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Characteristics of Parking Lot Runoff Produced by Simulated Rainfall



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EXECUTIVE SUMMARY

Urban stormwater runoff is currently one of the largest sources of pollutants discharged to the coastal oceans of southern California. However, the quality and quantity of stormwater runoff are highly variable. In particular, impervious (paved) surfaces directly affect a watershed's water quality. The goal of this study was to: (1) identify and measure constituent concentrations and toxicity found in parking lot surface runoff; (2) measure the effect of antecedent conditions on constituent accumulation between storms; and (3) investigate the effects of rainfall intensities and duration on runoff composition. A secondary objective was to assess the effects of traffic use and maintenance on the chemical composition and toxicity of parking lot runoff.

In order to control natural variability in precipitation, periodic rainfall simulations were used to quantify pollutant accumulation and washoff on two parking lots in the City of Long Beach for three months during the summer of 2000. Samples of surface runoff were analyzed for suspended solids, trace metals (Cd, Cr, Cu, Fe, Ni, Pb and Zn) in dissolved and particulate-bound phases, and 25 polycyclic aromatic hydrocarbons (PAHs). Among the metals studied, the highest mean concentrations in surface runoff samples were for Fe, Zn, Cu and Pb (810, 620, 40 and 40 $\mu\text{g/L}$, respectively). The Zn, Pb and Cu in the dissolved phase accounted for 65 to 81% of concentrations in surface runoff samples. Mean total PAH concentrations in surface runoff samples ranged from 0.08 to 180 $\mu\text{g/L}$.

Significant accumulation of mean constituent concentrations were observed for all constituents after 28 antecedent dry days, with the exception of total PAHs. Of the trace metals studied, Zn showed the largest accumulation in parking lot surface runoff, increasing by a factor of 3. Factors such as parking lot usage and maintenance did not affect the accumulation of runoff constituents. Similar concentrations of total suspended solids (TSS), trace metals, and total PAHs were found among high-use and low-use parking lots. Street sweeping as a maintenance activity did not reduce or improve runoff concentrations. However, the use of pressure washing did appear to reduce, but not completely remove, suspended solid and trace metal concentrations.

Washoff of all constituents was strongly inversely correlated with rainfall intensity and duration. Parking lot runoff samples collected during the first 10 min of a rain event contained the highest constituent concentrations indicative of a first-flush event. A "first flush" occurs when initial runoff during a storm has substantially higher concentrations than runoff later in the storm. Longer, simulated storms appeared to dilute parking lot runoff, and significantly lowered the average concentration of most constituents. Increases in rainfall intensity decreased the magnitude of the first flush, but the importance of rainfall intensities decreased with longer duration. Simulated rainfall, regardless of intensity, washed off most loose particles collected on the parking lot surface after approximately 15 min; concentrations of constituents collected after 15 min were generally low and less variable.

One hundred percent of simulated runoff samples were toxic, but not all species responded similarly after exposure to runoff samples. The sea urchin and marine bacteria were the most

sensitive organisms; the mysid was the least sensitive organism. Toxicity patterns were consistent with the accumulation and rainfall duration/intensity patterns of constituent concentrations. After 28 d of accumulation, toxicity in runoff samples increased by a factor of 6. When comparing runoff from either high-use or low-use parking lots, the magnitude of toxicity did not change. Similarly, the magnitude of toxicity between parking lots with and without street sweeping showed no difference. However, toxicity was reduced, but not completely eliminated, after pressure washing. A toxicity “first-flush” effect was present in runoff samples collected during the first 10 min of the simulated rain event. Runoff samples collected during this time interval were twice as toxic as runoff samples taken later during the storm event. This finding is in agreement with the results of chemical analyses of the samples, which showed the first portion of the runoff event to contain the highest constituent concentrations.

The toxicant characterization and identification experiments suggested that trace metals were an important contributor to toxicity. These evaluations targeted trace metals, particularly zinc, as constituents responsible for toxicity in the purple sea urchin fertilization test. This conclusion was based upon the following findings: (1) complexation of trace metals completely removed toxicity; (2) concentrations of dissolved zinc were sufficient to induce toxic responses; and (3) variations in zinc concentrations among samples were significantly correlated with toxic responses.

The rapid accumulation, the nearly complete washoff of constituent concentrations, and the level of toxicity observed from parking lot runoff in this study indicate that uncontrolled discharges of parking lot runoff have the potential to impact receiving water quality and may require remediation by appropriate stormwater BMPs. Targeting the first flush appears to be the most effective management scenario based upon the results herein. Additional simulated rainfall events are recommended for other constituents and for various land uses besides parking lots.

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I. INTRODUCTION

Urban stormwater runoff has been recognized as a leading source of contaminants to coastal oceans and inland waterways (U.S. EPA 1995a). Research has found a direct relationship between the amount of impervious surface in a watershed and the watershed's water quality (City of Olympia 1994). This research, which has been conducted in many geographic areas using many different variables and employing widely different methods, has yielded a surprisingly similar conclusion: stream degradation occurs at relatively low levels of imperviousness (~10%) (Booth and Reinelt 1993 and Shaver *et al.* 1995). In southern California, watersheds average 25% imperviousness; hence, the impacts of land development on the quality of surface runoff and on aquatic organisms are likely to be found in southern California.

Streets and parking lots comprise a large proportion of impervious area; runoff from these areas is therefore considered to be a significant source of chemical contamination to receiving waters. These pollutants are derived from wear of automotive parts (e.g., tires and brake pads), spills and leaks of automotive fluids (e.g., motor oil and coolant), and materials deposited on parking lots from the air (e.g., atmospheric deposition and wind transported pollutants) (Hoffman *et al.* 1985, Ellis *et al.* 1987, and Muschack 1990). During rainstorms, a portion of these pollutants are washed off and transported from the street surfaces to the urban storm drain system and discharged to local receiving waters. In a nationwide coring study of aquatic sediment quality by the U.S. Geological Service (Van Metre *et al.* 2000), a clear relationship was reported between increasing traffic volume and increasing PAH concentration. Traffic volume, therefore, seems to be an important factor affecting the type and accumulation of contaminant concentrations and is valuable as a measure for predicting runoff quality.

Contaminant accumulation and washoff are commonly assumed to be effective measures of runoff contamination in our semi-arid environment; however, the effectiveness of these measures has not been well quantified in southern California. The accumulation of contaminants on southern California streets and parking lots has become a focal point since periods of infrequent rainfall (long, dry periods without rain) followed by intense rainfall are common. Other factors have been shown to influence the quality of surface runoff including surface maintenance practices, the time of the year (season), and the intensity and duration of the storm. Storm intensity is strongly correlated to the type and quantity of pollutants found in stormwater runoff (Pitt and Shawley 1981, Spangberg and Niemczynowicz 1992). Measurements of stormwater discharges sampled in 1997-98 from the Santa Ana River in Santa Ana, California (Leecaster *et al.* 2001, Schiff and Tiefenthaler 2001, and Tiefenthaler *et al.* 2001) showed evidence of a seasonal flush of contaminants.

The goal of this report is to evaluate the effects of rainfall characteristics and antecedent conditions on the composition of parking lot surface runoff. The primary objective is to identify and measure contaminant and toxicity concentrations found in runoff from parking lots, assess the length of time required for constituents to re-accumulate once washed off, and investigate

how variations in intensity and duration of rainfall affect runoff composition. A secondary objective is to assess the effects of traffic use and parking lot maintenance on the chemical composition and toxicity of runoff.

II. METHODS

Experimental Design

This study was grouped into two major components: (1) The assessment of accumulation rates of selected contaminants over time and during discrete time periods. (2) The investigation of variations in rainfall intensities and durations affecting parking lot surface runoff concentrations to determine whether similar quantities of rainfall cause similar effects on contaminant concentrations over time (i.e., 6 millimeters of rainfall per hour [mm/hr] for 40 min vs. 25 mm/hr for 10 min). Possible interactions between treatments (i.e., low-use/maintained stations vs. high-use/unmaintained stations) were also examined.

A randomized factorial design was selected to measure the effects of a variety of treatments on contaminant accumulation and washoff on parking lots over time including: (1) low use (1 car/4 h--i.e., faculty parking); (2) high use (5 or more cars/h--i.e., public parking); (3) maintained stations vs. unmaintained stations (defined as the presence or absence of street sweeping); (4) rainfall intensities; and (5) rainfall durations. All rainfall simulations for the accumulation study were run for 20-min durations with a constant storm intensity of 13 mm/hr. The rainfall duration/intensity study had simulations that were run for the following time intervals: 0-10, 10-20, 20-40 and 0-20 min, using rainfall intensities of 6 (0.25 inches/h), 13 (0.5 in/h), and 25 (1 in/h) mm/hr. Treatments were assigned randomly among 27 test stations. The "first-flush" effect of storms was also evaluated.

Study Area

All samples were collected within the City of Long Beach, the fifth largest city in California with an estimated population of 440,000 citizens living in a 50-square-mile area. (City of Long Beach, Economic Development Bureau 1999). Long Beach is a port city bounded on its southern border by the Pacific Ocean. It has a semi-arid climate with an annual precipitation of only 30.5 centimeters (cm). An average 0.4 cm of rain falls each month from May to October, with 4.6 cm/month falling from November to April.

Sampling Sites

Two parking lots located within the Long Beach City College Liberal Arts Campus (LBCC LAC) at 4901 E. Carson Street in the City of Long Beach, California, were selected for monitoring runoff from parking lots (Figure II-1). The parking lots differed in daily traffic flow and maintenance practices. The parking lots have a combined capacity of 150 cars with a dimension of approximately 8 meters by 76 meters and a 4% grade. The lots operate seven days per week with five days at fill capacity. A total of 9 replicate sampling stations were located on the site off of Lew Davis Street, which received no maintenance. Eighteen sampling stations, representing both low-use and high-use as well as maintained and unmaintained conditions, were

located on the lot at Faculty Street. Six maintained stations (3 low use and 3 high use) were located in the southern portion of this lot and comprised approximately 30% of the total parking lot area. The land around the sites is mostly commercial. The sites, which were constructed of 100% asphalt, were used for both visitor and staff parking. Accessibility for runoff sampling was a consideration in site selection. Every effort was made to select sites which were as similar as possible in terms of condition and slope. The prevailing weather conditions were similar at all sites.

Dry conditions were prevalent in Long Beach from May to October of 2000, with less than a trace of rain at any of the two sites for a period of 160 d. Manual observation of traffic counts were recorded 1 d prior to each simulated rainfall event and averaged approximately 100 vehicles per day.

Rainfall Simulator

Rainfall simulation equipment and techniques were used for assessing the effects of rainfall on surface runoff. In this study, sampling was carried out using three identical rainfall simulators (spray rigs) designed to duplicate natural rainfall intensities. Each spray rig was comprised of polyvinylchloride (PVC) pipes with its own pressure gauge, flow meter, control valve, and fixed-rate Rainbird or Hunter PGM rotating polyurethane spray heads. One fixed-rate Rainbird spray head at 45/36 pounds per square inch (psi) and 5.0 liters per minute (L/min) produced a 3.8 m radius semicircle with an intensity of 13 mm/hr (Figures II-2 and II-3). This system provided a relatively uniform simulated rainstorm washing off 2 parking stalls measuring 18 m². Approximated rainfall intensities were determined for two types of storm events that occur in southern California. Typical (6 mm/hr) and worst-case (25 mm/hr) rainfall intensities were simulated using 2 Hunter spray heads with 0.75 gallon-per-minute (gpm) emitters while also varying the pressure and flow rate. Simulating rainfall for a period of 20 min at an intensity of 13 mm/hr resulted in a total runoff volume of 26.4 liters.

The rainfall simulators were designed to isolate and capture the entire portion of the surface runoff traveling off each sampling site. The surface runoff generated by the rainfall simulators was collected continuously during each run using a vacuum system that transferred the runoff into a 55-gallon plastic barrel. At the end of each simulation run, the runoff collected in each barrel was stirred vigorously to distribute the sediment evenly in the sample. Chemistry and toxicity samples were taken.

The source water for the rainfall simulators was obtained from hose bibs located around the perimeter of the campus' "Q & R" building. All test water passed through a portable filtration system to ensure removal of chlorine and sediments from the source water before it was supplied to the simulated rainfall systems (Figure II-4).

A series of quality assurance and quality control (QA/QC) performance evaluations were conducted on all rainfall simulators including evenness of spread and precision of pressure, flow rate and volume to determine accuracy of reproducibility among spray rigs. Rainfall simulator measurements were designed to be within approximately 20% coefficient of variation and were verified prior to the onset of each simulated rainfall run. At time zero (T0) all parking lots were

cleaned using cold, high-pressure washing to establish background values for contaminants. All simulated rainfall equipment was thoroughly cleaned after each simulation. Chemistry and toxicity blank samples were taken from the source water prior to each sampling period.

Parking Lot Maintenance

The effectiveness of street sweeping in improving the quality of parking lot runoff was measured by comparing runoff concentrations between maintained and unmaintained stations. Maintained test stations were cleaned on a weekly basis using the following procedure. One individual operated both the backpack blower and the brooms, and either blew or swept all visible loose debris and surface dirt into the path of a power vacuum truck for collection and removal.

Surface Runoff Sampling

From July 2000 until October 2000, 155 rainfall runoff samples were collected periodically from two parking lots located on a college campus in Long Beach, California. All samples were stored under refrigeration and analyzed for TSS, both total and dissolved metals (cadmium, chromium, copper, iron, lead, nickel, and zinc), 26 selected PAHs, and toxicity to 3 species. The rainfall intensity/duration experiment was conducted during the third month of the study in order to allow contaminants to accumulate.

During this study, three different duration type samples were collected. In order to generate the TSS pollutograph, discrete samples were taken every 2 min for 20 min at 6, 13, and 25 mm/hr rainfall intensities. This sampling scheme continued for 40 min at the 6 mm/hr intensity. For the accumulation study, rainfall simulations with an intensity of 13 mm/hr were run for a fixed time period (20 min) and a composited sample was taken. In the rainfall duration/intensity experiment, composited samples represented discrete time intervals. Samples representing 0-10 min and 10-20 min durations were taken at 6 and 25 mm/hr rainfall intensities, respectively. An additional rainfall duration sample representing 20-40 min was taken at the 6 mm/hr intensity. To facilitate a comparison with the accumulation study, simulations were also run for 20 min at a rainfall intensity of 13 mm/hr.

Analytical Chemistry

Suspended Solids

Total suspended solids were analyzed by filtering a 10 to 100 mL aliquot of stormwater through a tared 1.2 μm (micron) Whatman GF/C filter (EPA Method 160.2). The filters plus solids were dried at 60° C for 24 h, cooled, and weighed.

Polycyclic Aromatic Hydrocarbons

The PAHs were extracted, isolated, and analyzed using the procedures documented by EPA Method 8270C (U.S. EPA 1991). The PAHs were separated, identified, and quantified by capillary gas chromatography (GC) coupled to mass spectrometry (MS). Acenaphthene and

Pyrene were used for quality control check standards. Twenty-five specific PAHs were determined for this study. Total PAHs (Σ PAH) was computed as the sum of these values.

Trace Metal Analysis

Samples for total and dissolved trace metal analysis were prepared by digestion. Dissolved metals were defined as passing through a 0.45 μ m filter. A well-mixed, 25 mL aliquot of acidified sample was dispensed to a Teflon digestion vessel and 2 mL of ultra-pure HNO₃ (Optima, Fisher Scientific) were added, and the vessel was capped and sealed. The acidified samples were digested in a CEM MSP1000 Microwave Oven by ramping to 100 psi over 15 min and then holding at 100 psi for 10 min. After cooling, the digestate was centrifuged to remove any remaining residue from the sample. The supernatant with sample digest was transferred to a 15 mL test tube prior to analysis.

Inductively coupled plasma-mass spectroscopy (ICP-MS) was used to determine total and dissolved concentrations of inorganic constituents (aluminum, antimony, arsenic, beryllium, cadmium, chromium, copper, iron, lead, mercury, nickel, selenium, silver, and zinc) from sample digest solutions using a Hewlett Packard Model 4500 with Hewlett Packard Data Systems software and following protocols established by EPA Method 200.8, EPA Method 236.1 and 236.2, and by EPA Modified Method 245.1. The internal standard solution included rhodium and thulium. Instrument blanks were processed to identify sample carry-over. A spiked sample of known concentration was used as the laboratory control material. The Certified Reference Material was ERA 9970 and ERA 9977 (Environmental Resource Associates, WasteWatR Lot No. 9970 and 9977, respectively).

Data Analysis

Significant differences among mean concentrations were determined using one-way ANOVA, Kruskal-Wallis and Tukey tests ($p = 0.05$). This study examined potential differences between low-use and high-use stations and maintained and unmaintained stations. General comparisons were made for all treatments. To provide a more accurate assessment of the magnitude and trends of contaminant contributions from parking lot surface runoff, the mean contaminant concentrations from the combined low-use treatments from maintained and unmaintained stations were pooled and compared with those of the high-use treatments from maintained and unmaintained stations from the same time period.

Toxicity Measurement

Since the ultimate destination for most runoff from the City of Long Beach is the ocean, toxicity testing was conducted using three marine species: sea urchin, mysid, and bacteria. The toxicity testing program was designed to accomplish three objectives. The first objective was to determine the magnitude of toxicity in each runoff sample collected from either the accumulation or rainfall intensity and duration experiments. The sea urchin fertilization test was used to accomplish this objective. The second objective was to determine the relative sensitivity of various species to parking lot runoff. Selected samples from the accumulation experiment were tested with all three species (sea urchin, mysid, and bacteria) to accomplish this objective. The

final objective was to investigate the nature of the toxic components in parking lot runoff. To address this objective, Phase I toxicity identification evaluations (TIE) were conducted on selected samples using the sea urchin fertilization test.

All samples were adjusted to a constant salinity so only the effect of toxic constituents, not the effect of freshwater, was evaluated. Each sample was tested at a minimum of two concentrations in order to estimate the magnitude of toxicity present. The maximum sample concentration tested was 50% (i.e., 50% runoff sample and 50% seawater or salinity adjustment solution). The concentrations tested in the accumulation experiment varied from test to test in order to maximize the value of the results for estimating the median effect concentration (EC50) and no observed effect concentration (NOEC). In general, runoff samples from the high-use treatment groups of the accumulation experiment were tested at concentrations of 50, 25, 12, 6, and 3%, while the low-use treatment groups were tested at a reduced number of concentrations. All samples from the rainfall intensity and duration experiment were tested at concentrations of 50% and 12%.

Prior to the start of the project and during each sampling period, samples of water from the simulated rainfall delivery and collection system were collected and tested to verify that they were not causing toxicity.

Seas Urchin Fertilization

The purple sea urchin sperm cell test was performed as described by Chapman *et al.* 1995. Gametes were obtained from adult specimens of the purple sea urchin, *Strongylocentrotus purpuratus*, collected from a relatively uncontaminated area in northern Santa Monica Bay. In the test, sea urchin sperm are exposed to various concentrations of the test sample for 20 min at a temperature of approximately 15° C. Sea urchin eggs were then added to each sample and given 20 min for fertilization to occur. Preservative was then added to the samples and they were later analyzed under a microscope to determine the percentage of fertilized eggs. Comparing the fertilization success of the sample to that of the control determines the degree of toxicity.

Since the toxicity test uses a marine organism, the salinity of the runoff samples was adjusted to a typical seawater value by the addition of brine. Addition of the brine diluted the samples, restricting the highest concentration of sample tested to 50%. Additional test concentrations were prepared by adding laboratory seawater (filtered natural seawater collected from offshore Redondo Beach) to the samples. A brine control was included in the experiment to check for toxicity introduced by the salinity adjustment procedure. The brine control consisted of deionized water plus laboratory seawater and brine at the same concentration found in the most concentrated runoff sample tested.

A reference toxicant test was conducted concurrently with each test in order to document variability in test sensitivity. This test consisted of five concentrations of dissolved copper, ranging from 10 µg/L to 65 µg/L.

Mysid Survival and Growth

The mysid short-term chronic survival and growth bioassay was performed according to methods described in Klemm *et al.* 1994. Juvenile mysids of the species *Americamysis bahia* (formerly *Mysidopsis bahia*) were obtained from Aquatic Biosystems of Ft. Collins, CO. To perform the test, 5 animals are added to 250 mL polypropylene beakers containing 150 mL of sample with 8 replicates per concentration. The mysids are fed newly hatched *Artemia* daily. Each day the solution in the beakers is removed and renewed. The exposure period of 7 d is conducted at 26° C with a salinity of 30 g/Kg. At the end of the exposure period, the number of surviving animals is recorded and the survivors are dried and weighed. The endpoints for this test are percentage of survival and average individual dry weight compared to the control values.

The salinity of the runoff samples was adjusted by the addition of Forty Fathoms bioassay grade sea salts. Various test concentrations were prepared by diluting the salinity-adjusted runoff sample with 30 g/kg of laboratory seawater. A salt blank was included in each experiment to check for toxicity introduced by the salinity adjustment procedure. The salt blank consisted of deionized water plus sea salts and laboratory seawater at the same concentration found in the most concentrated runoff sample tested.

A reference toxicant test was conducted concurrently with each of the runoff tests in order to document variability in test sensitivity. This test consisted of five concentrations of dissolved copper, ranging from 100 µg/L to 350 µg/L. Both the survival and growth endpoints were examined for the reference toxicant exposure.

Bacteria Luminescence

Toxicity of the runoff samples to marine bacteria (*Vibrio fischeri*) was measured using the Microtox™ Rapid Toxicity Testing System. Two different tests were conducted on each sample, a 15-min short-term acute test and 24-h long-term chronic test. Samples for both procedures were analyzed using a Microtox M500 analyzer following the Microtox Comparison Test Method (Microbics Corporation 1995).

For the acute test, bacteria were added to triplicate cuvettes containing 1.5 mL of sample and incubated at 15° C. The salinity of the samples was adjusted by adding a saline solution. Microtox diluent was added to the samples to produce various test concentrations. The luminescence of each replicate was measured at 0, 5 and 15 min. Mean percent luminescence was then calculated as the average of the replicates within each concentration as normalized to the time zero value of each sample and corrected for natural light loss between zero and 15 min. Reproducibility of the test organism response was determined by testing a copper reference toxicant solution at a series of concentrations.

The Microtox chronic test procedure was similar to the acute method, except that the samples were tested in quadruplicate and incubated at 27° C for 24 h. Nutrient media were added to the test solution, with dilutions made using DIW and the Microtox control media solution. Luminescence at 24 h was measured and compared to the control value. Reproducibility of the

test organism response was determined by testing a copper reference toxicant solution at a series of concentrations.

Data Analysis

The NOEC (highest test concentration not producing a statistically significant reduction in fertilization or survival) and the EC50 or LC50 (concentration of runoff producing a 50% reduction in fertilization or survival, respectively) were calculated for each sample whenever suitable data were obtained. For the NOEC calculation, the data were arcsine transformed and then tested for homogeneity of variance and normal distribution. Data that met these criteria were then tested using the one-way analysis of variance (ANOVA) and Dunnett's multiple comparison test to identify differences between the control and each of the samples. Data that did not pass the test for homogeneity of variance and/or normal distribution were analyzed using the non-parametric Steel's Many-One Rank test. The EC50 or LC50 were calculated using probit analysis.

Toxicity Characterization

Phase I TIEs were conducted on runoff samples from months 2 and 3 of the accumulation experiment in order to determine the characteristics of the toxicants present. Each sample was subjected to treatments designed to remove selectively or neutralize classes of compounds (e.g., metals, nonpolar organics) and any associated toxins. Treated samples were then tested to determine the change in toxicity using the sea urchin fertilization test.

Four treatments were applied to each sample: particle removal, trace metal chelation, nonpolar organic extraction, and chemical reduction. With the exception of the organics extraction, each treatment was applied independently on a salinity-adjusted sample. A control sample (laboratory dilution water) was included with each type of treatment to verify that the manipulation itself was not causing toxicity. A reduced set of concentrations of untreated sample was tested at the time of the TIE to determine the baseline toxicity and control for changes in toxicity due to sample storage.

Ethylenediaminetetraacetic acid (EDTA), a chelator of metals, was added at a concentration of 60 mg/L to the test samples. Sodium thiosulfate (STS), a treatment that reduces oxidants such as chlorine and also decreases the toxicity of some metals, was added at a concentration of 50 mg/L to separate portions of each sample. The EDTA and STS treatments were given at least 1 h to interact with the sample prior to toxicity testing.

Samples were centrifuged for 30 min at 3000 X g to remove particle-borne contaminants and were then tested for toxicity. A portion of the centrifuged sample was also passed through a 12 mL Varian Mega Bond Elute C-18 solid phase extraction column in order to remove nonpolar organic compounds. The C-18 columns have also been found to remove some metals from aqueous solutions.

The used C-18 columns were stored under refrigeration for 1 to 2 months and then eluted in order to recover the retained toxic constituents. Each column was eluted sequentially with methylene chloride (MeCl₂) and hydrochloric acid (HCl) to recover the organic and metal

fractions. Each column was rinsed with deionized water to remove excess salts. MeCl₂ (100%) was then passed through the column and the eluate was collected. The column was then rinsed with methanol to remove any residual MeCl₂. Finally, 2 M HCl was passed through the columns and the eluate was collected. The MeCl₂ eluates were solvent exchanged into isopropanol. Dilutions of the organic and acid eluates were tested for toxicity using the sea urchin fertilization test.

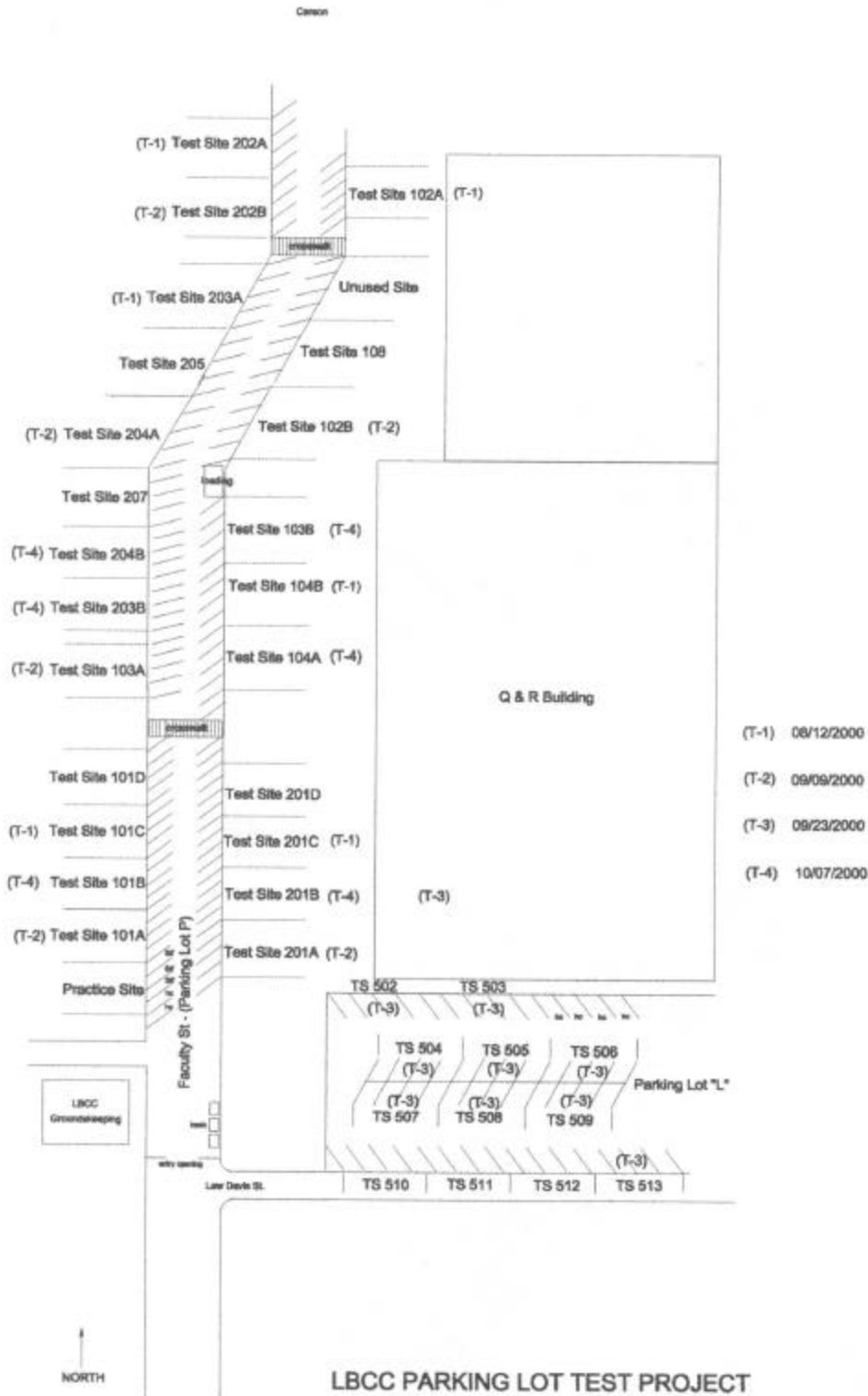


FIGURE II-1. Layout of the study area and sampling sites selected for monitoring runoff from parking lots located within the Long Beach City College Liberal Arts Campus (LBCC LAC) in the City of Long Beach, California.



FIGURE II-2. The simulated rainfall delivery and water collection system used for assessing the effects of rainfall on surface runoff.

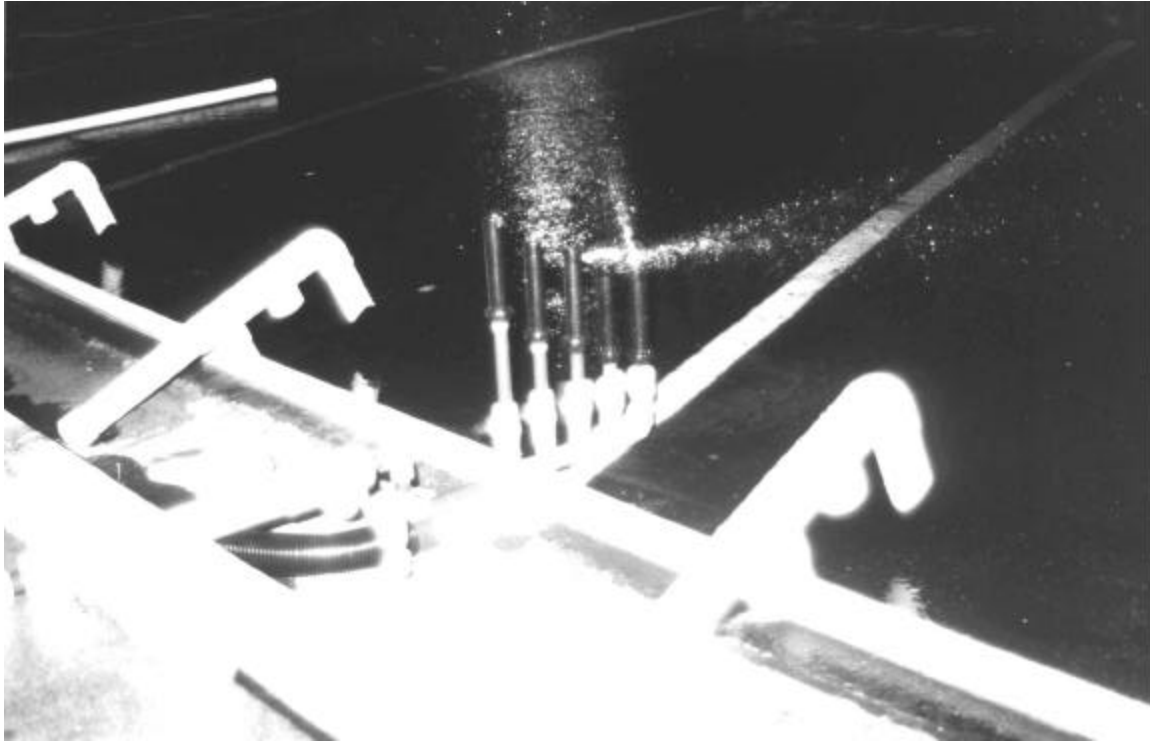


FIGURE II-3. Rainfall simulator in use.

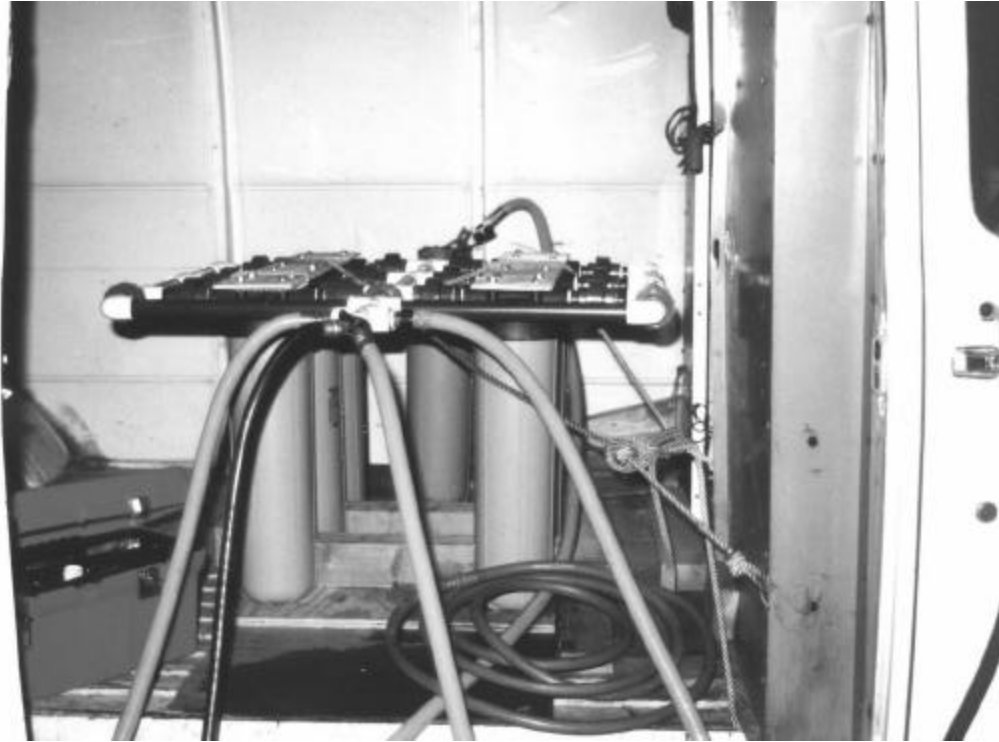


FIGURE II-4. Pre-treatment system used to ensure removal of chlorine and sediments from the source water before it was supplied to the simulated rainfall systems.

III. CONTAMINANT ACCUMULATION

Results

Rapid accumulation of all constituents was observed after 28 antecedent dry days (sampling month T1) with the exception of total PAHs (Figure III-1, Table III-1). Mean suspended solids concentrations increased from 29.2 mg/L to a maximum of 51.8 mg/L during this time period. Of the trace metals studied, zinc demonstrated the highest potential for accumulation in parking lot surface runoff (increasing by as much as 182%) at T1. After 28 d, all trace metals were detected in the dissolved phase and accounted for 31 to 81% of the total metals concentrations in parking lot runoff samples. Reported concentrations of dissolved zinc increased significantly from 200 µg/L to 553 µg/L between T0 and T1. In contrast, mean total PAH concentrations were highest (105 µg/L) at T0 and decreased 20% at T1 (Figure III-1, Table III-1).

Mean contaminant concentrations in subsequent sampling months (T2 and T3) tended to decrease relative to T1 (Figure III-1, Table III-1). For example, total zinc concentrations in parking lot surface runoff from T1 were about 1 to 4 times larger than the concentrations in runoff from other time periods. Monthly PAH concentrations gradually decreased to a minimum of 52.9 µg/L at T2 before a small increase to 53.3 µg/L at T3. Both of these time periods had significantly reduced mean concentrations from the initial (T0) pollutant concentration.

Average TSS concentrations measured at T0 were 26% lower than mean TSS precleaned concentrations (Figure III-1, Table III-1). All total and dissolved trace metals also had lower concentrations after the sites were cleaned, with the exception of cadmium and chromium, which increased by 30 and 8%, respectively. Mean total PAH concentrations decreased by 14% after cleaning. However, none of the lowered contaminant concentrations produced a statistically significant change.

Parking Lot Usage

Changes in parking lot use had little influence on surface runoff contaminant concentrations. Only 8 of 18 contaminants displayed higher runoff concentrations from the high-use stations compared to the low-use stations (Table III-2). However, no significantly different concentrations were found for any of the constituents among the treatments measured for parking lot runoff.

Mean contaminant concentrations followed similar temporal trends as observed in the accumulation study. Both low-use and high-use runoff within T1 had higher mean zinc concentrations (643 and 597 µg/L, respectively) than runoff from stations within T0 and T3. For copper, time periods T0 and T1 had much higher concentrations than T3. Suspended solids concentrations found in runoff from the high-use stations consistently increased from T0 to T2 (31.8 mg/L to 60 mg/L) before dipping during T3 (Figure III-2). On the low-use stations, TSS concentrations fluctuated from 29.2 to 51.8 mg/L. However, the monthly mean TSS concentrations did not vary significantly by use or time period. Concentrations of total PAHs exhibited a similar decreasing trend with respect to time.

Maintenance

Street sweeping was shown to have a minimal effect on parking lot runoff water quality because the sweeping practices used in this study removed very few contaminants. On the contrary, 15 of 18 contaminant concentrations were highest in runoff from maintained stations (Figure III-3, Table III-2). All constituent concentrations were not significantly different among maintenance sites.

As stated previously, the treatments within T1 exhibited higher monthly average TSS, total, and dissolved trace metal concentrations than any other month (Figure III-3). During T1, the mean total zinc concentration of 608 $\mu\text{g/L}$ at the unmaintained stations was up to 4 times larger than zinc concentrations measured in runoff from unmaintained stations during all other time periods. Even though average total zinc concentrations from unmaintained parking lots decreased over the study period, concentrations were substantially higher than at T0. Dissolved zinc concentrations exhibited a similar trend. For TSS, no significant differences existed between time periods; however, mean TSS values from maintained stations (82 mg/L) at T2 were much higher than values measured from unmaintained stations (29 mg/L). Mean total PAH concentrations found in surface runoff from maintained stations decreased considerably during each time period from 143 $\mu\text{g/L}$ at T0 to 47 $\mu\text{g/L}$ at T3. Similar decreased mean total PAH concentrations were also observed between unmaintained stations within T1 (96 $\mu\text{g/L}$) and unmaintained stations within T2 (48 $\mu\text{g/L}$), as well as between maintenance levels within T0 (maintained = 143 $\mu\text{g/L}$, unmaintained = 67 $\mu\text{g/L}$).

Discussion

Accumulation of Contaminant Concentrations

Although short-term accumulation was observed in the present study, long-term accumulation was not found. Contaminants accumulated relatively quickly on the parking lot surface (within 28 d). As the study continued, however, monthly average contaminant concentrations slowly decreased, approaching initial T0 level concentrations. Research on urban stormwater quality has indicated that pollutants accumulate on a street surface between sweeping and storm events. Physical removal processes, however, such as winds and rain or human activity (e.g., from the turbulence of traffic or by street sweeping) can limit the accumulation of solids and other pollutants from road and parking lot surfaces, obscuring the relationship between traffic volume, pollutant loads, and concentrations in runoff (Kerri *et al.* 1985, Pitt and Shawley 1981, Asplund 1980). Pitt and Sutherland (1982) estimated that the total mass concentration of pollutants that can accumulate on street surfaces is limited, requiring approximately two to three weeks to reach maximum levels.

Rainfall has the greatest potential to affect the accumulation of constituents. Unmeasurable amounts of rain fell on the parking lots between the sampling periods, reducing the number of antecedent dry days for events T2 and T3. Although these rainfall events did not appear to be significant, the amount of dry days prior to each of the last two sampling events were both less than two weeks. The effect of these trace quantities of rainfall is assumed to be negligible since rainfall did not pool and no flow was observed. Furthermore, we found that it takes an intensity of 6 mm of rain to fall for 15 min in order to wash off nearly all contaminants from the parking lot surface during the duration/intensity study (See Section IV).

Chemical processes can also limit the accumulation of potential pollutants on parking lot surfaces. Mean total PAH concentrations dropped significantly over the 3-month period of study. Hewitt and Rashad (1992) reported that between 70 and 99% of PAHs were removed from the road environment either by the atmosphere, volatilization, photo-oxidation, or other oxidation processes.

Traffic Usage

Vehicles are one of the major sources of pollutants, both directly and indirectly, in parking lot runoff (Hahn and Pfeifer 1994, Asaeda *et al.* 1996). Therefore, the amount of traffic on a given lot should influence the accumulation of pollutants on the parking lot surface. Our study did not establish a strong relationship between traffic volume and increased contaminant concentrations. Similar results were found when comparing runoff concentrations from highways of different traffic densities in studies by McKenzie and Irwin (1983) and Boucier *et al.* (1980). These studies found a weak correlation between TSS concentrations and average daily traffic (ADT), and no correlation of metal loadings with ADT. In another study, Stotz (1986) concluded that the amount of pollutants discharged has a higher correlation to the physical characteristics of the area than the traffic frequency.

Compared to mean cadmium concentrations, the relatively large arithmetic mean concentrations of total and dissolved zinc in parking lot surface runoff from the different treatments observed in this study support previous findings that automobiles are a large potential source of these constituents. Vehicles contribute contaminants directly into the environment from normal operation and wear to parts caused by friction. Road dust contaminated by tire wear products and zinc-plated metal erosion material contributes the highest levels of zinc to urban runoff (Kobriger and Geinopolos 1984, Smith and Lord 1990 and Lorant 1992). It is likely that these sources may have caused the high zinc concentrations observed in this study. Indirect or acquired contaminants are solids that are acquired by the vehicle for later deposition. Indirectly, vehicles contribute to parking lot contaminants by carrying solids from urban roadways. Indeed, Shaheen (1975) demonstrated that more than 95% of solids on a given road originate from sources other than the vehicles themselves.

Maintenance Effectiveness

The street sweeping practices performed in this study did not prove to be an effective measure for reducing the concentrations of most constituents in parking lot surface runoff. The objective was to remove dry-weather accumulations of contaminants, especially fine particulate matter, before they were washed off by rainwater, and thus reduce the potential for contaminant impacts on receiving waters. Studies by Pitt (1985), Maestri *et al.* (1985) and Gupta *et al.* (1981) reported that intensive street cleaning conducted three times a week using the traditional mechanical street cleaners showed no significant improvement in runoff water quality and was only effective in removing large solids. Most recently, studies conducted in the Pacific Northwest by Sutherland and Jelen (1997) and reported in the Runoff Report (1998), have evaluated the use of vacuum-assisted sweepers and regenerative-air sweepers to determine an optimum sweeping frequency. These improved sweeping mechanisms removed finer street surface materials than the standard mechanical street cleaning equipment, with measureable improvements in pollutant removal efficiency obtained with a sweeping frequency once every week or two.

TABLE III-1. Comparison of constituent accumulation over time. Values given are means and their standard deviations.

Parameter	Washoff Events				
	15-Jul-00 Preclean Mean (SD)	15-Jul-00 T0 Mean (SD)	12-Aug-00 T1 Mean (SD)	9-Sep-00 T2 Mean (SD)	7-Oct-00 T3 Mean (SD)
Suspended Solids (mg/L)	50 (25.4)	29.2 (11.7)	51.8 (14.1)	46.7 (37.2)	41.0 (10.8)
<u>Total Metals</u>					
Aluminum (µg/L)	315 (134.4)	250 (82)	533.3 (119.2)	423.3 (100.7)	421.7 (97)
Cadmium (µg/L)	0.7 (0.9)	1.3 (1.4)	2.5 (1.4)	0.9 (1.0)	0.0 (0)
Chromium (µg/L)	1.2 (1.6)	1.4 (1.1)	3.6 (0.5)	2.3 (0.5)	3.2 (0.4)
Copper (µg/L)	37.5 (13.4)	32.0 (9.2)	40.3 (7.2)	28.7 (6.8)	19.2 (3.2)
Iron (µg/L)	835 (7.1)	546.7 (154.5)	810.0 (174.4)	496.7 (130.1)	485.0 (97.4)
Lead (µg/L)	20 (11.3)	35.0 (9.2)	41.8 (10.6)	19.5 (8.5)	10.9 (2.2)
Mercury (µg/L)	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)
Nickel (µg/L)	16.3 (9.5)	14.2 (5.8)	20.7 (2.4)	16.5 (4.5)	9.2 (1.9)
Silver (µg/L)	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)
Zinc (µg/L)	530 (169.7)	220.0 (85.1)	620.0 (60.4)	395.0 (107.1)	230 (34.9)
Total PAHs (µg/L)	140 (14.1)	105 (46.0)	82.4 (33.7)	52.9 (10.7)	53.3 (6.8)
<u>Dissolved Metals</u>					
Aluminum (µg/L)	180 (70.7)	46.4 (27)	131.7 (62)	71 (33.4)	63.7 (4.2)
Cadmium (µg/L)	0 (0)	0.9 (1.0)	1.3 (1.2)	0.6 (0.8)	0.0 (0.0)
Chromium (µg/L)	0.9 (1.3)	1.0 (0.9)	2.3 (1.1)	1.5 (0.4)	1.9 (0.1)
Copper (µg/L)	32 (11.3)	27.3 (9.3)	28.5 (13.4)	19.3 (4.1)	13.5 (2.1)
Iron (µg/L)	285 (77.8)	263.3 (77.3)	286.7 (140.0)	118.7 (39.0)	66.2 (11.0)
Lead (µg/L)	9.7 (4.7)	32.3 (9.0)	22.8 (14.0)	10.9 (7.2)	3.6 (1.5)
Mercury (µg/L)	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)
Nickel (µg/L)	14.5 (7.8)	12.9 (5.8)	16.2 (7.7)	11.1 (2.6)	7.5 (1.1)
Silver (µg/L)	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)
Zinc (µg/L)	405 (176.8)	200 (78.9)	553.3 (50.5)	270.0 (89.4)	158.3 (18.4)

TABLE III-2. Comparison of parking lot runoff concentrations among parking lot usage and maintenance practices. Time periods were pooled and means with their standard deviations are reported.

Parameter	Pooled Time Periods (T1-T3)			
	Use		Maintained	
	Low Mean (SD)	High Mean (SD)	Yes Mean (SD)	No Mean (SD)
Suspended Solids (mg/L)	44.9 (19.3)	46.4 (27)	59.7 (23.4)	36.7 (19.4)
<u>Total Metals</u>				
Aluminum (µg/L)	506.7 (135.9)	412.2 (83.2)	546.7 (138.4)	415.8 (84.8)
Cadmium (µg/L)	0.9 (1.5)	1.4 (1.3)	1.1 (1.2)	1.1 (1.4)
Chromium (µg/L)	3.1 (0.6)	3 (0.8)	3.4 (0.8)	2.8 (0.6)
Copper (µg/L)	29.6 (8.8)	29.2 (12.2)	28.2 (8.7)	27.9 (11)
Iron (µg/L)	556.7 (122.2)	637.8 (256.2)	690 (170.1)	552.7 (189.1)
Lead (µg/L)	21.2 (12.4)	27 (17.4)	21.5 (11.6)	32.6 (24.3)
Mercury (µg/L)	0 (0)	0 (0)	0 (0)	0 (0)
Nickel (µg/L)	14.8 (4.5)	16.1 (6.7)	16.5 (5.8)	14.8 (5.1)
Silver (µg/L)	0 (0)	0 (0)	0 (0)	0 (0)
Zinc (µg/L)	427.8 (180.9)	402.2 (173.9)	426.7 (186.8)	359.3 (184.3)
Total PAHs (µg/L)	58.4 (9.8)	67.3 (33.3)	55.2 (9.9)	54.5 (35.7)
<u>Dissolved Metals</u>				
Aluminum (µg/L)	94.5 (54.7)	76.6 (47)	60.3 (9.1)	25.5 (36.1)
Cadmium (µg/L)	0.6 (1)	0.6 (1)	0.8 (0.9)	0.4 (0.9)
Chromium (µg/L)	2 (0.5)	1.8 (0.9)	2.1 (0.7)	1.7 (0.6)
Copper (µg/L)	22.2 (8.4)	18.7 (11.5)	22.3 (8.9)	18.7 (9.7)
Iron (µg/L)	166.6 (112.6)	147.8 (138.9)	183.2 (127.2)	142 (111.8)
Lead (µg/L)	11.3 (10)	13.6 (13.8)	11.8 (10)	19.3 (21.4)
Mercury (µg/L)	0 (0)	0 (0)	0 (0)	0 (0)
Nickel (µg/L)	12.2 (4.8)	10.9 (6.8)	13.3 (5.1)	11 (5.5)
Silver (µg/L)	0 (0)	0 (0)	0 (0)	0 (0)
Zinc (µg/L)	320 (166.9)	334.4 (187.4)	318.3 (171.9)	286.3 (185.3)

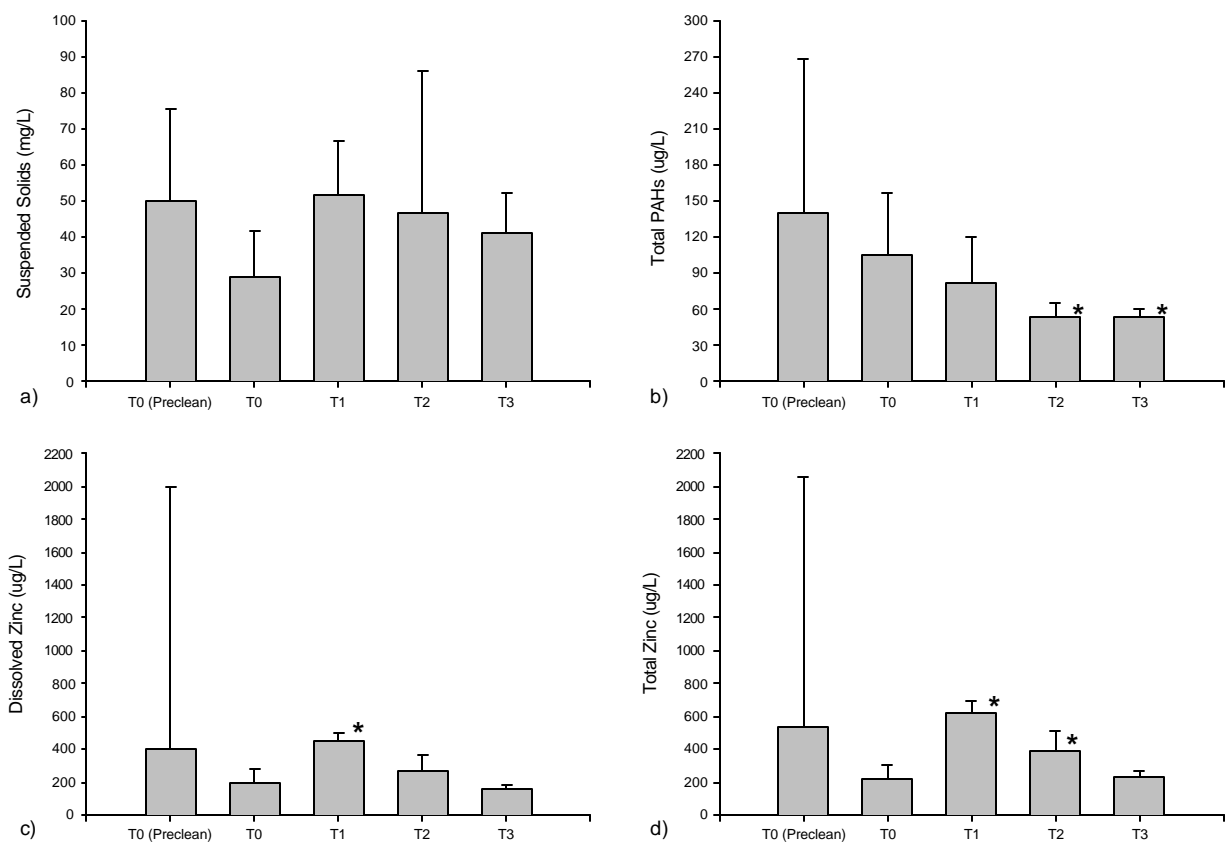


FIGURE III-1. Mean accumulation concentrations (± 95% C.I.) of (a) suspended solids, (b) total PAHs, (c) dissolved zinc and (d) total zinc in runoff from parking lots. Excluding precleaning, time steps are monthly. An asterisk denotes significant differences relative to the time zero sample.

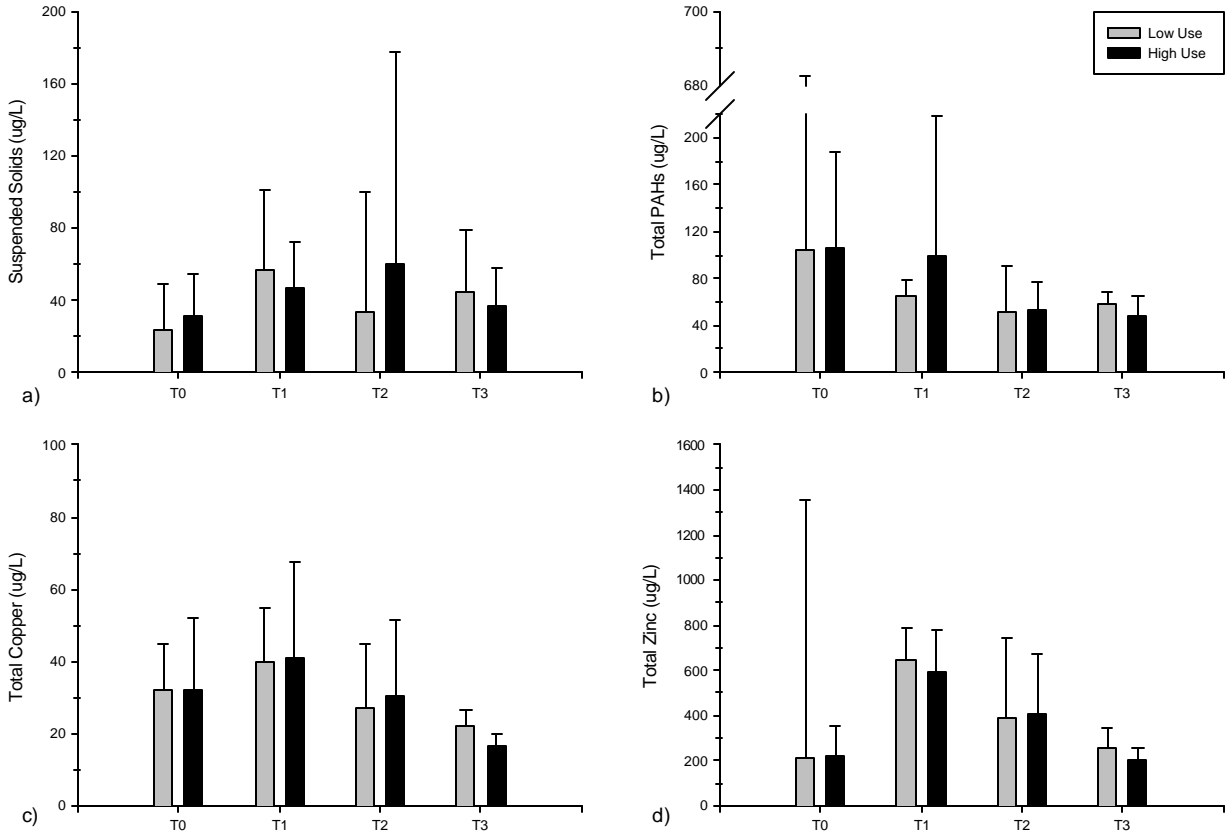


FIGURE III-2. Mean concentrations (\pm 95% C.I.) of (a) suspended solids, (b) total PAHs, (c) total copper and (d) total zinc in runoff from low-use and high-use parking lots over time.

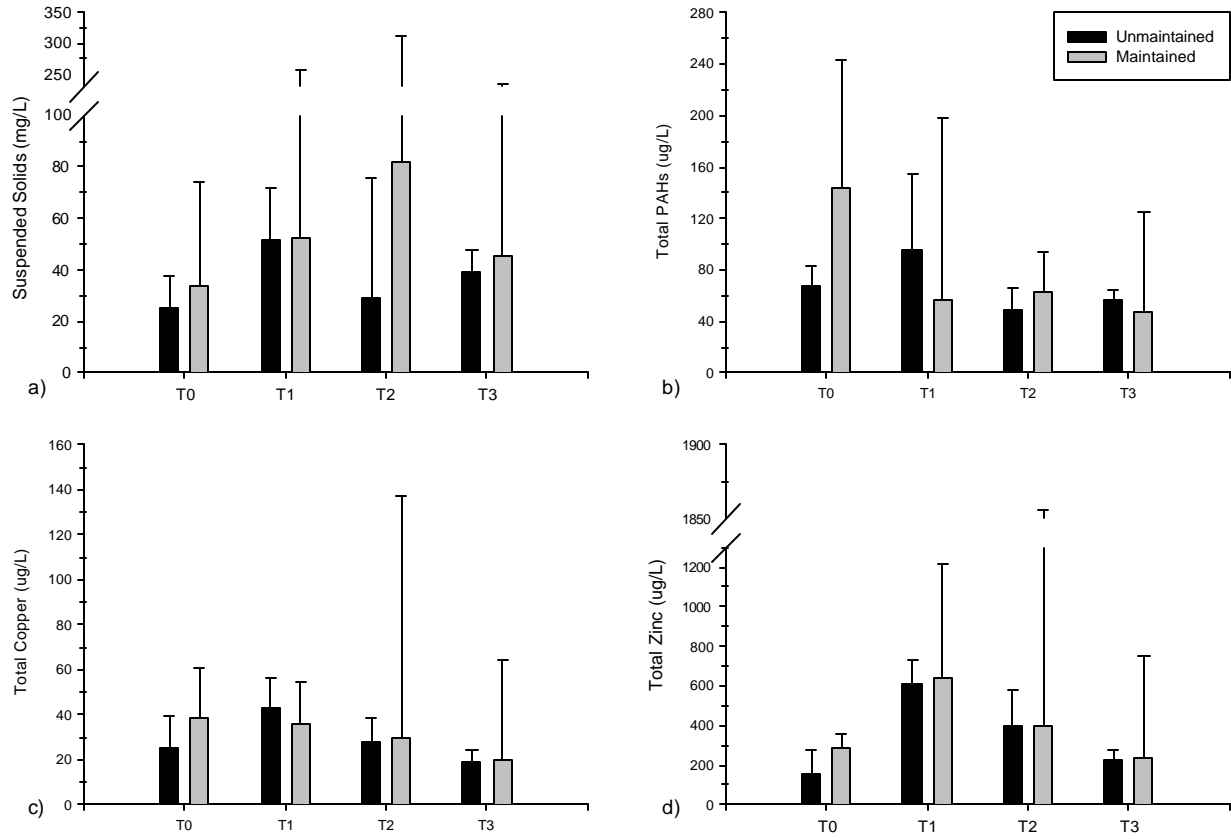


FIGURE III-3. Mean concentrations (\pm 95% C.I.) of (a) suspended solids, (b) total PAHs, (c) total copper and (d) total zinc in runoff from maintained and unmaintained parking lots over time.

IV. RAINFALL INTENSITY / DURATION

Results

Contaminant Washoff Patterns

Simulated rainfall washed off nearly all of the suspended solids that collected on the parking lot surface after approximately 15 min regardless of rainfall intensity. Higher concentrations were recorded during approximately the first 10 min for most constituents; however, the concentrations quickly reached a baseline concentration for the duration of the sampling period (Figure IV-1). The suspended solids concentrations varied from about 2 to 140 mg/L, with a decrease in concentrations with increasing rain intensity during these constant rain intensity tests. No concentrations higher than 52 mg/L occurred after approximately 10 min of rain. All TSS concentrations were less than 30 mg/L after approximately 15 min of rain. Suspended solids concentrations for all intensities showed slightly higher concentrations at the beginning (first flush) of the simulated storm events. The magnitude of the first-flush effect varied between intensities, ranging from 112 to 140 mg/L, and was more evident at the 6 mm/hr rainfall intensity.

Rainfall duration was the most important factor we observed. Washoff of all measured constituent variables was inversely correlated with duration at single or lumped rainfall intensities (Table IV-1, Figure IV-2). Longer simulated storms diluted parking lot runoff and significantly lowered the concentrations of contaminants. For example, mean suspended solids concentrations measured after 10 minutes significantly decreased from 57 mg/L to 16.2 mg/L measured during the 10-20 minute interval of the simulated storm ($F = 7.95$, $p = 0.00$) (Figure IV-2). At the end of the simulated storm event (20-40 min interval), mean suspended solids concentrations decreased to 11.7 mg/L and were significantly different from concentrations measured after 10 min ($F = 7.95$, $p = 0.00$). Simulated storm events with 20 minute rainfall durations had a mean TSS concentration of 28.7 and were not significantly different relative to the other time intervals.

Washoff of contaminant concentrations exhibited trends similar to TSS over different durations, but the importance of intensity was only detected at the shortest durations (Table IV-1, Figure IV-3). When durations were pooled, mean total zinc concentrations were highest (240 ug/L) at the 6 mm/hr rainfall intensity. More intense simulated storms had the same dilution effect on average pollutant concentrations, as did longer simulated storms, however, the concentrations were not significantly lower. Mean zinc concentrations were reduced to a minimum of 143 ug/L with 25 mm/hr of rainfall (Figure IV-3). The mean dissolved zinc concentrations ranged from approximately 51 to 338 ug/L, comprising a large percentage of the total zinc loadings. For all rain intensities, dissolved metals comprised up to 90% of the total metals.

DISCUSSION

Urban stormwater runoff is comprised of discharges from many separate source area components (parking lots, streets and highways) that are combined within the watershed drainage area before entering the receiving water. Bannerman *et al.* (1993) characterized parking lots as critical source areas contributing most of the runoff and contaminant loads during small rain events. One study in Toronto, Ontario by Pitt and McLean (1986), evaluated specific source areas to identify any possible trends of concentrations with rain volume. They found that lead and zinc concentrations were highest in runoff from paved parking areas and streets. Several other studies (Barrett *et al.* 1995, Driscoll *et al.* 1990, and Pitt 1985) measured runoff and contaminant concentrations on roads and highways.

To understand the potential impacts on water quality from surface runoff from parking lots, we compared the average constituent concentrations found in parking lot runoff to both the range of average national pollutant concentrations in highway runoff, and to the range of concentrations observed in the City of Long Beach's wet-weather stormwater monitoring program (Table IV-2). This comparison shows that the average concentrations in surface runoff from parking lots in Long Beach are at the lower end of range of concentrations for transportation land uses nationwide (FHWA 1998, Barrett *et al.* 1995). However, parking lot runoff concentrations generated during simulated rainfall events were similar to the concentrations measured in wet-weather discharges from the City of Long Beach during the winter of 2001 (Kinnetic Laboratories, Inc and SCCWRP, 2001). For example, the average concentrations of lead in parking lot runoff were lower than the range of mean runoff concentrations in transportation areas nationwide, but were within the range of concentrations measured in City of Long Beach wet-weather runoff. Interestingly, the ranges of mean zinc concentrations were similar among national transportation areas and the City of Long Beach, approximately 50 to 900 µg/L. The zinc concentration measured during simulated rainfall on a parking lot within the City of Long Beach was below the mid-range near 300 µg/L.

In this study, changes in rainfall duration were found to have the greatest effect on constituent concentrations. Parking lot runoff samples collected during the first 10 min of a rain event contained the highest constituent concentrations, indicating that a first-flush effect was present. After peaking during the first flush, constituent concentrations decreased and then remained relatively stable after approximately 15 min when most loose particles were washed off. Longer storms were found to dilute parking lot runoff and lower the variability in measured contaminant concentrations during this study. Rainfall intensity was also an important variable in determining removal of runoff constituents during a storm, but only during shorter durations (i.e., less than 15 min). Higher intensity storms produced higher concentrations during these small duration events. Others (Athayde *et al.* 1983; Irish *et al.* 1996) have documented a similar correlation among rainfall duration and intensity. For example, Dorman *et al.* (1988) found that concentrations of runoff pollutants were higher during shorter, low-volume storms.

The results of the intensity and duration experiments indicate that stormwater treatment systems that capture or treat the initial portion of stormwater discharge from parking lots are likely to provide the greatest benefit in terms of reducing constituent concentrations. This will, in turn,

help to reduce mass emissions, particularly for shorter storm events. However, several factors need to be considered when designing BMPs including sizing, trapping and treatment efficiency for specific constituents of concern, and flood protection among others.

TABLE IV-1. Comparison of constituent concentrations with varied intensities and durations. Mean concentrations with their standard deviations are reported.

Parameter	Intensity and Duration					
	6 mm/hr (0.25 in/hr)			13 mm/hr (0.5 in/hr)	25 mm/hr (1 in/hr)	
	0-10 min	10-20 min	20-40 (min)	0-20 min	0-10 min	10-20 min
	Mean (SD)	Mean (SD)	Mean (SD)	Mean (SD)	Mean (SD)	Mean (SD)
Suspended Solids (mg/L)	72.7 (18.1)	20.3 (6.5)	11.7 (5.2)	28.7 (14.6)	41 (13.3)	12 (3.1)
<u>Metals (Total)</u>						
Aluminum (µg/L)	1036.7 (172.7)	233.3 (177.5)	180 (55.9)	316.7 (73.5)	540 (114.7)	143.3 (26.1)
Cadmium (µg/L)	2.4 (0.6)	1 (0.8)	0 (0)	0.8 (0.6)	0.5 (0.8)	0 (0)
Chromium (µg/L)	7.7 (0.7)	4.1 (0.3)	2.2 (0.2)	2.6 (0.4)	4 (1.2)	1.8 (0.3)
Copper (µg/L)	54.3 (6.4)	27.3 (4.2)	10.3 (0.5)	19.7 (1.3)	29.7 (7.6)	10.3 (2.2)
Iron (µg/L)	556.7 (56.8)	446.7 (27.4)	216.7 (71.5)	560 (115.4)	610 (195.4)	266.7 (35.5)
Lead (µg/L)	168.7 (84.2)	93 (58)	27.7 (14.5)	61.7 (28.6)	48.7 (18.4)	18.7 (6.6)
Mercury (µg/L)	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)
Nickel (µg/L)	44.7 (7.4)	21.3 (4.7)	6.8 (0.9)	14 (2.3)	23.7 (6.9)	6.6 (1.3)
Silver (µg/L)	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)
Zinc (µg/L)	430 (47.5)	213.3 (35.5)	76.7 (3.2)	160 (8.5)	216.7 (26.1)	69.3 (10.6)
Total PAHs (µg/L)	8.5 (6.2)	4.3 (2.8)	2.7 (2.1)	5.5 (2.9)	3.3 (1)	1.6 (0.7)
<u>Metals (Dissolved)</u>						
Aluminum (µg/L)	78.7 (12.4)	92.7 (97.2)	0 (0)	0 (0)	0 (0)	25.7 (37.9)
Cadmium (µg/L)	2.1 (0.6)	0.9 (0.7)	0 (0)	0 (0)	0.5 (0.7)	0 (0)
Chromium (µg/L)	4.1 (0.4)	2.5 (0.2)	0.8 (0.7)	1.6 (0)	1.9 (0.6)	0.4 (0.5)
Copper (µg/L)	47.3 (5.2)	24.7 (4.8)	8.5 (0.9)	15.3 (1.8)	24.3 (9.4)	8 (2)
Iron (µg/L)	360 (64.4)	203.3 (40.3)	46.7 (35.5)	133.3 (26.1)	190 (30.7)	53.3 (39.4)
Lead (µg/L)	133.3 (77.4)	85.3 (63.1)	23.9 (16.4)	45.1 (28.7)	34 (12.6)	14.1 (7.2)
Mercury (µg/L)	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)
Nickel (µg/L)	41.3 (6.9)	19.3 (4.7)	6.4 (1.1)	12 (1.5)	21 (7.4)	5.8 (1.2)
Silver (µg/L)	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)
Zinc (µg/L)	336.7 (52.1)	170 (47.5)	56 (11.2)	104.7 (22.6)	156.7 (34.5)	50.7 (13.9)

TABLE IV-2. Average values of constituent concentrations in parking lot runoff compared to both highway runoff and wet-weather stormwater runoff concentrations (FHWA 1996, Kinnetic Laboratories, Inc and SCCWRP 2001, Barrett *et al.* 1995).

Constituent	City of Long Beach Paved Parking Lot Mean Concentrations	Range of Mean FHWA Highway Runoff Concentrations	City of Long Beach Wet Weather Stormwater Runoff Range of Concentrations
Suspended Solids (mg/L)	36	437 – 1147	24 - 350
<u>Metals (Total)</u>			
Cadmium (µg/L)	1	ND – 40	0.5 - 3.3
Chromium (µg/L)	3.1	ND – 40	1.9 - 10
Copper (µg/L)	28	22 – 7,033	8.9 - 78
Iron (µg/L)	524	2,429 – 10,300	350 - 9,700
Lead (µg/L)	45	73 – 1,780	10 - 59
Nickel (µg/L)	17	53	2.1 - 18
Zinc (µg/L)	293	56 – 929	51 - 960

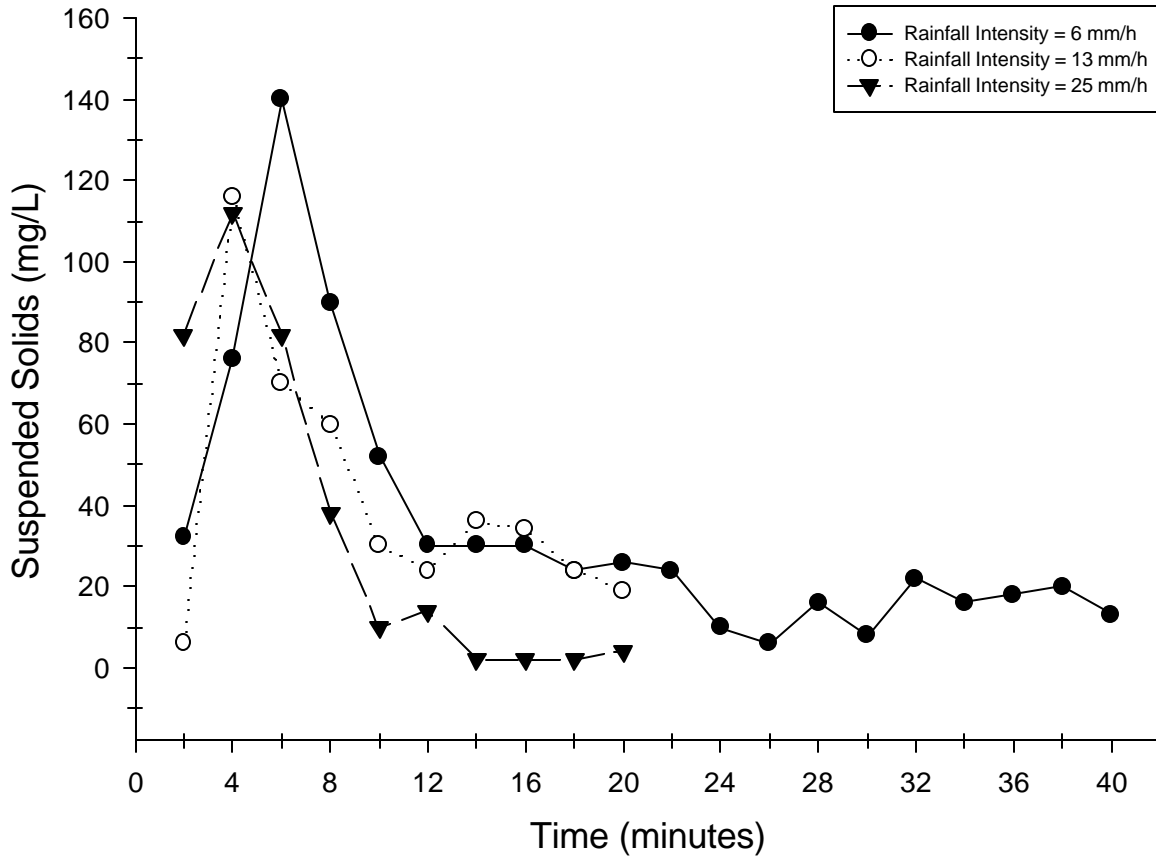


FIGURE IV-1. Wash-off patterns of suspended solids concentrations (mg/L) with 6, 13 and 25 mm/h simulated rainfall intensities.

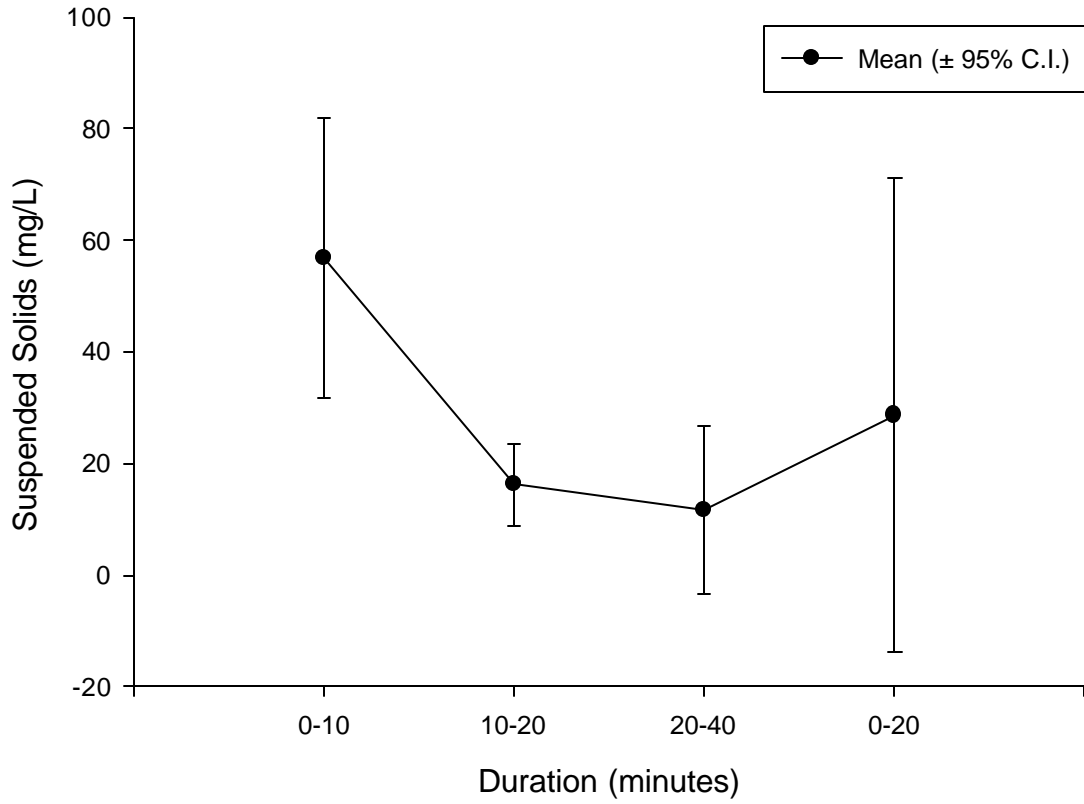


FIGURE IV-2. Concentrations of suspended solids (mg/L) versus rainfall duration. All intensities are pooled. Data are presented as mean values (\pm 95% C.I.).

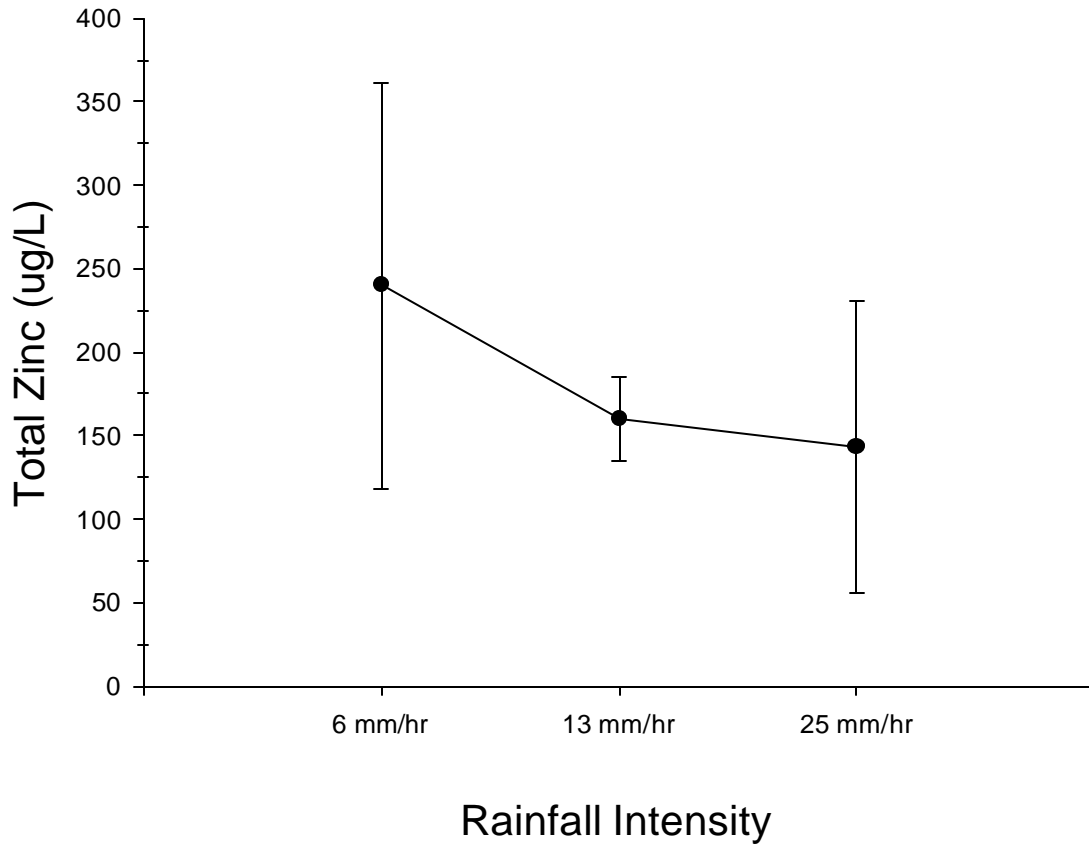


FIGURE IV-3. Mean concentration of total zinc (ug/L) (\pm 95% C.I.) versus rainfall intensities. All durations are pooled.

V. TOXICITY RESULTS

Comparative Toxicity to Marine Species

Each of the four test methods detected toxicity in the samples from sampling periods T2 and T3 (Table V-1). Toxicity was widespread among the three species used: sea urchins, mysids, and bacteria. Five of the six samples tested were toxic to all three species.

Responses to the month 2 samples (T2) were similar among the three samples tested (Figure V-1). Mysid survival was affected only at the highest concentration tested, 50%. The sea urchin fertilization and chronic Microtox tests always detected toxicity at lower concentrations, with the Microtox test showing the highest magnitude of response relative to the controls.

The relative responses of the three species showed a different pattern of response to the samples tested after 3 months of accumulation (Figure V-2). Mysid survival was less responsive, compared to the month 2 samples that were tested. In addition, the sea urchin test usually showed a greater relative response compared to the chronic Microtox test for the month 3 samples.

The mysid survival/growth and Microtox acute tests were the least sensitive methods overall. The NOECs for these two methods were usually $\geq 25\%$ and no toxicity was detected in 1 or 2 samples (Table V-1). In many cases, less than a 50% response was measured in the highest sample concentration tested ($EC_{50} > 50\%$). Mysid growth was a more sensitive response than survival in three of the five toxic samples (Table V-1). The reduction in mysid weight was relatively small, however, and did not exceed a 50% effect for any of the samples. The greatest growth effect was measured for sample 202B (T2), where the weight of mysids exposed to 25% sample was 57% of the control.

The sea urchin fertilization and chronic Microtox test methods were substantially more sensitive. Every sample tested was toxic to both species and the NOECs for these tests ranged from < 3 to 12% (Table V-1). The magnitude of response was similar between these tests; the EC_{50} s ranged from 14- $> 25\%$ and 7-31% for the sea urchin and chronic Microtox tests, respectively.

Accumulation Time Effects

Toxicity to sea urchin sperm was detected in every sample collected during the accumulation study (Table V-2). The magnitude of toxicity was similar among most samples collected within a time period. For example, the toxic units (TU) for the T3 samples were within a factor of 2 of each other and ranged from 4.3 TU to 8.8 TU. Samples collected at T2 showed the greatest variability in toxicity within a time interval. Toxicity for these samples ranged from < 4 TU to 10.8 TU. In all other cases, there was no more than a two-fold range of toxicity within a time interval (Table V-2).

Substantial differences in the mean level of toxicity were present among time intervals. The lowest level of toxicity and least variability were present in samples collected immediately after pressure washing the study sites (T0). All of the T0 samples had the highest NOEC (25%) and lowest toxic units (<2 TU to 2.7 TU) measured in the study (Table V-2). The mean toxicity in the T0 group (2.0 TU) was significantly lower than the average toxicity of all other groups, which ranged from 5.0 to 12.1 TU (Figure V-3).

The temporal variation of toxicity was similar to the pattern observed for most of the chemical constituents. The highest magnitude of toxicity was present in samples collected following 1 month of accumulation (T1). The average toxicity of these samples was significantly greater than the toxicity at T0 or prior to cleaning (Figure V-3). Toxicity in the T2 and T3 samples declined by approximately 50% relative to T1, but these differences were not statistically significant from the T1 mean.

Variations in traffic use did not have a consistent effect on toxicity. High traffic use sites tended to have greater toxicity in the T1 samples, but the differences were relatively small (Figure V-4). An opposite trend was observed for the T2 and T3 samples. Toxicity within these intervals tended to be approximately 50% lower in samples from high traffic areas (Figure V-4).

Variation in maintenance level produced no discernible effect on toxicity of samples from most of the sampling events. Maintained high use sites were approximately twice as toxic at T2 (Figure V-4). The difference in toxicity between maintained and unmaintained sites was much less for all other sampling events.

Rainfall Intensity and Duration Effects

Sea urchin fertilization tests of the runoff samples collected during the intensity and duration study detected toxicity in every sample. The magnitude of toxicity was quite variable among treatments, ranging from 2.6 to 13.8 TU (Table V-3). However, little variability in toxicity was present among the samples within a treatment group. Less than a two-fold difference in toxicity was found among the three replicate samples within each intensity/duration group (Table V-3).

Differences in both rain intensity and duration had a pronounced and predictable effect on toxicity. Toxicity was inversely related to both of these factors, as illustrated in Figure V-5. For the same duration interval (i.e., 10-20 min), toxicity decreased as rainfall intensity increased from 6 mm/hr to 25 mm/hr. Samples collected later in the rainfall event at the same intensity always contained less toxicity.

The toxicity data also indicated that an interaction between intensity and duration was present. For example, the relative decrease in toxicity between the 0-10 min and 10-20 min intervals at 6 mm/hr was less (31 %) than the change (54 %) measured at an intensity of 25 mm/hr.

The magnitude of toxicity present in the various intensity/duration groups was determined in large part by the portion of the rainfall event captured in the sample. This relationship is evident when toxicity is plotted relative to the volume of simulated rainfall represented by a sample (Figure V-6). For example, the highest toxicity was present in samples that contained runoff

from the first 15 L of flow. A similar amount of toxicity was present in samples that contained runoff corresponding to 13.2-26.4 L of runoff, even though the intensity of the simulated rainfall varied four-fold (6-25 mm/hr).

Toxicant Characterization

Phase I TIEs were conducted on one runoff sample from each of the T2 and T3 sampling events. Similar results were obtained for each sample (Figures V-7 and V-8): both the EDTA addition and C-18 extraction treatments eliminated most of the toxicity. Extraction of nonpolar organic compounds from the samples using a C-18 column was the most effective treatment; this procedure eliminated essentially all of the toxicity. Addition of EDTA to complex cationic trace metals (e.g., copper and zinc) eliminated 44 to 76% of the toxicity.

The two other TIE procedures, the removal of particles and addition of sodium thiosulfate (to reduce oxidants), were not effective in reducing toxicity. The TIE results also indicated that toxicity in the samples was stable during short-term storage; no significant change in toxicity was found between the initial measurement and the TIE baseline measurement conducted 2 d later.

Chemical analysis of the TIE samples indicated that detectable concentrations of three potentially toxic constituents (zinc, copper, and total PAH) were present. Of these three constituents, only zinc was present at a sufficiently high concentration to cause substantial toxicity (Figures V-7 and V-8). Limited data are available that describe the toxicity of individual PAHs to sea urchin sperm, but unpublished SCCWRP data for several PAHs indicates that concentrations of ≥ 100 $\mu\text{g/L}$ are needed to produce toxicity. The PAH concentrations in these samples were below 30 $\mu\text{g/L}$, which suggested that these organics were unlikely to be responsible for much of the sample toxicity.

Correlation analysis of the chemistry and toxicity data for all test samples supported the hypothesis that the runoff toxicity was likely related to trace metals. Significant correlations were obtained for both the total and dissolved forms of most metals, with no significant correlation between PAH concentration and toxicity (Table V-4). Correlations were highest (>0.6) for total and dissolved chromium, total aluminum, total nickel, and total and dissolved zinc.

Plots of the chemistry and toxicity data corroborate the correlation results. A clear trend of increased toxicity at higher concentrations of total Cr or dissolved Zn is evident (Figure V-9). However, variations in the concentration of TSS or PAH show little relationship with toxicity.

The correlation results indicate that the concentrations of the primary cause of toxicity in these samples covary with the metals concentrations, but they do not prove that metals are the cause. Other (unmeasured) constituents that occur with metals in runoff may be the cause of toxicity.

Elution of the C-18 columns with solvent recovered a portion amount of toxicity (Figure V-10). The eluate was toxic when tested at a concentration that was 1.5-3x greater than the original concentration of the test sample. The inability of solvent elution to recover all of the toxicity

removed could be due to several factors, inability of the solvent to remove all of the organics from the column, degradation of the toxicants during storage of the column between extraction and elution, and the binding of inorganic toxicants that are not soluble in the solvent (e.g., metals) to the column.

The binding of copper and zinc to C-18 columns has been observed in a previous study (Schiff *et al.* 2001); thus, an attempt was made to elute metals from the C-18 columns with an acid solution. The acid eluate of both columns was much more toxic than the solvent eluates (Figure V-10). All of the acid eluates, tested at 0.8-3x of the original sample concentration, were highly toxic to sea urchin sperm. Some toxicity was present in the blank for the acid eluate sample, but the unusual dose response pattern for this sample suggests that this toxicity may be an outlier.

The concentration of dissolved zinc in the runoff samples ranged from 140 to 620 ug/L. The toxic units of zinc corresponding to these concentrations (calculated using laboratory-derived EC50s for these metals) is greater than the number of toxic units measured using the sea urchin fertilization test (Figure V-11). This result indicates that a sufficient concentration of zinc was present in each of the runoff samples to account for all of the toxicity measured. Dissolved copper in these samples ranged from 0 to 37 µg/L, corresponding to less than 10% of the toxicity of any sample.

Discussion

The results of this study indicate that runoff from transportation land uses, such as parking lots and roadways, are an important source of toxicity in urban runoff. All of the simulated runoff samples measured in the present study were toxic, and the magnitude of toxicity was usually higher than that measured in other urban stormwater samples. For example, composite stormwater samples collected from the Los Cerritos Channel in Long Beach, California, during 2001 contained fewer than 4 TU (Kinnetic Laboratories, Inc. and SCCWRP 2001), whereas nearly all parking lot runoff samples contained greater than 4 TU. Samples from the Los Cerritos Channel contained the highest magnitude of toxicity among the Long Beach stormwater sampling locations during the 2000/2001 NPDES monitoring program.

The high relative sensitivity of the sea urchin fertilization test found in this study are similar to those obtained in other recent studies. Two previous studies have used multiple marine species to measure the toxicity of urban stormwater. In each case, the sea urchin fertilization test was more sensitive than the 7-d mysid survival and growth test (Kinnetic Laboratories, Inc. and SCCWRP 2001, SCCWRP 1999).

The Microtox chronic test was similar in sensitivity to parking lot runoff as the sea urchin fertilization test. Both test methods detected toxicity in all six samples analyzed as part of the method comparison study (Table V-1). In addition, the magnitude of toxicity, as indicated by the EC50, was similar between these two test methods. These results indicate that the chronic Microtox test procedure may be useful for stormwater toxicity monitoring and research. However, the acute Microtox is of limited value for stormwater assessment in Long Beach. The acute test failed to detect toxicity in several samples that contained approximately 5 TU of chronic Microtox toxicity.

The accumulation study results indicated that typical street/parking lot maintenance activities (i.e., sweeping) were not effective for reducing runoff toxicity. Manual sweeping of the study sites did not significantly affect runoff toxicity levels. However, more rigorous cleaning activities may be effective in reducing stormwater toxicity. For example, pressure washing of the study sites at the beginning of the experiment reduced the toxicity of the runoff by a factor of 3. Toxicity was not eliminated by pressure washing, indicating that more research is needed to identify the most effective methods for eliminating stormwater toxicity.

Toxicity measurements at different time intervals indicated that a toxicity first-flush effect was present. Runoff samples collected during the first 10 min of a rain event were approximately twice as toxic as runoff from later portions of the simulated storm (Figure V-5). This finding was in agreement with the results of chemical analyses of the samples, which showed the first portion of the runoff event to contain the highest constituent concentrations. These results indicate that stormwater treatment systems that capture or treat the initial portion of stormwater discharge from parking lots are likely to provide the greatest benefit in terms of reducing toxic constituents.

The results of the intensity and duration experiment also illustrate the importance of collecting a sample of known and representative composition for stormwater monitoring programs. Failure to capture the initial phase of stormwater runoff may underestimate the magnitude of toxicity present and variations in sample compositing methods may increase the variability in the results.

The toxicant characterization and identification experiments, though limited in number, suggested that parking lot runoff toxicity to sea urchins was due primarily to metals, especially zinc. These results are similar to the results of TIEs from other studies, which have identified zinc as a primary toxicant of concern in stormwater runoff from Ballona Creek in Los Angeles, California, and Chollas Creek in San Diego, California (Bay *et al.* 1999, SCCWRP 1999). The TIE experiments also determined that the toxic constituents of parking lot runoff were confined to the dissolved fraction, which is usually a more biologically available form than particulate metals. This finding has implications for the design of BMPs to reduce stormwater toxicity. The BMPs that are based primarily on particulate removal are not likely to be effective in reducing the toxicity of stormwater runoff from parking lots.

TABLE V-1. Comparison of toxicity test responses for three marine species. Data for the mysid test are based on the most sensitive of either the survival (s) or growth (g) endpoints, as indicated by the letter following the value.

Sample	Time	Use/ Maintenance	NOEC (%)				EC50 (%)			
			Sea Urchin	Mysid	Microtox Acute Chronic		Sea Urchin	Mysid	Microtox Acute/Chronic	
202B	T2	H/U	12.5	<25g	6	6	>25	36.8s	>50	10.4
204A	T2	H/U	12.5	25s	6	12	19.7	37.5s	>50	15.9
201A	T2	H/M	3	25s	25	<3	13.5	42.4s	>50	6.7
203B	T3	H/U	6	25g	≥50	6	20.5	>50	>50	20.0
204B	T3	H/U	6	≥50	≥50	12	22.4	>50	>50	31.0
201B	T3	H/M	3	25g	25	<3	23.2	>50	>50	15.5

TABLE V-2. Summary of parking lot toxicity results during the accumulation study. Toxic units are calculated using either the sea urchin fertilization NOEC (TUc) or EC50 (TU). EC50s for the T0 (after cleaning) samples were estimated by graphical interpolation, EC50s for other samples were calculated using probit analysis.

Sample	Time	Use/Maintenance	NOEC (%)	TUc	EC50 (%)	TU
103B	T0	L/U (preclean)	3	33	20.4	4.9
204A	T0	H/U (preclean)	3	33	19.3	5.2
Mean	T0	preclean	3	33	19.8	5.0
101B	T0	L/U (postclean)	25	4	50 ^a	2.0
103B	T0	L/U (postclean)	25	4	>50	<2.0
201A	T0	H/M (postclean)	25	4	37 ^a	2.7
201C	T0	H/M (postclean)	25	4	46 ^a	2.2
204A	T0	H/U (postclean)	25	4	44 ^a	2.2
203B	T0	H/U (postclean)	25	4	53 ^a	1.9
Mean	T0	postclean	25	4	55.2	2.0
102A	T1	L/U	<12	>8	8.7	11.5
104B	T1	L/U	<12	>8	10.9	9.2
101C	T1	L/M	<12	>8	10.7	9.3
202A	T1	H/U	<3	>33	8.2	12.2
203A	T1	H/U	<3	>33	7.2	13.9
201C	T1	H/M	<3	>33	6.1	16.4
Mean	T1		<8	>13	8.6	12.1
102B	T2	L/U	3	33	12.0	8.3
103A	T2	L/U	3	33	9.3	10.8
101A	T2	L/M	3	33	11.7	8.5
202B	T2	H/U	12	8	>25	<4
204A	T2	H/U	12	8	19.7	5.1
201A	T2	H/M	3	33	13.5	7.4
Mean	T2		6	25	19.4	7.0
103B	T3	L/U	3	33	13.5	7.4
104A	T3	L/U	3	33	12.4	8.1
101B	T3	L/M	3	33	11.4	8.8
203B	T3	H/U	6	17	20.5	4.9
204B	T3	H/U	6	17	22.4	4.5
201B	T3	H/M	3	33	23.2	4.3
Mean	T3		4	28	17.2	6.3

TABLE V-3. Toxicity to sea urchin sperm of parking lot runoff collected at different intensity/duration combinations. Samples representing up to four time intervals were collected at each intensity. The EC50 was calculated by linear interpolation of the fertilization data.

Sample	Intensity (mm/hr)	0-10 minutes		10-20 minutes		20-40 minutes	
		EC50 (%)	TU	EC50 (%)	TU	EC50 (%)	TU
502R1	6	6.5	15.4	10.5	9.5	27	3.7
505R2	6	8.5	11.8	10.5	9.5	29	3.4
507R3	6	7	14.3	10.5	9.5	28	3.6
Mean	6	7.3	13.8	10.5	9.5	28.0	3.6
503R1 ^a	13			21 ^a	4.8 ^a		
504R2 ^a	13			21 ^a	4.8 ^a		
509R3 ^a	13			26 ^a	3.8 ^a		
Mean^a	13			22.7^a	4.5^a		
506R1	25	17	5.9	34	2.9		
508R2	25	26	3.8	57	1.8		
513R3	25	14	7.1	32	3.1		
Mean	25	19.0	5.6	41.0	2.6		

^aSamples representing a rainfall interval of 0-20 minutes.

TABLE V-4. Spearman correlation coefficients between sea urchin fertilization toxic units and runoff chemical parameters for all samples analyzed. N = 42 for all analyses.

Constituent	Correlation Coefficient	P value
TSS	0.4175	0.0062
Total PAH	-0.0006	0.9967
Dissolved Al	0.4707	0.0018
Total Al	0.6689	<0.0001
Dissolved Cd	0.4326	0.0044
Total Cd	0.4003	0.0088
Dissolved Cr	0.6932	<0.0001
Total Cr	0.7927	<0.0001
Dissolved Cu	0.4278	0.0049
Total Cu	0.5424	<0.0001
Dissolved Fe	0.3371	0.0293
Total Fe	0.3975	0.0094
Dissolved Pb	0.0280	0.8595
Total Pb	0.2708	0.0824
Dissolved Ni	0.4939	<0.0001
Total Ni	0.6375	<0.0001
Dissolved Zn	0.6293	<0.0001
Total Zn	0.6547	<0.0001

Mercury and silver are not included in the table because the chemistry values were all nondetectable.

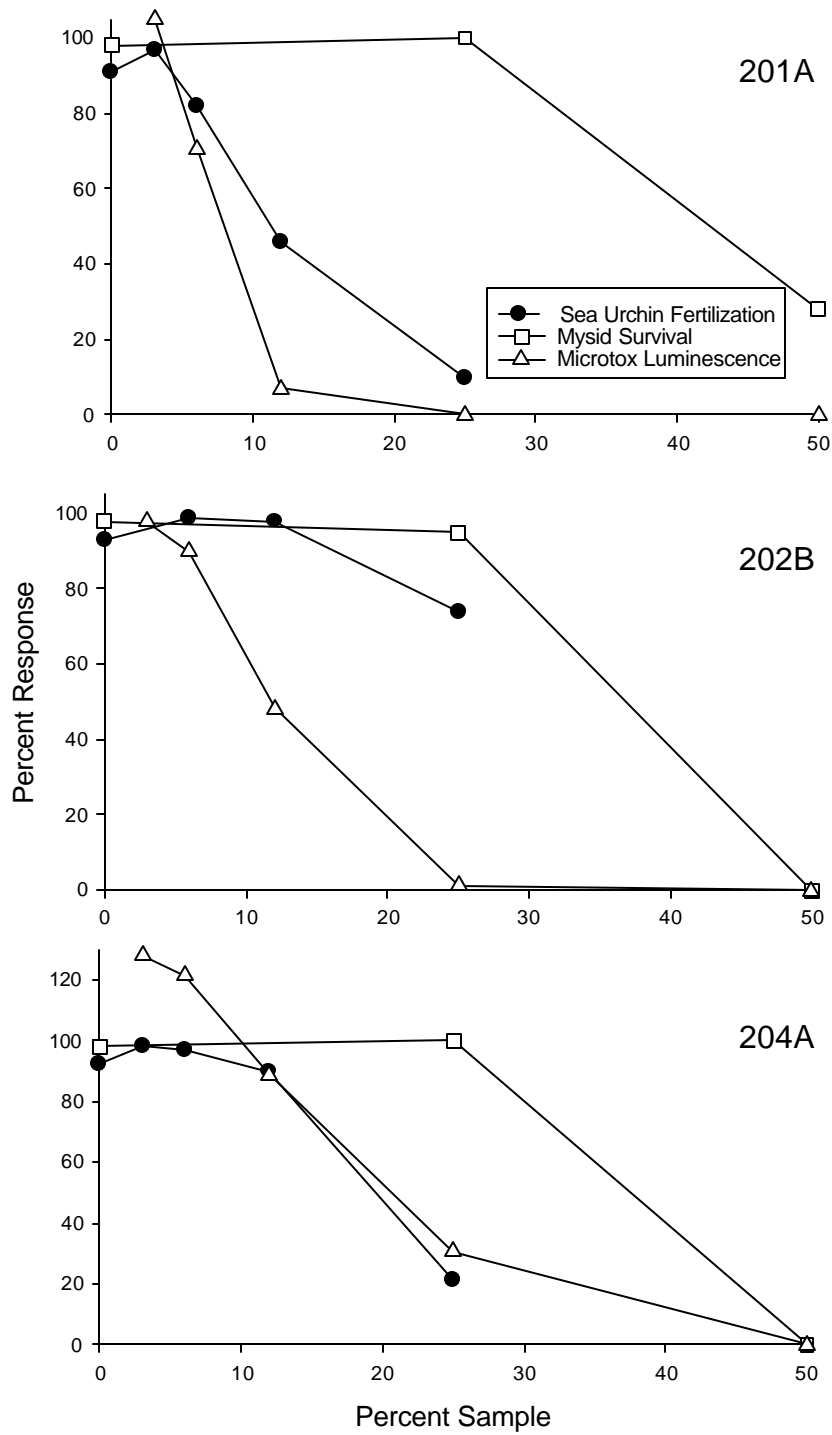


FIGURE V-1. Response of three marine species to runoff samples after 2 months of accumulation. Only data for the chronic version of the Microtox test are shown.

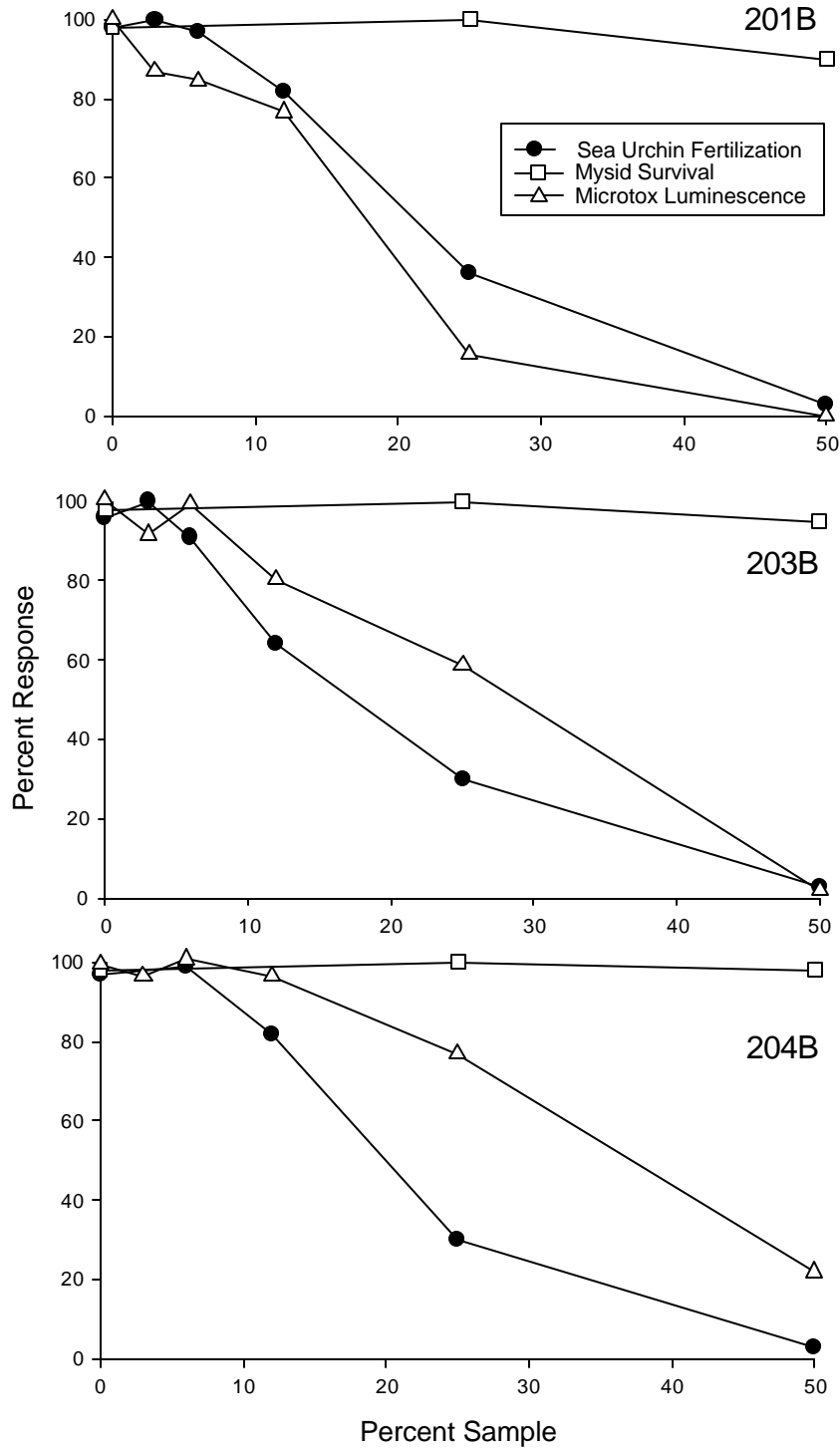


FIGURE V-2. Response of three marine species to runoff samples after 3 months of accumulation. Only data for the chronic version of the Microtox test are shown.

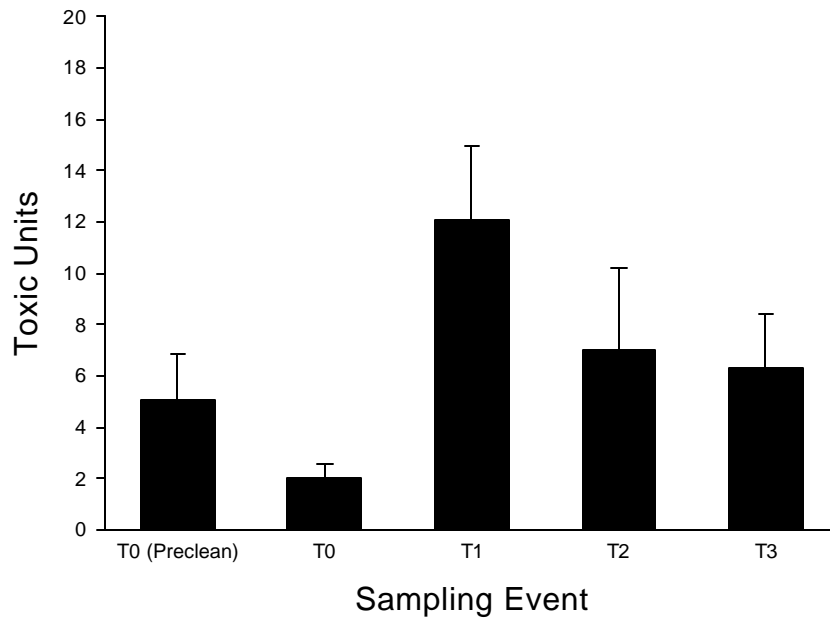


FIGURE V3. Variation in parking lot runoff toxicity using sea urchin sperm during a 3-month accumulation period (maintenance and use groups combined). Values are the mean + upper 95% confidence interval.

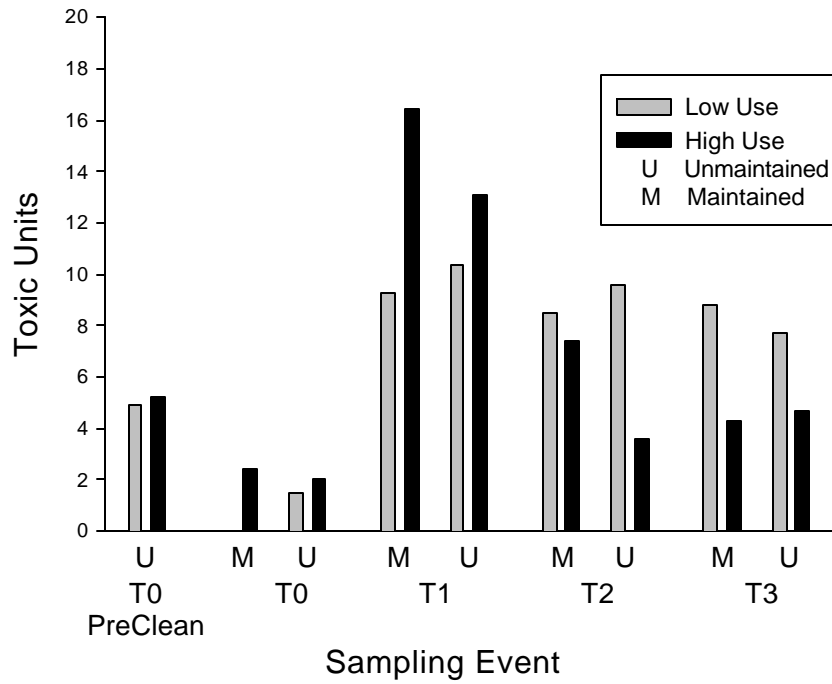


FIGURE V4. Toxicity of parking lot runoff samples to sea urchin sperm during a three-month accumulation period. Data are the means of two samples except for the maintained sites, where n=1.

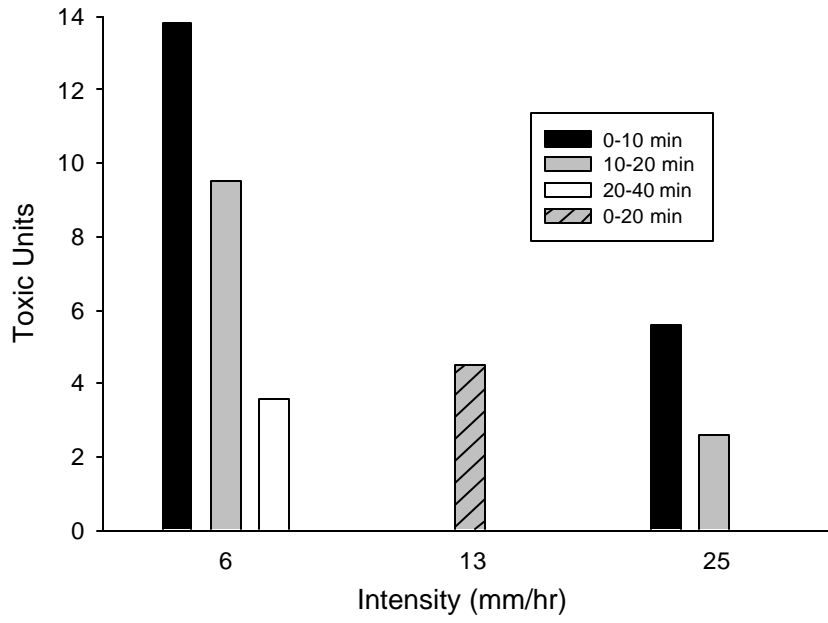


FIGURE V-5. Average toxicity of runoff samples collected at different intensity and duration combinations.

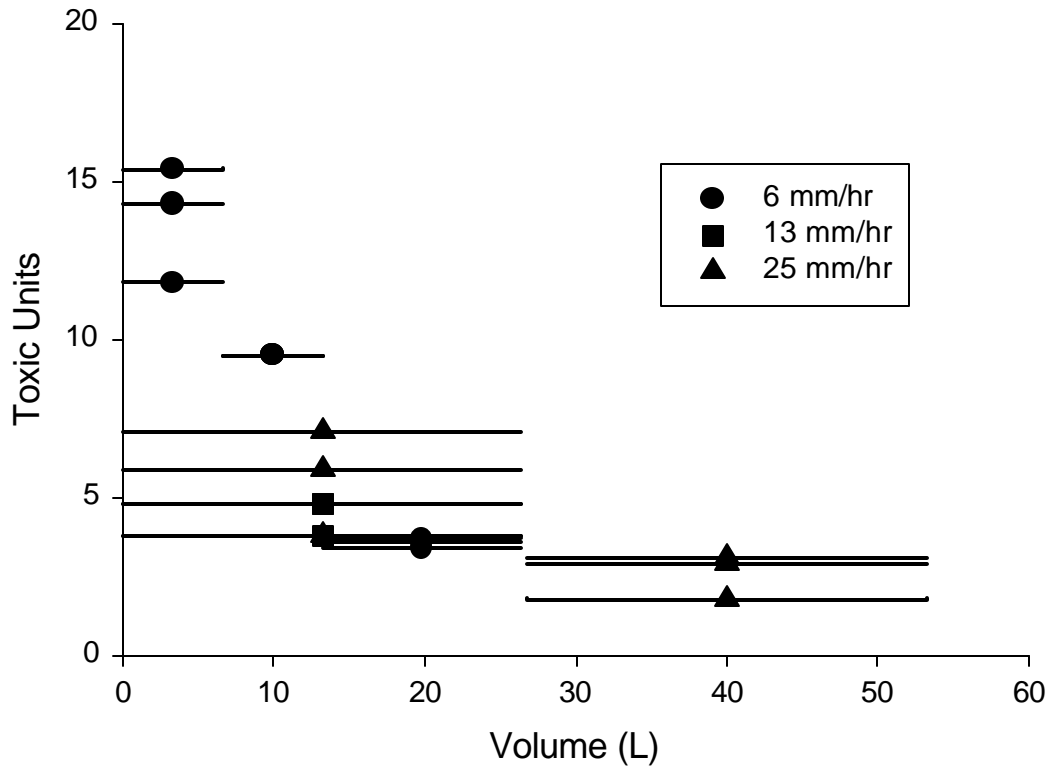


FIGURE V-6. Relationship of toxicity to portion of the rainfall event sampled. The horizontal lines indicate the portion of the runoff flow sampled, with 0 liters representing the start of runoff.

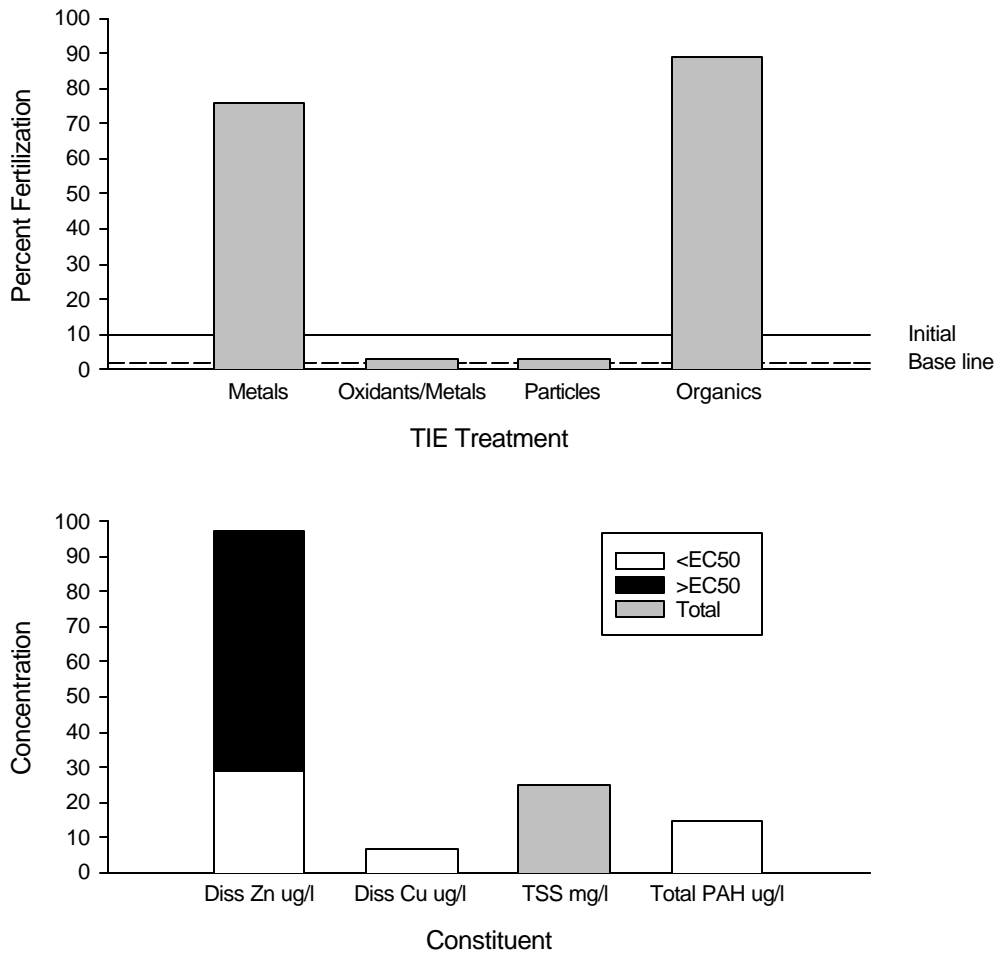


FIGURE V-7. Summary of TIE results for a runoff sample (201A) following 2 months of accumulation. Constituent concentrations shown in the bottom plot have been adjusted for the dilution of the sample (0.25x) used for toxicity testing. The black portion of each bar indicates the portion of the concentration that is greater than the EC50 for the constituent.

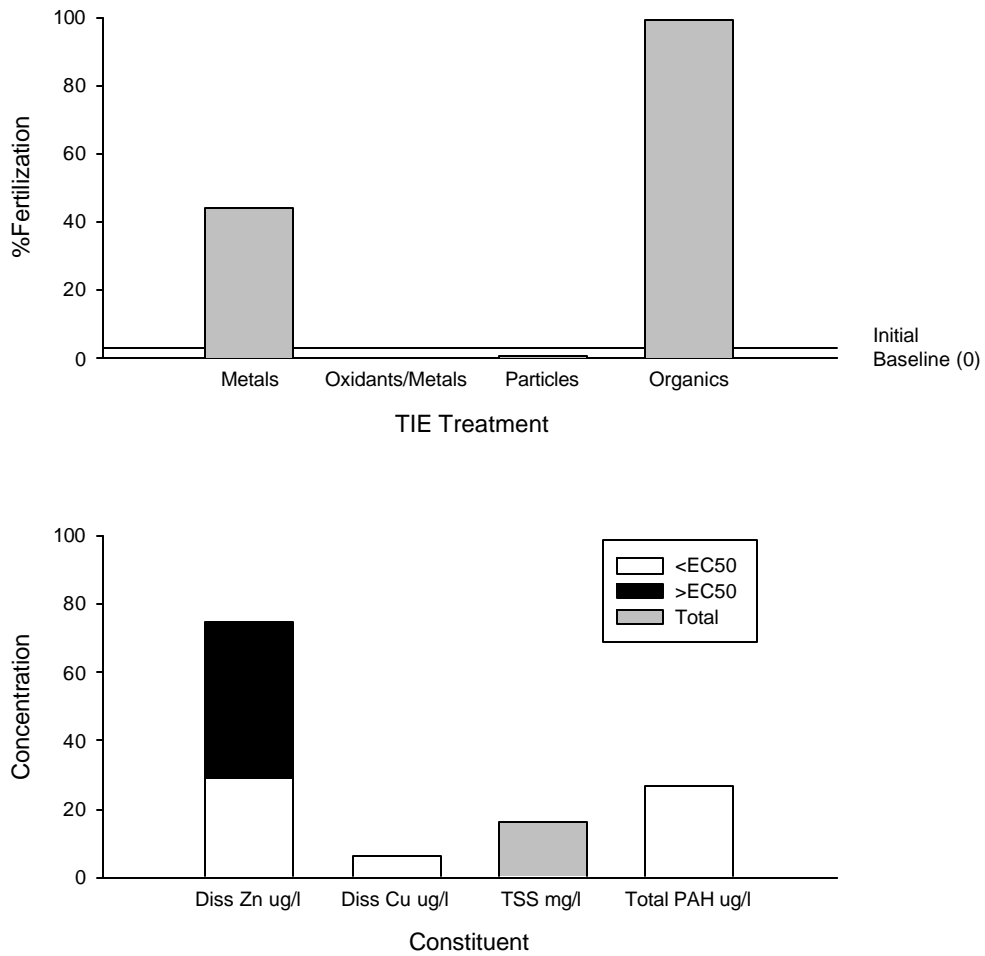


FIGURE V-8. Summary of TIE results for a runoff sample (203B) following 3 months of accumulation. Constituent concentrations shown in the bottom plot have been corrected for the dilution of the sample (0.5x) used for toxicity testing. The black portion of each bar indicates the portion of concentration that is greater than the EC50 for the constituent.

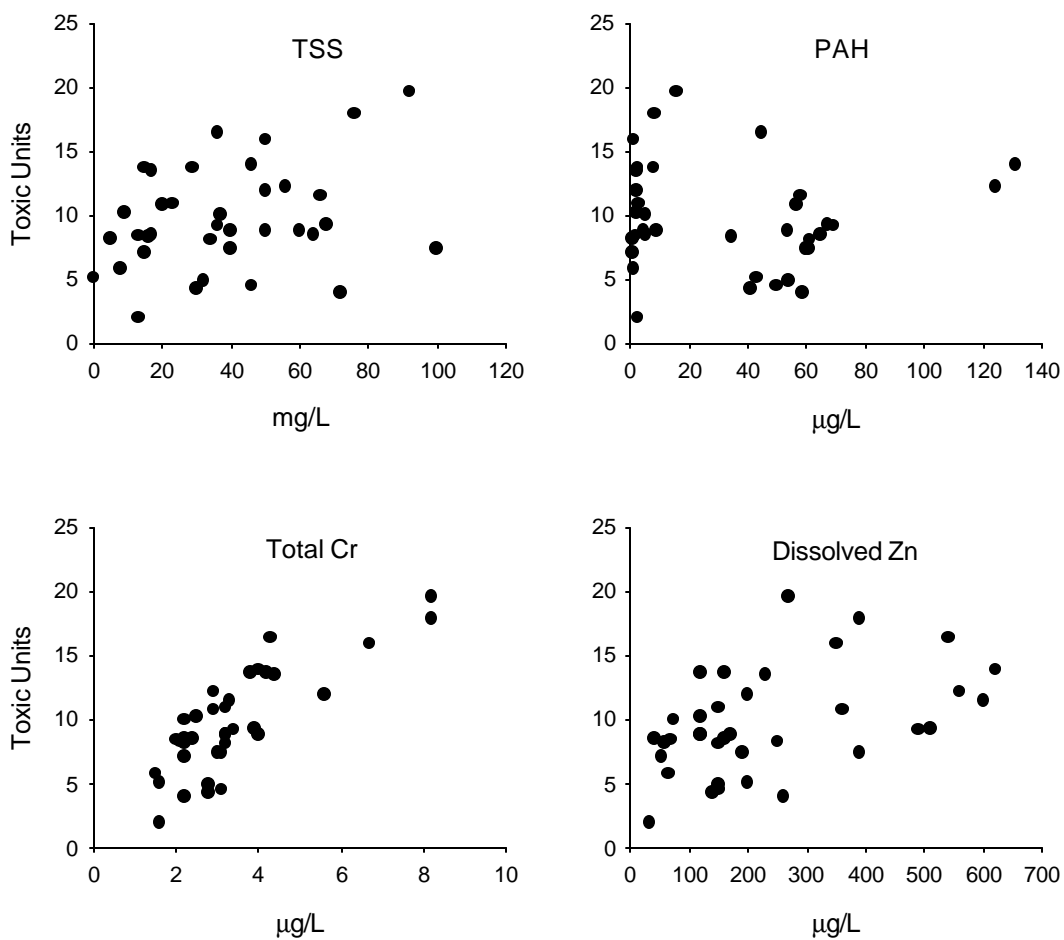


FIGURE V9. Relationship of toxicity (sea urchin fertilization test) to concentration for selected runoff constituents.

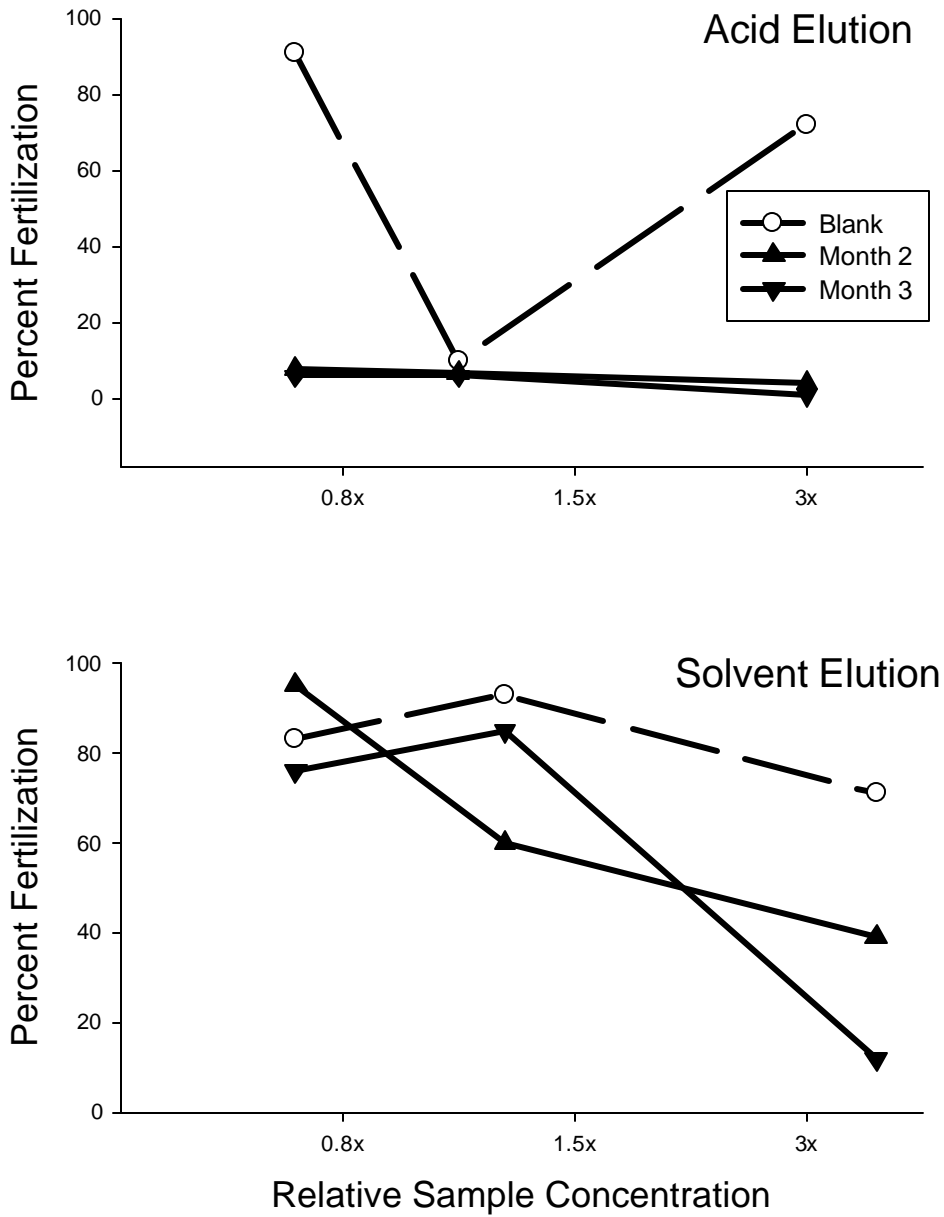


FIGURE V-10. Toxicity of acid or solvent eluates of C-18 column used for TIE. Concentration is expressed relative to the highest concentration tested in the Phase I TIE test.

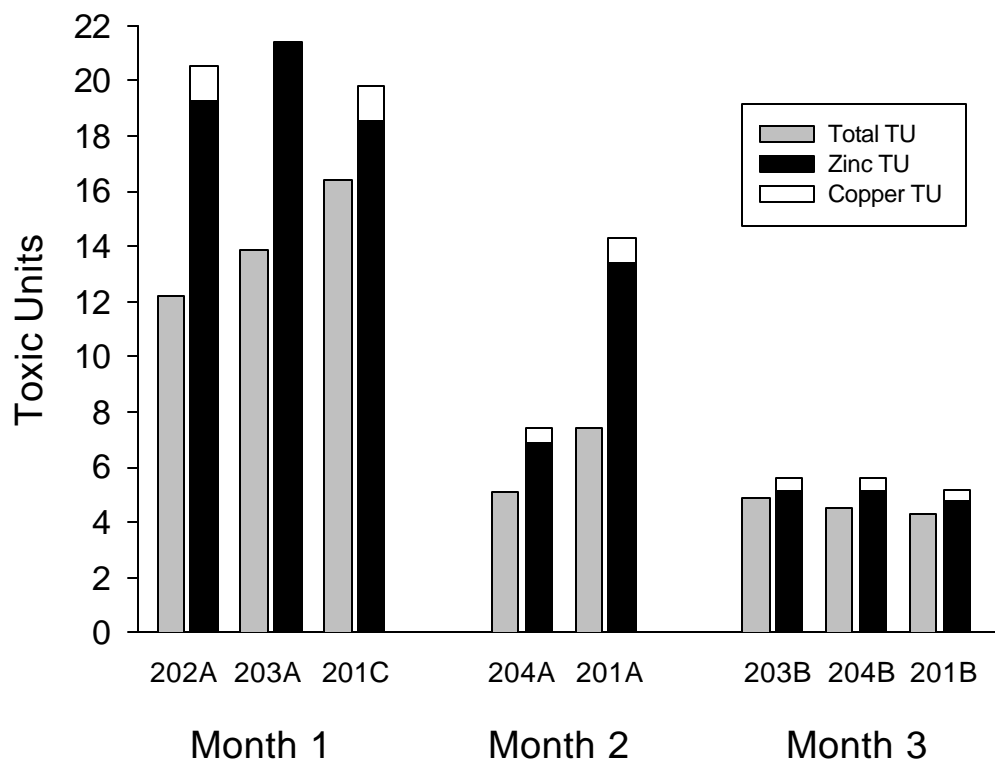


FIGURE V-11. Comparison of measured and calculated toxic units for runoff samples analyzed during the accumulation experiment. Calculated toxic units are based on the concentration of dissolved zinc and copper in the sample.

VI. CONCLUSIONS

- *Accumulation of most constituents occurred within 28 d.*

Seventeen of 18 constituents had increased concentrations relative to the T0 sampling, ranging from 20-181%, in runoff samples collected after one month of accumulation. Zinc showed the highest accumulation, increasing by nearly a factor of 3 during the antecedent time period. Only total PAH did not increase; concentrations of PAH declined by 20%.

-- The variability in temporal patterns remains unexplained.

Constituent concentrations peaked during the first month of accumulation and then decreased in months 2 and 3. Physical factors other than those addressed in this study may play a role in increasing or decreasing the accumulation of constituents on parking lot surfaces including human activities, indirect vehicle deposition, wind, and atmospheric deposition, among others. This study measured time over a period of months; shorter time scales (days to weeks) are needed to explain these types of patterns and interactions.

- *Parking lot usage did not affect the accumulation of runoff constituents.*

Similar concentrations of TSS, trace metals, and total PAH were observed between parking lots with ≤ 4 cars per hour and parking lots with > 5 cars per hour.

- *Parking lot maintenance did not affect the accumulation of runoff constituents.*

Parking lots where street sweeping was employed as a maintenance activity had similar runoff concentrations compared to parking lots without street sweeping. Improved street sweeping technology or alternative BMPs will be required to reduce concentrations of contaminants in runoff. Current street sweeping technology may be effective, however, in reducing other types of runoff-transported pollution such as trash or debris.

- *Pressure washing appeared to be partially effective in reducing the accumulation of runoff constituents.*

Mean constituent concentrations in parking lot runoff were lower after pressure washing compared to mean constituent concentrations in parking lot runoff immediately following precleaned rainfall simulations. Some constituents, in particular zinc, were reduced by as much as 50%.

- *Runoff constituent concentrations were inversely correlated with rainfall duration and intensity. Rainfall duration was more important than intensity during this study.*

The TSS concentrations varied by one order of magnitude between samples collected at 2 min and samples collected 12 min after the onset of rain, indicating the presence of a first flush. Moreover, more than 75% of the TSS load was washed off in the first 15 min of the simulated storms. The “first-flush” effect was more pronounced during less intense simulated rain events, but the importance of rainfall intensity decreased with longer storm duration.

- *Toxicity was consistently measured in parking lot runoff, but not all species responded similarly to exposure to runoff samples.*

One hundred percent of simulated runoff samples elicited toxic responses. The sea urchin and marine bacteria were the most sensitive organisms; the mysid was the least sensitive organism. The level of toxicity observed in samples exposed to parking lot runoff was higher than the level observed during the Long Beach wet-weather monitoring program.

- *Toxicity patterns corresponded with constituent accumulation and rainfall intensity/duration patterns.*

Toxicity in runoff samples increased by a factor of six after one month of accumulation. The magnitude of toxicity between runoff from high-use and low-use parking lots showed no consistent difference. Similarly, the magnitude of toxicity between parking lots with or without street sweeping was similar. A toxicity first-flush effect was also present in runoff samples collected during the first 10 min of a rain event. Runoff samples collected during this time interval were twice as toxic as runoff samples collected from later portions of the simulated storm.

- *Trace metals were an important contributor to toxicity.*

The TIEs identified trace metals, particularly zinc, as the constituent responsible for toxicity in the purple sea urchin fertilization test. This conclusion was based upon the following findings: (1) complexation of trace metals completely removed toxicity; (2) concentrations of dissolved zinc were sufficient to induce toxic responses; and (3) variations in zinc concentrations among samples were significantly correlated with toxic responses.

VII. RECOMMENDATIONS

- *Parking lot BMPs that focus on initial storm flows will be most effective.*

A large first-flush effect was observed during this study. Suspended solids concentrations were highest and nearly 75% of the mass emissions occurred in the first 15 min of the simulated rainfall events. Capturing or treating these initial storm flows, particularly at relatively small temporal scales (0-15 min), would likely be most effective at reducing concentrations and loads of runoff constituents.

- *Managers should give priority to reducing dissolved trace metals in runoff treatment programs.*

Dissolved trace metals, in particular zinc, were identified as the constituents responsible for toxicity to marine organisms such as the purple sea urchin. This finding has been observed in wet-weather discharges from watersheds throughout southern California. Most structural BMPs today do not attempt to ameliorate dissolved constituents in wet-weather runoff.

- *Additional maintenance strategies need to be tested.*

Parking lot sites that received street sweeping every two weeks showed no difference when compared to parking lot sites that received no street sweeping. However, some moderate decreases in constituent concentrations were observed in runoff samples following pressure washing as a maintenance activity. Additional maintenance strategies, such as, improved street sweepers (i.e. regenerative air sweepers), should be evaluated to assess their effectiveness. Existing maintenance strategies should be retested using additional variable factors (i.e., land uses, constituents, antecedent dry periods, etc.)

- *The accumulation study design needs to be refined.*

A significant increase in constituent concentrations and toxicity was observed after one month of accumulation. However, most constituent concentrations and some toxicity levels decreased in subsequent months, indicating that secondary factors may influence the accumulation of toxics on parking lot surfaces. Future studies should attempt to account for these factors by measuring wind speed and direction, rainfall, and other variables while decreasing the time interval between sampling events.

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