness Factor
TKN	Total Kjeldahl Nitrogen
TOC	Total Organic Carbon
TSS	Total Suspended Solids
VSS	Volatile Suspended Solids
US EPA	United States Environmental Protection Agency
USWS	United States Weather Service

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EXECUTIVE SUMMARY

“First flush” is a phenomenon that is associated with the occurrence or belief that the first portion of stormwater runoff in a storm event is the most contaminated. While most researchers believe that the first portion of runoff does have higher contaminant concentrations, opinions vary as to the importance of the increased concentrations, and whether the actual mass of the first flush is a significant portion of the total runoff mass. Lay people generally believe there is a first flush, and associate hazardous driving conditions with the onset of rainfall. There is also a general believe that the first rainfall of a new rainy season is the most contaminated (seasonal first flush), and washes out several months of contaminant buildup. The concept of seasonal first flush is applicable to climates such as California, which have distinct wet and dry seasons.

This study has identified several types of first flushes, but all, with the exception of “seasonal first flush” indicate the discharge of greater concentrations or mass in the early part of a storm event. The term first flush can be used to describe the discharge of any contaminant. For example, a first flush that is associated with particles or litter will be reported as “particle first flush” or “litter first flush,” respectively.

The first flush study was jointly performed by the University of California at Los Angeles (UCLA) and the University of California at Davis (UCD). Most of the data presented in this report were collected by UCLA from three representative highway sites in west Los Angeles, California. Much effort went into developing a quantitative way of defining the mass first flush. Various other aspects of first flush were also investigated such as: water quality during storm events, litter characteristics, correlations among contaminants, first flush of organics, litter and particles, models for the build up and washoff of pollutants, new methods for measuring oil and grease, grab and composite sampling strategies.

The existence of a first flush may present alternative opportunities for stormwater pollutant reduction strategies. First, the cost of treatment, such as a stormwater BMP, is more dependent on the volume of water to be treated than the contaminant concentrations. Second, removal efficiency is greater at higher concentrations and zero at lower concentrations. These phenomena have been demonstrated using catch basin inserts, sorbers and sedimentation devices. The emerging American Society of Civil Engineers database on stormwater treatment BMP trials has also shown this effect.

1. INTRODUCTION

1.1 Overview of the First Flush Phenomenon

The "**first flush**" phenomenon is generally assumed for rainfall events, and can be described as a concentration first flush or a mass first flush. A concentration first flush occurs when the first runoff has high concentration relative to runoff later in the storm event. A mass first (concentration times flow rate) is flow dependent and it will occurs when both concentration and the initial runoff is high relative to mass emission rate in the later runoff. Concentration first flushes have been frequently reported, but mass first flushes have rarely been quantified. For example, most of the parameters monitored for all the events in this study had higher concentrations at the beginning of the runoff than later in the runoff. Mass first flushes were less frequently observed and with lower magnitudes. This is due to the nature of the runoff, which generally has lower flow rate at the beginning of the storm than in the middle of the storm. Therefore, the mass emission rate in the middle of the storm event may be greater than at the beginning of the storm event, in spite of lower concentrations in the middle of the storm. The concept can be applied to any particular constituent or water quality parameter. Therefore, a first flush in total organic carbon (TOC), for example, can be called a TOC first flush.

The concept of first flush can also be applied to a rainfall season. In California and many other areas of the world, rainfall occurs over distinct periods. For example, the bulk of the rainfall in Los Angeles occurs from approximately November to March, with the months of January and February usually having the greatest rainfall. The long dry period from April or May to October allows contaminants to build up. The first large rainfall of the season, occurring any time from October to January, generally mobilizes the built-up contaminants, creating a larger discharge. This phenomenon is called a "**seasonal first flush**."

In this report the term first flush will be used as follows:

First flush	The discharge of a larger mass or higher concentration in the early part of a storm relative to the later part of the storm. The term can be applied to any contaminant. The magnitude of the first flush will depend on site specific conditions, but the term first flush is applicable.
Seasonal first flush	The discharge of a larger mass or higher concentration of the first storm or first few storms of a rainy season, relative to storms later in the season.

Both terms can be applied to any water quality parameter and constituents such as metals, litter, particles, toxicity, turbidity, etc. and both terms can be used to describe a mass first flush or a concentration first flush. The modifiers of the terms indicate if it is a mass or a concentration.

Various ways have been previously proposed to quantify mass first flush, and absolute quantitative definitions have been offered. An early definition offered by Bertrand-Krajewski *et al.* (1998) is typical and suggested the existence of a first flush if 80% of the pollutant mass is emitted in the first 30% of the runoff. Other definitions and observations have been offered, and will be discussed in greater detail later (Thornton and Saul, 1987; Geiger, 1987; Vorreiter and Hickey, 1994; Saget *et al*, 1995; Gupta and Saul, 1996; Sansalone and Buchberger, 1997; Larsen *et al*., 1998; Sansalone *et al*., 1998; Deletic, 1998). They all in some way suggest a higher pollutant mass emission rate in the early part of the storm than in the later part, and the early part is generally considered the first 20 to 40% of the runoff volume. In this report and in earlier papers (see Bibliography at the end of this report, which lists our previously submitted or published reports and papers), we have proposed a mass first flush ratio or MFF, which quantitatively describes the mass first flush and is sufficiently broad to apply to any initial portion of the storm.

It is possible to have a concentration seasonal first flush as well as a mass seasonal first flush. The techniques used to describe a mass first flush can also be used to describe a mass seasonal first flush. Occasionally, when investigators are describing both the first flush of a single storm and an entire season, they may use the term “**storm first flush**” to emphasize that the first flush is for a single storm event. In this study, he term “storm first flush” is not used. The term first flush always refers to a single storm event and seasonal first flush will always be used for an entire season.

Evidence collected in this study, combined with other datasets from Southern California, have provided the first quantitative demonstration of a seasonal first flush. The existence of a seasonal first flush presents opportunities and challenges stormwater management.

The presence of a mass first flush depends on a number of factors, which will be discussed in greater detail throughout the report. Often one sees or reads of an investigator describing a very large watershed, and noting that a first flush was not observed. Such conclusions are naïve, because in a large watershed, stormwater must be transported a great distance to a single discharge point, or mouth of the watershed. Therefore, the time of travel of the runoff from various places in the watershed to the monitoring point is different (time of travel is the elapsed time for a quantity of stormwater to flow from the point of generation to the monitoring point). In this case, the first flush from each small area in the watershed arrives at the mouth of the watershed at different times, which mixes the smaller first flushes of each area into a broad discharge pattern. Therefore, the first flush from one area is mixed with runoff from other areas that occurred much later in the storm.

The definition of large watershed for this context is a function of the time of travel. The first flush of pollutants observed in this study was generally within the first few minutes to the first hour after detecting observable runoff. First flushes are much less likely to occur in large watersheds.

The imperviousness of the watershed or catchment area also affects the first flush. Highly impervious surfaces create high velocities that easily transport solids or scour contaminants from surfaces, and runoff occurs almost immediately at the beginning of rainfall. Previous work performed in our laboratory (Lau *et al*, 1998), evaluated Ballona Creek and Malibu Creek during rainfall events. Flow appeared in the Ballona Creek watershed (~70% impervious) 10 to 15 minutes after the beginning of measurable rainfall. The same rainfall did not produce additional runoff in Malibu Creek until 10 to 12 hours after the beginning of measurable rainfall. The quickly occurring runoff, or short time of travel provided by highly impervious watersheds, provides more opportunity for first flushes.

The bulk of our efforts have been devoted to estimating the mass first flush of highway emissions, with the objective of proposing methods to improve the effectiveness of best management practices (BMPs) that take advantage of the first flush. Highways catchments are landuses that are likely to have a first flush. They are generally impervious and small. Our three sites, which were picked in 1998 as “typical” of for the Department’s sites, are 0.6 to 1.6 hectares and are more than 95% impervious. Runoff appears only a few minutes after measurable rainfall. The nature of the Department’s sites, and by implication many sites for other state departments of transportation (DOT), may provide an excellent opportunity for improved stormwater management at reduced cost because of the likelihood of first flushes.

A BMP that takes advantage of the first flush is sometimes called “first flush friendly” and an example of such a BMP is an infiltration/sedimentation basin. An infiltration/sedimentation basin could be operated in one of two ways: it could be operated as a flow through device, which would remove some portion of the contaminants such as suspended solids, throughout a storm event. For large storms, over the design frequency of the basin, some portion of the flow rate would be bypassed, or the basin would operate at high flow rate and reduced efficiency. An alternative way of operating the basin is to fill the basin with the first runoff, and bypass the remaining runoff. The second strategy provides greater opportunity the small particles to settle, and will be a superior strategy if there is a significant mass first flush. The definition of “significant” will depend on site-specific issues, which we will address later in the report.

Our findings suggest that for most pollutants, the second strategy is preferable. Generally, 30 to 50% of the pollutants in highway runoff from a single storm event are contained in the first 10 to 20% of the runoff volume. This can mean that treating the first 20% of the flow can treat 50% of the pollutants. Conversely, uniformly treating 20% of the flow during the entire storm would treat only 20% of the mass. The ratio of mass treated to volume treated in the first case is 2.5 and in the second case is 1.0. Generally, the cost of managing stormwater is more related to the volume than the concentration, which means that the first strategy will be much more cost effective than the second strategy. Also, emerging information collected by others (Strecker et al. 2001) and our laboratory (Lau and Stenstrom, 2002) shows that BMPs are generally more effective in treating higher concentrations than lower concentrations (i.e., the removal efficiency of a catch basin insert or a sedimentation basin may be close to zero at low concentrations, and as high as 70% or more at high concentrations). Therefore, applying BMPs to the first runoff, when the concentrations are higher, will be a more effective strategy for two reasons: 1) the most contaminated runoff is being treated, and if there is bypassing it will be less contaminated runoff that occurs later in the storm, and 2) the BMPs are likely to have higher removal efficiencies treating the more contaminated runoff.

The first flush or seasonal first flush can represent an opportunity to achieve higher pollutant reductions at lower cost or effort. For example, the Department has been required to remove litter from highway catch basins at the end of the summer. The seasonal first flush presents an opportunity to remove six to nine months of litter buildup in a single cleaning. If a seasonal first flush did not exist, the monthly cleanings might be needed to remove the same mass of litter.

1.2 Focus of the Report

This report describes the results of an extensive study to characterize and quantify the first flush of highway pollutants from three sites near UCLA, and to report on data collected by two consultants funded by the Department at other sites in District 7. The study was conducted over four years and includes storms monitored from 1999 to 2003, or four wet seasons.

1.3 Report Organization

This report is organized to be brief yet comprehensive. It is complemented by a CD that includes all data and graphical representations in PDF format.

The report is organized in chapters. The introduction chapter summaries the important concepts to be realized by taking advantage of the first flush in highway stormwater management, focus of the report and the report organization. Chapter 2 describes methodology and summarizes analytical methods and sampling strategies. Chapter 3 summaries the water quality results, providing summaries, such as the event mean concentrations (EMCs), for the various parameters. Chapter 4 presents the first flush results and discussion in the following order: meaningful definition of first flush for practical implication, organic (PAH) first flush, litter first flush, particle first flush and seasonal first flush. Chapter 5 presents additional topics related to first flush that include: preliminary treatment evaluation strategy with respect to first flush pollutant loads, a new method to monitor oil and grease, and sampling issue-composite versus grab sampling. Chapter 6 summarizes the information presented in chapter 4 and 5. Full results are compiled in a CD as summary tables and graphs and presented in Appendices A through K.

A series of technical memorandums are also included in the appendix. The technical memorandums were issued to the Department much earlier than the final report and were designed to provide early availability of the results. A bibliography of the papers presented at conferences and submitted or published in journals is listed at the end of this report. The technical memorandums along with technical papers provide greater detail or more explanation than contained in the final report, which allows a more readable, compact final report. The main report includes only the most important parts of the technical memorandums and technical papers.

2. METHODOLOGIES

2.1 Description of Monitoring Sites

Three monitoring stations were used for the UCLA-sampled first flush studies. They were selected by the Department in 1999, based on five major criteria: clearly defined runoff area, personnel safety, proximity to UCLA, representativeness and access to the flow stream. Table 2.1 summarizes the site characteristics. Initially the sites were labeled by the Department as UCLA 1, 2 and 3. Later the Department assigned numbers to the sites as 7-201, 7-202, and 7-203. Some of the early reports and publications use the “UCLA-n” designation, and later reports and publications use the “7-20n” designation.

Figure 1 shows the location of the sites. The sub-watersheds are delineated by bold blue lines. Red lines show major freeways. The light blue object north of Site 1 is the Sepulveda Dam flood protection area. It is close to Site 1, but is hydraulically separated from the site. The travel time travel by automobile to the sites from ULCA via freeways is usually less than 15 minutes, but can be more during high traffic conditions. Additionally, the sites can be reached in about the same time via surface streets. Easy and quick site access was important in order to reach the sites quickly to catch the first flush

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

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

Monitoring site 7-203 was located on the east side of the IS 405 Freeway just south of the point where it passes over Santa Monica Boulevard. This site was constructed as a monitoring site previously by the Department. It has a 24-inch diameter plastic corrugated pipe (smooth on the inside, corrugated on the outside) which collects runoff from the northbound, east side of the freeway. The curb was opened to collect runoff from the shoulder, and no runoff can enter the site in any other way, including the freeway and shoulder south of the site. It has no sound walls. It has AC power and a small house (approximately 2.5 square with a pitched roof approximately 3 ft high in the center) to hold an automatic sampler. The small house was reused to contain the composite sampler after the first year of our study. As the runoff exits the pipe there is a gap of 20 cm, which creates a free waterfall for sampling.

Table 2.1 Summary description of UCLA monitoring stations

Site characteristics/ parameter	**Monitoring Site**		
	7-201	**7-202**	**7-203**
Freeway/postmile	US 101 PM 17	IS 405 PM 34.8	IS 405 PM 30.8
Location	Eastbound US 101	IS 405 Freeway and Sepulveda	North Bound IS 405 and Santa Monica Blvd.
Drainage area (m^2)	12802	16918	3917
Freeway type	Grade	Fill	Cut
Annual average daily traffic	328,000	260,000	322,000
Longitude	34.16	34.10	34.05
Latitude	-118.48	-118.48	-118.44

All three sites were virtually 100 percent impervious, and the runoff coefficient was usually 0.9 to 0.95. Each site was equipped in the first year with an American Sigma rain gage and flow meter. The flow meter recorded flow and rainfall in one-minute intervals. In the second year a composite sampler was added to each site and it was also an American Sigma device. Data from each site was downloaded into a laptop, Windows-based computer after the end of each storm.

The three sites were also used for litter collection during the second and third years of the study. Litter bags, with 6 mm octagonal openings were attached to the corrugated pipes. An aluminum collar fabricated in the UCLA shops was used for Sites 1 and 2. The collar clamped to the outside of the corrugated pipes, and had an opening at the top that allowed the sampling team access to the free waterfall with a scope. Figures 2.2, 2.3 and 2.4 show several pictures of the sites.

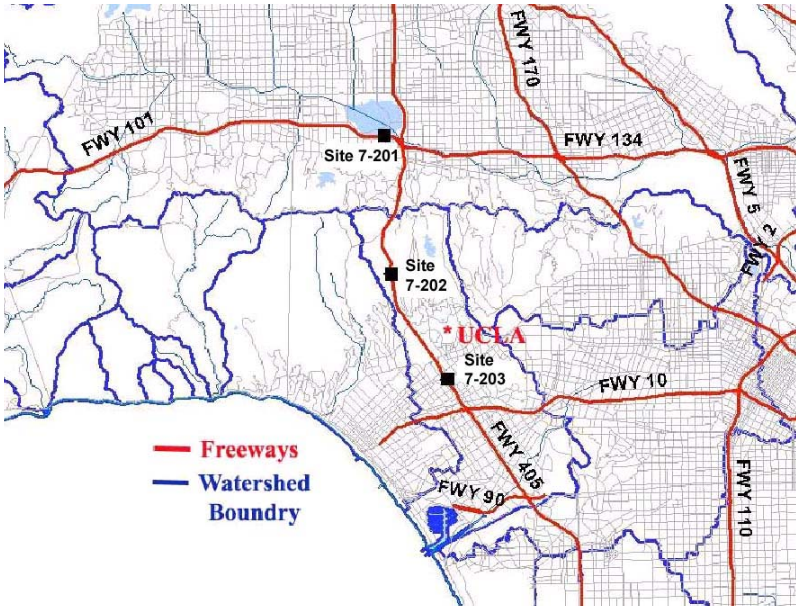


Figure 2.1 Locations of UCLA Sites 1 to 3 (Department's designation 7-201, 7-202, 7-203)

Figure 2.2 Pictures of Site 1, clockwise from the top: **1)** site from a distance of 30 meters; **2)** drainage pipe showing free waterfall and cables for level and velocity sensors, and **3)** rain gage above the sound wall.

Figure 2.3 Pictures of Site 2, clockwise from the top: **1)** site from a distance of 15 meters, showing rain gage, rain protection enclosure, PVC pipe for cables. The discharge is obscured by the brush; **2)** drainage pipe showing free waterfall and PVC pipe for cables for level and velocity sensors, and **3)** freeway looking north showing the four inlet grates.

Figure 2.4 Pictures of Site 3, clockwise from the top: 1) site from a distance of 50 meters, looking north, showing drainage pipe (an early picture, taken before our study) 2) drainage pipe showing rain gage and dry/wet collection containers from an earlier study. The free water fall is at the end of the black pipe, and 3) site entrance from shoulder, looking south.

The sites were maintained by the Department during the study. Maintenance was coordinated with District 7 personnel and occasionally the UCLA team had to perform brush removal. Site 3 shows additional equipment for dry and wet deposition sampling, but was not part of our study. It was especially important at Site 3 to contain the overhead growth, to prevent interference with the rain gage.

2.2 Sampling Strategies

Weather forecasting was an important aspect of the sampling. It was necessary to obtain the most reliable forecast in order to avoid time consuming and frustrating mobilizations for storms that did not occur, as well as making sure that the teams were prepared for the real events. A variety of forecasting methods were used. The long term (3 to 5 day) forecasts by the US Weather Service (USWS) were useful to prepare the teams for upcoming events, in order to check the equipment and replace batteries. UCLA's Department of Atmospheric Sciences also provided useful forecasts. When USWS forecast suggested that a storm probability was greater than 50%, the sampling teams were mobilized to each sampling site, to within 5 to 10 minutes travel time to each site. After some practice, USWS Doppler radar was useful in predicting the beginning of rainfall. Approximately 80% of the storms approached the sampling sites from the north west (i.e., Santa Barbara) and active rainfall could be observed as it traveled to the sites. Storms that came from a southerly direction (i.e., Santa Catalina Island) were less predictable.

Detecting the first flush required grab samples to be collected throughout the storm but especially in the early runoff period. Grab samples can be collected manually or can be collected with automated samplers having multiple bottles. Multi-bottle samplers were not available and manual sampling was used. The manual sampling also provided greater flexibility, allowing larger sample volumes to be collected as well as special samples using different bottles. The sampling strategy was perfected in the first year and a consistent protocol was used in the second and later years. Automatic flow-weighted composite samplers were also added in the second year.

In the first year (1999-2000), five grab samples were collected in the first hour of runoff followed by two or three grab samples collected in the following two to three hours, which were combined to create a composite sample. This strategy adequately characterized the initial runoff but was inadequate to characterize later runoff, and especially for long storms with a lengthy period of light rainfall. The mass contribution of the runoff late in the storm was significant compared to the mass in the early runoff.

In the second year, five grab samples were again collected in the first hour, followed by one grab sample per hour for the next 7 hours, providing a total of 12 grab samples. For storms lasting less than 8 hours, fewer grab samples were collected. For storms lasting longer than 8 hours, an additional one or two grab samples were collected in the period from 8 hours to the end of the storm. In the first year, all samples were analyzed. In later years, storms that were sampled but were too short to produce a sufficient number of samples to create pollutographs were not analyzed.

The highly impervious nature of the sites created runoff soon after the beginning of rainfall. Even though the time of travel from UCLA to the sites was short, it was still necessary to mobilize the sampling teams before the beginning of rainfall in order to collect the first runoff. Three teams of two people each were used in the early part of the storm when more frequent sampling occurred. After the first few hours of the storm event, the sample team was reduced to one or two teams and the other team members worked in the laboratory on analytical methods.

The sampling teams generally arrived at the sampling site prior to the start of the storm event. Sampling began as soon as the flow was observed at the collection point, or if runoff had already begun, as soon the teams arrived.

Runoff samples were collected from the storm drain outfall (or drain pipe) using a polypropylene scoop, and then transferred to 4-L amber glass bottles. In all cases samples were collected from a free waterfall. The bottles were then transported to the laboratory at UCLA immediately after collection and refrigerated at 4°C until analyzed. Generally the first five bottles were transported to the laboratory after the first hour, and one or two more trips were made as the storm progressed. Returning samples to the laboratory at frequent intervals was not particularly burdensome, because of its close proximity and because the team wanted to get out of the rain and warm up in the hour between samples. The time between the sample collection and receipt of samples at UCLA laboratory was less than 4 hours. This became important in the last year of the study, when particle size distribution (PSD) was being measured. Changes in the PSD were observable after 10 to 12 hours of storage. Therefore a holding time of 6 hours was established for particle size distribution analysis.

Samples were collected in 4-L amber glass bottles. The bottles were prewashed and kept in the laboratory cold room prior to the storm. As soon as samples arrived at the laboratory they were mixed and divided into sub samples for different analysis. In the first three years of the study, the most time-critical analysis was filtration for metals analysis, which must be completed within 24-hours of sample collection. Later the particle size distribution became the most time-critical analysis, which needed to be preformed within six hours of sample collection. Additional sample were collected for particle size analysis, depending on the types of analysis being performed, which is described in more detail later in the report.

In the second and third year of the study, litter samples were collected, using a large, reusable bag with 6-mm openings. The draw-string bag was placed over discharge of each pipe to capture the entire flow, but still allowed the grab samples to be collected from a free water fall. Three bags were collected for each site for each storm. The first bag was installed before the beginning of the storm, and removed after 1 hour of runoff. A second bag was then installed and was removed after 8 hours or the cessation of grab sample collection. The third bag was installed and was left in place until the next day, well after the end of the storm. It was retrieved and all bags for all sites were transported to an outside lab under contract with the Department for performing the litter analysis. The bags were cleaned and reused.

Autosamplers (Sigma 900MAX, American Sigma) were installed at all three monitoring locations prior to the second storm season (2000-2001) begins. Flow-weighted composite samples was collected and analyzed for the same suite of contaminants, except oil and grease.

2.3 Constituents and Analytical Methods

The water quality parameters were selected based on the Department's Storm Water Monitoring Protocols (California Department of Transportation, 2000a), in compliance with the NPDES permits. Table 2.2 shows the selected water quality parameters and their corresponding analytical methods. All analyses were performed as soon as the samples were collected, and within the recommended holding time. All analyses were performed in the UCLA Water Quality Laboratory, except for metals analysis. The metal samples were filtered and digested at UCLA, but the final analysis was done using an ICP/AE instrument at the Castaic Water Laboratory (a State certified laboratory).

Polynuclear aromatic hydrocarbons (PAHs) were also monitored, but not as routinely as the other constituents. Both dissolved and particulate bounded PAHs were analyzed according to US EPA Methods (SW-846, 1999): Method 3535 was used for dissolved PAHs and Method 3546 was used for particulate-bound PAHs. Both fractions were analyzed using a Finnigan 4000 Quadrapole mass-spectrometer with a Varian 3400 gas chromatograph. A splitless injector (at 290^{o}C) was used for sample injection onto a 30 m x 0.25 mm i.d. DB-5ms capillary column (J&W Scientific). The GC temperature was programmed at 30^{o}C for 4 min., 30^o - 300^o at 6^{o}C/min and 300^{o}C for 30 min. Mass spectral data were collected by using a scan range of 35 - 500 amu and a scan rate of 1 scan/s. A total of 41 PAHs were analyzed using this method.

2.4 Rainfall and Monitored Events

The number of monitored events was impacted distribution of rainfall. Figure 2.5 shows the rainfall that occurred during the four years and compares the total for each year. The vertical bars show the monthly rainfall. It is clear that the majority of the rainfall usually occurs in January and February, and almost no rainfall occurs between May and October. This rainfall pattern is associated with Mediterranean climates, and will be important in analyzing the seasonal first flush noted earlier. Based upon the amounts of rainfall that occurred each year, year 1 (1999-2000) was an average year. Years 2 and 4 (2000-2001 and 2002-2003) were wet years. Year 3 (2001-2002) was an extremely dry year. The study years followed the general monthly trends, although 2002-2003 had no rainfall in January and more than average rainfall in March.

Figure 2.6 shows the rainfall arranged as a probability plot. The 50% probability storm for the UCLA sites was 18 mm. The largest single storm was over 100 mm.

Table 2.2 Constituents monitored

Parameters	Units	Reporting Limits	Analytical Method	Holding Time and Preservation
Conventionals				
Total suspended solids	mg/L	2	EPA[1] 160.2	7 days; refrigerated at 4°C
Turbidity	NTU	1	EPA 150.1	48 hours; refrigerated at 4°C
Conductivity	μmho/cm	1	EPA 180.1	28 days; refrigerated at 4°C
pH	pH	0.01	EPA 120.1	Analyze immediately
Hardness	mg/L as $CaCO_3$	2	EPA 130.2	6 months; acidify with HNO_3 to pH < 2
Chemical oxygen demand	mg/L	2	EPA 410.0	Analyze as soon as possible
Dissolved organic carbon	mg C/L	1	EPA 415.1	7 days; acidify to pH <2 with H_3PO_4
Nutrients				
Ammonia[2]	mg /L	0.01	EPA 350.3	Analyze as soon as possible
Nitrite[2]	mg /L	0.01	EPA 354.1	48 hours; refrigerated at 4°C
Nitrate[2]	mg /L	0.1	EPA 300.0	48 hours; refrigerated at 4°C
Total Kjeldahl Nitrogen[2]	mg /L	0.1	EPA 351.4	7 days; refrigerated at 4°C, acidify to pH <2 with H_2SO_4
Ortho-Phosphate[3]	mg /L	0.1	EPA 300.0	48 hours; refrigerated at 4°C
Phosphorus (Dissolved and Total)[3]	mg /L	0.03	EPA 200.7	48 hours; refrigerated at 4°C
Organics				
Particulate PAHs	μg/L	1–5 x 10^{-3}	EPA 3535	7 days; refrigerated at 4°C
Dissolved PAHs	μg/L	1–5 x 10^{-3}	EPA 3546	7 days; refrigerated at 4°C
Oil and grease	mg/L	1	C18 SPE[4]	28 days; acidify to pH < 2 with HCl
Metals (dissolved and total)			EPA 200.7	Filter immediately, acidity to pH < 2 with HNO_3
Cadmium, chromium, nickel, zinc	μg/L	1		
Copper		3		
Lead		5		
Microbiological				
Total coliform	MPN/100 ml	2	SM[5] B9221	24 hours
Fecal coliform	MPN/100 ml	2	SM C9221	24 hours

EPA Methods and Guidance for Analysis of Water (USEPA, 1999)

[2] Reported as mg nitrogen per liter

[3] Reported as mg phosphorus per liter

[4] Lau and Stenstrom (1997)

[5] Standard Methods (1999)

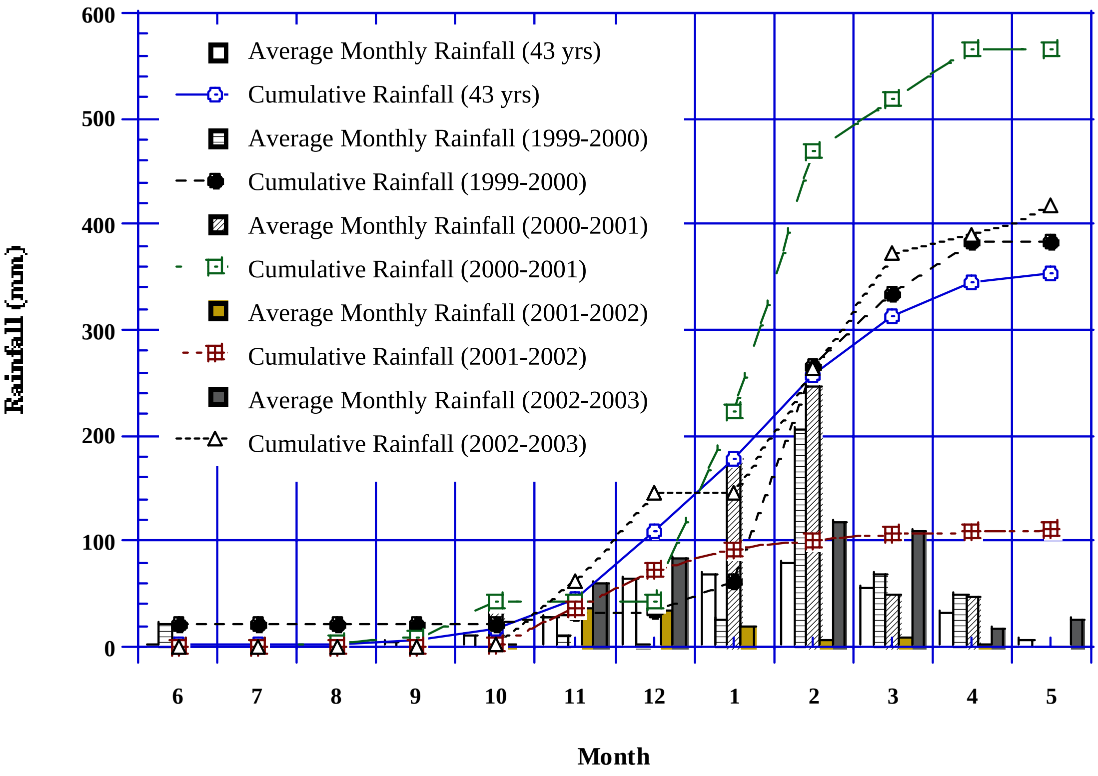


Figure 2.5 Rainfall during the study.

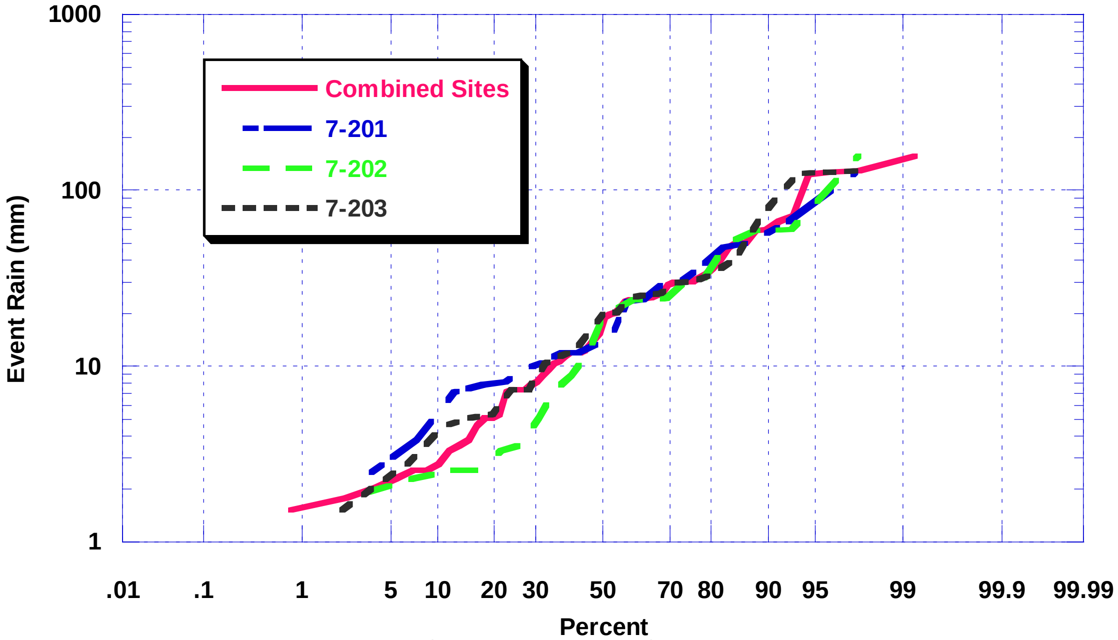


Figure 2.6 Rainfall probabilities for all three sites.

Tables 2.3 to 2.7 show the monitored storm events for each year. Generally, all large storm events were monitored. Storm events that followed an earlier storm within 24 to 36 hours were generally not monitored. A special effort was made to insure that the first storm of each rainy season was monitored. Appendix A shows the sampled event parameters in greater detail and also includes the events sampled by the consultants in years two and three.

Table 2.3 Basic statistics of storm events

Site		**Total Rainfall (mm)**	**Max. Intensity (mm/hr)**	**Antecedent Dry Day**	**Storm Duration (hr)**	**Ave. Rainfall Intensity (mm/hr)**
7-201	No. of storm events	30	29	30	30	30
	Min. / Max.	1.3 / 127.0	3.0 / 51.8	1.0 / 69.4	2.0 / 47.5	0.1 / 10.7
	Median / Mean	13.8 / 25.0	12.2 / 18.4	11.7 / 15.6	10.1 /12.1	1.7 / 2.6
	Standard Dev.	28.3	17.0	16.0	11.2	2.6
7-202	No. of storm events	32	32	32	32	32
	Min. / Max.	1.8 / 156.0	3.0 / 61.0	1.0 / 192.2	0.5 / 46.5	0.2 / 11.3
	Median / Mean	20.2 / 26.4	12.2 / 18.9	12.6 / 22.3	8.2 / 10.9	2.1 / 3.0
	Standard Dev.	32.0	18.4	34.8	11.1	2.9
7-203	No. of storm events	35	33	34	35	35
	Min. / Max.	0.5 / 128.5	3.0 / 51.8	0.3 / 192.3	1.4 / 52.2	0.1 / 8.9
	Median / Mean	15.5 / 25.1	21.3 / 21.1	11.7 / 21.9	7.3 / 10.6	2.2 / 2.8
	Standard Dev.	30.3	12.8	34.1	11.1	2.3
Combined sites	No. of storm events	97	94	96	97	97
	Min. / Max.	0.5 / 156.0	3.0 / 82.3	0.3 / 192.3	0.5 / 52.2	0.1 / 11.3
	Median / Mean	15.5 / 25.5	15.2 / 19.5	11.7 / 20.1	8.6 / 11.2	2.0 / 2.8
	Standard Dev.	30.0	16.1	29.8	11.0	2.6

Table 2.4 Events sampled in Year 1 (1999-2000)

Site ID	Date	Event Rain (mm)	Max. Intensity (mm/hr)	Antecedent Dry (days)	Peak Flow (L/s)	Cumulative Precipitation (mm)
7-201	01/17/00	1.27	3.05	17	0.32	1.27
	01/25/00	17.02	6.10	8	16.84	18.29
	01/30/00	2.54	3.05	5	1.14	20.83
	02/10/00	7.37	12.19	10	15.71	28.19
	02/11/00	18.54	15.24	1	46.37	46.74
	02/20/00	90.68	51.82	4	139.49	137.41
	02/27/00	3.30	6.10	4	6.18	140.72
	03/05/00	45.72	-	2	11.89	186.44
	03/08/00	17.78	12.19	2	22.21	204.22
	04/17/00	13.21	12.19	40	16.99	217.42
7-202	11/20/99	1.78	15.24	12	5.86	1.78
	01/17/00	1.78	3.05	17	0.32	3.56
	01/25/00	25.15	6.10	8	16.84	28.70
	01/30/00	12.70	6.10	5	1.14	41.40
	02/10/00	11.68	12.19	10	15.71	53.09
	02/11/00	25.15	24.38	1	46.37	78.23
	02/20/00	92.46	82.30	4	139.49	170.69
	02/27/00	7.37	15.24	4	6.18	178.05
	03/05/00	50.80	36.58	2	15.52	228.85
	03/08/00	23.37	12.19	2	22.21	252.22
	04/17/00	44.45	27.43	40	66.62	296.67
7-203	11/08/99	1.27	-	-	0.28	1.27
	12/31/99	0.51	-	41	0.28	2.54
	01/17/00	1.52	3.05	17	0.85	4.06
	01/25/00	18.29	6.10	8	16.99	22.35
	01/30/00	13.46	6.10	5	14.16	35.81
	02/10/00	14.99	24.38	10	15.57	50.80
	02/12/00	21.08	24.38	2	14.16	71.88
	02/20/00	58.93	45.72	4	24.92	169.67
	02/27/00	10.16	12.19	4	5.66	210.57
	03/04/00	5.84	24.38	6	11.33	216.41
	03/08/00	18.80	12.19	2	2.27	276.10
	04/17/00	56.39	51.82	40	19.82	332.49

Table 2.5 Events sampled in Year 2 (2000-2001)

Site ID	Date	Event Rain (mm)	Max. Intensity (mm/hr)	Antecedent Dry (days)	Peak Flow (L/s)	Cumulative Precipitation (mm)
7-201	10/26/00	23.88	9.14	33.63	27.13	32.51
	01/08/01	3.81	3.05	69.39	12.15	52.83
	01/10/01	127.00	51.82	1.98	63.12	179.83
	02/10/01	13.21	21.34	14.20	22.96	239.27
	02/19/01	7.11	6.10	5.36	8.52	375.16
	02/24/01	14.48	6.10	0.97	5.01	391.67
	03/04/01	11.94	6.10	4.02	10.39	473.20
	04/20/01	8.13	12.19	13.17	9.97	552.45
7-202	10/26/00	23.88	9.14	33.63	11.75	32.51
	01/08/01	5.08	3.05	69.39	4.62	54.10
	01/10/01	155.96	60.96	1.94	36.08	210.06
	02/19/01	23.88	15.24	4.84	17.08	375.41
	02/24/01	19.05	6.10	0.99	9.37	396.49
	03/04/01	8.89	12.19	4.02	18.41	474.98
	04/06/01	30.23	12.19	31.13	38.62	542.80
7-203	10/26/00	25.91	30.48	33.58	7.26	34.54
	01/08/01	5.33	6.10	69.36	5.80	56.39
	01/10/01	128.52	36.58	1.96	21.58	184.91
	02/10/01	15.49	21.34	14.21	11.41	246.63
	02/19/01	30.23	21.34	5.33	20.73	405.64
	02/24/01	11.43	9.14	0.99	3.34	419.10
	03/04/01	5.08	6.10	4.02	3.28	493.78
	04/06/01	25.40	21.34	31.57	9.88	556.77

Table 2.6 Events sampled in Year 3 (2001-2002)

Site ID	Date	Event Rain (mm)	Max. Intensity (mm/hr)	Antecedent Dry (days)	Peak Flow (L/s)	Cumulative Precipitation (mm)
7-201	11/12/01	7.87	3.05	11.90	68.44	9.40
	11/24/01	47.24	51.82	11.64	75.67	56.64
	12/20/01	10.67	21.34	6.26	24.65	68.33
	01/27/02	11.94	6.10	27.13	11.18	80.26
	02/17/02	2.03	3.05	20.38	4.71	82.30
7-202	10/30/01	3.30	6.10	192.20	14.25	3.30
	11/12/01	11.94	33.53	13.10	82.37	15.24
	11/24/01	50.29	51.82	11.69	123.97	65.53
	12/14/01	3.56	12.19	19.77	34.73	69.09
	01/27/02	31.75	15.24	27.13	30.27	123.44
	02/17/02	7.37	6.10	20.27	13.20	130.81
	03/06/02	2.54	3.05	17.61	3.91	133.35
	03/17/02	2.29	6.10	10.66	13.26	135.64
7-203	10/30/01	2.79	6.10	192.30	4.79	2.79
	11/12/01	7.37	27.43	13.10	12.88	10.16
	11/24/01	29.72	39.62	11.69	17.58	39.88
	12/20/01	12.19	33.53	6.31	13.88	54.10
	01/27/02	24.64	24.38	27.14	10.20	78.74
	02/17/02	7.37	9.14	20.31	9.80	86.11
	03/07/02	4.57	12.19	17.39	6.04	90.68
	03/17/02	10.41	24.38	10.60	16.40	101.09

Table 2.7 Events sampled in Year 4 (2002-2003)

Site ID	Date	Event Rain (mm)	Max. Intensity (mm/hr)	Antecedent Dry (days)	Peak Flow (L/s)	Cumulative Precipitation (mm)
7-201	11/07/02	28.96	12.19	40.13	21.10	30.23
	11/29/02	9.65	39.62	20.23	29.36	39.88
	12/16/02	29.72	18.29	16.43	49.41	76.45
	12/19/02	36.07	24.38	3.25	69.69	112.01
	02/11/03	23.37	18.29	44.27	24.95	146.81
	03/15/03	66.55	45.72	11.68	88.09	445.77
	05/02/03	50.29	51.82	18.10	77.84	495.81
7-202	11/07/02	58.67	18.29	41.21	109.44	58.42
	11/29/02	1.78	6.10	19.97	10.79	60.20
	12/15/02	2.54	6.10	16.21	18.86	62.23
	12/16/02	59.94	42.67	1.21	154.61	121.16
	02/11/03	24.38	15.24	44.26	37.99	204.72
	04/14/03	21.34	21.34	27.85	137.79	475.24
7-203	11/07/02	71.37	15.24	40.16	15.80	72.64
	11/29/02	1.52	6.10	19.96	0.93	74.17
	12/16/02	40.64	30.48	0.27	57.57	117.86
	12/19/02	32.51	18.29	3.09	25.06	151.13
	02/10/03	20.07	15.24	44.12	19.44	182.63
	03/15/03	123.19	39.62	11.68	48.32	538.48
	04/12/03	19.81	30.48	27.85	39.79	558.29

3. WATER QUALITY RESULTS

The large body of data collected over the four years to quantify the first flush has utility to describe the various parameters associated with highway runoff. To the best of the authors' knowledge, these three sites may have been more extensively monitored for a larger variety of parameters than any other highway sites. Since many of the site specific parameters for the three sites are similar (e.g., rainfall, average daily traffic, location, etc.) the pooled data represents an even larger data resource.

The parameters were monitored in two ways after the first year of the study: using a series of grab samples, and automatically sampled, flow-weighted composite samples. A flow weighted composite sample can be calculated from a series of grabs if the flow rates were simultaneously measured. The flow weighted composite sample, whether collected by an automated instrument or calculated from a series of grab samples, is called an event mean concentration or EMC. There are several procedures, and in Chapter 4 we describe some of the benefits of the various approaches. Before we present the EMCs of water quality parameters, we will show a proper method to compute the EMC from grab samples.

3.1 Computation of Event Mean Concentrations (EMCs)

Mathematically, EMCs can be defined as total pollutant mass (*M*) discharged during an event divided by total volume (*V*) discharge of the storm event.

$$EMC = \frac{M}{V} = \frac{\int C(t)Q(t)dt}{\int Q(t)dt} \tag{3.1}$$

In equation 3.1, $C(t)$ is a smooth real-valued function of time that represents the pollutant concentration curve, and $Q(t)$ is also a smooth real-valued function of time that represents the stormwater flow rate curve. However, in practice, the integrals are not by the functions of $Q(t)$ and $C(t)$ but approximations created by discrete measurements of $Q(t)$ and $C(t)$. If we assume we measure the concentration and the flow rate based on equal time-interval in a storm event, the EMC can be estimated as

$$EMC = \frac{\sum_i c_i q_i}{\sum_i q_i} \tag{3.2}$$

where q_i and c_i are the measurements for the discharge rate and pollutant concentration in the i^{th} interval. From the point of view of approximating the continuous functions in equation 3.1, the more measurements we take, the more accurate approximation we can obtain by equation 3.2. When we view the measurements of the flow rate as the weights, equation 3.2 becomes the discharge-weighted average throughout the storm event, as follows:

$$EMC = \sum_i w_i c_i \tag{3.3}$$

$$w_i = \frac{q_i}{\sum_i q_i} \tag{3.4}$$

where w_i is the flow weight, and $\sum_{i=1}^{n} w_i = 1$. In practice, one common situation is the number of concentration measurements does not match the number of flow measurements. Generally there are many fewer concentration measurements, because concentration measurements are much more expensive and time consuming; flow measurements can be easily and automatically obtained by the instrument. For most situations the weights must be adjusted for each concentration measurement in equation 3.3. One of the reasonable ways to adjust the weights is to use the discharge volume. One approach (Charbeneau and Barrett, 1998) splits the discharge volume from the mid-point between two consecutive concentration measurements. Figure 3.1 shows this approach, and the adjusted weight can be written as:

$$w_i = \frac{V_i}{\sum_i V_i} \tag{3.5}$$

where V_i is the corresponding discharge volume for the i^{th} concentration measurement. This mid-discharge splitting method can also be applied for measurements at unequal time-interval bases. Alternatively, if the concentration measurements are based on constant discharge volume, the weighted average of $w_i c_i$ form is reduced to the arithmetic average. Ideally, automated samplers can collect samples in proportion to discharge volume. Additionally there are always slight errors (noise) in sample volume and pace that change the equal weights. Thus, an EMC can be calculated using a series of flow-weighted grab samples.

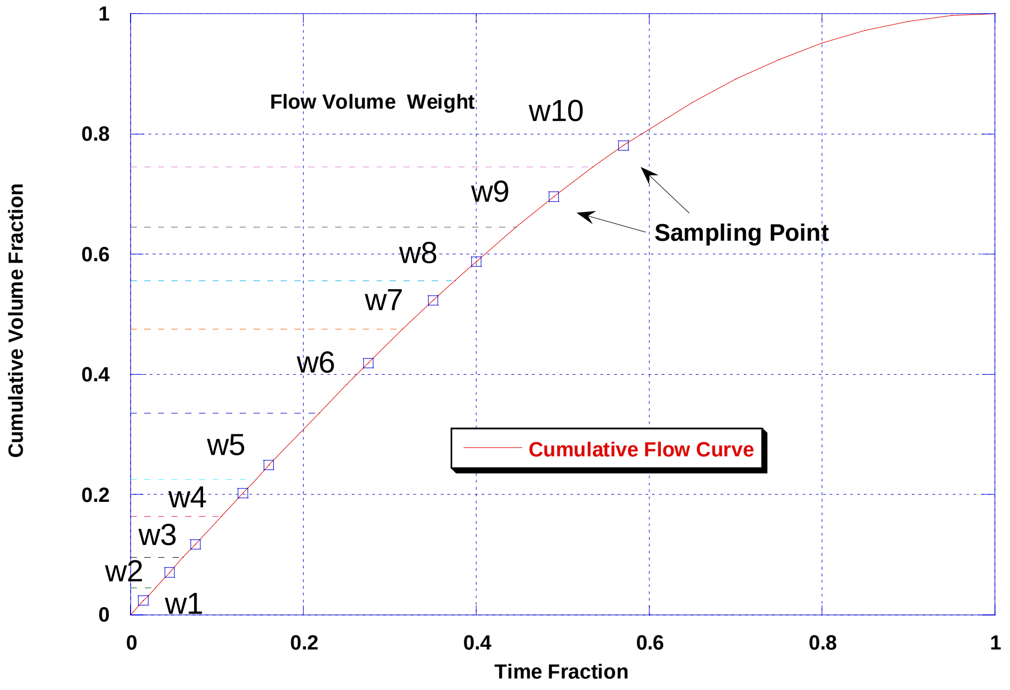


Figure 3.1 Example of flow weighing for EMC calculations.

The EMCs shown in this report were calculated from grab samples, using flow weights as described, unless noted otherwise.

3.2 EMCs of Water Quality Parameters

Table 3.1 shows the mean, median and EMCs for the pollutants measured during the four years of the study. The different estimates of the concentration are provided to show the variability. The maximum values for some values are startlingly high; for example, the maximum value of COD is 2282.8. These high numbers would have been unobserved if only automatic composite samplers had been used.

Table 3.1 Basic statistics of principal EMCs and grab samples for combined sites

Parameters	**No. of cases[1]**	**Mean of EMCs**	**Median of EMCs**	**Mean of Grabs**	**Median of Grabs**	**Min. of EMCs**	**Max. of EMCs**	**Std. Dev. of EMCs**
TSS (mg/L)	62 / 569	67.7	57.6	71.3	45.9	8.8	466.4	62.9
Turbidity (NTU)	62 / 569	46.8	33.0	52.0	31.9	10.9	170.5	39.2
Cond. (µmho/cm)	62 / 569	239.0	135.0	315.1	157.0	23.4	1991.7	302.7
Hardness (mg/L)	62 / 569	78.4	50.7	104.9	48.4	6.8	598.0	95.6
COD (mg/L)	62 / 569	252.3	119.8	321.3	138.5	19.3	2282.8	373.0
DOC (mg/L)	62 / 544	67.6	29.4	81.4	29.3	2.9	848.8	126.8
Oil & Grease (mg/L)	62 / 569	14.0	9.3	18.1	10.6	1.5	80.2	14.6
TKN (mg/L)	62 / 569	9.7	4.1	11.6	4.7	0.8	111.3	16.4
NH_3-N (mg/L)	62 / 569	4.6	1.4	5.5	1.3	0.1	65.0	9.7
NO_2-N (mg/L)	62 / 569	0.3	0.2	0.5	0.2	0.0	3.0	0.4
NO_3-N (mg/L)	62 / 552	2.7	1.2	3.2	1.5	0.0	34.7	5.3
Total P (mg/L)	43 / 564	0.9	0.4	895.8	437.1	0.1	8.2	1.6
PO_4-P (mg/L)	45 /138	0.3	0.1	653.2	355.0	0.0	2.7	0.5
Dissolved P (mg/L)	62 / 566	0.7	0.2	740.1	291.0	0.1	7.3	1.3
Total Cd (µg/L)	24 / 361	2.5	1.4	3.0	1.1	0.5	20.2	3.9
Total Cr (µg/L)	58 / 563	10.1	8.8	10.5	8.4	2.4	40.1	6.3
Total Cu (µg/L)	62 / 564	93.1	55.7	113.9	64.7	16.2	920.8	125.2
Total Ni (µg/L)	62 / 563	20.0	11.2	23.3	12.8	2.3	253.7	33.9
Total Pb (µg/L)	47 / 556	33.0	25.0	24.6	19.2	4.6	239.1	38.1
Total Zn (µg/L)	62 / 558	506.4	267.9	564.9	274.0	83.4	8881.3	1137.0
Dissolved Cd (µg/L)	43 / 299	1.3	0.5	2.4	0.8	0.5	17.8	2.7
Dissolved Cr (µg/L)	58 / 495	2.8	2.0	3.5	2.3	0.5	19.3	2.8
Dissolved Cu (µg/L)	62 / 566	65.9	35.4	85.5	39.2	5.3	735.3	103.9
Dissolved Ni (µg/L)	62 / 558	15.7	7.9	18.9	8.7	0.5	229.2	31.3
Dissolved Pb (µg/L)	47 / 392	4.9	3.6	6.0	4.1	0.5	43.5	6.5
Dissolved Zn (µg/L)	62 / 562	415.4	177.7	465.5	184.0	42.4	8150.0	1055.7

[1] Number of events / total number of grab samples

Of particular interest are the particulate forms of the metals, since they have the greatest opportunity for removal through removal of the suspended solids. Soluble metals are much more difficult to remove, requiring ion exchange, precipitation or reverse osmosis.

Table 3.2 shows the percentage of the metals that are sorbed to suspended solids. The percentage sorbed ranges from nearly zero to 100%. In general, Cd, Cr and Pb are particulate-bound and Cu, Ni and Zn are more associated with the dissolved phase.

In future projects the association between metals and particles will be further investigated. There is evidence in our study, mostly anecdotal at present, that the soluble metals are not in equilibrium and that sorption to particles is continuing well after 24 hours. Our protocol required metal samples to be filtered within 24 hours (essentially ending the sorption process), but were generally filtered in less than 12 hours. In a future project, we hope to investigate the rate of sorption and equilibrium of soluble metals during the 24 hours after sample collection. If the metals equilibrium is shifting towards the particulate phase, it is a useful finding for BMP selection, since BMPs can generally remove pollutants sorbed to suspended solids than soluble pollutants.

Table 3.2 Summary statistics for particulate-bound metals (% of total metals sorbed to solids)

		Site 1	**Site 2**	**Site 3**	**Combined**			**Site 1**	**Site 2**	**Site 3**	**Combined**
No. of cases	Cd	130	164	150	444	Standard Dev	Cd	27.7	33.8	30.9	31.7
	Cr	171	192	193	556		Cr	19.0	15.3	15.4	16.9
	Cu	172	192	200	564		Cu	15.7	20.6	22.8	20.8
	Ni	172	192	200	564		Ni	20.9	22.4	24.6	23.0
	Pb	163	192	200	555		Pb	18.3	15.2	18.7	17.9
	Zn	166	192	200	558		Zn	20.9	26.1	19.1	22.7
Minimum	Cd	6.9	0.0	5.0	0.0	Maximum	Cd	100.0	100.0	100.0	100.0
	Cr	0.2	16.0	30.2	0.2		Cr	100.0	100.0	100.0	100.0
	Cu	0.2	2.3	2.1	0.2		Cu	91.5	84.0	85.3	91.5
	Ni	0.3	0.9	1.4	0.3		Ni	100.0	87.5	90.6	100.0
	Pb	23.2	25.3	7.5	7.5		Pb	100.0	100.0	99.5	100.0
	Zn	0.8	1.2	0.3	0.3		Zn	92.1	93.4	78.7	93.4
Median	Cd	57.2	50.0	50.0	50.0	Mean	Cd	69.4	53.7	58.2	59.8
	Cr	71.4	74.8	74.4	73.7		Cr	66.3	73.8	73.9	71.5
	Cu	26.1	42.4	25.7	31.1		Cu	29.2	42.0	32.7	34.8
	Ni	22.2	31.9	28.8	27.9		Ni	28.2	35.4	35.3	33.2
	Pb	90.8	92.5	81.7	87.6		Pb	84.0	86.5	77.1	82.4
	Zn	21.4	33.6	19.6	24.1		Zn	27.8	36.5	25.3	29.9

Note: Site 1, 2 and 3 are 7-201, 7-202 and 7-203, respectively.

3.3 Correlation among Water Quality Parameters

The correlation among pollutants and TSS is also interesting and important. Tables 3.3 and 3.4 show the correlations. The numbers above the line are the Pearson correlation coefficient, frequently referred to as "R." Below the line are the probabilities associated with obtaining a random result with the same value of R (lower numbers indicate less likelihood of a random or artifactual finding). Generally, probabilities less than 0.05 are considered significant results.

The organic or oxygen demanding pollutants shown in Table 3.3 are particularly significant. The COD and DOC are highly correlated, suggesting that the COD is primarily composed of organic compounds, and not reduced inorganic, such as nitrite, sulfur compounds and certain metals. This is also an important correlation for an important finding described later between Oil and Grease and COD. The high correlations suggest one of two things: either the two correlated pollutants are measuring the same material, or that the sources of the pollutants are similar or release the pollutants in similar ways.

For the case of COD and DOC, the two parameters are measuring similar properties. The DOC measures the amount of organic carbon, but not its oxidation state. For COD, the tendency to react with oxygen is measured. The two are related depending on the form of the carbon. For example, methane, the most reduced form of organic carbon, has an oxygen demand weight ratio of 5.6 (e.g., 5.6 grams of oxygen are consumed for each gram of methane oxidized). For a highly oxidized form of carbon, such as carbon monoxide, the ratio is only 1.3. The high correlation between COD and DOC suggests that the oxygen-consuming pollutants are organic and have relatively consistent oxidation state.

The high correlations between different metals probably suggest similar sources. For example, metals used in manufacturing are frequently alloys, such as brass, which is an alloy of Cu, Zn and Pb. Brass particles would show all three metals in the analysis.

The poor correlation of particulate Cd and TSS shows that the sorbed Cd varies with TSS concentration. Even though the percentage sorbed is high, as shown in Table 3.2, a treatment system removing particulates would have a varying Cd removal rate. The high variability associated with Cd may be in part related to its low concentration, which is usually near the detection limits of the analytical procedures.

Table 3.3 Correlation analysis results among non-metals and TSS

Water Quality Parameter	TSS	COD	DOC	O & G	TKN	NH_3-N	T-P
TSS	1	0.40	0.34	0.38	0.40	0.39	0.35
COD	0.00	1	0.95	0.83	0.84	0.79	0.74
DOC	0.00	0.00	1	0.98	0.89	0.88	0.60
O & G	0.00	0.00	0.00	1	0.89	0.85	0.84
TKN	0.00	0.00	0.00	0.00	1	0.84	0.87
NH_3-N	0.00	0.00	0.00	0.00	0.00	1	0.81
Tot. P	0.00	0.00	0.00	0.00	0.00	0.00	1

- above the diagonal : Pearson's Coefficient "r"
- below the diagonal : Probability Values (P-Value)

Table 3.4 Correlation analysis results for particulate phase metals and TSS

Parameter	TSS	Part. Cd	Part. Cr	Part. Cu	Part. Ni	Part. Pb	Part. Zn
TSS	1	0.02	0.59	0.58	0.57	0.60	0.60
Part. Cd	0.67	1	0.02	0.30	0.26	0.62	0.75
Part. Cr	0.00	0.60	1	0.75	0.70	0.65	0.70
Part. Cu	0.00	0.00	0.00	1	0.85	0.70	0.83
Part. Ni	0.00	0.00	0.00	0.00	1	0.70	0.75
Part. Pb	0.00	0.00	0.00	0.00	0.00	1	0.74
Part. Zn	0.00	0.00	0.00	0.00	0.00	0.00	1

- above the diagonal : Pearson's Coefficient "r"
- below the diagonal : Probability Values (P-Value)

4. FIRST FLUSH RESULTS AND DISCUSSION

This chapter discusses the measured first flush of the various monitored parameters. The parameters have been ranked according to the magnitude of the first flush. In order to rank the first flush, a new parameter was developed, called the mass first flush ratio (MFF). Other first flush characteristics discussed in this chapter include PAHs, litter, and particles (based upon particle counting methods and not TSS). The results of seasonal first flush have also been discussed in this chapter..

4.1 Meaningful Definition of First Flush for Practical Application

The first flush of the highway runoff sites were characterized with mass first flush ratios. As noted in the introduction, this ratio is a quantitative method of concepts proposed earlier. It quantifies the mass of emitted pollutants as a function of the storm progress, as indicated by the normalized runoff volume (e.g., 0 to 1, with 1 being the total volume). It is defined as follows:

$$MFF_n = \frac{\dfrac{\int_0^{t_1} C(t)Q(t)dt}{M}}{\dfrac{\int_0^{t_1} Q(t)dt}{V}} \tag{4.1}$$

In equation 4.1, MFF is the mass first flush ratio, and is dimensionless; n is the index or point in the storm, and corresponds to the percentage of the runoff, ranging from 0 to 100%. M is the total mass of emitted pollutant, V is the total runoff volume, C(t) and Q(t) are the pollutant concentration and runoff volume as functions of time. The terms have the same meaning as used earlier in equation 3.1 that defined the EMC.

By definition, the MFF is equal to zero at the storm beginning and always equals 1.0 at the end of the storm. Values greater than 1 indicate that normalized mass is being discharged faster than the normalized volume, or a first flush.

The MFF can be defined or visualized graphically, and Figure 4.1 shows the concept for a hypothetical storm. The normalized pollutant mass emission is plotted as a function of the normalized flow volume. This line is sometimes called a “load graph.” The MFF can be calculated at any point on the curve by dividing the Y axis value by the X axis value.

In Figure 4.1, two points were selected at normalized runoff volumes of 0.1 and 0.3, or 10 and 30% of the storm volume (i.e., n = 10 and n = 30). The intersection of the load graph for 10 and 30 are 0.45 and 0.66. This means that 45% of the pollutant mass was discharged in the first 10% of the runoff, and 66% of the mass was discharged in the 20% of the runoff. The MFF ratio is the quotient of the normalized pollutant mass divided by the normalized pollutant volume. Figure 4.1 shows the MFF_{10} = 4.5 and MFF_{30} = 2.2. To calculate the percentage of pollutant discharged at a point in the storm using the MFF ratio, the index is multiplied by the ratio, or 10 x 4.5 =45% or 30 x 2.2 = 66%.

Calculating the first flush requires a series of grab samples, or at least two flow weighed composite samples. The ratio can be conveniently calculated using the series of grab samples as shown in the previous chapter for EMC calculation. Alternatively, a full storm composite sample, as normally collected, can be used for the denominator of the MFF ratio. The numerator can be a second flow-weighted composite sample, which must be collected from the storm beginning to the point in the storm corresponding to n. The MFF ratio or knowledge of the first flush cannot be determined from routine monitoring data, and the data collected in this study are unique among the Department's stormwater monitoring programs.

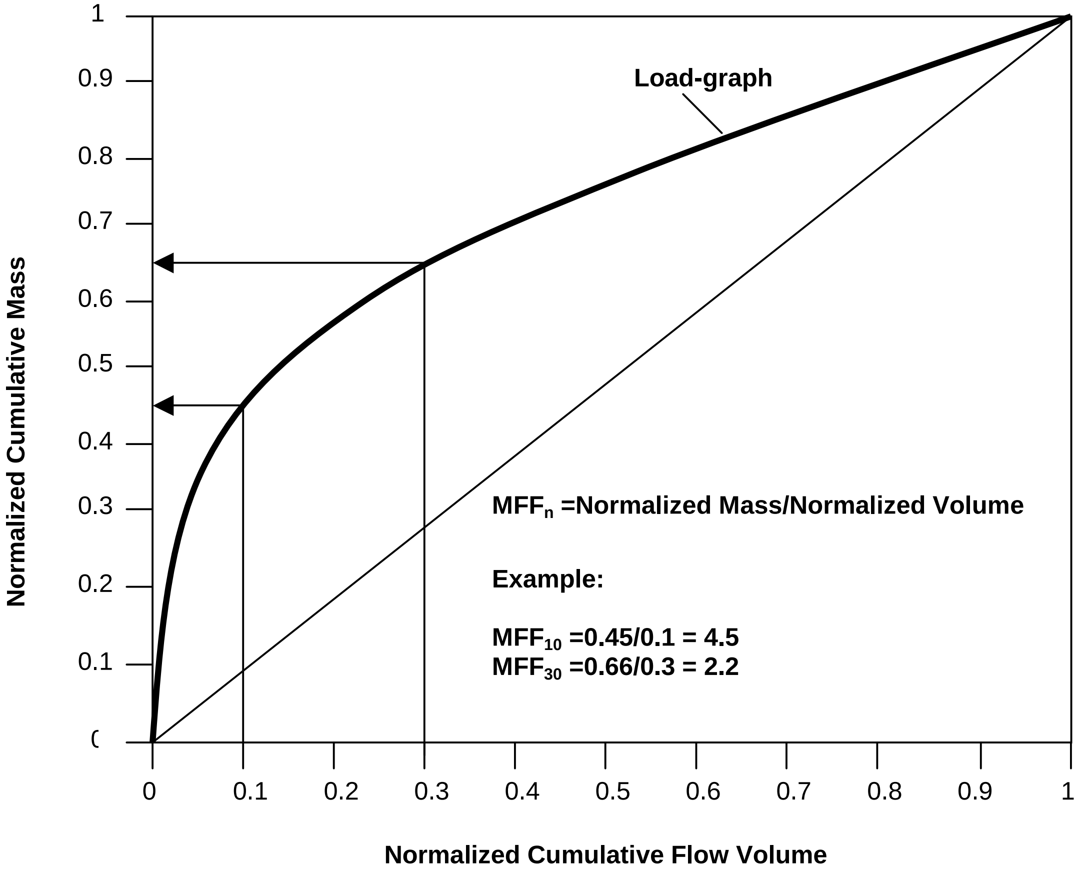


Figure 4.1 Load graph example of MFF calculation.

The MFF ratio can be related to another concept called the partial EMC or PEMC. The PEMC is a flow weighted composite sample, collected from the storm beginning to a point in the storm, as described in the previous paragraph. The MFF ratio can be defined as follows, and is numerically the same as calculated from equation 4.1

$$MFF_n = PEMC_n/EMC \qquad (4.2)$$

MFF ratios have been calculated for the last three years of the study (data from the first year was not suitable, since the tail of the storm was monitored with only a composite sample). The appendix contains the MFF ratios, calculated from 10 to 50% of the storm, for all events and for all parameters.

Table 4.1 shows the MFF_{20} ratios for all three UCLA sites and the pooled data for all three sites, for 26 pollutants. They are ranked by magnitude. Generally the chemical oxygen demanding (COD) or organics indicating pollutants (DOC, O&G, TKN) have the highest MFF ratios. It should be expected that they have similar ratios, since they are highly correlated, as shown in the last chapter. The fact that their values are high suggests that they are washed or scoured from the sites early in the storm.

Table 4.1 Ranked mass first flush ratios for MFF_{20}

Rank	**7-201**		**7-202**		**7-203**		**Combined Sites**	
	Parameters	**Median**	**Parameters**	**Median**	**Parameters**	**Median**	**Parameters**	**Median**
1	COD	1.740	Dissolved Ni	2.086	DOC	2.511	Dissolved Ni	1.943
2	Total P	1.706	DOC	2.005	Dissolved Ni	2.405	DOC	1.942
3	Dissolved P	1.688	NH_3-N	2.000	COD	2.326	TKN	1.895
4	TKN	1.589	Total Zn	1.999	TKN	2.180	COD	1.883
5	Dissolved Ni	1.577	Dissolved Cu	1.982	Dissolved Cu	2.122	NH_3-N	1.882
6	Oil & Grease	1.567	COD	1.948	NH_3-N	2.099	Dissolved P	1.748
7	TSS	1.559	TKN	1.944	TSS	1.980	TSS	1.718
8	NH_3-N	1.558	Dissolved Zn	1.927	Total Ni	1.864	Total P	1.717
9	DOC	1.522	Dissolved P	1.862	Total Cu	1.792	Oil & Grease	1.699
10	Total Ni	1.489	Total Ni	1.845	Oil & Grease	1.787	Dissolved Cu	1.680
11	Total Zn	1.484	Total Cu	1.714	Dissolved P	1.747	Total Ni	1.680
12	Dissolved Zn	1.428	Oil & Grease	1.709	Total P	1.747	Total Zn	1.666
13	Conductivity	1.416	Total P	1.703	Conductivity	1.741	Dissolved Zn	1.657
14	Dissolved Cu	1.401	NO_3-N	1.486	Dissolved Zn	1.661	Total Cu	1.644
15	Total Cu	1.396	Total Cd	1.459	Total Zn	1.652	Conductivity	1.538
16	NO_2-N	1.392	Turbidity	1.429	Hardness	1.607	Hardness	1.484
17	Total Cr	1.358	TSS	1.416	NO_3-N	1.573	NO_2-N	1.371
18	Turbidity	1.299	Dissolved Pb	1.377	NO_2-N	1.369	NO_3-N	1.345
19	Total Pb	1.225	PO_4-P	1.366	Dissolved Pb	1.339	Turbidity	1.288
20	Hardness	1.200	Dissolved Cr	1.349	Total Cd	1.269	Total Cd	1.264
21	Dissolved Cr	1.152	Total Pb	1.323	Total Cr	1.224	Total Pb	1.230
22	Total Cd	1.074	Dissolved Cd	1.307	Total Pb	1.131	Total Cr	1.223
23	Dissolved Cd	1.001	NO_2-N	1.251	Turbidity	1.093	Dissolved Pb	1.206
24	Dissolved Pb	1.000	Hardness	1.227	Dissolved Cd	1.091	Dissolved Cr	1.172
25	PO_4-P	1.000	Conductivity	1.214	Dissolved Cr	1.040	Dissolved Cd	1.087
26	NO_3-N	0.983	Total Cr	1.200	PO_4-P	1.000	PO_4-P	1.000

The range or statistical variability of the MFF ratios is also important. Table 4.1 shows only the median values. Figures 4.2 and 4.3 show notched box plots of the MFF_{10} to MFF_{50} ratios for combined sites for COD, TSS and the six metals of most interest to the Department (Cd. Cr, Ni, Pb, Cu and Zn). The bar plots show the 25% and 75% percentiles (edges of the bar), the median (notch of the bar), confidence intervals (5%, upper and lower knees), fences and outliers. Different software produces slightly different notch bar plots. Systat 10.2 (Richmond, CA) was used to produce all the notched bar plots in this report. The advantage of notched bar plots over standard bar plots is the ability to observe statistical differences in categories. If the knees of the notches do not overlap, there is a significant difference in the categories.

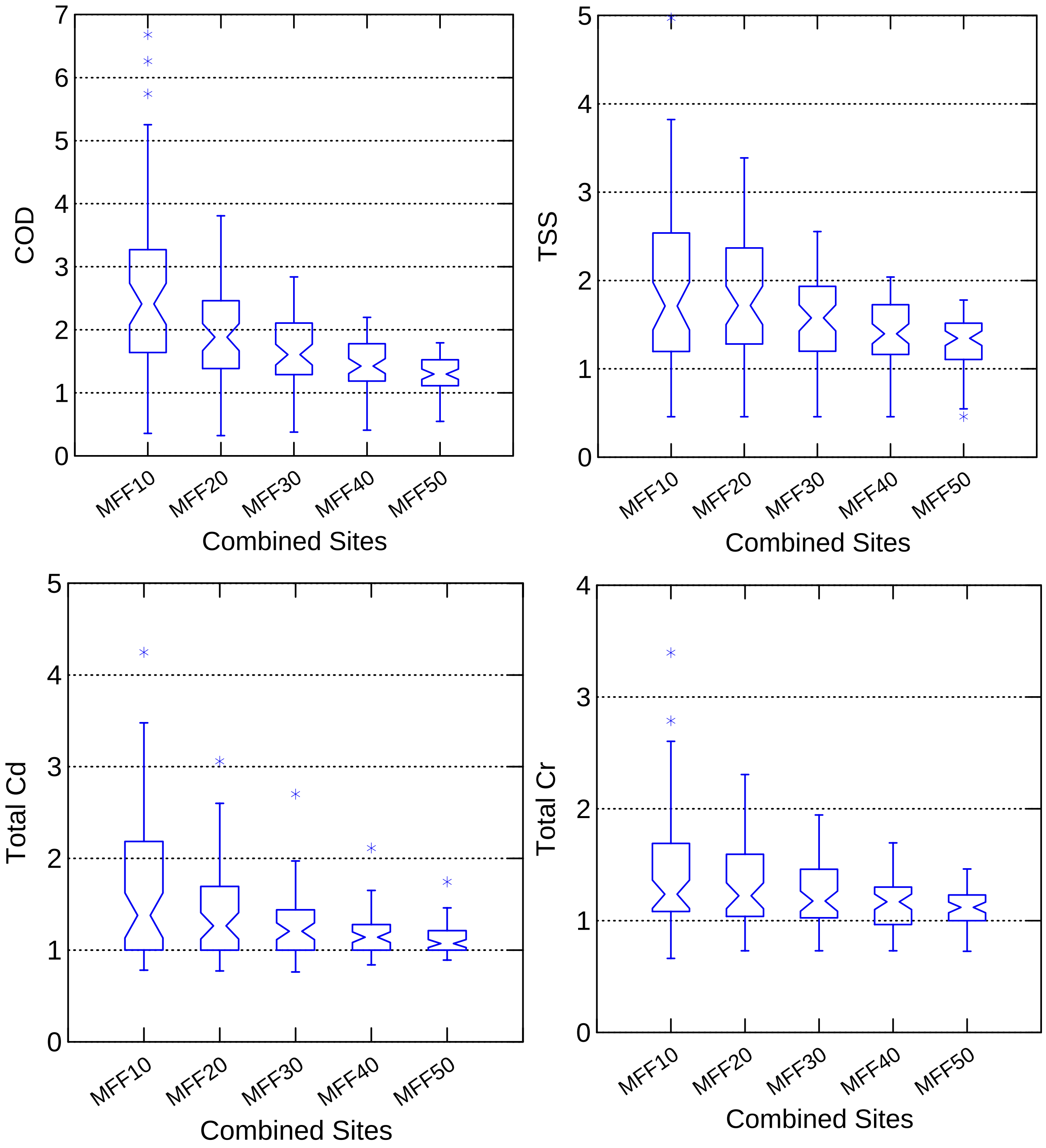


Figure 4.2 Notched bar graphs for MFF ratios (10 to 50%) for COD, TSS, Total Cd and Total Cr for the combined sites (The number of cases is 58 for COD and TSS, and 62 for metals).

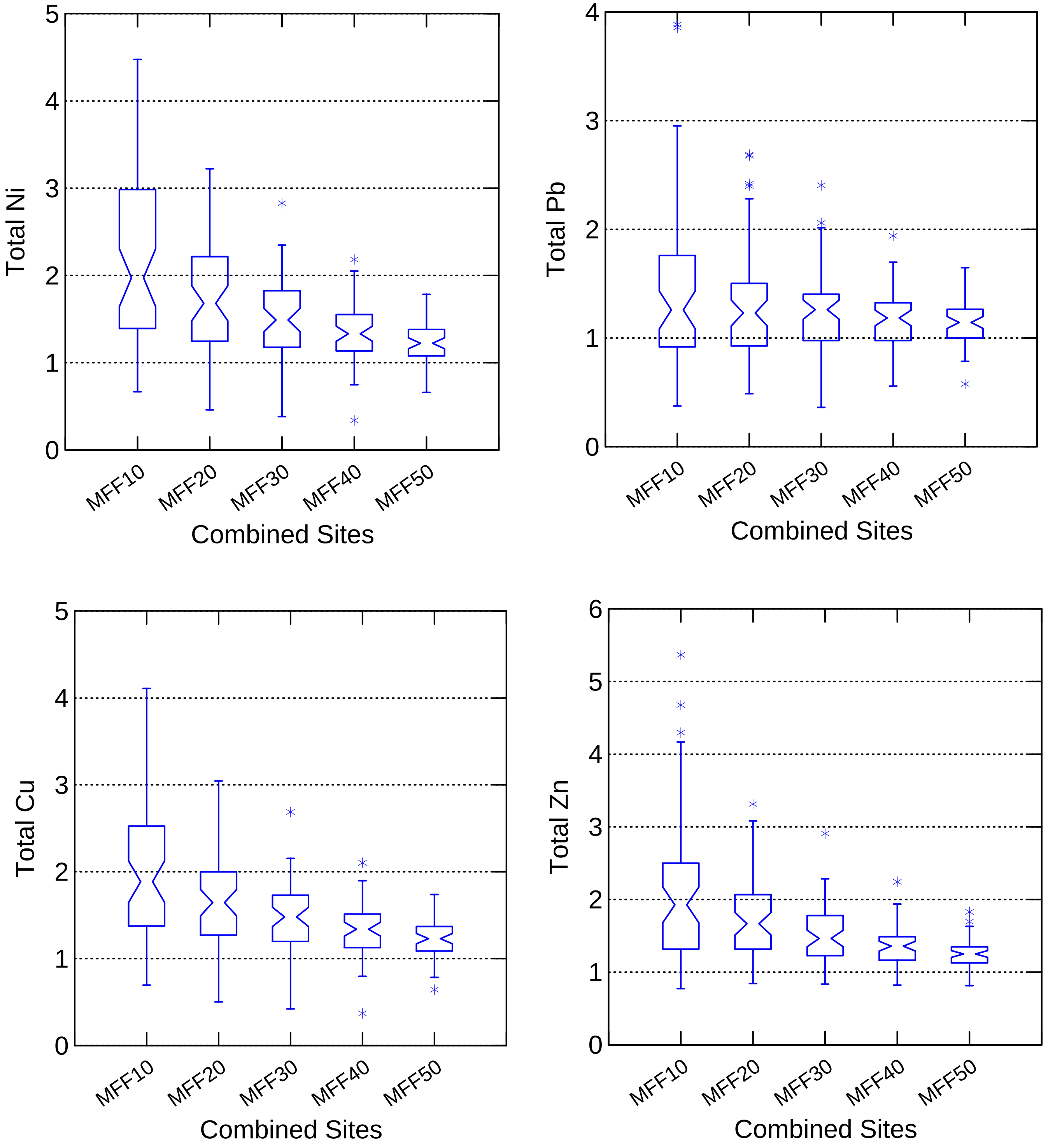


Figure 4.3 Notched bar graphs for MFF ratios (10 to 50%) for Total Ni, Pb, Cu and Zn for the combined sites (The number of cases is 58 for COD and TSS, and 62 for metals).

Ratios for the individual sites, including those monitored by the consultants are shown in the appendix. All the ratios measured in this investigation decline with increasing runoff volume. It is possible that a ratio at a larger flow volume could be larger than a ratio for a smaller volume, but an unusual runoff behavior would have to occur.

As noted earlier the MFF ratios for the different pollutants are in many cases highly correlated, and the correlations are shown in the appendices. Unfortunately, no significant correlations have been found yet between MFF ratios and storm and site parameters, such as ADD, ADT, rainfall intensity, and total rainfall. At present the Pearson-type correlations, which are useful for describing linear relationships, have been investigated. There are other opportunities to detect meaningful relationships. Techniques that will be investigated in our future work will include component analysis, Bayesian analysis and neural networks. These have been successfully applied by our group (Ha, et al, 2003) for determining relationships among water quality parameters and land use. These tools are better in detecting non-linear relationships.

4.2 PAH First Flush

Polynuclear aromatic hydrocarbons (PAHs) are often associated with highway runoff and combustion residuals. PAHs are included in organic measurements such as COD and DOC, but are generally so low in concentration that there first flush behavior cannot be determined from these measurements. In order to measure the first flush of PAHs, 32 different PAHs were measured at three sites over the study. At first, both soluble and particulate phase PAHs were measured. Soluble phase PAHs were rarely above the detection limit of 5 ng/L, and the analysis was abandoned. Particulate phase PAHs were found, and Table 4.2 shows typical results. Figure 4.4 shows the MFF ratios for total PAHs.

Table 4.2 Particulate phase PAHs for Site 1, 2001-2002 season

PAH Compound	**EMC (ng/L)**							
	10/30	**11/12**	**11/24**	**12/14**	**1/27**	**2/17**	**3/7**	**3/17**
Napthalene	28	6		17	6	2		11
Acenapthylene								
Acenapthene								
Fluorene								
Phenanthrene	83	24	14	54	21	22	29	42
Anthracene	14			14				
Fluoranthene	226	53	31	277	59	73	98	166
Pyrene	511	128	73	532	134	144	220	356
Benz[a]anthracene	93	24	17	102	24	29	31	50
Chrysene	332	85	51	295	86	108	179	241
Benzo[b]fluoranthene	57	41	22	124	38	38	25	84
Benzo[k]fluoranthene	60	11	9	59	13	20	22	30
Benzo[a]pyrene	147	48	28	124	44	48	71	113
Indeno[1,2,3,cd]pyrene	65	16	9	24	8	7		31
Dibenzo(ah)anthracene				0				
Benz[g,h,i]perylene	296	86	41	229	73	74	100	195
Total PAHs	1882	529	300	1852	511	568	778	1327

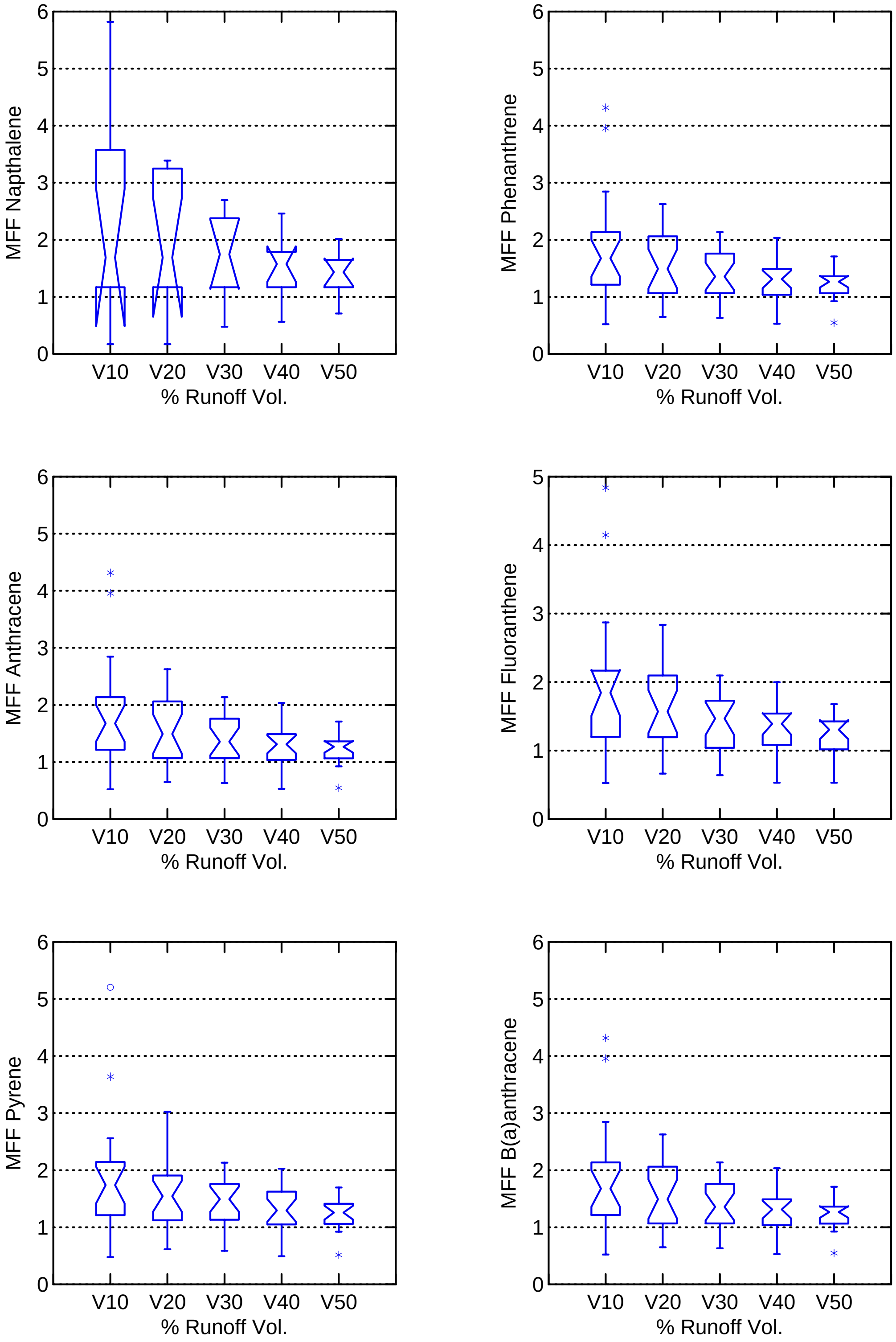


Figure 4.4 Notched bar graphs showing MFF ratios for various PAHs.

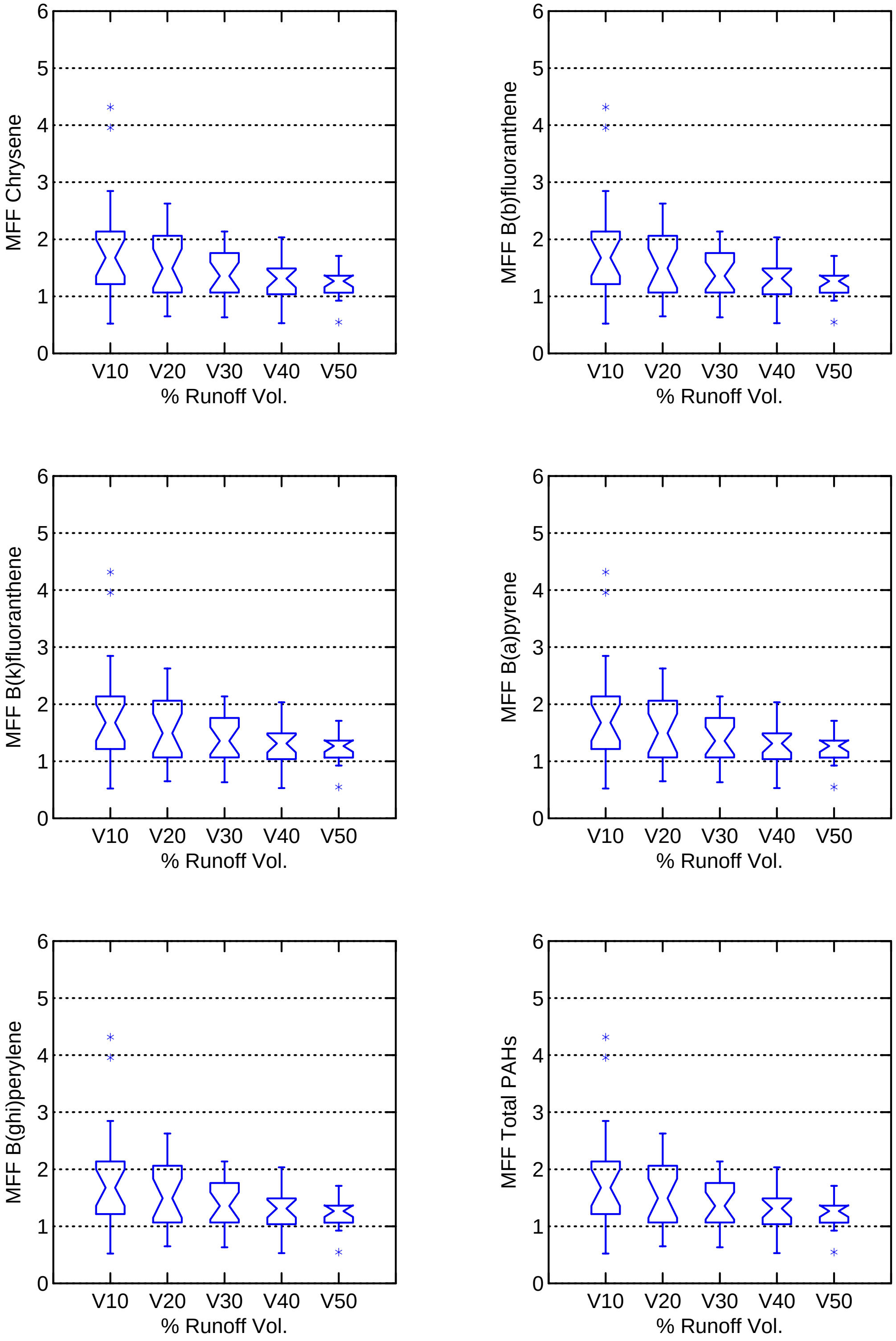


Figure 4.4 (Continued) Notched bar graphs showing MFF ratios for various PAHs.

PAHs generally showed a first flush in the same order as organic pollutants such as COD and DOC, and enhanced removal of PAHs will occur if BMPs that treat the first flush are used.

4.3 Litter First Flush

Litter is generally not considered a water quality parameter, but has been regulated by the Los Angeles Regional Water Quality Control Board under its total maximum daily load (TMDL) program. The Department's first flush criterion for litter is defined as the litter mass fraction within the first two hours of the storm event. If more than 50% of the mass is emitted during the first two hours, it is called a first flush. The litter first flush observation based on the litter ratio is presented in Table 4.3 for selected events. The occurrence of a first flush was not consistently observed at all monitoring sites during the same storm event. Similarly, review of the litter pollutographs and load-graphs indicate that the first flush phenomenon was occasionally observed in all sites during certain storm events. Table 4.3 shows that site 6-20F most consistently exhibited a first flush. During the storm event of January 10, 2001, site 6-20F, 8-23C and 23 showed significant first flush effects, but there was none present for site 7-202 and 7-203. This storm event also had the highest relative rainfall intensity of the season.

Table 4.3 Fraction of litter occurring in the first 2 h of runoff [a]

Parameters		Gross Pollutant Wet Weight	Gross Pollutant Wet Volume	Litter Wet Weight	Litter Wet Volume	Litter Air Dry Weight	Litter Air Dry Volume	Biodegradable Dry Weight	Biodegradable Dry Volume
7-202	10/26/01	0.02	0.03	0.04	0.05	0.03	0.06	0.03	0.04
	1/8/01	0.98	0.95	0.98	0.97	0.96	0.97	0.97	0.98
	1/10/01	0.05	0.11	0.53	0.39	0.48	0.5	0.5	0.63
7-203	10/26/01	0.92	0.73	0.85	0.62	0.81	0.61	0.64	0.4
	1/8/01	0.94	0.9	0.98	0.96	0.98	0.96	0.98	0.95
	1/10/01	0.2	0.27	0.59	0.31	0.38	0.34	0.49	0.37
	2/10/01	0.25	0.26	0.15	0.13	0.12	0.1	0.15	0.1
	2/19/01	0.61	0.57	0.85	0.71	0.92	0.74	0.75	0.57
6-20F	10/26/00	0.23	0.29	0.33	0.35	0.29	0.34	0.24	0.31
	1/10/01	0.98	0.96	0.94	0.96	0.96	0.94	0.97	0.94
	1/26/01	0.87	0.88	0.94	0.96	0.96	0.96	1	0.93
	2/10/01	0.97	0.95	0.99	0.93	0.99	0.94	0.99	0.93
8-23C	10/26/00	0.19	0.2	0.14	0.12	0.12	0.12	0.16	0.14
	1/10/01	0.77	0.68	0.58	0.7	0.53	0.62	0.77	0.7
	2/24/01	0.22	0.32	0.37	0.43	0.37	0.33	0.46	0.33

[a] Due to low rainfall in 2001-2002 monitoring season, limited litter data were collected.

Gross pollutant and litter data were also reviewed and compared on a multi-event basis to evaluate a potential effect of the first storm event of the season. It was hypothesized that the first storm event of the season would have the highest relative amount of litter mass, volume and mass loading compared to subsequent storm events. Table 4.3 shows that the first monitored storm event of the season did not produce a relatively greater amount of litter when compared to the subsequent storm events. The existence of a first flush and the mass of gross pollutants may be a function of the total or maximum intensity of rainfall. Gross pollutants are retained on the surfaces and in catch basins and pipes, and a minimum flow may be required to mobilize them. If the first rainfall of the season is large but lengthy with low intensity, gross pollutants may not be mobilized. Conversely, a short, intense rainfall may mobilize more pollutants.

The ratio of biodegradable to non-biodegradable litter was calculated for each event and site. The values varied considerably during each storm event. Site 6-20F, the site with the highest normalized litter mass loading, consistently had higher amounts of biodegradable litter. Site 7-202 had more non-biodegradable litter. On average for all sites, a slightly greater percentage (approximately 60%) of biodegradable litter was measured in the first flush of the storm events. This was consistent with individual storm event observations where lighter biodegradable litter appeared to be washed out first, leaving the relatively heavier non-biodegradable litter to wash out with the remainder of the storm event during the peak flow periods.

Gross pollutant and litter data were evaluated as pollutographs (concentration versus time) and load-graphs (mass loading rate versus time) for each event and site. The litter concentrations were calculated as the dry litter mass divided by the total flow volume during the time of the litter sample collection. The litter mass loading rates were calculated as the dry litter mass divided by the elapsed time of litter collection, and normalized by the catchment area. These plots were compared to the respective hydrographs to determine the potential relationships to flow intensity and storm duration. The plots were also used to determine whether a first flush effect (i.e., relatively higher litter concentrations early in the event, followed by a decrease in concentration after a period of time) was present. Figure 4.5 shows an example of combined litter pollutograph and load-graph for the first event of the season. The first event of the season at site 7-201 shows very high dry litter concentration and load in first hour.

Evaluation of the litter load-graphs, however, presented no clear observations of a first flush phenomenon. In many instances, the litter mass loading rates were not highest during the first portion of a storm event; the highest litter mass loading rate was observed later in the storm event, after the peak flow had occurred.

Figure 4.6 shows the normalized wet gross, vegetation and litter rates for each event at site 7-203. The storm event, October 30, 2001, is the first storm at site 7-203. The mass rate is not higher compared to other events. The mass rates vary to event-to-event and influenced by several factors such as antecedent dry days and total rainfall. A regression model was developed to describe litter EMC as a function of antecedent dry days and total rainfall. Detail information on regression model and additional litter characterization is presented elsewhere (Kim, et al., 2004).

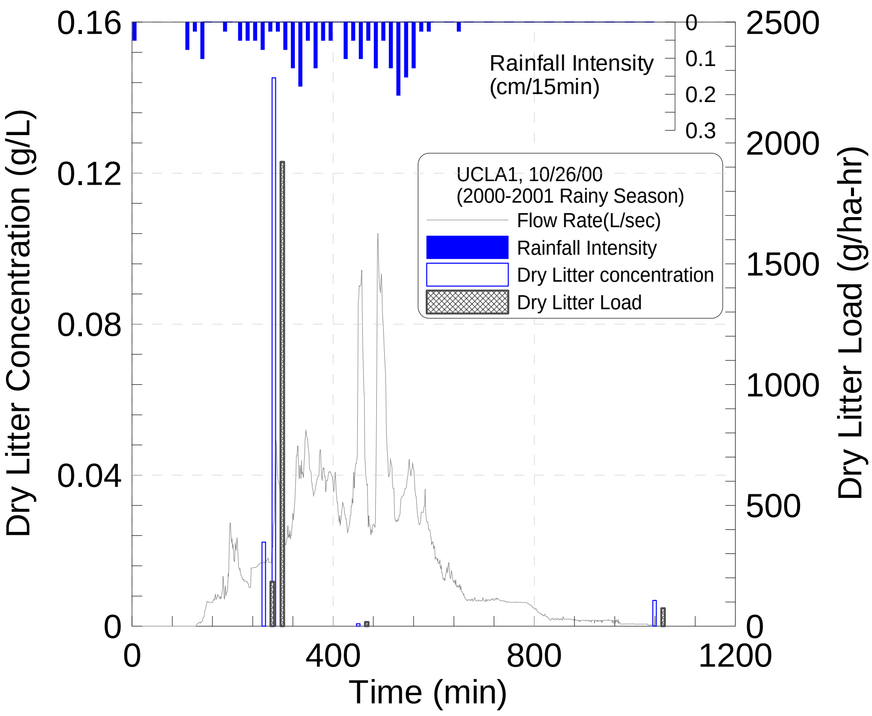


Figure 4.5 Litter polluto- and load-graphs for a storm event (with hydrograph shown in background).

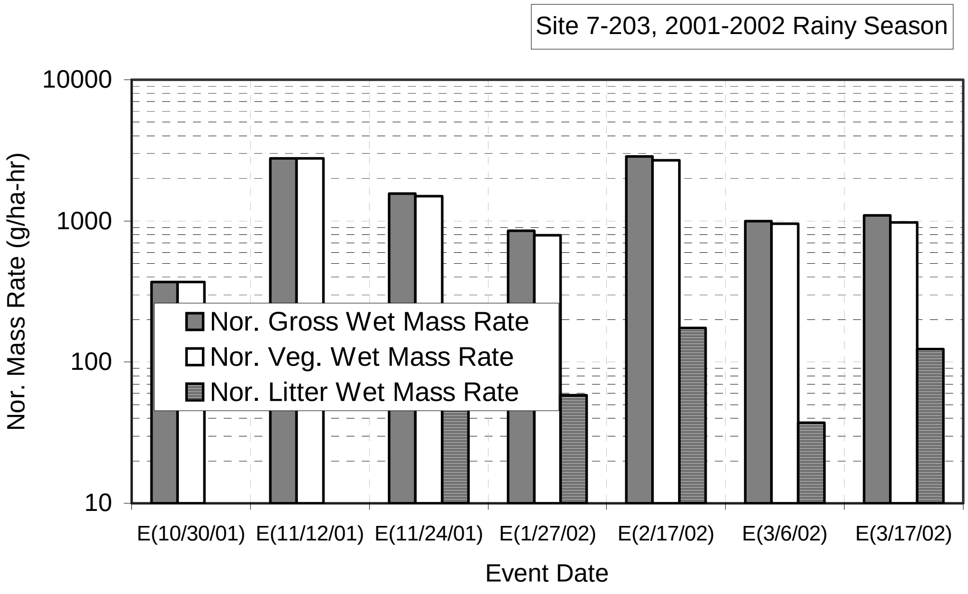


Figure 4.6 Normalized mass rates as function of catchment area and storm duration.

4.4 Particle First Flush

During the third year of the project, a particle size analyzer was acquired which can measure the number of particles from 2 to 1000 μm (Nicomp, Santa Barbara, California, PSS AccuSizer 780 Optical Particle Sizer module equipped with an auto-dilution system and a LE1000-2SE Light Scattering/Extinction sensor). This instrument has never been used in stormwater monitoring and required new protocols to be developed to reliably and accurately quantify the particles in highway runoff. The work on this topic is embryonic, and is the subject of our future work. The appendices include the entire text of a technical memorandum on its use.

The developed protocol included the following components:

1. Storage time. Sample storage is limited to 6 hours. After 6 hours, there is a noticeable aggregation in particle size. Therefore composite samples cannot be used (the time in the sampler is usually longer than 6 hours)
2. Bottle cleaning. Sample bottles must be rigorously clean and a protocol was developed that limited spurious particles to less than 250/ml, which was adequately compared to the range of particles in stormwater, which was 10^4 to 10^7/ml.
3. Mixing. Samples stored in bottles for even a few minutes need to be mixed so that a representative subsample can be collected. A mixing protocol was developed that insured a representative sample. The mixing had to be adequate to resuspend all particles without shearing them into smaller particles.
4. A series of reproducibility measurements were made. Generally the reproducibility of the method is within 5% for particles less than 30 μm, where many particles are usually present. For the larger ranges (200 μm and larger), the reproducibility may only be 20 to 50%, which can be created by one additional particle or one less particle.

Particle analysis was performed on 3 storms. Figure 4.7 shows pollutographs as well as the particle size distributions for the series of grab samples. The upper graphs show the runoff flow, rainfall intensity, TSS, turbidity, conductivity, median particle size and the particle size distribution for each grab sample. The upper graph shows the points in the pollutographs where grab samples were collected. The lower graphs show the number of particles as a function of particle size. Each grab sample corresponds to a line on the lower graphs. Sampling times are shown to locate the particle size function to a point on the pollutographs. It is easily observed that the number of particles declines dramatically as the storm progresses. Samples later in the storm have many fewer particles (note the scale change on the lower PSD axis in Figure 4.7). The median particle diameter decreases as the storm proceeds, which means that the larger particles are washed out faster than the smaller particles.

Figure 4.8 shows the Particle number first flush ratios (PNFF) which are calculated exactly the same as MFF ratios, except that particle numbers are used instead of concentrations. The PNFF can be calculated for the entire size distribution or for smaller intervals. Figure 4.8 shows that the smaller particles had $PFFN_{20}$ as low as 2.0. The larger particles had median ratios higher than 3.0.

The work on particle analysis is just beginning, but we expect to be able to develop quantitative designs for sedimentation-type BMPs based on the particle size and the pollutant concentrations on the particles. Work is being done as part of our follow-on project in 2004-2005 to measure pollutant concentrations as a function of particle size, as well as collecting more particle size information.

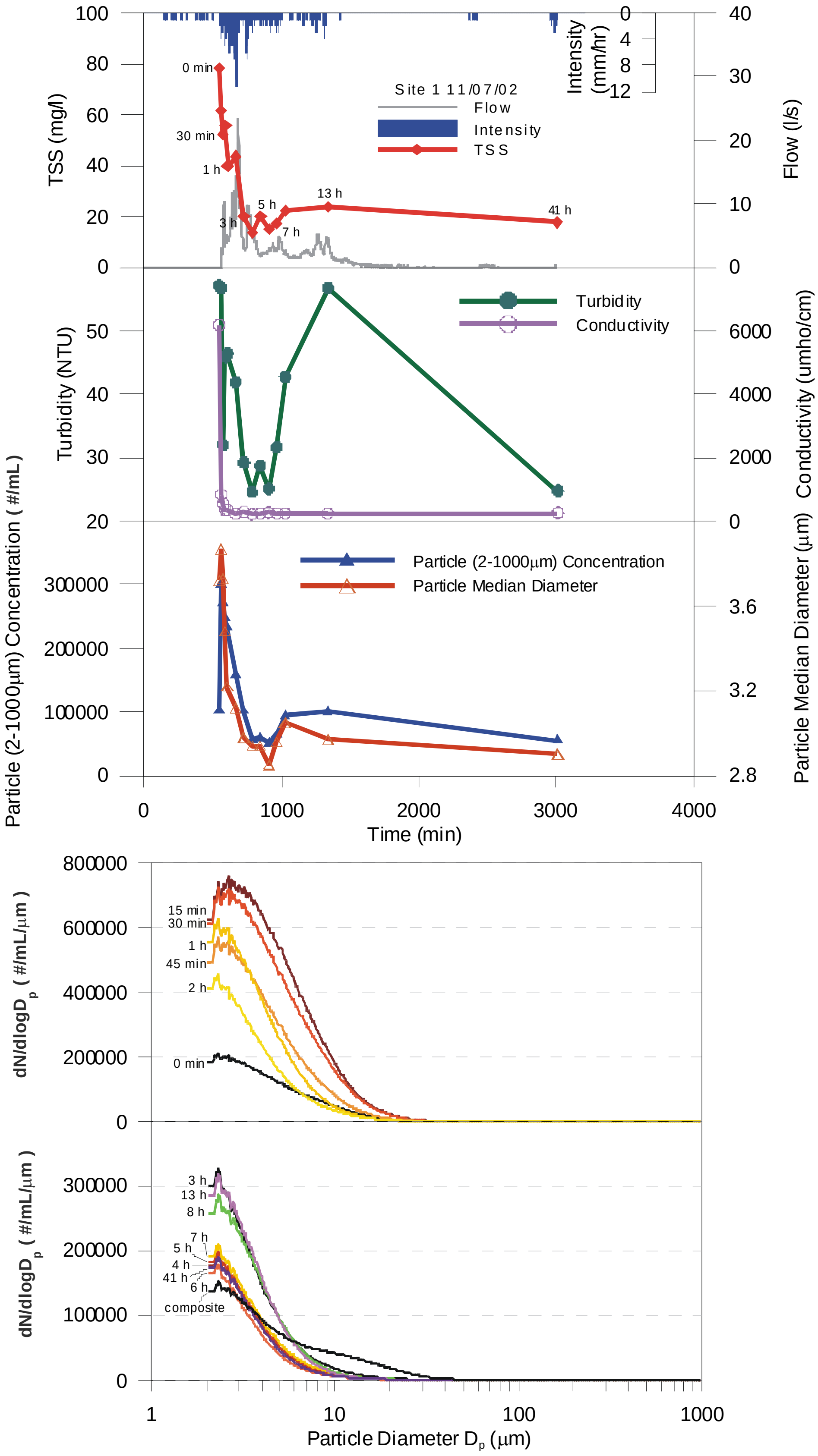


Figure 4.7 Pollutograph and particle size distribution for Site 7-201, even 11/07/02

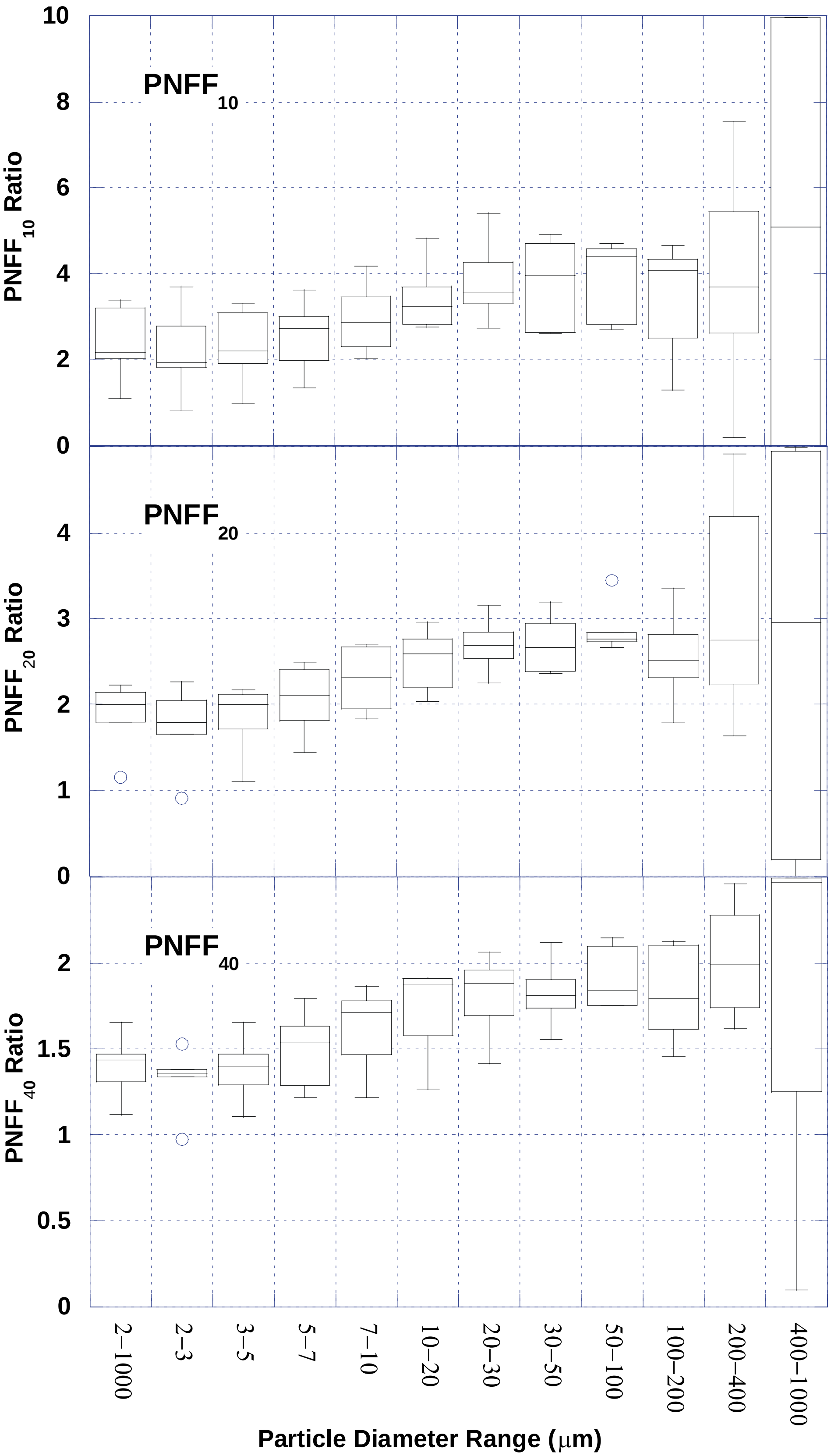


Figure 4.8 Particle number first flush ratio

4.5 Seasonal First Flush

The same method of quantifying an event first flush can be applied to seasonal first flush. Most parts of California have wet and dry seasons, often characterized as a Mediterranean climate. Figure 2.5 showed the rainfall season for Southern California as November to March, with most rain occurring in January and February. Figure 4.9 shows the average California rainfall patterns in Los Angeles and Sacramento and compares them to two locations in New England (Connecticut).

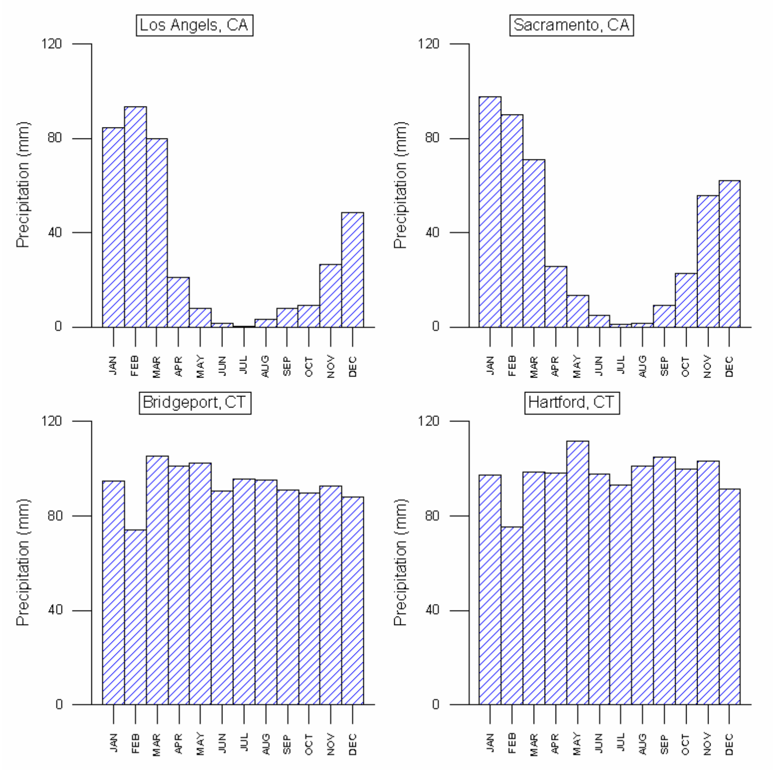


Figure 4.9 Monthly average Rainfall in Los Angeles, Sacramento, Bridgeport, and Hartford during 1971-2000

The long periods of dry weather in California, essentially from April to October, provide a long period for pollutant build up. The existence of the long dry period should be viewed as an opportunity as opposed to a problem. For example, the Department has already taken advantage of the seasonal rainfall by scheduling its insert cleaning in the late summer or early autumn. This should be viewed as an opportunity because the Department, in a single cleaning, can collect approximately 6 months of accumulated debris and litter. In a more common rainfall environment, monthly cleanings would be required to collect 6 months of accumulation, and even then, debris would be discharged with the frequent rains.

To examine the magnitude of the seasonal first flush and its impact on BMP design, several datasets were examined to determine the differences in runoff of the first storm of the season or early storms of the season and later storms (see Table 4.4). It was necessary to enlarge our study because the required analysis must pool each season's rainfall events into a single observation. Therefore, even though the first flush data collected in this study are, to the authors knowledge, the most extensive highway runoff dataset in existence, still more data were needed. The first flush data were combined with the data from the Department's statewide monitoring program, as well as two other datasets collected in or near Los Angeles County. The other datasets had, in so far as possible, similar landuses to transportation landuse. The Industrial General Permit dataset covered some transportation landuse, but many landuses were similar to the Department's maintenance facilities and parking areas.

Table 4.4 Summary of datasets used for seasonal first flush evaluation

Name of Monitoring Program	**Sponsoring or Managing Agency**	**Monitoring year**	**Monitoring Area**	**Primary Land Use**	**No. observations**
Industrial Activities General Permit	Los Angeles Regional Water Quality Control Board, (LARWQCB)	from 1992 to 2003	County of Los Angeles	Industrial	~ 6500 events from many sites over two years
Land Use Monitoring	Los Angeles County Department of Public Works (LACDPW)	from 1996 to 2001	near LAX	Transportation	24 events from 1 site over three years
First Flush Highway Runoff Characterization [a]	California Department of Transportation (Department)	from 1999 to 2003	IS 405 and US 101 freeway near UCLA (3 sites)	Transportation (Highway)	71 events from 3 sites over three years
Statewide Highway Runoff Monitoring [b]	California Department of Transportation (Department)	from 1997 to 2003	California (statewide)	Transportation (Highway)	237 events from 25 sites over three years

[a] Performed by the Civil & Environmental Engineering Department, University of California, Los Angeles.
[b] Part of the Department's state-wide stormwater runoff monitoring program, Department (2003).
[C] Transportation includes surface roads, while highway includes only freeways.

In order to compare different seasons and different sites and monitoring programs, a common parameter to reflect the point in the rainy season was needed. Ideally, the runoff of each site could be used, and added to produce an accumulated runoff for the entire season. Unfortunately, such runoff data was rarely available, and even the Department's statewide monitoring program does not have such data (not all storms were sampled, and in some cases, the actual runoff data is too voluminous to be reported). For other studies such as the Industrial Activities General Permit, runoff is not required and is not usually measured (Stenstrom and Lee, 2005).

To create a common parameter for all datasets, rainfall was used. Rainfall data were collected from the nearest gauge and added to produce an accumulated rainfall. For some datasets it was difficult to locate the correct rain gages. For the Department's datasets, this was much easier since rainfall was usually measured at the monitoring station. The accumulated rainfall was then normalized, so that all years would produce a scale from 0 to 1.0. Next, the concentrations of the pollutants of interest were plotted as a function of accumulated rainfall.

Figure 4.10 shows four graphs of various pollutants for selected years of data from this study. The rainfall of each storm is plotted along the top, as well as the ADD. Because the rainfall is cumulative, it is not possible to determine the time between rainfall events from the horizontal axis. The horizontal axis is frequently used for time in stormwater studies, and it natural to assume that the horizontal axis is linear in time. The cumulative rainfall is the appropriate parameter to plot for this analysis, since the rainfall washes out the pollutants. The rainfall is not a linear function of time. The opportunity for pollutants to accumulate between rainfall events is quantified by ADD.

It is clear from the graph that the first storms of the season have higher concentrations. In some cases the first storm was small which biased the concentration, but in general, with very few exceptions, and declining trend in concentrations is observed for almost every parameter. The appendices to this report include a copy of the technical memorandum devoted to the topic, and can be consulted for more information on individual events or datasets.

The MFF ratios can be applied to those datasets with runoff volume. Both of the Department’s datasets can be analyzed in this way. Figure 4.11 shows the load graph for four metals, TSS and COD for the first flush study. Each point represents a storm in each season. The MFF ratio is equal to the Y coordinated divided by the X coordinate. Values above the diagonal indicated a seasonal first flush. The vast majority of the points are above the diagonal, with points for copper being commonly found in the upper part of the figure. The majority of the points for lead are below the diagonal line.

Figure 4.12 shows a similar analysis for the data from the Department’s statewide sampling program. Virtually all the metals show a seasonal first flush.

As stated before, the existence of a seasonal first flush provides an opportunity. The first storms of the season carry a higher mass load of pollutants; therefore developing BMPs that treat all of the first storms will be a better strategy than trying to treat a fraction of all storms throughout the season. An example might be infiltration basins that dry out over the summer, which allows them to capture and retain the first few storms of the wet season.

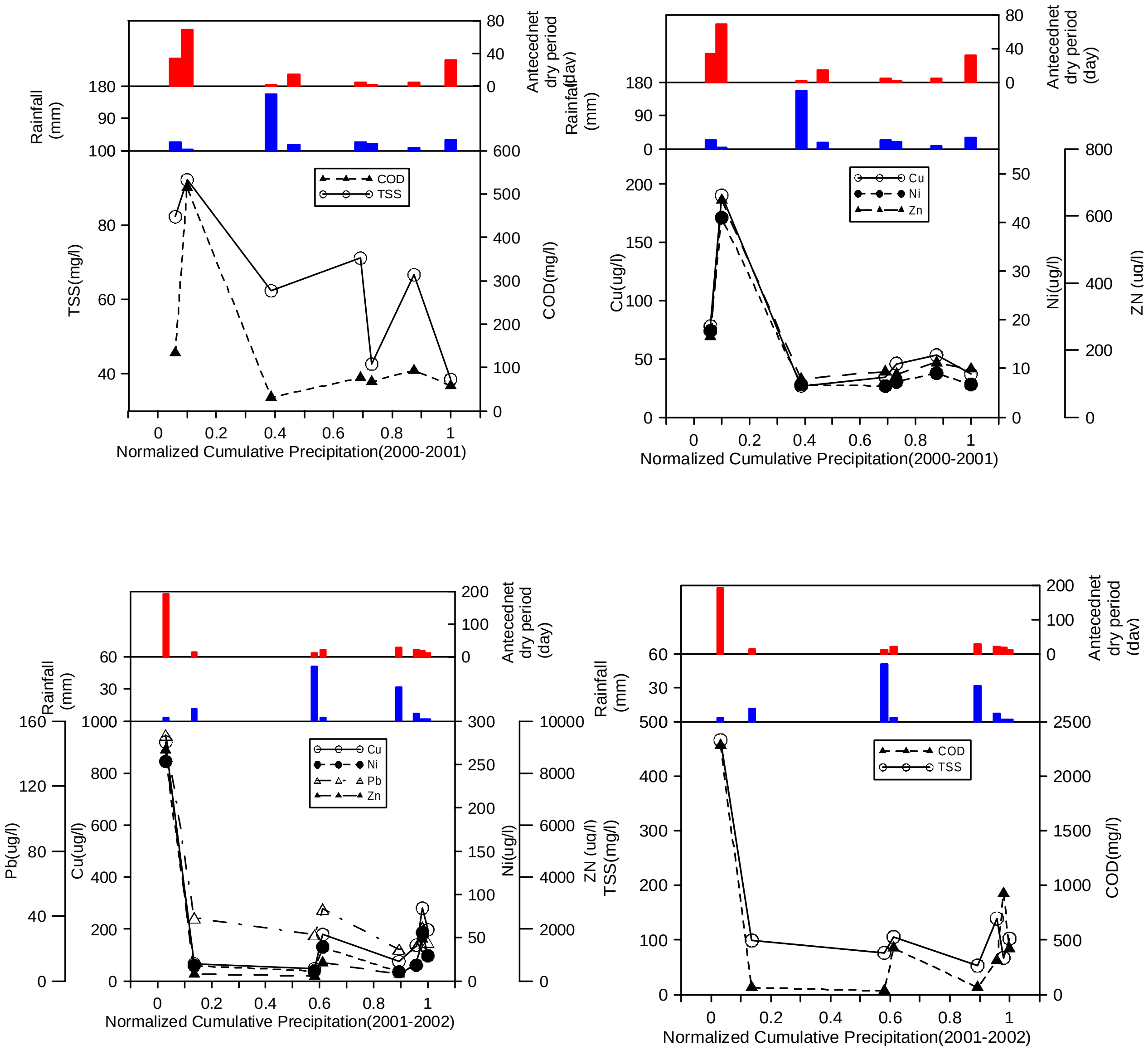


Figure 4.10 Concentrations of various pollutants versus normalized cumulative rainfall for selected monitoring events for the first flush highway runoff dataset

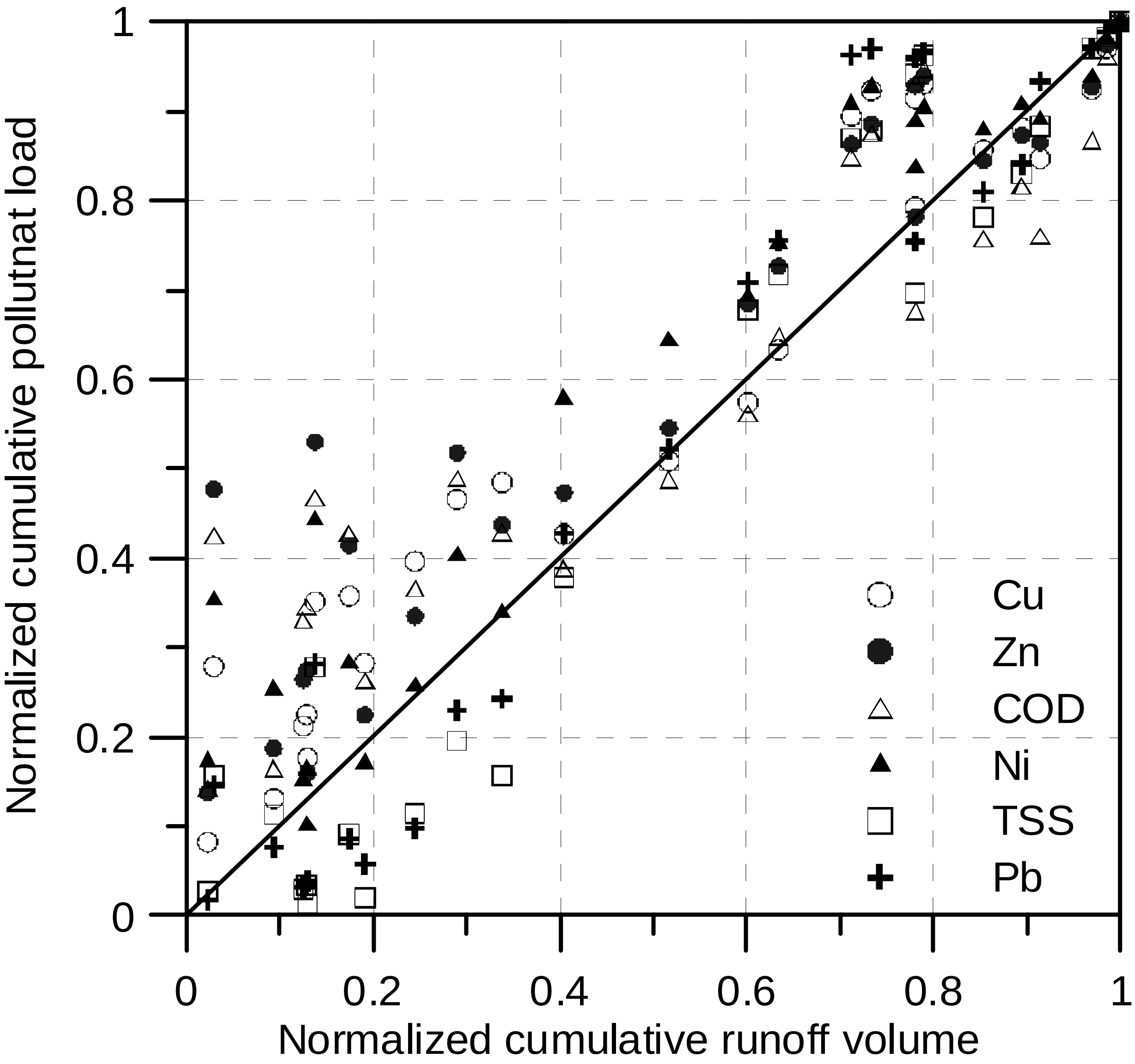


Figure 4.11 Load graphs of four metals, TSS and COD for the first flush study sites

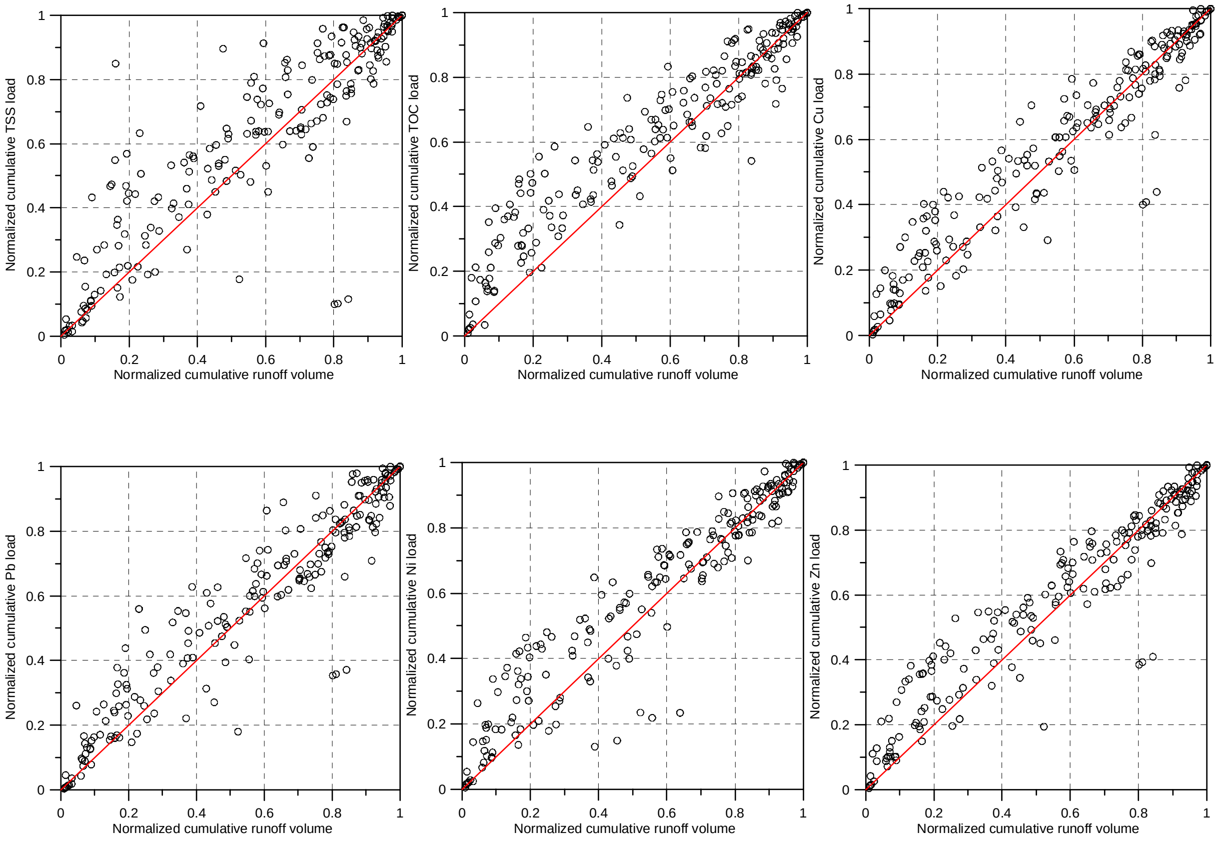


Figure 4.12 Load graphs for metals for the Department's statewide monitoring program sites

5. TOPICS RELATED TO FIRST FLUSH

5.1 Treatment Strategies with Respect to First Flush Pollutant Load

The MFF ratios plotted and tabulated in the figures and appendices can be very useful to the Department in estimating potential removals of BMPs. Since it will not be possible to design and construct BMPs that can treat all of the runoff from all sites for all storms, there must be a probabilistic goal for treatment.

The Los Angeles Regional Water Quality Control Board’s example is useful for demonstration. The Board adopted a regulation that requires all new developments to capture or treat the runoff from first 25 mm (1 inch) of rainfall. This rainfall corresponds to a 60% storm for the monitored sites, as shown in Figure 2.6. For storms larger than 60%, some portion of the flow must be bypassed. For very large storms, perhaps only 30 or 40% of the flow can be treated. If only 30% of the flow is treated, the BMP, because of the first flush, has an opportunity to remove not just 30% of the pollutants, but 30% times the MFF_{30} ratio of the pollutants. Using COD as an example, the MFF_{30} is approximately 1.6, and a BMP that treats 30% of the flow would in fact treat 48% of the COD mass.

MFFs can be used to better define the potential removal of BMPs that are “first flush friendly.” This term is coined to describe a BMP that treats the first runoff and bypasses later runoff, without washing out the material retained from the earlier part of the storm. Detention basins are one example of a BMP that can be operated in first flush friendly mode. BMPs operated as first-flush friendly may be 2 to 4 times as effective as other BMPs when only a portion of the runoff volume can be treated. Other, more detailed examples of this advantage will be presented later.

Using the MFF ratios provided through this study, the Department can revise upwards its predictions for BMP removal rates, based upon the expected volumes to be treated. For small storms that are completely captured by BMPs, the removals will not change, but for larger storms, which are the most expensive to manage, the mass removals will be greater.

In order to estimate the potential benefits of treating early runoff as compared to runoff later in the season, we defined an effectiveness factor as a function of cumulative runoff volume. In the expected situation of having limited funding for BMP construction, applying BMPs to runoff with higher pollutant concentrations will generally be more beneficial. Also there is growing evidence that suggests that BMPs removal efficiencies are higher in runoff with higher concentrations (Strecker et al., 2001; Lau and Stenstrom, 2002).

The effectiveness factor at a specific cumulative runoff volume is calculated as follows:

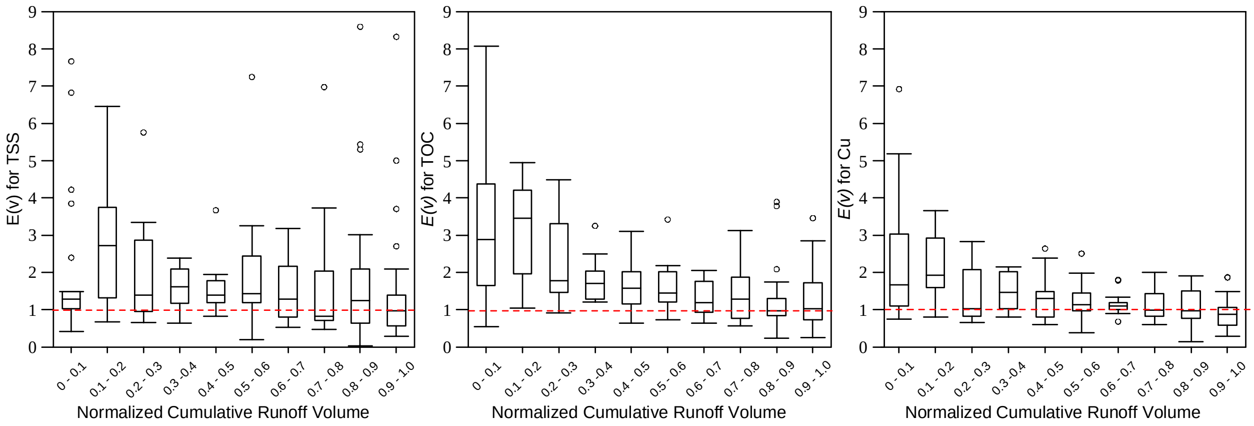
$$E(V) = \frac{(Mv/v)}{(1-Mv)/(1-v)} \tag{5.1}$$

where *E(V)* is the effectiveness factor at a specific cumulative runoff volume *V*, and *Mv* is the normalized cumulative mass at a specific normalized cumulative runoff volume, *v*.

The effectiveness factor has the same utility as the MFF ratio. Values close to 1 are obtained if there is no first flush. Higher values are observed with greater first flush.

Figure 5.1 shows the effectiveness factor calculated for TSS, TOC and four metals for the Department's state wide monitoring program results. The factor was calculated at 10 runoff volume intervals. The dashed line at 1.0 shows the expected value of the effectiveness factor for constant pollutant concentrations or no first flush. The data are plotted as box plots (no confidence intervals).

It is readily apparent that treating the early runoff in the season is several times more effective than treating the later runoff. The results suggest that the Department's efforts to implement BMPs should address the early storms as effectively and completely as possible. Such a strategy will maximize the benefits of the applied BMPs.



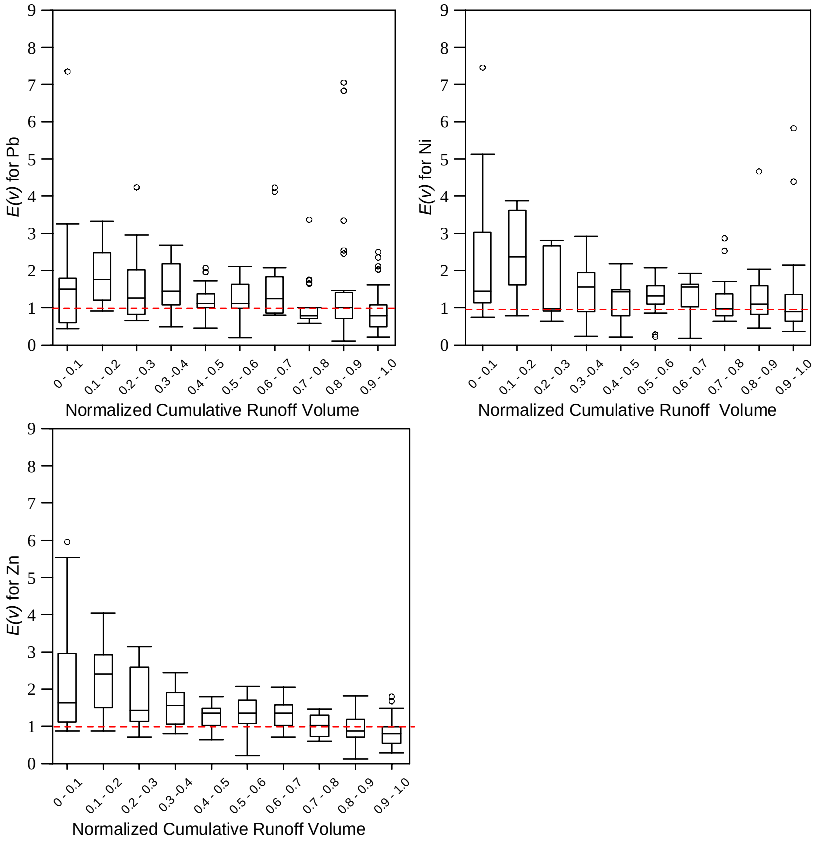


Figure 5.1 Effectiveness factor calculated for ten volume intervals for data from the Department’s statewide monitoring program

5.2 A New Methodology to Monitor Oil and Grease

Monitoring for O&G presents special problems because automated samples are not recommended for O&G samples collection (American Public Health Association 1998). Carry over from one sample to the next is caused by oil and grease retention in the sampler tubing. Automated samplers are also avoided when measuring toxicity, due to the introduction of artifactual toxicity from tubing, pumps and containers. Otherwise, automated samplers generally work well, can be left unattended and can be triggered automatically to insure that the very beginning of runoff is sampled. The sampler is programmed to collect many small samples over the entire storm event to insure representativeness.

It is difficult to measure the EMC of O&G in stormwater because a series of grab samples must be collected. If ten samples are collected, the analytical costs are ten times greater and the additional sampling labor maybe even more expensive. Also, the first part of a storm event maybe missed by the sampling team, since the rains will occur at an inconvenient times and the sampling team may have a great distance to cover.

To avoid the complexity and cost of collecting a series of grab samples, a single grab sample is often substituted for the composite sample or the series of grab samples. This strategy reduces the cost, but potentially creates bias due to the timing of the grab sample.

O&G usually exhibits a first flush and Table 4.1 showed that the MFF ratios for O&G were among the highest. Earlier publications document some of the findings on O&G first flush (Lau et al. 2002; Ma et al. 2002). Therefore, a sample collected early in the runoff event will have higher concentration than a sample collected later in the storm event. The critical question is when to collect the grab sample so that it most closely approximates the EMC.

The first flush dataset presented a unique opportunity to develop a methodology for predicting the best time for collecting a grab sample. The existence or more than 60 storm events monitored with 12 grab samples each was used to answer the question of when to sample. Also, correlations were investigated to determine if other parameters might be more useful in estimating the EMC.

Figure 5.2 shows the concept of best time to sample. The O&G concentration declines from a high value at the beginning of the storm to a low value at the end of the storm. This was typically observed in our samples. It is readily apparent from this graph that a sample collected early in the storm overestimates the EMC and a sample collected later in the storm underestimates the EMC. For this event, the idea time to collect a sample is at 133 minutes. Unfortunately there is no way for the sampling team to know this, and if they were to take multiple grabs to determine the best time, it would defeat the purpose of knowing the best time.

To estimate the best time, oil and grease samples from the first three years of the study were analyzed. A Matlab program was written to "read" the pollutographs and calculate the best time. The same program was also written to interpolate between data points on the pollutographs, so sampling times could be simulated. In this way the Matlab program could tabulate the best time for all pollutographs, as well as indicating the O&G concentration that would have been measured if a specific sampling time had been used.

The Matlab program could then be used to calculate the answer to the question “What if all storms had been sampled at 30 minutes” or similar questions. Using this program, a range of sampling strategies was evaluated. The first strategy simulated was random sampling. A random time was selected for sampling each storm and the results were tabulated. Next, fixed times were used, such as 15 minutes into the storm, 1 hour, etc., or at the end of the storm. Next, averages and regressions were used. For example, regressions were performed between storm characteristics and the best times to sample. In some cases, the storm parameters are not known before the storm, which means that weather predictions would have to be used, further complicating the samplers’ job.

Finally, correlations with other parameters were investigated. Both dissolved organic carbon and COD measure the O&G. They also include organic compounds or oxygen demanding compounds that are not O&G. Correlations were made to determine if consistent ratios among the parameters exist.

Table 5.1 shows the results of all strategies. The left most column describes the sampling strategy. The next column shows the number of storms that was included in the analysis. The next three columns show the goodness of fit in different ways. For regression, the R^2 are shown and for other cases the root mean square errors (RMS, equal to the square root of the sum of squares divided by the number of observations) are shown. Finally, the last column shows the bias. The bias is the average difference between the observed EMC and the predicted EMC from the sampling strategy. The observed EMC is the EMC calculated from the series of 8 to 12 grab samples.

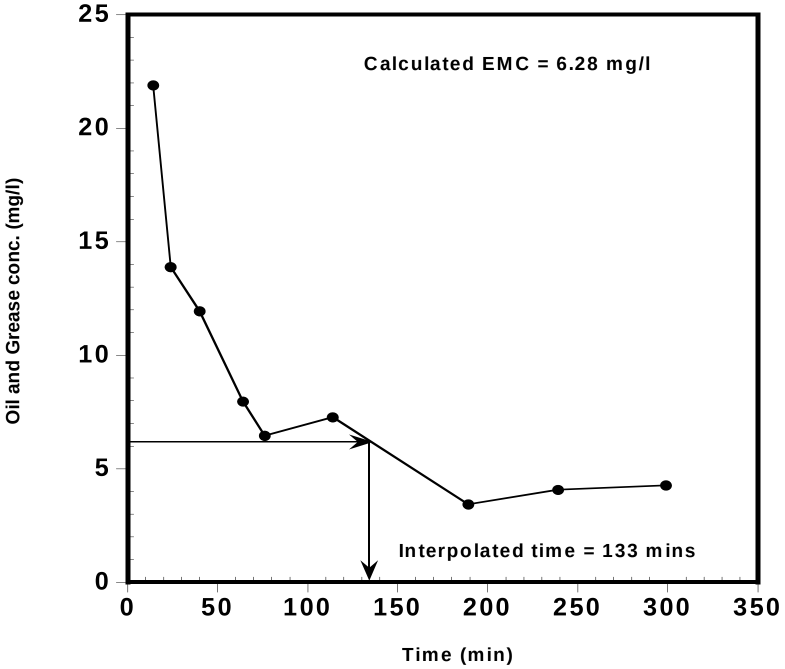


Figure 5.2 Illustration of the best time to collect a grab sample to approximate the EMC

Table 5.1 Results of best sampling time simulations and regressions

Sampling strategy or regression method	**No. of Obs.**	**R^2**	**RMS Error (mg/L)**	**Bias (mg/L)**
Random grab sampling time	22	0.54	9.40	1.15
Strategy 1: Timed sample strategies after beginning of runoff				
0.25 hr	22		32.4	23.8
1 hr	22		3.47	1.39
2 hr	22		3.91	-2.07
3 hr	18		3.92	-2.54
4 hr	15		3.59	-0.88
5 hr	14		3.13	-1.21
6 hr	9		2.19	-1.38
Storm end	22		3.52	-1.96
Strategy 2: Best sampling time from event and site variables				
Post storm measured parameters				
Total rainfall	22	0.96	1.99	-0.27
Duration of runoff	22	0.92	2.64	-0.22
Total rainfall and duration of runoff	22	0.96	1.96	-0.26
Total rainfall, duration of runoff, and ADD	22	0.97	2.72	0.73
Predicted parameters				
Total rainfall	22	0.89	2.98	0.39
Duration of runoff	22	0.95	2.22	-0.40
Total rainfall and duration of runoff	22	0.88	3.19	0.37
Total rainfall, duration of runoff, and ADD	22	0.92	3.46	1.18
Strategy 3: *EMC* of O&G from site and event variables				
ADD	22	0.82	3.84	-0.01
ADD and total rainfall	22	0.83	3.79	0.00
Logarithm of ADD and total rainfall	22	0.84	3.60	-0.42
Strategy 4: Correlation to composite COD or DOC measurement				
COD Eq. (13)	22	0.90	2.90	0.07
DOC Eq. (14)	22	0.90	2.84	0.01

The first strategy is random timing, which is probably the most common current strategy. The sampling team travels to the site and collects the grab sample when they are able. This strategy had an RMS error of 9.4 mg/L and on average was 1.15 mg/L higher than the EMC. The timed strategies produced the expected results. Samples collected in the first 15 minutes were much higher than the EMC, on average being 23.8 mg/L higher than the EMC. If the storm is sampled after 1 to 4 hours, the grab sample is pretty good and the bias ranges from -1.39 to 2.45 mg/L. Sampling at the end of the storm is also biased on the negative side.

The second set of strategies shows the results of the regression methods. The time to sample in these methods was based upon regressions of the storm parameters. The first group used the post storm parameters, and it is not realistic because they are not known until after the storm. The second group used simulated weather predictions, which provided estimates that were +/- 50% of the actual values. This group of simulations provided results with RMS errors of 2 to 3.5 mg/L, and the bias was nearly zero, which is expected from a regression.

The third group used ADD and total rainfall for predicting the oil and grease concentration. This strategy used no sample for O&G, just a regression from the ADD and./or the total rainfall. The RMS error for this method was only slightly larger than the error associated with strategies that used a sample.

The final group used a simple correlation with COD or DOC. This is the method of choice and provides an accurate answer with the least sampling effort. If COD and DOC are being measured it is a simple matter to estimate the O&G EMC from the COD or DOC EMC. The value of R^2 is nearly as high as the other methods, and no O&G sample is required.

$$\text{O\&G}_{\text{EMC}} = 3.705 + 0.037 \times \text{COD}_{\text{EMC}} \qquad R^2 = 0.90 \tag{5.2}$$

$$\text{O\&G}_{\text{EMC}} = 0.15 + 0.28 \times \text{DOC}_{\text{EMC}} \qquad R^2 = 0.90 \tag{5.3}$$

These results have important consequences for the Department. It is recommended that the Department end O&G sampling, and correlate O&G to either COD or DOC. This change may require regulatory approval, but the analysis provides powerful support for its approval.

A word of caution is needed. The reason the correlation of O&G to COD or DOC works well is the nature of the stormwater. The organics in highway runoff are mostly compounds that are classified as O&G. For other stormwaters or wastewaters, the correlation may be poor, since the organics in the waters may be carbohydrates or proteins, which do not extract into the organic phase during O&G analysis. A general discussion and review of O&G is helpful in understanding the makeup of O&G (Stenstrom, et al, 1986). The appendices of this report contain the full text of the technical memorandum on this topic.

5.3 Sampling Issue: Composite Samples versus Grab Samples

In order to evaluate different sampling strategies, it is necessary to simulate many events and to add stochastic component (noise) to make the simulation realistic. A COD regression model was used top perform this simulation, as follows:

$$E(\log COD \mid \mathbf{x}) = 6.08 - 0.60 \log CumRs + 0.40 \log AtDry - 0.16 \log AtRs \tag{5.4}$$

where,

COD = chemical oxygen demand concentration (mg/L),
CumRs = cumulative rainfall, corresponding to grab sample collection time, (0.01 inch increments),
AtDry = antecedent dry period before monitored events, days and
AtRs = previous event’s precipitation before the monitored event, (0.01 inch increments)

Figure 5.3 shows the model’s fitted values vs. the observations. The COD model can be used to predict any number of concentrations for a given hydrograph. In this way, collecting any number of grab samples can be simulated. A random component is added (white noise) which has mean zero and a variance equal to the variance in the original data. A special simulation will use equation (4.4) to generate COD concentrations at one-minute intervals. This special simulation will be used as the benchmark in simulation tasks and is the shortest possible sampling frequency, since the rainfall and flow data are collected at one-minute intervals. The EMC is then calculated using equation 3, where the weights are the discharge rates.

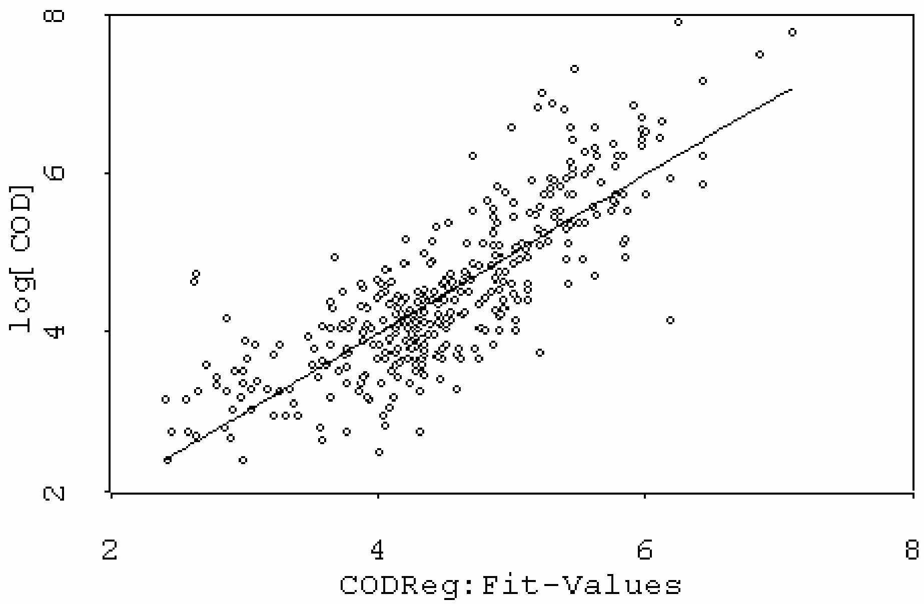


Figure 5.3 Regression's fitted values vs. observation

In order to illustrate this one-minute simulation, one real event is used for demonstration. Figure 5.4 shows the original and the smoothed event hydrographs. The smoothed hydrograph will be used in simulation to correct fluctuations in original data. Figure 5.5 shows the histogram of 1000 simulated EMCs. The original sample mean is 116.36 (mg/L), and the mean of the simulations is 116.25 (mg/L).

To compare other sampling strategies, simulations were performed using different numbers and different strategies for collecting samples during typical storm events (e.g., random, equally spaced in time, equal volume, etc.). A total of 35 different rainfall patterns, corresponding to actual observed patterns in our monitoring program, were used. Table 5.2 summaries the events. Each type of simulation will generate a distribution of EMCs after multiple runs. Simulations that use more samples will produce EMCs that are closer to the original sample EMC. The value of differing numbers of samples as well as the strategy can be compared.

Five types of sampling strategies were evaluated. Type 1 used random timing of the samples. The simulation assumes a sample set with specified size (*n*) that is randomly collected from all possible time elements during each tested event. It is a random permutation of size *n* for a sequence. Theoretically, this is the most general case for a sample set with fixed size. The influence of sample size on EMC results is evaluated simulating 10, 20, 40, 60, and 100 samples per event. Type 2 used equal-time sampling. To avoid the extreme result of a sample sequence, each selected sample sequence was randomly shifted forward or backward in a range (10 minutes). Type 3 used equal-rainfall interval sampling by simulating the sample collection at equal intervals of rainfall depths. Type 4 used equal discharge-volume sampling. No weighting noise was assumed in this task (i.e., the weightings are perfectly known, without measurement error). Type 5 was similar to Type 4, except that random noise was applied to the weighting factors (i.e., the discharged volumes cannot be perfectly measured).

Table 5.2 Hydrologic characteristics for 35 monitored events

Hydrologic Property	Average	StdDev	Minimum	Median	Maximum
Total Rainfall (in)	1.17	1.54	0.08	0.67	6.14
Max Rain Intensity (in/hr)	0.31	0.33	0.02	0.19	1.28
Discharge Volume (gal)	75022	99293	1799.5	36808	374217
Max Discharge Rate (gpm)	340	304	17	258	1465
Rain Duration (min)	660.5	512.7	93	610	2376

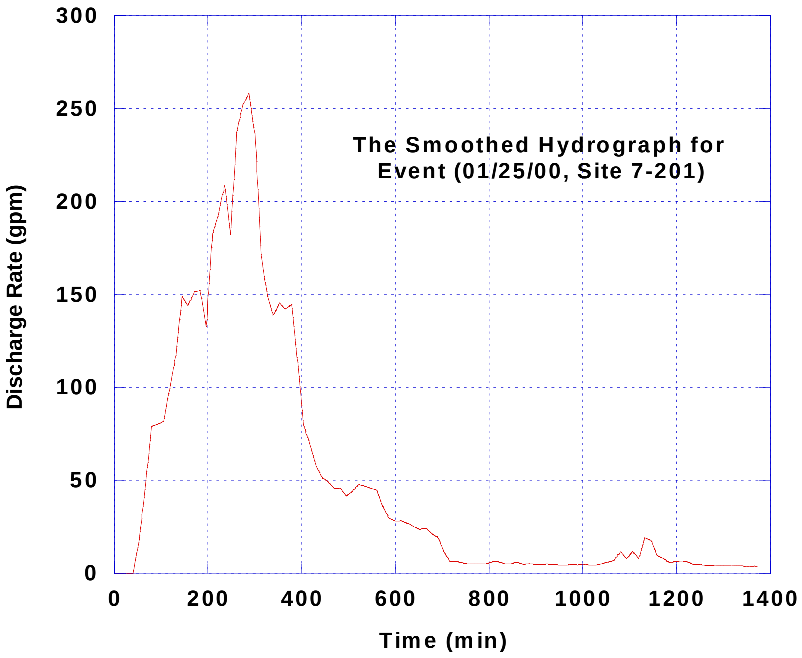


Figure 5.4 Smoothed hydrographs (event recorded on 01/25/00, Site 7-201)

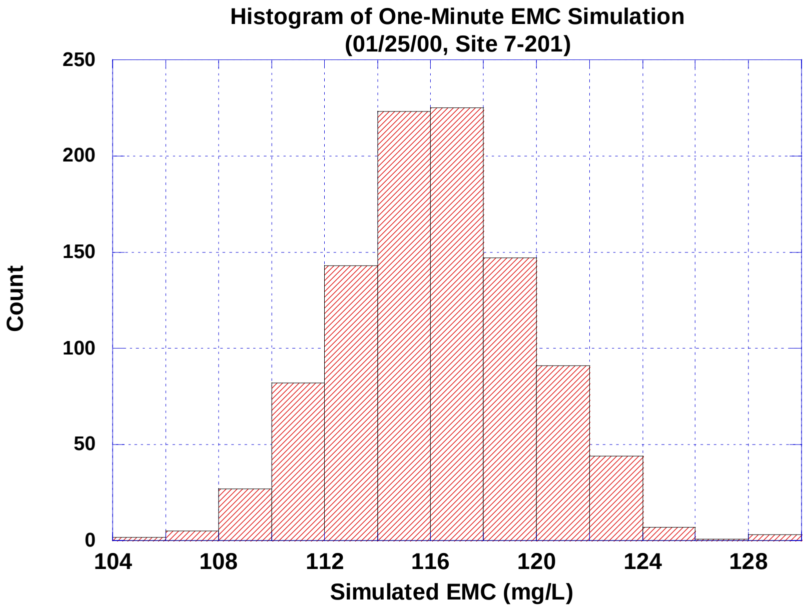


Figure 5.5 Sampling distribution for one-minute EMC simulation
(event recorded on 01/25/00, Site 7-201

The results of the various simulations for different types of sampling strategies are presented in a series of figures. The figures show the distribution of simulated EMCs for each number of samples. Figure 5.6 (top) is a box plot and shows the results for Type 1. The worst error percentage can be up to 80% for *n* = 10. The average error percentages for *n* = 10, 20, 40, 60, and 100, are 47.0%, 30.2%, 19.5%, 15.3%, and 11.6% respectively. The medians of errors are slightly lower than the averages. The corresponding standard deviations are 13.9%, 7.2%, 4.1%, 2.9% and 2.2%. Type 1 is a benchmark on the influence of sample size for estimating EMCs, and is the most general sampling strategy.

Figure 5.6 (middle) shows the sample distributions Type 2. Only one outlier was found for each *n*. The worst case is for *n* = 10 with error of approximately 66%, which is much improved over Type 1. The average error percentages for *n* = 10, 20, 40, 60, and 100, are 37.2%, 21.7%, 15.2%, 12.4%, and 9.2% respectively. The medians of errors are generally the same as the averages. The corresponding standard deviations are 11.1%, 4.4%, 2.7%, 2.8% and 1.7%. These statistics show an improvement over random sampling.

Figure 5.6 (bottom) shows the sample distributions from Type 3. Although several outliers were found for *n* = 10, the worst case is approximately 30%, which is much improved over Type 2. The average error percentages for *n* = 10, 20, 40, 60, and 100, are 23.9%, 17.5%, 13.5%, 11.9%, and 10.5% respectively. The medians of errors are generally the same as the averages. The corresponding standard deviations are 2.2%, 2.2%, 2.6%, 3.2% and 3.7%, a large improvement over time sampling.

Figure 5.7 (top) shows the sample distributions from Type 4. It is obvious on plot that this is the best result from the aspect of outliers, averages, or variances. The average error percentages for n = 10, 20, 40, 60, and 100, are 23%, 16.6%, 12.0%, 9.7%, and 7.5% respectively. The medians are generally the same as the averages. The corresponding standard deviations are 2.5%, 1.6%, 1.2%, 1.0% and 0.7%. Figure 5.7 (bottom) shows the sample distributions for Type 5. This is the same strategy as Type 4, except that the weights are not perfectly measured. The average error percentages for n = 10, 20, 40, 60, and 100, are 23.5%, 17.1%, 12.3%, 10.1%, and 7.8% respectively. The corresponding standard deviations are 2.1%, 1.6%, 1.3%, 0.9% and 0.8%. The effect of imperfect weights is not very large.

This analysis has shown that a flow weighted composite sample can be viewed as a series of grab samples summed with weights that reflect the flow. To evaluate the error of using a limited number of grab samples and the strategy for collecting the samples, a series of simulations was performed using a COD correlation, random noise and hydrographs from 35 different storm events.

The results show that a series of 10 grab samples provides a relatively poor estimate of the EMC, with median errors of 40% for randomly timed samples to 23% for samples collected at equal flow volumes. If the number of grab samples increases to 20, the error is reduced to 30% for randomly timed samples to 16% for samples collected at equal flow volumes. Even if 100 samples are collected, the error is still nearly twice as large as the minimum possible error, when samples are collected each minute.

The best strategy is to collect the grab samples at equal flow volume intervals. Equal rainfall interval is the second choice, with equal timing and random timing being less desirable strategies.

The results show that automatic flow weighted composite samples, which can be programmed to collect several hundred samples per storm, are far superior to a series of grab samples, even if 100 grab samples are used. If automatic composite samplers can be used without chemical or physical biases (e.g., such as the concerns of sample carry-over when sampling for oil and grease, or the introduction of artifactual toxicity), they are always preferred.

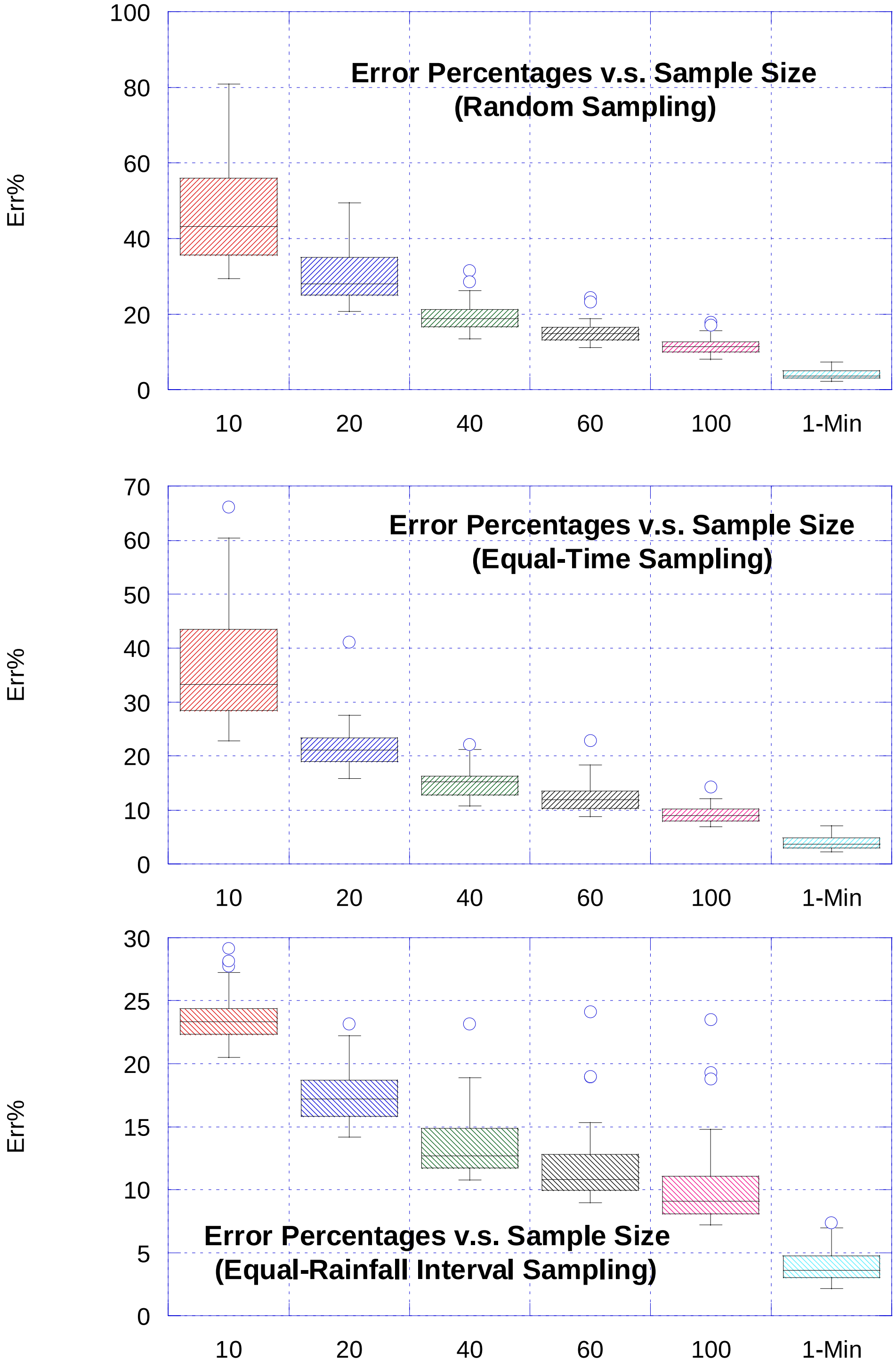


Figure 5.6 Sampling distributions for random time (top), equal time (middle) and equal rainfall interval (bottom) (with n = 10, 20, 40, 60, and 100) plus one-minute simulation

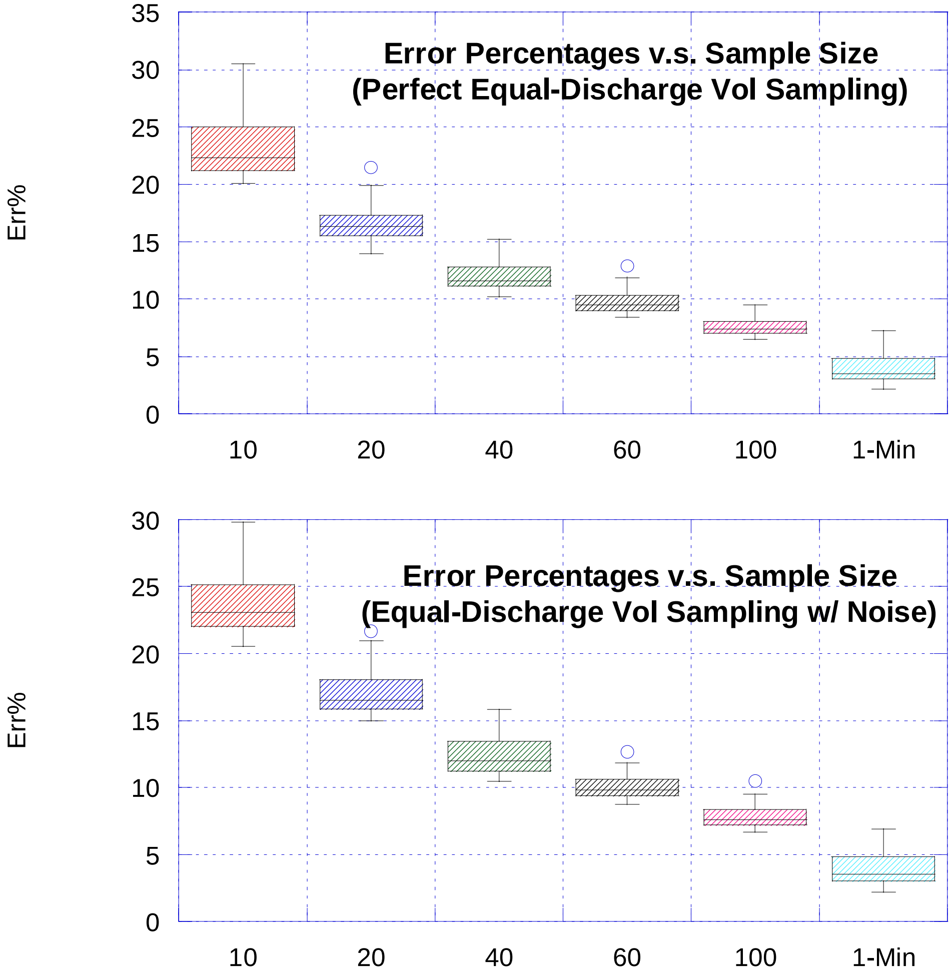


Figure 5.7 Sampling distributions for perfect equal-discharge volume sampling (top) and equal-discharge volume sampling with noise (bottom) (as n = 10, 20, 40, 60, and 100) plus one-minute simulation

6. SUMMARY

The California Department of Transportation sponsored a four-year stormwater monitoring study to investigate first flush phenomenon. The Department of Civil and Environmental Engineering at the University of California, Los Angeles (UCLA) in collaboration with the Center for Environmental and Water Resources Engineering at the University of California, Davis (UCD) conducted the investigation. UCLA collected the bulk of data and performed the analysis of the results. Consultants under contract with the Department sampled several sites in the first two years of the study, and assisted in the initial set up the sites and monitoring equipment.

Three highly urbanized representative highway sites near UCLA were selected for this study. Two sites were located on IS 405 near Santa Monica Boulevard and the Getty Center and the third site was located on the intersection of US 101 and IS 405. The sites were instrumented with rain gauges, flow meters and automatic composite samplers. Consultants monitored two different sites in the 1999-2000 and three different sites in the 2000-2001. Nearly all analysis and discussion presented in this report are based on the results obtained from the UCLA monitoring data, although data from both consults are included with the UCLA monitoring data in the Appendix.

In the first year, five grab samples were collected during the first hour of runoff followed by two or three manually composited samples in the following two to three hours. In the second, third and forth years, five grab samples were again collected in the first hour, followed by one grab sample per hour for the next 7 hours, providing a total of 12 grab samples. For storms lasting less than 8 hours, fewer grab samples were collected. For storms lasting longer than 8 hours, an additional one or two grab samples were collected in the period from 8 hours to the end of the storm.

The grab samples were collected from the storm drain outfall (or drain pipe) using a polypropylene scoop, and then transferred to 4-L amber glass bottles. In all cases samples were collected from a free waterfall. The bottles were transported to the laboratory at UCLA immediately after collection and refrigerated at 4°C until analyzed. Generally the first 5 bottles were transported to the laboratory after the first hour, and one or two more trips were made as the storm progress. The time between the sample collection and receipt of samples at UCLA laboratory was less than 4 hours. This became important in the last year of the study, when particle size distribution (PSD) was being measured. Measurable changes in PSD occurred within 12 hours after sample collection.

Numerous water quality parameters, nutrients, metals (particulate and dissolved), oil and grease were routinely monitored for the duration of the study. Other constituents that were monitored less frequently include indicator organisms and polynuclear aromatic hydrocarbon (PAHs). All analyses were performed within the recommended holding time using US EPA and Standard Method protocols. In addition, during the second and third year of the study, litter samples were collected. A large mesh, draw-string bag (6 mm opening) was placed over the entire flow from each site to collect litter. Three bags were collected for each site for each storm. The first bag was installed before the beginning of the storm, and removed after 1 hour of runoff. A second bag was installed and was removed after 8 hours or the end of grab samples. The third bag was installed and was left in place until the end of the storm.

It was retrieved and all bags for all sites were transported to an outside lab under contract with the Department for performing the litter analysis.

Major results and findings of the study are summarized in the following paragraphs.

6.1 Definition of First Flush Phenomenon

First-flush is a phenomenon that is associated with the belief that the first runoff in a storm event is the most contaminated. Most researchers believe that the first runoff does have higher contaminant concentrations, but opinions vary as to the importance of the increased concentrations, and whether the actual first flush mass is a significant portion of the total runoff mass. Lay people generally believe there is a first flush, and associate hazardous driving conditions with the onset of rainfall. The study has devoted a great deal of effort to developing a quantitative definition of first flush. In areas which have distinct seasonal rainfall patterns, such as California, a similar concept, called seasonal first flush exists. A mathematical concept was developed (described in section 4) that can be applied to different types of first flush phenomena, defined as follows:

> First flush – the concept that pollutants are more concentrated at the beginning of a rainfall event than in the later parts of a rainfall event. The concept can be applied to the mass discharge of contaminants (e.g., mass first flush) or the concentration (e.g. concentration first flush).
>
> Seasonal first flush - the concept that pollutants are more concentrated in the runoff of the first few storms of a rainy season than in the storms that occur later in the season. The concept can be applied to the mass discharge of contaminants (e.g., mass first flush) or the concentration (e.g. concentration first flush). The existence of a seasonal first flush requires an extended dry period before the rainy season.

6.2 Pollutograph and First Flush of Pollutants

The EMC measured through flow-weighted composite samples is perhaps the best, single descriptor of stormwater contaminant concentration and is generally preferred in any monitoring study. Unfortunately, the EMC provides no information on the temporal variability of contaminant concentrations. It cannot be used to characterize first flush. Analysis of a series of grab samples, while more expensive, provides the temporal pollutant variability throughout the storm hydrograph. This temporal variability is usually illustrated through pollutographs by plotting constituent concentration vs. duration of the storm event. A large concentration of pollutant at the beginning of the event with a gradual decrease of the pollutant concentration towards the end of the storm event is an indication of first flush.

The results of this study revealed a large change in concentration of most contaminants as a storm progresses. For example, the first sample may have had more than 500 mg/L chemical oxygen demand (COD) but the EMC may have been only 100 mg/L. The reduction occurs because the pollutant mass may be washed out of the site, or may be diluted by higher runoff flow rate as the storm progresses. By reporting only the EMC concentrations, the high initial concentrations are not recognized. This may be significant for BMP selection, since BMPs generally perform better at higher influent concentrations. Using the EMC for BMP evaluation may underestimate overall BMP removal rates.

6.3 Load-graph and Mass First Flush Ratio

The graph of normalized cumulative mass versus normalized cumulative volume is usually referred to as "load-graph" and can be used to examine the mass first flush phenomenon. The mass first flush ratio is defined as the normalized discharged constituent mass divided by the normalized runoff volume for a specific runoff volume. For example, a MFF_{10} ratio of 4.5 implies that 45 percent of pollutant mass is transported in the first 10 percent of the runoff volume. The greater the MMF_n ratio, the larger the mass first flush. The MFF always approaches 1.0 as the normalized runoff volume approaches 1.0. For a pollutant to have a first flush the mass first flush ratio (MFF_n), must be greater than 1.

6.4 Organic (PAHs) First Flush

Dissolved polyaromatic hydrocarbons (PAHs) were generally at or below detection limits. However, particulate PAHs were dominant and in most cases, first flushes of particulate PAHs were exhibited. The mass first flush ratio generally was above 2 for the first 20% of the runoff volume, and in some cases as high as 2.8. The results suggest that best management practices (BMPs) that address particulate phase contaminants in the initial runoff can have greater effectiveness for particulate PAH removal than other types of BMPs.

6.5 Litter First Flush

Results obtained indicate that a first flush of gross pollutants was generally observed. Gross pollutants were defined as being larger than 6 mm and were classified into three categories: vegetation, biodegradable litter, and non-biodegradable litter. The gross pollutants were 90% vegetation and 10% litter. Approximately 50% of the litter was composed of biodegradable materials. However, a greater percentage of biodegradable litter was normally collected in the first flush. No statistically significant correlations of litter production were noted, although the event mean concentrations show an increasing trend with antecedent dry days and a decreasing trend with total runoff volume or total rainfall. The mass emission rates will be useful to estimate total litter production for developing total maximum daily loads for litter.

6.6 Seasonal First Flush

The seasonal first flush issue was addressed by plotting the concentrations of the various water quality parameters as a function of normalized rainfall for several years. Results revealed that the constituents' concentrations decline as the season progresses. This indicates that treating stormwater early in the season is more effective than treating runoff late in the season. The engineering opportunities to exploit these differences were beyond the scope of this study and have not been explored. Similar trends in other water quality parameters and the data from the Department's statewide monitoring program (Department's report CTSW-RT-03-065.51.42) also show a seasonal first flush.

6.7 Particle First Flush

In the fourth year of the study, particle size distribution was measured during the various stages of the hydrograph. The numbers of particles were measured over the range of 2 to 1000 μm. It was observed that the numbers of particles declined dramatically as the storm progressed. Preliminary analysis of particle size distribution indicated the occurrence of a natural aggregation. This natural aggregation of particles required that analysis be performed as soon as possible, but in no case longer than six hours after sample collection of the sample. Analysis of samples older than six hours could be biased due to particle aggregation. Samples collected using automatic composite samplers had lesser numbers of small particles and greater numbers of large particles than grab samples. The holding time during the composite sample collection allowed particles to aggregate. Therefore, composite samplers are not recommended for collecting samples for PSD analysis.

More than 97% of the particles were less than 30 μm in diameter. Particle concentration and size generally decreased rapidly as the storm progressed. Rapid increases in particle numbers occurred after rapid increases in rainfall or runoff, and were accompanied by increases in turbidity and total suspended solids concentration. Particles showed an obvious first flush, with median of PFF_{20} of approximately 2, indicating that 40 % of total particles were carried in the first 20 % of runoff volume. Larger particles showed a stronger first flush effect than smaller particles.

The availability of particle size distribution measurements will greatly increase our understanding of treatment mechanisms. BMPs can be sized to remove particles larger than a specific size, which will allow more scientific evaluation of BMPs. Work is underway to measure pollutant concentrations as a function of the particle size.

6.8 BMP Evaluation based on First Flush

As part of this study, the MFF ratios have been calculated for all storms and monitored constituents. The mean mass first flush ratios at 10, 20, 30, 40 percent runoff volume were computed and ranked for all constituents. The use of the MFF ratios, as opposed to an arbitrary definition of first flush, allows BMPs to be evaluated for a continuum of conditions. The MFF values can be used in evaluating BMPs, especially those that are “first flush friendly,” meaning that the treatment system can capture or treat the early runoff and associated pollutant mass.

To estimate the potential benefits of treating pollutants in the early runoff, either as the first flush of a storm event or a seasonal first flush, a treatment effectiveness factor (TEF_n) as a function of MFF_n was introduced. Computation of TEF for 10, 20, 30 and 40 percent of the normalized cumulative runoff volume showed a value between 2 to as high as 7. A TEF_{10} of 7 means that treating the first 10 percent of the stormwater runoff volume will be 7 times more effective than treating an equal volume of runoff at a later time in the storm event.

6.9 Correlation among Water Quality Parameters

Results showed that there are strong correlations among many of the water quality parameters and particularly among parameters that measure organic content (e.g., COD, total or dissolved organic carbon, etc). COD shows a particularly high correlation with other parameters. There are strong correlations among metals, such as zinc and copper, and the dissolved and particulate phase concentrations are highly correlated as expected. TSS is not as well correlated to other water quality contaminants as we have previously thought. The high degree of correlation among parameters raises questions about the need for such extensive monitoring of all parameters. It may not be necessary to measure all parameters for routine monitoring. For example, it may be possible to measure only one organic quality parameter, such as TOC or COD. TOC is easy to measure and generates no laboratory hazardous wastes as COD. It is easier and more reliable than oil and grease measurement. The degree of correlation is very high among soluble and total metals. Therefore it may be possible to measure only total metals. The utility in reducing the number of parameters will depend on the monitoring purpose. For BMP selection, the difference in soluble and total metals is important, since most BMPs generally cannot remove soluble metals. For routine monitoring, it may be possible to substitute total metals and calculate the soluble metal from the correlation.

6.10 New Method to Measure Oil and Grease Concentration

Oil and grease can generally not be sampled with an automatic sampler because the oil adheres to tubing and sample bottle surfaces. The adsorbed oil reduces the sampled value and can carry over to the following sample. Most agencies choose to take one grab sample instead of a composite sample. If the oil and grease sample is collected early in the storm, it will likely be greater than the EMC. If it is collected later in the storm, it can be lower. There is no distinct time in a storm event to collect a single oil and grease sample to be representative of the entire storm event. The most representative time to collect a sample ranges from 2 to 5 hours after the beginning of rainfall, and depends on many factors.

Correlation between O&G and other organic constituents, such as chemical oxygen demand (COD) or dissolved organic carbon (DOC) was shown to be a better method to estimate the oil and grease EMC. Most importantly, COD and DOC can be collected using automatic samplers. Strong correlation (R^2= 0.9) between these aggregate organic constituents and oil and grease were found. A linear mathematical relationship was derived and for highway runoff, and the composite sample analyzed for DOC was the best method to estimate O&G event mean concentration.

6.11 Sampling Issue: Automatic versus Grab Sampling

It is generally known that flow weighted composite samples provide more accurate and precise information than a grab sample. During the course of this research, questions were raised about the accuracy of flow-weighted automated composite samplers, and whether they provide better information than a series of composite samples that are flow-weight averaged to produce a calculated composite sample.

To answer this question, a series of simulations were performed to “mimic” the runoff flow rate and concentrations observed in the first two years of our study. Random noise was added to simulate the stochastic nature of stormwater. The degree of noise was selected to match the variability in the actual observations. Next an automated sampler and flow weighted grab samples were simulated. The automated sampler was simulated by rapidly sampling the runoff at short intervals, simulating the “squirts” that the automated composite samplers collect in proportion to flow rate. Grab samples were simulated in a similar fashion, but at randomly timed intervals.

More than 1000 simulations were performed and the result showed that and EMC estimated by averaging 10 grab samples will have a mean error of 42 % difference as compared to a flow weighed composite sample, collecting small sample volumes every minute. The error decreases with the number of samples and approaches 12% for 100 grab samples. In general, however, it is shown that a large number of grab samples is needed to approximate the flow weighted composite sample. Thirty grab samples per storm event provided a good estimate of a composite sample. To detect a first flush, it is necessary to take even more samples or to weight the samples towards the beginning of the storm. The superiority of the automatic sampling equipment is demonstrated, and the results show that investigators using only a few grab samples to characterize an event would not be able to observe a first flush.

In Conclusion

The existence of a first flush, either a storm or a seasonal first flush, may present opportunities for managers and regulators to affect better pollutant reduction programs. Treating early runoff that has higher contaminant concentrations may be a better policy than treating a similar fraction of the entire runoff volume. This will be true for two reasons. The first reason is the cost of treatment is generally more dependent more on the volume of water to be treated than the contaminant concentration. The second reason relates to the way that stormwater BMPs function; removal efficiency is greater at higher concentrations. Treatment efficiency at low concentrations is nearly zero, but significant removal can be obtained at higher concentrations. The emerging ASCE database on BMP trials shows this effect.

The Department’s future development programs to reduce pollutants from stormwater may take advantage of first flush for removal of specific contaminate at local watershed basis.

REFERENCES

American Public Health Association. (1998). *Standard methods for the examination of water and wastewaters*, 20th Ed., Washington, DC.

Barrett, M.E., Irish, L.B., Jr., Malina, J.F., Jr., and Charbeneau, R.J. (1998). "Characterization of highway runoff in Austin, Texas, area." *J. Envir. Engrg.*, 124(2), 131-137.

Bertrand-Krajewski, J., Chebbo, G., and Saget, A. (1998). "Distribution of pollutant mass vs. volume in stormwater discharges and the first flush phenomenon." *Wat. Res.*, 32(8), 2341-2356.

Charbeneau, R.J., and Barrett, M.E. (1998). "Evaluation of methods for estimating stormwater pollutant loads." *Wat. Environ. Res.*, 70(7), 1295-1302.

Deletic, A. (1998). "The first flush load of urban surface runoff." *Wat. Res.*, 32(8), 2462-2470.

Deletic, A.B., and Mahsimivic, C.T. (1998). "Evaluation of water quality factors in storm runoff from paved areas." *J. of Environ. Engr*, 124(9), 869-879.

Deletic A., Ashley, R., and Rest, D. (2000). "Modeling input of fine granular sediment into drainage systems via gully-pots." *Wat. Res.*, 34(15), 3836-3844.

Department (2000a). *Caltrans storm water monitoring & research program : 2000-2001 water quality data-reporting protocols*, Div. of Environmental Analysis, California Department of Transportation, Sacramento.

Department (2000b). *Sampling and analysis plan, Caltrans 2000-2001, first flush characterization study.* Department's document No. CTSW-RT-00-044. CA.

Department (2000c). *Litter monitoring guidance manual.* Department's document No. CTSW-RT-00-025. CA.

Department (2003). *Discharge Characterization Study Report*. Department's document N0. CTSW-RT-03-065.51.42

Geiger, W. (1987). "Flushing effects in combined sewer systems." *Proc. 4th Int. Conf. Urban Drainage*, 40-46, Lausanne, Switzerland.

Gupta, K., and Saul, A.J. (1996). "Specific relationships for the first flush load in combined sewer flows." *Wat. Res.*, 30(5), 1244-1252.

Ha, H. and M.K. Stenstrom, "Identification of Land Use with Water Quality Data in Stormwater Using a Neural Network," *Water Research*, Vol. 37, pp 4222-4230, 2003.

Irish, L.B., Jr., Barrett, M.E., Malina, J.F., Jr., and Charbeneau, R.J. (1998). "Use of regression models for analyzing highway storm-water loads." *J. of Environ. Engr.*, 124(10), 987-993.

Kim, L-H., M. Kayhanian, M. and M.K. Stenstrom (2004)"Event Mean Concentrations of Litter from Highways during Storms," *Science of the Total Environment*, Vol. 330, pp. 101-113.

Larsen T., Broch, K., and Andersen, M.R. (1998). "First flush effects in an urban catchment area in Aalborg." *Wat. Sci. & Tec.*, 37(1), 251-257.

Lau, S-L, S. Bay and M.K. Stenstrom (1998) "Impact of Wet Weather Runoff to Santa Monica Bay - A Case Study," Proceedings of the 1st Biannual Water Environment Federation Asia Conference, Singapore, March 8-11, Vol. 2, pp 221-232.

Lau, S. L., J-S Ma, M. Kayhanian and M.K. Stenstrom, "First Flush of Organics in Highway Runoff," Proceedings of the 9th International Conference on Urban Drainage, Portland Oregon. October 8-13, 2002.

Lau, S-L and M.K. Stenstrom (2001) "Best Management Practices to Reduce Pollution from Stormwater in Highly Urbanized Areas," WEF Tech, Chicago, IL, September 30-October 3.

Lau, S-L., and Stenstrom, M.K., (1997). "Solid phase extraction for oil and grease analysis." *Wat. Environ. Res.*, 69(3), 368-374.

Legret, M., and Pagotto, C. (1999). "Evaluation of pollutant loadings in the runoff waters from a major rural highway." *Sci. Total Environment*, 235, 143-150.

Ma, J-S, S. Khan, Y-X Li, L-H Kim, H. Ha, S-L Lau, M. Kayhanian, and M.K. Stenstrom, "Implication of Oil and Grease Measurement in Stormwater Management Systems", Proceedings of the 9th International Conference on Urban Drainage, Portland Oregon. October 8-13, 2002.

Ma, J-S, S. Khan, Y-X Li, L-H Kim, S. Ha, S-L Lau, M. Kayhanian, and M.K. Stenstrom, "First Flush Phenomena for Highways: How It Can Be Meaningfully Defined," ", Proceedings of the 9th International Conference on Urban Drainage, Portland Oregon. October 8-13, 2002.

Ma, J.S. (2002) "Characteristics of Pollutants in Highway Runoff: Regression, Representativeness, and First Flush," Ph.D. Dissertation, University of California, Los Angeles, Los Angeles, CA.

Ngabe, B., Bidleman, T.F., and Scott, G.I. (2000). "Polycyclic aromatic hydrocarbons in storm runoff from urban and coastal South Carolina." *Sci. Total Environment*, 255, 1-9.

Osuch-Pajdzinska, E., and Zawilski, M. (1998). "Model of storm sewer discharge. I: description." *J. of Environ. Engr.*, 124(7), 593-599.

Saget, A., Chebbo, G., and Bertrand-Krajewski, J. (1995). "The first flush in sewer system. *Proc. 4th Int. Conf. Sewer Solids-Characteristics, Movement, Effects and Control*, 58-65, Dundee, UK.

Saget, A., Chebbo, G., and Bertrand-Krajewski, J. (1995). "The first flush in sewer system." *Proc. 4th Int. Conf. Sewer Solids-Characteristics, Movement, Effects and Control*, 58-65, Dundee, UK.

Sansalone, J.J., and Buchberger, S.G. (1997). "Partitioning and first flush of metals in urban roadway storm water." *J. of Environ. Engr.*, 123(2), 134-143.

Sansalone, J.J., Koran, J.M., Smithson, J.A., and Buchberger, S.G. (1998). "Physical characteristics of urban roadway soils transported during rain events." *J. of Environ. Engr.*, 124(5), 427-440.

Stenstrom, M.K., S. Fam and G.S. Silverman (1986) "Analytical Methods for Quantitative and Qualitative Determination of Hydrocarbons and Oil and Grease in Wastewater," *Environmental Technology Letters,* Vol. 7, pp 625-636.

Stenstrom, M.K. and Lee, H (2005) Final Report: Industrial Storm Water Monitoring Program Existing Statewide Permit Utility and Proposed Modifications, to the Los Angeles Regional Water Quality Control Board, Los Angeles, CA.

Strecker, E.W., Quigley, M.M., Urbonas, B.R., Jones, J.E., Clary, J.K., (2001). "Determining urban storm water BMP effectiveness." *Journal of Water Resources Planning And Management-ASCE*, 127(3), 144-149.

Thornton, R.C., and Saul, A.J. (1987). "Temporal variation of pollutants in two combined sewer systems." *Proc. 4th Int. Conf. Urban Drainage*, 51-52, Lausanne, Switzerland.

Vorreiter, L., and Hickey, C. (1994). "Incidence of the first flush phenomenon in catchments of the Sydney region." *Nat. Conf. Publication-Inst. of Engr.*, 3, 359-364, Australia.

US EPA (1999). *SW-846: Test Methods for Evaluating Solid Waste, Physical/Chemical Methods*. Office of Solid Waste, US EPA.

Wu, J. S., Allan, C. J., Saunders, W. L., and Evett, J. B. (1998). "Characterization and pollutant loading estimation for highway runoff", *J. Environ. Eng.*, 584-592.

BIBLIOGRAPHY (as of September 2005)

Published Journal Papers

1. Kim, L-H., M. Kayhanian, M. and M.K. Stenstrom, “Event Mean Concentrations of Litter from Highways during Storms,” *Science of the Total Environment*, Vol. 330, pp. 101-113, 2004.
2. Lee, H. S-L. Lau, M. Kayhanian, and M.K. Stenstrom, “Seasonal first flush phenomenon of urban stormwater discharges”, *Water Research*, Vol. 38, pp 4153-4163, 2004.
3. Kim, L-H, M. Kayhanian, S-L Lau, and M.K. Stenstrom, “A New Modeling Approach for Estimating First Flush Metal Mass Loading,” *Water Science and Technology*, Vol. 51(3-4), pp. 159-167, 2005.
4. Li, Y, S-L Lau, M. Kayhanian, and M.K. Stenstrom, “Particle Size Distribution in Highway Runoff,” *Journal of the Environmental Engineering*, ASCE, Vol. 131, pp 1267-1276, 2005.
5. Kayhanian, M. And M.K. Stenstrom, " Mass Loading of First Flush Pollutants with Treatment Strategy Simulations." *Transportation Research Record (Hydrology, Hydraulics, and Water Quality)*, No. 1904, pp 133-143. 2005.
6. Kim, L.H., M. Kayhanian, K.D. Zoh, and M.K. Stenstrom, “Modeling of Highway Runoff,” *Science of the Total Environment*, Vol. 348, pp 1-18, 2005.

In press Journal Papers

1. Khan, S, S-L Lau, M. Kayhanian, and M.K. Stenstrom, “Oil and Grease Measurement in Highway Runoff – Sampling Time and Event Mean Concentrations,” *Journal of the Environmental Engineering*, ASCE, 2004.
2. Han, Y-H, S-L Lau, M. Kayhanian and M.K. Stenstrom, “Correlation Analysis Among Highway Stormwater Runoff Pollutants and Characteristics,” *Water Science and Technology*, 2005.
3. Kim, L-H, J. Kang, M. Kayhanian, K-I Gil, M.K. Stenstrom and K-D Zoh, “Characteristics of Litter Wastes in Highway Runoff,” *Water Science and Technology*, 2005.

Submitted Journal Papers

1. Li, Y., S-L Lau, M. Kayhanian, and M.K. Stenstrom, “Dynamic Characteristics of Particle Size Distribution in Highway Runoff: Implications for Settling Tank Design,” *Journal of the Environmental Engineering*, ASCE, 2004.
2. Li, Y., S-L Lau, M. Kayhanian, and M.K. Stenstrom, “Application of Particle Size Distribution Highway Runoff: Optimization of Settling Tank Design to Remove Particles and Metals,” *Journal of the Environmental Engineering*, ASCE, 2005.
3. Kim, L-H, M. Kayhanian, and M.K. Stenstrom, “Estimation of Accumulated Pollutant Mass.” *Journal of the Environmental Engineering*, ASCE, 2005.

Conference Papers

1. Stenstrom, M.K, Lau, S-L, Lee, H-H, Ma, J-S, Ha, H., Kim, L-H, Khan, S. and M. Kayhanian, “First Flush Stormwater Runoff from Highways,” ASCE EWRI Conference, Orlando, FL, May 24, 2001.
2. Ma, J-S, S. Khan, Y-X Li, L-H Kim, H. Ha, S-L Lau, M. Kayhanian, and M.K. Stenstrom, “Implication of Oil and Grease Measurement in Stormwater Management Systems”, Proceedings of the 9th International Conference on Urban Drainage, Portland Oregon. October 8-13, 2002.
3. Lau, S. L., J-S Ma, M. Kayhanian and M.K. Stenstrom, “First Flush of Organics in Highway Runoff,” Proceedings of the 9th International Conference on Urban Drainage, Portland Oregon. October 8-13, 2002.
4. Ma, J-S, S. Khan, Y-X Li, L-H Kim, S. Ha, S-L Lau, M. Kayhanian, and M.K. Stenstrom, “First Flush Phenomena for Highways: How It Can Be Meaningfully Defined,” ”, Proceedings of the 9th International Conference on Urban Drainage, Portland Oregon. October 8-13, 2002.
5. Kim, L-H, M. Kayhanian and M.K. Stenstrom, “Prediction of Event Mean Concentrations and First Flush Effects Using a Mass Interpolation Wash-off Model for Highway Runoff,” Proceedings of the 6th IWA International Conference on Diffuse Pollution, Amsterdam, pp 227-235, October 1, 2002.
6. Lau, S-L, M. Kayhanian and M.K. Stenstrom, “Mass First Flush of Organic Contaminants in Highway Runoff,” Paper 3Q5K13, Proceedings of the IAW-Asia Pacific Regional Conference, Oct. 19-23, 2003, Bangkok, Thailand.
7. Stenstrom, M.K., M. Ma and M. Kayhanian, “Sampling Issues: Composite versus Grab,” Proceedings, StormCon, Palm Desert, CA, July 26-29, 2004
8. Kayhanian, M., S. Khan and M.K. Stenstrom, “A New Method to Estimate Oil and Grease Event Mean Concentration in Roadway Runoff,” Proceedings, StormCon, Palm Desert, CA, July 26-29, 2004
9. Kayhanian, M, T.M. Young, and M.K. Stenstrom, “Limitation of Current Solids Measurements in Stormwater Runoff,” *Stormwater*, Vol. 6, No. 5.
10. Lau, S-L, M. Kayhanian and M.K. Stenstrom, “PAHs and Organic Pollutants in Highway Runoff,” IWA ASPIRE Conference, Singapore, July 10-15, 2005, paper 7F5.
11. Li, Y, M. Kayhanian, S-L Lau and M.K. Stenstrom, “Particle-Based Pollutant Removal BMPs,” Proceedings, StormCon, Orlando, Fl, July 18-21, 2005.
12. Kayhanian, M. S. Ha and M.K. Stenstrom, “Constituents’ Annual Loading Estimation form Highways,” 10th ICUD Conference, Copenhagen, Denmark, August 21-26, 2005.