Toxicity of Parking Lot Runoff After Application of Simulated Rainfall

D. Greenstein, L. Tiefenthaler, S. Bay

Southern California Coastal Water Research Project, 7171 Fenwick Lane, Westminster, California 92683

Received: 6 February 2003/Accepted: 23 December 2003

Abstract. Stormwater runoff is an important source of toxic substances to the marine environment, but the effects of antecedent dry period, rainfall intensity, and duration on the toxicity of runoff are not well understood. In this study, simulated rainfall was applied to parking lots to examine the toxicity of runoff while controlling for antecedent period, intensity, and duration of rainfall. Parking areas were divided into high and low use and maintained and unmaintained treatments. The parking stalls were cleaned by pressure washing at time zero. Simulated rainfall was then applied to subplots of the parking lots so that antecedent periods of 1, 2, and 3 months were achieved, and all of the runoff was collected for analysis. On a separate parking lot, rainfall was applied at a variety of intensities and durations after a 3-month antecedent period. Runoff samples were tested for toxicity using the purple sea urchin fertilization test. Every runoff sample tested was found to be toxic. Mean toxicity for the sea urchin fertilization test ranged from 2.0 to 12.1 acute toxic units. The toxicity increased rapidly during the first month but then decreased approximately to precleaning levels and remained there. No difference in toxicity was found between the different levels of use or maintenance treatments. The intensity and duration of rainfall were inversely related to degree of toxicity. For all intensities tested, toxicity was always greatest in the first sampling time interval. Dissolved zinc was most likely the primary cause of toxicity based on toxicant characterization of selected runoff samples.

Many studies have found urban stormwater runoff to be toxic to aquatic organisms (Heaney et al. 1999). Toxicity has been found for both small watersheds, such as streets and industrial sites (Malthe et al. 1995; Marsalek et al. 1999; Pitt et al. 1995), as well as larger urban creeks and rivers (Bay et al. 1997; Jirik et al. 1998; Rives and Gersberg 1999; Schiff et al. 2002). In study, nearly half of the samples were characterized as having moderate to extreme toxicity (Pitt et al. 1995). The presence of toxicity in runoff indicates that contamination is present at harmful levels and can have important implications for environmental management such as triggering the development of total maximum daily loads or the implementation of treatment processes. An understanding of the factors affecting the occurrence and magnitude of toxicity is essential to the development of effective management strategies for runoff quality.

Storm characteristics—such as the time between storms (antecedent period), storm intensity, and storm duration—have the potential to affect runoff toxicity, but the influence of these factors is poorly understood. Most of the work on antecedent period and storm characteristics has focused on contaminant loadings, not toxicity. In one study, the concentration of metals in runoff was found to vary by season (Zartman et al. 2001). The effect of antecedent period on runoff composition is variable (Barrett et al. 1995; Lee et al. 2002), and the intensity of rainfall has been implicated as an important factor in the concentration of metals in runoff (Sansaline et al. 1996). Anecdotal evidence from storm-water monitoring programs indicates that storm characteristics also have important effects on toxicity. Longer antecedent periods between storms have been associated with the presence of increased toxicity (Bay et al. 1999; Kinetic Laboratories Incorporated, Southern California Coastal Water Research Project 2001), and much greater runoff toxicity has been measured during early-season storms in some studies (Bay et al. 2003; Schiff and Stevenson 1996). However, differences in location, scale, year, and methods among these toxicity studies make it difficult to derive conclusions regarding the effects of storm characteristics.

One of the limits to our understanding of how storm characteristics affect toxicity is the uncontrolled variation in rainfall that occurs during storm events. The study of runoff toxicity during natural storm events provides no control over the intensity or duration of the rainfall or the period between storms. Without these controls, questions as to whether the toxicity of runoff changes as length of time between storms increases and whether there is a difference in toxicity of runoff between short, intense rain and longer, gentle rain are difficult to answer.

In this study, we used simulated rainfall so that all aspects of the precipitation event were controlled. The study was conducted on parking lots to capture all of the runoff and to provide for replication. Runoff from roadways and parking lots has been found to have high levels of contaminants and to be toxic to freshwater and marine organisms (Malthe et al. 1995; Pitt et al. 1995).

Correspondence to: D. Greenstein; email: darring@sccwrp.org
The project had four objectives concerning different runoff issues. The first objective was to determine the effect of different antecedent periods on runoff quality by testing adjacent sites at antecedent intervals of 1, 2, and 3 months. The next two objectives were explored as part of the antecedent period study. One was to establish what effect the use level of the parking lot had on toxicity, with high use equating to many cars parked for short periods versus low use equating to fewer cars and longer periods. The second was to determine if normal parking lot maintenance procedures had an effect on runoff quality. The final objective was to determine the effect of differing rainfall intensities and durations on the quality of the runoff. In addition to testing the differential toxicity from the treatments described above, this study had the additional goal of determining the cause of observed toxicity through the application of toxicity identification evaluation (TIE) methods.

Methods

Study Design

The sampling design consisted of two major components. The first was an antecedent period experiment to measure the effects of contaminant accumulation after 1, 2, and 3 months without rain. The antecedent period experiment also included separate treatments for maintenance and level of parking lot use. Each month, simulated rainfall was applied to parking lot subplots designated for the particular treatments, and the runoff was tested for toxicity.

The second major component was a one-time rainfall intensity and duration experiment that was performed after three months' accumulation. For this part of the study, simulated rainfall was applied to parking lot subplots at combinations of three intensities and three durations of rainfall. Runoff samples from each combination of factors were tested for toxicity.

This study was conducted during summer 2000, during which time no measurable natural rainfall occurred. The parking lots used were located on the Liberal Arts Campus of the Long Beach City College and were constructed of asphalt. Two separate parking lots were used for each of the components. The parking lots were divided into multiple study plots, each consisting of two parking stalls with a total area of 18 m². All runoff samples throughout the study were tested for toxicity using the purple sea urchin fertilization test.

The antecedent period experiment consisted of 18 study plots that consisted of high and low use and maintained and unmaintained treatment groups assigned using a randomized block design. High-use parking stalls had a high turnover rate, with many cars occupying a stall one at a time for short periods (Tiefenthaler et al. 2003). Low-use sites had fewer cars parked for longer periods. During peak periods, all stalls were in use. Maintained sites had weekly leaf blowing and sweeping; unmaintained sites did not. Before the study, simulated rainfall was applied to representative plots, and the runoff was collected to establish the baseline toxicity level. All plots were then pressure washed at time zero, and simulated rainfall was again applied and the runoff tested. For 3 months, at 1-month intervals six plots were rainfed on and tested; one high-use maintained, two high-use unmaintained, one low-use maintained, and two low-use unmaintained plots each month. Simulated rainfall was applied to each of these plots at a rate of 13 mm/h for 20 minutes, and all of the runoff was collected for testing. Each plot was sampled only once during the experiment.

In the second part of the study, we tested runoff after the application of rainfall at different intensities and durations. Three months after pressure washing the lots, nine plots were subjected to the following rainfall regimes. Three replicate plots were used for each of the intensities, which were 6, 13, and 25 mm/h (0.25, 0.5, and 1 in./h), a range from typical- to worst-case intensities for the study area. Samples were collected from each plot at varying durations. For the 6 and 25 mm/h intensities, samples were taken after 10 minutes and then after 20 minutes, the second sample contained only runoff from simulated rainfall between the 10- and 20-minute periods. For the 6 mm/h treatment, an additional sample was taken after 40 minutes that only contained runoff from the 20- to 40-minute period. Only one sample was collected for the 13 mm/h treatment after 20 minutes of rainfall and matched the duration and intensity for the antecedent period portion of the study.

The rainfall simulator consisted of a manifold with lawn sprinkler heads that sprayed water in a semicircular pattern wetting an area of 1.19 m² (Tiefenthaler et al. 2003). The simulated rain fell from a height <1 m. Source water for rainfall simulation was taken from campus taps and passed through a series of activated carbon and particle filters. The runoff collection apparatus consisted of perforated polyvinyl chloride (PVC) pipes positioned along the boundaries of the plot. The PVC pipe was attached to a 55-gallon plastic barrel with a tight fitting lid, which in turn was attached to a vacuum. When the vacuum was turned on, runoff was drawn through the PVC pipe on the plots, through the tubing, and finally into the barrel. At the end of the rainfall application, the collected water was mixed thoroughly in the barrel, and an aliquot was removed for toxicity testing.

Toxicity Measurement

This study was part of a larger project investigating the effect of urban runoff on marine test species. We therefore chose to use the purple sea urchin sperm cell test as described by the United States Environmental Protection Agency (USEPA 1995). Gametes were obtained from adult specimens of the purple sea urchin, Strongylocentrotus purpuratus. Sea urchin sperm were exposed to various concentrations of the test sample for 20 minutes at a temperature of approximately 15°C. Eggs were then added to each sample and given 20 minutes for fertilization to occur. The samples were preserved and later examined under a microscope to determine the percentage of fertilized eggs.

The salinity of the runoff samples was adjusted to typical seawater concentration by the addition of hypertonic brine with a salinity of approximately 68 g/kg. Addition of the brine diluted the samples, which resulted in the highest sample concentration tested being 50%. Additional test concentrations were prepared by adding laboratory seawater to the samples. A brine control was included in each experiment to test for toxicity introduced by the salinity adjustment procedure.

Each sample was tested at a minimum of two concentrations. Samples from the high-use treatment groups were tested at concentrations of 50%, 25%, 12%, 6%, and 3%, whereas low-use treatment groups were tested at a decreased number of concentrations because of limited resources. All samples from the rainfall intensity and duration experiment were tested at concentrations of 50% and 12%. Samples of water from every part of the rainfall application and runoff collection systems were tested to verify that no part of the system was causing toxicity.

To determine the chemical constituents responsible for the observed toxicity, phase 1 TIEs were conducted on selected samples. Each sample was subjected to treatments designed to selectively remove or neutralize different classes of compounds (e.g., metals, nonpolar organics). Treated samples then underwent testing with the sea urchin fertilization test to determine if any change in toxicity had occurred.

Four treatments were applied to each sample: particle removal, trace metal chelation, extraction of nonpolar organic compounds, and chemical reduction. The treatments were based on EPA methods (USEPA 1996). A sample of laboratory water was included with each type of treatment to verify that the manipulation was not causing toxicity. The
untreated sample was retested at the time of the TIE to control for changes in toxicity related to sample storage. Ethylenediaminetetraacetic acid (EDTA), a chelator of metals, was added to test samples to achieve a final concentration of 60 mg/L. Sodium thiosulfate, a treatment that chemically reduces oxidants such as chlorine and also decreases the toxicity of some metals, was added to a final concentration of 50 mg/L to separate portions of each sample. Samples were centrifuged for 30 minutes at 3000g to remove particle-borne contaminants. A portion of the centrifuged sample was passed through a 12-ml Varian (Palo Alto, CA) Mega Bond Elute C-18 solid phase extraction column to remove nonpolar organic compounds. The C-18 columns have also been found to remove some metals from aqueous solutions.

The C-18 columns were eluted sequentially with methylene chloride (MeCl₂) and hydrochloric acid to recover the organic and metal fractions that had bound to the columns. The MeCl₂ eluates were solvent exchanged to isopropanol. The eluates in isopropanol and the acid eluates were then diluted with seawater and tested for toxicity using the sea urchin fertilization test.

Analytical Chemistry

Details of the chemical analysis can be found in Tiefenthaler et al. (2003). Briefly, all chemical analysis were performed on 100% runoff samples. Total suspended solids were analyzed gravimetrically using EPA method 160.2. Samples for total and dissolved metals were analyzed using EPA methods 200.8, 236.1, 236.2, and 245.1. Inductively coupled plasma–mass spectrometry was used for all metals analyses. Polycyclic aromatic hydrocarbons (PAHs) were extracted, isolated, and analyzed using EPA method 8270 C.

Data Analysis

To make comparisons between the relative toxicity of the various treatments, the no-observed-effect concentration (NOEC, the highest concentration not producing a statistically significant decrease in fertilization or survival) and the concentration of runoff producing a 50% decrease in fertilization (EC50) were calculated for each sample. For the NOEC calculation, the data were arcsine transformed and then tested for homogeneity of variance (Bartlett's test) and normal distribution (Shapiro–Wilk's test). Data meeting these criteria were then tested using one-way analysis of variance 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 nonparametric Steel's Many-One Rank test (USEPA 1995). The EC50 was calculated using probit analysis. To make comparisons between treatments and to determine the relative contribution of chemical constituents to observed toxicity, the EC50 data were converted to acute toxic units (TUa = 100/EC50). All NOEC and EC50 calculations were performed using ToxStat version 3.5. Spearman's rank correlations were performed on chemistry concentrations and toxicity data to determine statistical associations between contaminants and toxicity.

Results

Antecedent Period Effects

Runoff samples collected immediately after the clearing (T0) were much less toxic than the preclearing samples. All of the T0 samples had the highest NOEC (25%) and lowest TUa (< 2 to 2.7) measured in the study (Table 1). When the data for all use and maintenance groups are combined, a sixfold increase in toxicity was observed after a 1-month antecedent period relative to the T0 samples. The toxicity decreased by nearly a factor of two for the second month, and the third month's results were very similar to those for the second month. Both the 2- and 3-month samples had mean TUa values that were similar to the samples taken before the sites were pressure washed (Table 1).

Toxicity to sea urchin sperm was observed in every sample collected during the accumulation study, including the samples taken immediately after the parking lot cleaning (Table 1). The magnitude of toxicity was similar among most samples collected within a time period. Samples collected after 2 months' accumulation showed the greatest variability in toxicity within a time interval. Toxicity for these samples ranged from < 4 to 10.8 TUa. In all other cases, there was no more than a twofold range of toxicity within a time interval (Table 1).

Level of Use and Maintenance Effects

Variations in parking lot use did not have a consistent effect on toxicity. High-use sites tended to have greater toxicity in month-1 samples, but the differences were relatively small (Figure 1). The opposite trend was observed for the month-2 and -3 samples. Toxicity within these intervals tended to have approximately 50% less toxicity in the high-use than low-use sites (Figure 1). The level of maintenance that a site received had no discernible effect on toxicity for most of the sampling intervals. Maintained high-use sites at month 2 were approximately twice as toxic as unmaintained high-use sites (Figure 1). The difference in toxicity between maintenance levels was much less for the remaining intervals.

Rainfall Intensity and Duration

Variations in both simulated rain intensity and duration had a pronounced and predictable effect on toxicity. Toxicity was inversely related to both of these parameters (Table 2). For any given duration interval, toxicity decreased as rainfall intensity increased from 6 mm/h to 25 mm/h. Samples collected after longer durations at the same intensity always were less toxic. A wide range in magnitude of toxicity was exhibited between treatments: mean TUa ranged from 2.6 to 13.8 (Table 2).

The toxicity data also indicated that there was an interaction between intensity and duration. For example, the relative decrease in toxicity after 10 minutes and after 20 minutes of rainfall at 6 mm/h was less (31%) than the change (54%) measured at an intensity of 25 mm/h. The magnitude of toxicity present in each intensity and duration group was largely determined by the total amount of rainfall that had preceded the sampling time. The samples with the greatest toxicity were those collected first at any given intensity (Table 2).

Every sample of runoff collected during the rainfall intensity and duration phase of the study was toxic to the sea urchin sperm cell test. Little variability was present among the samples within any treatment group, the maximum standard deviation was 26. Less than a factor of two difference in toxicity
Table 1. Summary of parking lot runoff toxicity results during each of three months of accumulation (mean ± SD; maintenance and use groups combined)

<table>
<thead>
<tr>
<th>Time</th>
<th>N</th>
<th>NOEC (%)</th>
<th>EC50 (%)</th>
<th>TUa</th>
</tr>
</thead>
<tbody>
<tr>
<td>Preclean</td>
<td>2</td>
<td>3 ± 0</td>
<td>19.8 ± 0.8</td>
<td>5.0 ± 0.2</td>
</tr>
<tr>
<td>T0 postclean</td>
<td>6</td>
<td>25 ± 0</td>
<td>55.0 ± 22.7*</td>
<td>2.0 ± 0.6</td>
</tr>
<tr>
<td>Month 1</td>
<td>6</td>
<td>&lt;8 ± 5</td>
<td>8.6 ± 1.9</td>
<td>12.1 ± 2.8</td>
</tr>
<tr>
<td>Month 2</td>
<td>6</td>
<td>6 ± 5</td>
<td>19.4 ± 15.4*</td>
<td>7.0 ± 3.1</td>
</tr>
<tr>
<td>Month 3</td>
<td>6</td>
<td>4 ± 2</td>
<td>17.2 ± 5.4</td>
<td>6.3 ± 2.0</td>
</tr>
</tbody>
</table>

Notes: Toxic units were calculated using the sea urchin fertilization test EC50 (TUa). EC50s for the T0 (after pressure washing) samples were estimated by graphic interpolation. EC50s for the remaining samples were calculated using probit analysis.

* One site did not exhibit enough toxicity to calculate an EC50. A value that equaled twice the highest concentration tested was used in the calculation of the mean.

EC50 = concentration of runoff producing a 50% decrease in fertilization or survival; NOEC = no-observed-effect concentration; TUa = acute toxic units.

---

Fig. 1. Toxicity (TUa) of parking lot runoff samples from various use and maintenance combination sites to sea urchin fertilization test during each of the 3 months of accumulation. Data are the means of two samples except for maintained and T0 sites where n = 1. Error bars represent the standard deviation.

---

**Toxicity Identification**

Phase I TIEs were conducted on one runoff sample from each of the month-2 and -3 sampling events: a high-use maintained plot in month 2 and a high-use unmaintained plot in month 3. The TIE baseline testing also indicated that the samples were stable during short-term storage (< 5 d) because there was no appreciable difference in toxicity between the initial and TIE baseline samples (Figures 2 and 3).

For each sample, both the EDTA addition and C-18 extraction treatments were effective at eliminating most of the toxicity (Figures 2 and 3). The most effective treatment was the extraction of nonpolar organic compounds using a C-18 column, which eliminated nearly all of the toxicity. Addition of EDTA eliminated 44% to 76% of the toxicity. The two other TIE manipulations, the removal of particles and addition of sodium thiosulfate, were not effective in decreasing toxicity.

Elution of the C-18 columns with organic solvent recovered only a portion of the expected toxicity (Figure 4). When the original samples were tested, <5% of the eggs were fertilized, which is what would be expected in the eluates if all of the toxicity were recovered. After the column was eluted with solvent and the eluate concentrated to 1.5 times the original sample concentration, the fertilization rate was >60% (Figure 4). It was not until the sample was concentrated to 3 times the original concentration that a greater amount of toxicity was recovered. An attempt was made to elute metals from the C-18 columns with an acid solution. The acid eluates were not expected to be toxic unless metals were being extracted from the columns. All of the acid eluates were highly toxic to sea urchin sperm (Figure 4). Some toxicity was observed in the acid eluate blank sample, but the unusual dose-response pattern suggested that this was caused by a procedural artifact.

Chemical analysis of the samples indicated that detectable concentrations of three potentially toxic constituents (zinc, copper, and total PAH) were present (Tiefenthaler et al. 2003). Of these, only zinc was present at a sufficiently high concentration to cause substantial toxicity (Figures 2 and 3). Limited data are available on the toxicity of individual PAHs to sea urchin sperm, but unpublished data from our laboratory for several PAHs indicates that concentrations ≥ 100 μg/L are needed to produce toxicity. The PAH concentrations in the runoff were < 30 μg/L, suggesting that these compounds were unlikely to be responsible for much of the sample toxicity.

Significant correlations were obtained for both the total and dissolved forms of most metals and toxicity, but no significant correlation was observed between total PAHs and toxicity (Table 3). Correlations were highest (>0.6) for total and dissolved chromium, total aluminum, total nickel, and total and dissolved zinc. In our laboratory, over multiple exposures, we have found the EC50 for zinc to be approximately 22 μg/L. The concentration of dissolved zinc in the parking lot samples ranged from 140 to 620 μg/L. The toxic units for zinc corresponding to these concentrations are as much as 28 and were always greater than the number of toxic units measured for the sea urchin fertilization test (Table 1). This indicates that the concentration of zinc was sufficient in each of the runoff samples to account for all the observed toxicity. The EC50 for copper in our laboratory exposures is approximately 35 μg/L.
Table 2. Toxicity to sea urchin fertilization of parking lot runoff collected at different simulated rainfall intensity and duration combinations

<table>
<thead>
<tr>
<th>Sample</th>
<th>Intensity (mm/h)</th>
<th>0–10 minutes</th>
<th>10–20 minutes</th>
<th>20–40 minutes</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>EC50 (%)</td>
<td>TUs</td>
<td>EC50 (%)</td>
</tr>
<tr>
<td>302R1</td>
<td>6</td>
<td>6.5</td>
<td>15.4</td>
<td>10.5</td>
</tr>
<tr>
<td>505R2</td>
<td>6</td>
<td>8.5</td>
<td>11.8</td>
<td>10.5</td>
</tr>
<tr>
<td>507R3</td>
<td>6</td>
<td>7</td>
<td>14.3</td>
<td>10.5</td>
</tr>
<tr>
<td>Mean</td>
<td>6</td>
<td>7.3</td>
<td>13.8</td>
<td>10.5</td>
</tr>
<tr>
<td>303R1a</td>
<td>13</td>
<td>21</td>
<td>4.8</td>
<td>21</td>
</tr>
<tr>
<td>304R2a</td>
<td>13</td>
<td>26</td>
<td>3.8</td>
<td>26</td>
</tr>
<tr>
<td>309R3a</td>
<td>13</td>
<td>22.7</td>
<td>4.5</td>
<td>22.7</td>
</tr>
<tr>
<td>Mean*</td>
<td>13</td>
<td>17</td>
<td>5.9</td>
<td>34</td>
</tr>
<tr>
<td>506R1</td>
<td>25</td>
<td>26</td>
<td>3.8</td>
<td>57</td>
</tr>
<tr>
<td>508R2</td>
<td>25</td>
<td>25</td>
<td>7.1</td>
<td>32</td>
</tr>
<tr>
<td>513R3</td>
<td>25</td>
<td>19.0</td>
<td>5.6</td>
<td>41.0</td>
</tr>
</tbody>
</table>

Notes: Samples representing up to three time intervals were collected for each intensity. The EC50 was calculated by linear interpolation of the fertilization data.

*Samples representing a rainfall interval of 0 to 20 minutes.

EC50 = concentration of runoff producing a 50% decrease in fertilization or survival; TUs = acute toxic units.

---

Dissolved copper in the parking lot samples ranged from 0 to 37 μg/L, contributing at most only one toxic unit and accounting for <10% of the toxic units of any sample.

Discussion

The results of this study show that runoff from parking lots is an important source of toxicity in urban storm water. All of the simulated rainfall runoff samples from this project were found to be toxic. The magnitude of toxicity was often greater than that observed in other urban storm-water samples. Storm-water samples collected from various channels in southern California usually had <4 TUs (Kinetic Laboratories 2001; Schiff et al. 2002), whereas nearly all of the parking lot runoff samples exhibited >4 TUs. A similar result was observed for dissolved...
in small watersheds dominated by a specific land use, such as parking lots, than in storm channels draining more larger and more diverse watersheds. Other researchers have identified parking lots as critical source areas for contaminants in commercial and industrial land use areas (Bannerman et al. 1993).

The lack of an increase in toxicity after the first month of accumulation was contrary to what has been observed in studies on larger watersheds in southern California. Previous work has indicated that longer antecedent periods lead to greater toxicity in storm channels (Bay et al. 1999; Kinetic Laboratories 2001). However, other researchers have found that antecedent period is a poor predictor of storm-water quality; a positive association was found in some studies, and no relationship was found in others (Barrett et al. 1995; Lee et al. 2002). In studies of accumulation of street dirt, it was found that maximum observed loadings were often reached in ≤30 days (Heaney et al. 1999). A study conducted on particulate loading to streets found that accumulation decreases with time because losses from wind-carried fugitive dust increase with higher loadings (Pitt and Sutherland 1982). The findings for streets are similar to the results from our study, which indicate that the toxic constituents accumulated rapidly but after a month reached a maximum level. This implies that any treatment of the parking lot to decrease toxicity, such as washing, would have to be conducted more often than monthly to be effective.

Results from this study indicated that the typically used maintenance activities, such as sweeping and dust removal, were ineffective for decreasing the toxicity of parking lot runoff. These methods would mostly be effective at removing particulates. Street sweepers are not effective at removing fine particles with which metals might be associated (Leibens 2001). However, most of the toxicity is expected to be associated with constituents that dissolve into the runoff. This is supported by the ineffectiveness of the particle removal step in the TIE at decreasing toxicity. The more rigorous pressure washing that was done at the beginning of the study decreased the toxicity of the runoff by a factor of three. The fact that pressure washing did not completely eliminate toxicity indicates that more research is needed to identify the most effective means of eliminating runoff toxicity.

The lack of difference in toxicity between the high- and low-use treatments may be associated with a couple of different factors. It is possible that the presence of automobiles on a site, whether for long or short periods, may deposit the same amount of contaminants. Although the number of cars and duration of use varied, all of the parking stalls were used during peak periods. A second factor is that contaminants may be deposited on the parking lots from other sources. Aerial deposition has been implicated as an important source of cadmium, copper, and lead (Davis et al. 2001). Measurement from the rainfall intensity and duration component indicated the presence of a first-flush effect for toxicity. Runoff samples collected during the first 10 minutes of a simulated rain event were approximately twice as toxic as runoff from later samples. This finding agreed with the results of chemical analyses of the samples, which showed the first portion of the runoff event to contain the highest constituent concentrations (Tiefenthaler et al. 2003). The 25 mm/h intensity of simulated rainfall showed a much lower level of toxicity than the 6 mm/h intensity after 10 minutes. This was likely an

---

**Table 3.** Spearman correlation coefficients between sea urchin fertilization toxic units and chemical concentrations for all samples analyzed

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Correlation Coefficient</th>
<th>p value</th>
</tr>
</thead>
<tbody>
<tr>
<td>TSS</td>
<td>0.418</td>
<td>0.006</td>
</tr>
<tr>
<td>PAH (total)</td>
<td>-0.001</td>
<td>0.997</td>
</tr>
<tr>
<td>Al (dissolved)</td>
<td>0.471</td>
<td>0.002</td>
</tr>
<tr>
<td>Al (total)</td>
<td>0.669</td>
<td>&lt; 0.001</td>
</tr>
<tr>
<td>Cd (dissolved)</td>
<td>0.433</td>
<td>0.004</td>
</tr>
<tr>
<td>Cd (total)</td>
<td>0.400</td>
<td>0.009</td>
</tr>
<tr>
<td>Cr (dissolved)</td>
<td>0.693</td>
<td>&lt; 0.001</td>
</tr>
<tr>
<td>Cr (total)</td>
<td>0.793</td>
<td>&lt; 0.001</td>
</tr>
<tr>
<td>Cu (total)</td>
<td>0.542</td>
<td>&lt; 0.001</td>
</tr>
<tr>
<td>Cu (dissolved)</td>
<td>0.428</td>
<td>0.005</td>
</tr>
<tr>
<td>Fe (dissolved)</td>
<td>0.337</td>
<td>0.029</td>
</tr>
<tr>
<td>Fe (total)</td>
<td>0.398</td>
<td>0.009</td>
</tr>
<tr>
<td>Pb (dissolved)</td>
<td>0.228</td>
<td>0.060</td>
</tr>
<tr>
<td>Pb (total)</td>
<td>0.271</td>
<td>0.082</td>
</tr>
<tr>
<td>Ni (dissolved)</td>
<td>0.494</td>
<td>&lt; 0.001</td>
</tr>
<tr>
<td>Ni (total)</td>
<td>0.638</td>
<td>&lt; 0.001</td>
</tr>
<tr>
<td>Zn (dissolved)</td>
<td>0.629</td>
<td>&lt; 0.001</td>
</tr>
<tr>
<td>Zn (total)</td>
<td>0.655</td>
<td>&lt; 0.001</td>
</tr>
</tbody>
</table>

Notes: N = 42 for all analyses. Mercury and silver concentrations were nondetectable for all samples and are not included in correlation analyses.
artifact of our sample collection method. Four times the volume of runoff was collected in the 25 mm/h than in the 6 mm/h, effectively diluting the first flush effect at the higher intensity. These results indicate that storm-water treatment systems that capture or treat the initial portion of storm-water discharge are likely to provide the greatest decrease in toxic constituents. The toxicant characterization and identification component suggested that the toxicity of the parking lot runoff to the sea urchin fertilization test was primarily caused by metals. Given its high concentrations in the samples, zinc is the most likely cause of the metal toxicity. These results are similar to those of TIEs from studies of storm-water runoff identified zinc as a primary toxicant of concern in Ballona Creek in Los Angeles and Chollas Creek in San Diego (Bay et al. 2003; Schiff et al. 2002). Motor vehicles are a likely source of this zinc; high levels are found in brakes, motor oil, and tires (Davis et al. 2001). Motor oils have been found to contain > 0.1% zinc (Zieba-Palus and Koscieniak 2000). TIEs conducted on lake leachate toxic to freshwater organisms indicated that zinc was the cause of the observed toxicity (Nelson et al. 1994). Vehicles may supply zinc either directly to the parking lot from fluid leakage or by transporting zinc-laden road dust.

The removal of toxicity by the C-18 column is usually interpreted as an indication that nonpolar organics are a source of toxicity. In this study, no organic chemicals were measured in the runoff at concentrations high enough to be expected to cause toxicity to the sea urchin fertilization test. Furthermore, the fact that elution of the C-18 columns with organic solvents recovered only a small portion of the toxicity indicates that nonpolar organics were not a source of toxicity. The recovery of toxicity by elution with acetonitrile indicates that the column extracted metals from the sample. However, no chemical analysis was performed to verify what constituents were eluted in either the organic or acetic phase. We previously found that C-18 columns were capable of removing toxic quantities of copper and zinc from spiked water samples (Schiff et al. 2002).

The correlation analysis of the toxicity and chemistry results indicates a strong association between several metals and toxicity. However, each of these metals is also highly correlated with one another, and the concentrations of most of the metals were not high enough to cause toxicity to the organisms used in this study. The only metals that were measured at concentrations sufficient to cause toxicity were copper and zinc. The toxic units calculations, however, indicate that only zinc was present at concentrations high enough to account for the observed toxicity. The TIE treatments also determined that the toxic constituents in the parking lot runoff were associated with the dissolved fraction rather than particulates. Similarly, the chemistry data indicated that most of the metals were associated with the dissolved phase (Tiefenthaler et al. 2003). These findings have implications for the design of best management practices (BMPs) to decrease storm-water toxicity. BMPs based primarily on particulate removal are unlikely to be effective in decreasing the toxicity of storm-water runoff from parking lots.

Acknowledgments. The authors thank the employees of Property Prep, Inc., and Wastewater Remediation for construction of the rainfall simulators and their work in the field sampling. We also thank the following Southern California Coastal Water Research personnel who assisted in the toxicity studies and field sampling: Jeffrey Brown, Dario Diehl, Ehren Doris, Kim Johnson, Julie Kalman, Andrea Steinberger, and David Tsukada. We additionally thank two anonymous reviewers for their valuable comments.

References