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# Toxicity of parking lot runoff after simulated rainfall

**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-use and low-use, and into maintained and unmaintained treatments. The parking stalls were cleaned by pressure washing at time zero. Simulated rainfall was then applied to the parking lots at monthly intervals for three months with all of the runoff being collected for analysis. 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 (TUa). The toxicity increased rapidly during the first month, but then dropped approximately to pre-cleaning 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 the degree of toxicity. For all of the 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.

## INTRODUCTION

Many studies have found urban stormwater runoff to be toxic to aquatic organisms (Heaney *et al.* 1999a). Toxicity has been found for both small watersheds, such as streets and industrial sites (Maltby *et al.* 1995, Pitt *et al.* 1995, Marsalek *et al.* 1999) and larger urban creeks and rivers (Bay *et al.* 1997, Jirik *et al.* 1998, Riveles and Gersberg 1999, Schiff *et al.* 2002). In one study, nearly one-half of the samples were characterized as having moderate to extreme toxicity (Pitt *et al.* 1995). Most studies have focused on determining the land-use type or specific chemical causing toxicity. A complete understanding of all of the factors that affect toxicity is necessary to make management decisions to reduce toxicity.

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While a great deal of research has been conducted on issues regarding environmental effects of stormwater, there are still many gaps in our understanding of these effects (Heaney *et al.* 1999b). Many factors have the potential to affect the degree of runoff toxicity, including the time between storms (antecedent period), storm duration, and intensity of rainfall; but these factors are poorly understood. There has been no direct study of how these factors affect toxicity. Some previous studies have indicated that longer antecedent periods between storms are associated with increased toxicity (Bay *et al.* 1999, KLI and SCCWRP 2001). Other studies have pointed to the importance of seasonal effects to runoff quality; where early-season storms exhibited much greater toxicity than late-season storms, with little apparent effect of antecedent period (Schiff and Stevenson 1996, Bay *et al.* 2003). Most of the work on antecedent period and storm characteristics has focused on contaminant inputs. A review of such studies found that the effect of antecedent period was variable (Barrett *et al.* 1995). The intensity of rainfall has been implicated as an important factor in the amount of particulate-bound metals that are washed off (Sansalone *et al.* 1996).

One of the limits to our understanding of how storm characteristics affect toxicity is a lack of control of the rainfall. It is very difficult to study the effects of storm characteristics when relying upon natural rainfall to provide runoff. The drawback to relying on natural storm events is that there is no control over intensity or duration of the rainfall, nor the period between storms. Without these controls, it is difficult to answer two critical questions: (1) Does the toxicity of runoff change as length of time between storms increases?; and (2) Is there a difference in toxicity of runoff between short, intense rain and longer, gentler rain?

In this study, we used simulated rainfall so that all aspects of the precipitation event were controlled.

The study was conducted on parking lots in order 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 (Maltby *et al.* 1995, Pitt *et al.* 1995).

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 monthly over three months. The second objective was to determine the effect of differing rainfall intensities and durations on the quality of the runoff. The remaining 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 parked for longer periods. The second was to determine whether normal parking lot maintenance procedures had an effect on runoff quality. 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 a three-month antecedent period experiment to measure the effects of contaminant accumulation over differing time periods. 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, which was performed after three months of accumulation. For this part of the study, simulated rainfall was applied to parking lot subplots at varying intensities and durations. Runoff samples from each combination of factors were tested for toxicity.

This study was conducted during the summer of 2000. The parking lots used were located on the Liberal Arts Campus of 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. Every study plot was cleaned by pressure washing at the start of the study period. Immediately before and after the cleaning, simulated rainfall was applied to representative plots and the runoff was collected to establish the baseline toxicity level. 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 were assigned to treatment groups using a randomized block design. Use level, maintenance type, and antecedent period were the factors. Each of the plots was designated as to length of antecedent period and whether it was high or low use and maintained or un-maintained. High-use parking stalls had a high turnover rate, with many cars occupying a stall 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. Maintenance consisted of weekly leaf blowing and sweeping. Simulated rainfall was applied to one high-use, maintained (H/M), two high-use un-maintained (H/U), one low-use maintained (L/M), and two low-use un-maintained (L/U) plots each month, for three consecutive months. Simulated rainfall was applied to each of these plots at a rate of 13 mm/h for 20 minutes, and the runoff was collected for testing. Each plot was sampled only once during the experiment.

The rainfall intensity and duration experiment was conducted using nine plots, which were randomly assigned to one of three intensity groups. 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). Samples were collected from each plot at varying durations. For the 6 and 25 mm/h intensities, samples were taken representing 0-10 min and 10-20 min of simulated rainfall. For the 6 mm/h treatment, an additional sample was taken representing 20-40 min. Only one sample was collected for the 13 mm/h treatment, which represented 0-20 minutes of rainfall and matched the duration and intensity of the monthly sampling.

The rainfall simulator consisted of a manifold with lawn sprinkler heads that sprayed water in a semi-circular pattern (Tiefenthaler *et al.* 2003). 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 PVC pipes positioned along

the boundaries of the plot. The PVC pipe was attached to a plastic barrel, which in turn was attached to a vacuum. Runoff was drawn through the PVC pipe and collected in 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

The purple sea urchin sperm cell test was performed as described by U.S. EPA (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 min at a temperature of approximately 15°C. Eggs were then added to each sample and given 20 min for fertilization to occur. The samples were then 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 hypersaline brine. 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%, 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%. 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 observed toxicity, Phase I 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 whether 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. 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 due 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 (STS), a treatment that 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 min at 3000 X g to remove particle-borne contaminants. A portion of the centrifuged sample was 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 C-18 columns were eluted sequentially with ~~methylene chloride (MeCl<sub>2</sub>)~~ and hydrochloric acid to recover the organic and metal fractions that had bound to the columns. The MeCl<sub>2</sub> 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.

### Data Analysis

To make comparisons between the relative toxicity of the various treatments, the NOEC (highest concentration not producing a statistically significant reduction in fertilization or survival) and the EC50 (concentration of runoff producing a 50% reduction in fertilization or survival, respectively) were calculated for each sample. 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 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 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 (TU<sub>a</sub> = 100/EC50). 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 cleaning (T0) were much less toxic than the pre-cleaning samples. All of the T0 samples had the highest NOEC (25%) and lowest toxic units (<2 to 2.7 TUa) measured in the study (Table 1). A six-fold increase in toxicity was observed after a one-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 the second month's results. Both the two-month and three-month samples had mean TUa values that were similar to the samples that were 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 following the parking lot cleaning (Table 1). The magnitude of toxicity was similar among most samples collected within a time period. Samples collected after two months of 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 two-fold range of toxicity within a time interval (Table 1).

### Level of Use 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 sites than low-use sites (Figure 1).

### Maintenance Effects

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.

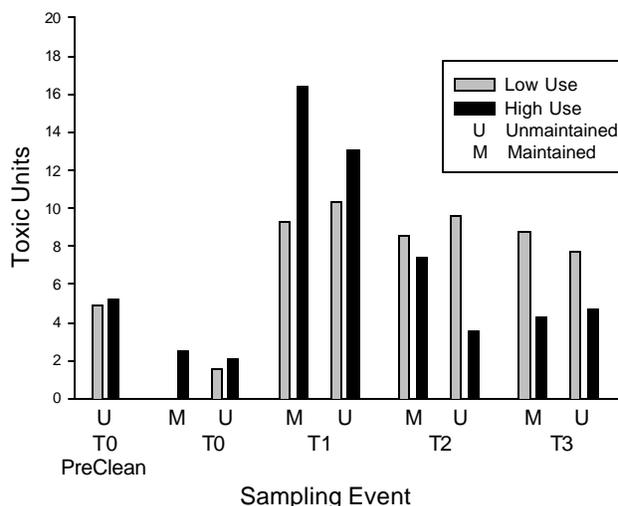
### Rainfall Intensity and Duration

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 (Figure 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 the 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 between the 0-10 min and 10-20 min intervals 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/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 that contained the first 4 mm of total rainfall (Table 2).

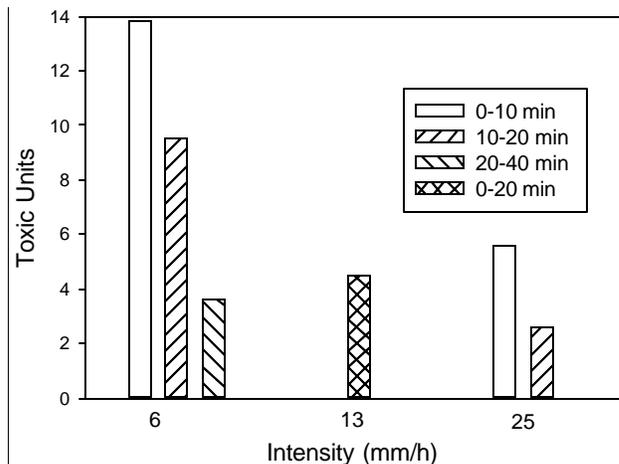
Every sample of runoff collected during the rainfall intensity and duration phase of the study was toxic to the sea urchin sperm cell test. Little variability was present among the samples within any treatment group. Less than a factor of two difference in toxicity was detected among the three replicate sites within each intensity/duration group (Table 2).

**Table 1. Summary of parking lot runoff toxicity results during the three-month accumulation period (mean  $\pm$  standard deviation; maintenance and use groups combined). Toxic units are calculated using the sea urchin fertilization test EC50 (TUa). The EC50s for the T0 (after pressure washing) samples were estimated by graphical interpolation. The EC50s for the remaining samples were calculated using probit analysis.**

Time	N	NOEC (%)	EC50 (%)	TUa
T0 Preclean	2	3 $\pm$ 0	19.8 $\pm$ 0.8	5.0 $\pm$ 0.2
T0 Postclean	6	25 $\pm$ 0	55.0 $\pm$ 22.7 <sup>a</sup>	2.0 $\pm$ 0.6
Month 1	6	<8 $\pm$ 5	8.6 $\pm$ 1.9	12.1 $\pm$ 2.8
Month 2	6	6 $\pm$ 5	19.4 $\pm$ 15.4 <sup>a</sup>	7.0 $\pm$ 3.1
Month 3	6	4 $\pm$ 2	17.2 $\pm$ 5.4	6.3 $\pm$ 2.0



**Figure 1. Toxicity (TUa) of parking lot runoff samples from various use and maintenance combination sites to sea urchin fertilization test during the 3-month accumulation period. Data are the means of two samples except for maintained sites, where n=1.**



**Figure 2. Mean toxicity (TUa) to the sea urchin fertilization test from runoff samples collected at different simulated rainfall intensity and duration combinations.**

**Table 2. Toxicity to sea urchin sperm of parking lot runoff collected at different simulated rainfall intensity and duration combinations. Samples representing up to three time intervals were collected for each intensity. The EC50 was calculated by linear interpolation of the fertilization data.**

Sample	0-10 minutes				10-20 minutes			20-40 minutes		
	Intensity (mm/h)	EC50 (%)	TUa	Rainfall (mm)	EC50 (%)	TUa	Rainfall (mm)	EC50 (%)	TUa	Rainfall (mm)
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	
<b>Mean</b>	<b>6</b>	<b>7.3</b>	<b>13.8</b>	1	<b>10.5</b>	<b>9.5</b>	2	<b>28</b>	<b>3.6</b>	4
503R1 <sup>a</sup>	13				21 <sup>a</sup>	4.8 <sup>a</sup>				
504R2 <sup>a</sup>	13				21 <sup>a</sup>	4.8 <sup>a</sup>				
509R3 <sup>a</sup>	13				26 <sup>a</sup>	3.8 <sup>a</sup>				
<b>Mean<sup>a</sup></b>	<b>13</b>				<b>22.7<sup>a</sup></b>	<b>4.5<sup>a</sup></b>	4			
506R1	25	17	5.9		34	2.9				
508R2	25	26	3.8		57	1.8				
513R3	25	14	7.1		32	3.1				
<b>Mean</b>	<b>25</b>	<b>19</b>	<b>5.6</b>	4	<b>41</b>	<b>2.6</b>	8			

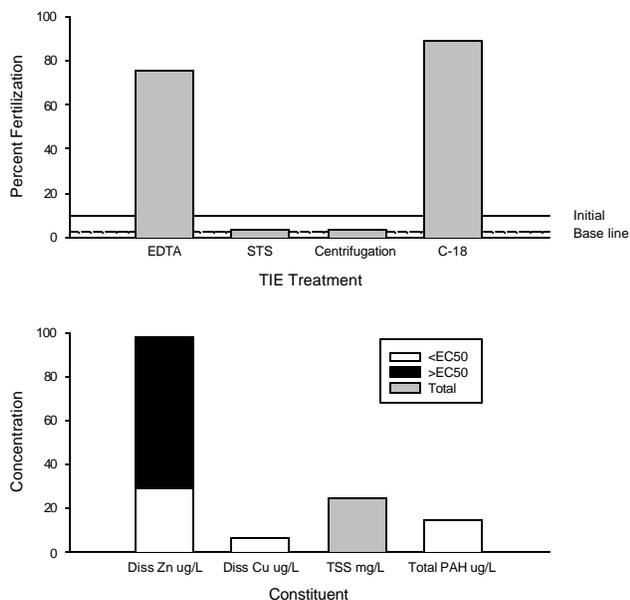
<sup>a</sup>Samples representing a rainfall interval of 0-20 minutes.

## Toxicity Identification

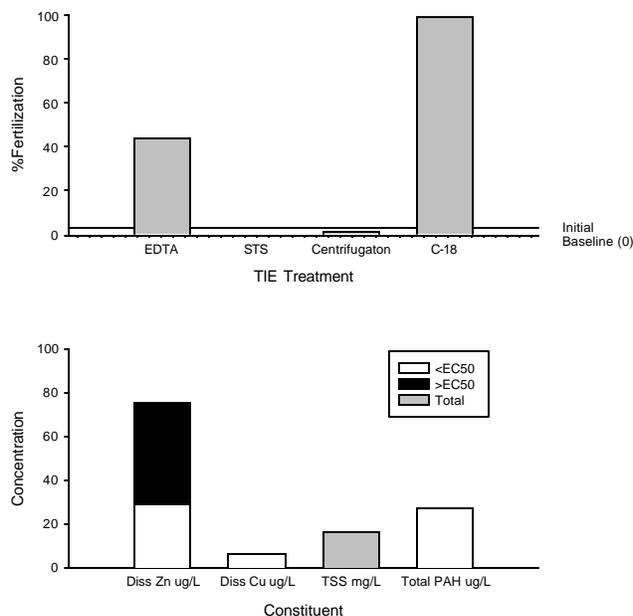
Phase I TIEs were conducted on one runoff sample from each of the Month 2 and 3 sampling events. For each sample, both the EDTA addition and C-18 extraction treatments were effective at eliminating most of the toxicity (Figures 3 and 4). The most effective treatment was the extraction of nonpolar organic 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 reducing toxicity. The TIE baseline testing also indicated that the samples were stable during short-term storage, as there was no appreciable difference in toxicity between the initial and TIE baseline samples (Figures 3 and 4).

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 3 and 4). Limited data are available on the toxicity of individual PAHs to sea urchin sperm, but unpublished SCCWRP data



**Figure 3. TIE results for a runoff sample 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 represents the portion of the concentration that is greater than the EC50 for that constituent.**



**Figure 4. TIE results for a runoff sample following 3 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 represents the portion of the concentration that is greater than the EC50 for that constituent.**

for several PAHs indicate that concentrations of  $\geq 100 \mu\text{g/L}$  are needed to produce toxicity. The PAH concentrations in the runoff were below  $30 \mu\text{g/L}$ , 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. The concentration of dissolved zinc ranged from 140 to  $620 \mu\text{g/L}$ . The toxic units for zinc corresponding to these concentrations (calculated from laboratory-derived EC50s) are greater than the number of toxic units measured for the sea urchin fertilization test (Figure 5). This indicates that the concentration of zinc was sufficient in each of the runoff samples to account for all of the observed toxicity. Dissolved copper in these samples ranged from 0 to  $37 \mu\text{g/L}$ , contributing less than 10% of the toxic units of any sample.

Elution of the C-18 columns with organic solvent recovered only a portion of the expected toxicity

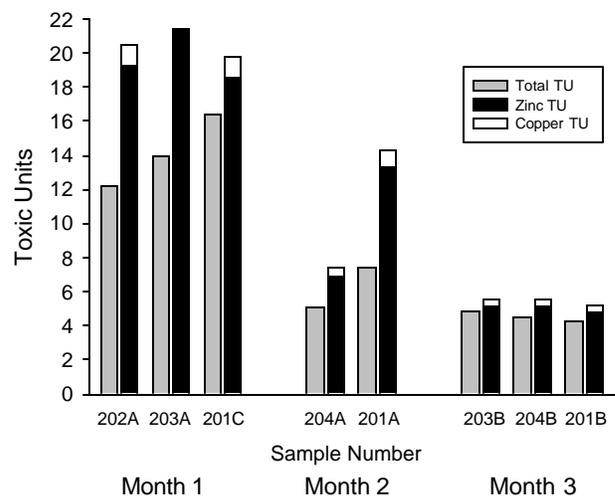
**Table 3. Spearman correlation coefficients between sea urchin fertilization toxic units and chemical concentrations for all samples analyzed. N = 42 for all analyses. Mercury and silver concentrations were nondetectable for all samples, so are not included in correlation analyses.**

Constituent	Correlation Coefficient	P value
TSS	0.418	0.006
PAH (Total)	-0.001	0.997
Al (Dissolved)	0.471	0.002
Al (Total)	0.669	<0.001
Cd (Dissolved)	0.433	0.004
Cd (Total)	0.400	0.009
Cr (Dissolved)	0.693	<0.001
Cr (Total)	0.793	<0.001
Cu (Dissolved)	0.428	0.005
Cu (Total)	0.542	<0.001
Fe (Dissolved)	0.337	0.029
Fe (Total)	0.398	0.009
Pb (Dissolved)	0.028	0.860
Pb (Total)	0.271	0.082
Ni (Dissolved)	0.494	<0.001
Ni (Total)	0.638	<0.001
Zn (Dissolved)	0.629	<0.001
Zn (Total)	0.655	<0.001

(Figure 6). When the original samples were tested, less than 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% or greater (Figure 6). 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 6). Some toxicity was observed in the acid eluate blank sample, but the unusual dose-response pattern suggests that this was due to a procedural artifact.

## DISCUSSION

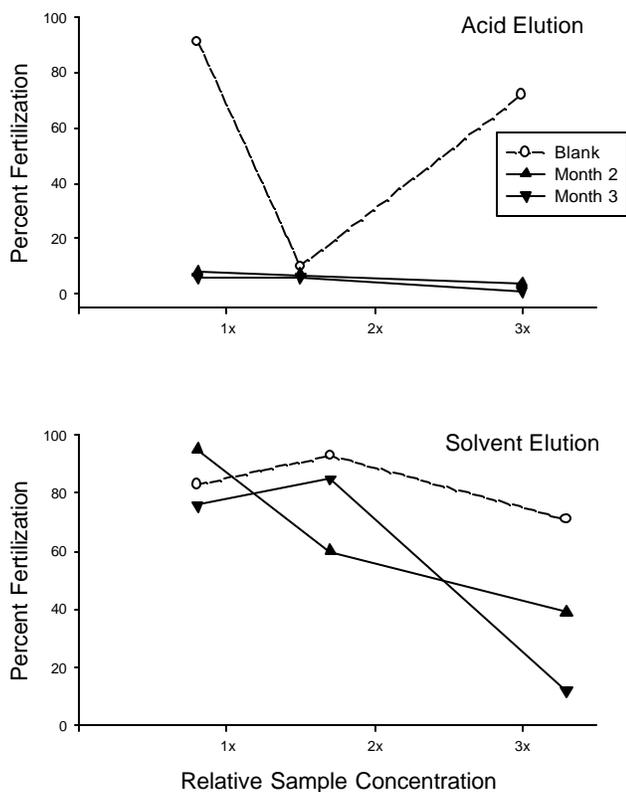
The results of this study demonstrate that runoff from parking lots is an important source of toxicity in



**Figure 5. Comparison of measured and calculated acute toxic units (TUa) for runoff samples analyzed during the 3 months of accumulation. Calculated toxic units are based on the concentration of dissolved zinc and copper in each sample. For one of the Month 2 samples, the toxic units could only be expressed as < 4 and are therefore not included on the plot.**

urban stormwater. 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 stormwater samples. Stormwater samples collected from various channels in southern California usually had less than 4 TUa (KLI and SCCWRP 2001, Schiff *et al.* 2002), while nearly all of the parking lot runoff samples had greater than 4 TUa. A similar result was observed for dissolved metals; the concentrations in the parking lot runoff were always higher than in the storm channel samples (Tiefenthaler *et al.* 2003), indicating that toxic constituents are more concentrated in small watersheds dominated by a specific land use, such as parking lots, than in storm channels draining 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, KLI and SCCWRP 2001). However, other researchers have found that antecedent period is a poor predictor of stormwater quality, with a positive association found in some



**Figure 6. Toxicity of acid or solvent eluates of C-18 columns used for the TIE. Concentration is expressed relative to the highest concentration tested in the Phase I TIE.**

studies and no relationship found in others (Barrett *et al.* 1995). In studies of accumulation of street dirt, it was found that maximum observed loadings were often reached in 30 d or less (Heaney *et al.* 1999a). A study conducted on particulate loading to streets found that accumulation decreases with time, as losses from wind-carried fugitive dust increase with higher loadings (Pitt and Sutherland 1982). The findings for streets are similar to 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 reduce 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 reducing the toxicity of parking lot runoff. These methods would mostly be effective at removing particulates. 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 reducing toxicity. The more rigorous pressure washing that was done at the beginning of the study reduced 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 vehicle 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. While the number of cars and duration of use varied, all of the parking stalls were in use 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).

Measurements from the rainfall intensity and duration component indicated the presence of a first-flush effect for toxicity. Runoff samples collected during the first 10 min 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 after 10 minutes. This was likely an 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, diluting out the first-flush effect at the higher intensity. These results indicate that stormwater treatment systems that capture or treat the initial portion of stormwater discharge are likely to provide the greatest reduction in toxic constituents.

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 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 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. Further, the fact that elution of the C-18 columns with organic solvents only recovered a small portion of the toxicity indicates that nonpolar organics were not a source of toxicity. The recovery of toxicity by elution with acid 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 acid phase. We have 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 toxicant characterization and identification component suggested that the toxicity of the parking lot runoff to the sea urchin fertilization test was primarily due to 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 stormwater runoff, which have identified zinc as a primary toxicant of concern in Ballona Creek in Los Angeles and Chollas Creek in San Diego (Schiff *et al.* 2002, Bay *et al.* 2003). Automobiles are a prime source of zinc with high levels found in brakes, motor oil, and especially tires (Davis *et al.* 2001).

The TIE treatments also determined that the toxic constituents in the parking lot runoff were associated with the dissolved fraction, as opposed to particulates. Similarly, the chemistry data indicated that most of the metals were associated with the dissolved phase (Tiefenthaler *et al.* in press). These findings have implications for the design of best management practices (BMPs) to reduce stormwater toxicity. The BMPs that are based primarily on particulate removal are unlikely to be effective in reducing the toxicity of stormwater runoff from parking lots.

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