Evaluation of urban non-point source runoff of hazardous metals entering Santa Monica Bay, California

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Abstract Significant amounts of non-point source runoff enter the Santa Monica Bay from the Ballona Creek Watershed during wet weather flow. The primary objective of this study was to determine the concentrations of hazardous metal pollutants associated with the aqueous and suspended solid phases during wet weather flow. A calculation of the mass of the pollutants for each storm was conducted. Other objectives of this study were to evaluate during a storm event the relationships between (1) soluble and sorbed metals, (2) storm flow and pollutant loading, including a determination if a first flush was present, and (3) total mass loading of pollutants and relative pollution loading from three watershed sub-basins. This study focused on the urbanized watershed of Ballona Creek, which is approximately 330 km^2 (127 miles^2) in size and developed primarily with residential and light commercial industries. In the 1997–98 rain season, an El Niño year, two storm events were monitored by the collection of hourly grab samples. An initial storm monitored Ballona creek, while a second storm also monitored Ballona Creek along with two smaller sub-watersheds, Centinela Channel and Sepulveda Channel. The results indicated the suspended solids phase primarily transported the mass for five of the six hazardous metals studied: cadmium, chromium, copper, lead, and nickel. Arsenic was found primarily in the aqueous phase.

Keywords Heavy metals; non-point sources; urban runoff; wet weather flow

Introduction

The Ballona Creek watershed is the most significant non-point source of pollution to the Santa Monica Bay during wet weather flow. At approximately 330 km^2 (127 miles^2), this watershed is the largest in the region and is extensively developed. The land use is 61% residential, 17% commercial, 15% parks or open space, and 7% industrial. Ballona Creek is primarily lined with concrete, and all of its tributaries are either concrete channels or covered culverts. Thus, the vast majority of the precipitation within the watershed is conveyed to the ocean along with its entrained load of trash and pollutants. From past studies it has been determined that significant amounts of metals and organic pollutants come from the Ballona Creek watershed (Suffet *et al.*, 1997).

The primary objective of this study was to determine the types and concentrations of pollutants associated with aqueous and suspended solids emanating from the Ballona Creek watershed during the course of storm events. Secondary objectives of this study were to evaluate during a storm event the relationships between (1) soluble and sorbed metals, (2) storm flow and pollutant loading, including a determination if a first flush was present, and (3) total mass loading of pollutants and relative pollution loading from three watershed sub-basins.

To achieve the objectives, several rainfall events were sampled from November 1997 through March 1998. This paper focuses in on two large storms: December 5–6, 1997 and March 25, 1998. Both storms were sampled hourly with the December storm sampling lasting 31 hours and the March storm sampled for 17 hours.

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Methods

Three sampling locations were used for this study to gather information on each of the three sub-watersheds: Ballona Creek, Sepulveda Channel and Centinela Channel. Sampling for Ballona Creek was located at the Sawtelle Boulevard Bridge; a location upstream of the intersection of the two large tributaries, Sepulveda and Centinela Channels. Sepulveda Channel was sampled approximately one quarter mile upstream of its confluence with Ballona Creek. Centinela Channel was sampled approximately one half mile upstream of its confluence with Ballona Creek.

Storm samples were collected by taking 5–10 L grab samples, once per hour, for the two storms. The grab samples were taken by lowering a large polypropylene bucket into the storm drain by rope and samples were scooped from the storm drain. The samples were then poured into 4 L amber glass bottles and sealed with Teflon-lined caps. After collection, all samples were transported back to UCLA for filtration. Samples were stored at 4°C and filtered as soon as possible. Samples were filtered using a stainless steel, Teflon-lined Millipore 142 mm Hazardous Waste Filtration System with an integral 1.5 L reservoir. Samples were filtered in 1 litre increments using pressure filtration (40 psi of Nitrogen gas) through 142 mm, 0.7 m pure glass (no binder) TCLP filters (Whatman, Inc., Cat # 1825142). The filters were previously acid washed with 50% HNO_3, rinsed with Milli-Q water and oven dried at 100°C. For each sample, the filtrate was collected and stored at 4°C for water quality analysis. Drying of the filter paper was done by placing anhydrous calcium chloride desiccant (8 mesh) at the bottom of a pre-cleaned glass jar. The filter paper was placed on top of the desiccant, separated from the desiccant by using folded weighing paper and then resting the filter paper with the suspended solids on the weighing paper. Samples were dried in the absence of light for at least 48 hours before digestion.

The filters containing the suspended solids were digested by a modified version of EPA Method 3050B. The particular digestion procedure used was the one specified for subsequent analysis ICP/AE. The only modification was a doubling of the acid volumes to account for the presence of the filter. For the filtrate samples that were collected in glass bottles and stored at 4°C, 3 drops of concentrated HNO_3 (trace metal grade) was placed in a 30 mL Nalgene LDPE bottle for trace metal analysis. To the bottle, 30 mL of the filtrate was added.

Since the samples were collected and filtered from 2 hours to 48 hours after the storm, the concentrations represent the soluble fraction of the total sample that is in equilibrium with the solid phase and dissolved phase present in the sample bottle at the time of filtering. It should be pointed out that the data do not necessarily represent the percent soluble phase at the pH of the storm water or at the time of sampling.

To evaluate the toxicity of storm water, this research takes a unique approach in evaluating the suspended sediments. Long *et al.* (1995) developed the ERLs, Effects Range-Low, and the ERMs, Effects Range-Median, as guidelines to evaluate bottom sediments. Concentrations below the ERL represent a minimum effects range where ecologic effects would rarely be observed. Concentrations equal to and above the ERL and below the ERM represent a range in which effects would occasionally occur. Concentrations equal to or higher than the ERM represent a range in which effects would frequently occur. Since it is likely that the suspended sediments will be deposited in Santa Monica Bay, this research compares the ERLs and ERMs with the suspended sediment concentration as a tool to indicate the potential hazard to the environment.

To evaluate the toxicity of total metal concentrations, the Event Mean Concentrations (EMC) were calculated (Sansalone and Buchberger, 1997) and compared to the Chronic Toxicity to Aquatic Life (CTAL) from California's Ocean Plan (SWRCB, 1997).

To determine if there was a first flush, the percent of the total pollutant load was compared with the percent of the runoff load (Sansalone and Buchberger, 1997 and Deletic, 1998). For this study, all first flush calculations were conducted at 25% of the runoff load. For example, for the December storm, 25% of the runoff load occurred at 10:21 PM. The percent mass load for each compound was calculated by integrating the mass of the compound to the time when 25% runoff load occurred (10:21 PM) and then dividing by the total mass load to obtain the percentage. For this paper, a first flush effect is defined if the mass of compound is greater than 25%.

Results and discussion

A series of storms were sampled from November 1997 through March 1998 when over 94 cm (37 in.) of rain fell on Los Angeles during this El Niño year as compared to the long term average of 38 cm (15 in.) of rain. The December 5–6, 1997 storm yielded 6.0 cm (2.36 in.) of rain. It had not rained for the previous 6 days. Sampling began at 11:30 am on December 5, 1997 and ended at 5:30 pm on December 6. An estimated 5.7×10^9 L of water during this storm was transported by the Ballona Creek sampling station.

For the March 25, 1998, sampling began at 2:45 am and ended at 6 pm. The March storm yielded almost 10.1 cm (4 in.) of rain and was the largest storm of the season. This storm occurred after over 76 cm (30 in.) of rain fell during this El Niño season. An estimated 6.1×10^9 L of water was transported by Ballona Creek at the sample station location, which was 4.2 times the amount of runoff for the Sepulveda watershed (1.5×10^9 L) and 16 times the amount for the Centinela watershed (0.39×10^9 L).

Table 1 shows the percentages of the total mass on the suspended solids. As shown by the table, only arsenic was found primarily in the aqueous phase, while the other metals were primarily found in the suspended solid phase. The variability in the percentage for arsenic was largely due to the limited number of detections of arsenic in the suspended solid phase (8 detections in 28 samples for December, 9 detections in 45 samples for March).

For the other five metals, the December storm had less of a percentage of particulate-bound metals than the March storm. Although it is not precisely known why more of the metals were found in the dissolved phase for the December storm, this may be part of a seasonal first flush where metals that have been deposited over the dry season are mobilized in the dissolved phase during the first storms of the wet season and are either discharged to the receiving waters or are bound to the particulate phase for future transport.

In Table 2, the total metal EMCs are shown with the discharge standards for California. The majority of the pollutants, arsenic, cadmium, chromium, and nickel, had concentrations that are below the discharge standards. However, lead and copper concentrations violated the discharge standards. During the March storm, lead violated the discharge standard at two locations, Ballona and Sepulveda. Total copper concentrations, which averaged 20 μg/L for the EMCs greatly exceeded the CTAL limit of 5 μg/L for both storms and all sampling locations.

With the exception of copper, data from the Ballona sampling station showed that the December storm had lower total concentrations than the March storm. Although this would seem to contradict a seasonal first flush, the longer antecedent dry period before the March

Table 1 Percent of the total metal on the suspended solids (particulate-bound phase)

Location	Date	As	Cd	Cr	Cu	Pb	Ni
Ballona	12/5–6/97	30%	61%	51%	40%	77%	61%
Ballona	3/25/98	23%	72%	84%	87%	98%	100%
Sepulveda	3/25/98	2%	77%	71%	70%	97%	72%
Centinela	3/25/98	40%	89%	93%	89%	99%	98%

Table 2 Event Mean Concentrations (EMCs) for total metal concentration with the CTALs

		As (µg/L)	Cd (µg/L)	Cr (µg/L)	Cu (µg/L)	Pb (µg/L)	Ni (µg/L)	TSS (g/L)
CTALs		19	8	18	5	22	48	
Ballona	12/5–6/97	0.9	0.5	2.2	24	19	6.5	0.07
Ballona	3/25/1998	3.4	1.2	6.7	19	41	7.8	0.25
Sepulveda	3/25/1998	4.2	1.1	12	23	21	13	0.38
Centinela	3/25/1998	2.1	0.4	3.3	13	11	4.2	0.22

storm may explain part of this result. Furthermore, the March storm mobilized a much higher concentration of Total Suspended Sediments (TSS) than the December storm. Since Table 1 showed that much of the pollutants were carried in the suspended solid phase, it is reasonable that a larger load of suspended sediments would lead to a higher total metal concentration.

Comparison of the total concentration of metals for the three watersheds for the March storm generally showed that the smallest watershed, Centinela, had the lowest total concentration of metals. Further efforts should investigate which watershed attributes contributed to the lower total metal concentrations in the Centinela watershed.

The December storm hydrograph, with the concentration of lead in the suspended solid phase is shown in Figure 1. Table 3 shows the EMC for suspended sediments and compares the EMC with the ERLs and ERMs. Figure 1 shows a large variation in the lead concentration throughout the hydrograph. Although the data is not shown, the other metals also showed a large amount of variability in the particulate-bound concentrations and had no discernable trend.

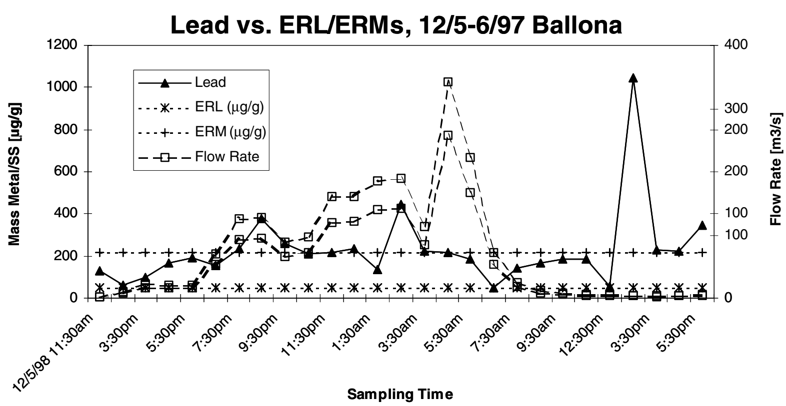

Figure 1 Lead concentration (suspended sediments) plotted with the ERL, and ERM and the storm hydrograph for the Ballona Creek sampling station

Table 3 ERLs and ERMs shown with the suspended sediment EMC

		As (µg/g)	Cd (µg/g)	Cr (µg/g)	Cu (µg/g)	Pb (µg/g)	Ni (µg/g)
ERL		8.2	1.2	81	34	46.7	20.9
ERM		70	9.6	370	270	218	51.6
Ballona	12/5–6/97	3.8	3.9	15	130	199	53
Ballona	3/25/1998	3.2	3.4	22	67	162	31
Sepulveda	3/25/1998	4.4	2.6	30	53	55	33
Centinela	3/25/1998	0.2	1.5	11	43	49	13

Arsenic and chromium had concentrations below their ERLs. This indicates that if the suspended sediments are deposited in the estuary, there would be a low likelihood of ecological effects. Nickel concentrations were unique in that one station for the March storm had an EMC that was below the ERL, while the EMC from the December storm was greater than the ERM. All the other metals had EMCs in-between the ERLs and the ERMs. Ecological effects occasionally occur in this range. This shows that the concentration of metals on the suspended sediments may be causing ecological damage to Santa Monica Bay.

Generally, the metal concentrations on the suspended solids for the Ballona watershed showed some variation between the March and December storms. However, there was no consistent trend between the sampling dates. Centinela had lower concentrations of metals in the suspended sediment phase than the Ballona and Sepulveda sampling stations, which is consistent with earlier observations made for the total concentrations.

Figure 2 shows the cumulative runoff and load for Ballona Creek for the December storm. Table 4 shows the cumulative mass at 25% of the runoff volume. The table and the figure indicate that a first flush was present for arsenic and copper for the December storm. This may be attributed to these metals being present primarily in the dissolved phase for that storm, and therefore easily mobilized during the storm. Other metals generally did not show the presence of a first flush during the December storm and were similar to the TSS level. Data for the three sample locations for the March storm did not indicate the presence of a first flush. As shown in Table 2, the March storm had a higher concentration of suspended solids. However, since the suspended solids had only 10% of the cumulative load at 25% of the cumulative runoff, it is not surprising that the metals, which were primarily in the suspended solid phase, did not indicate the presence of a first flush.

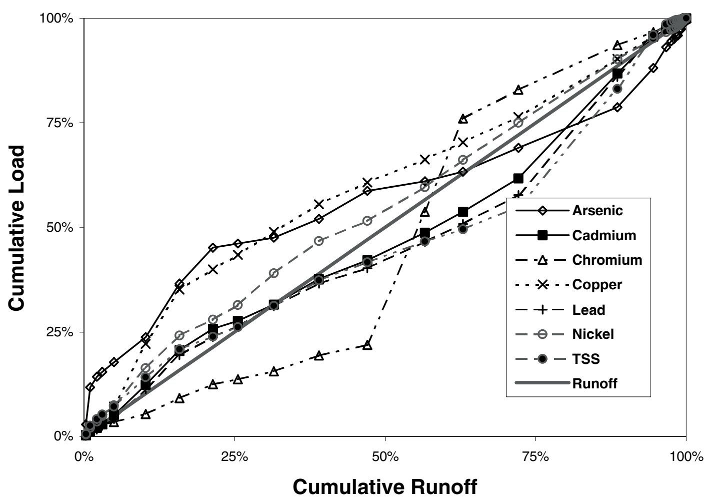

Figure 2 Cumulative runoff and load for Ballona Creek 12/5–6/1997. A first flush determination is made at 25% of the cumulative runoff

Table 4 Cumulative load (mass) of the metals at 25% of the runoff volume. This point of runoff is used for the determination of the presence of a first flush for the storm

Location	Date	As	Cd	Cr	Cu	Pb	Ni	TSS
Ballona	12/5–6/97	45%	27%	14%	43%	26%	31%	21%
Ballona	3/25/1998	23%	16%	7%	18%	11%	11%	10%
Sepulveda	3/25/1998	14%	17%	11%	15%	20%	15%	10%
Centinela	3/25/1998	17%	24%	20%	9%	20%	26%	9%

This research has shown that the wet weather storm flow contains large amounts of heavy metals at concentrations that are potentially hazardous to the environment. Cadmium, chromium, copper, lead and nickel were transported primarily in the suspended solid phase, while arsenic was transported primarily in the dissolved phase. The pollutants discharged during storm events, which have high flows due to the urbanization of this watershed, have little opportunity to be removed prior to being discharged into Santa Monica Bay. Therefore, future efforts to lower the wet weather pollutant loads should focus on management practices that limit the amount of pollutants that are being generated.

Conclusions

Wet weather flow for this urban watershed carries a significant amount of hazardous metals into the receiving water. By determining the types and amount of metals transported in the storm flow, ways to lessen the impacts to the ecosystem can be identified. By using the types of analysis presented in this paper, the nature and magnitude of pollutants and their potential impact to the receiving watershed have been identified.

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