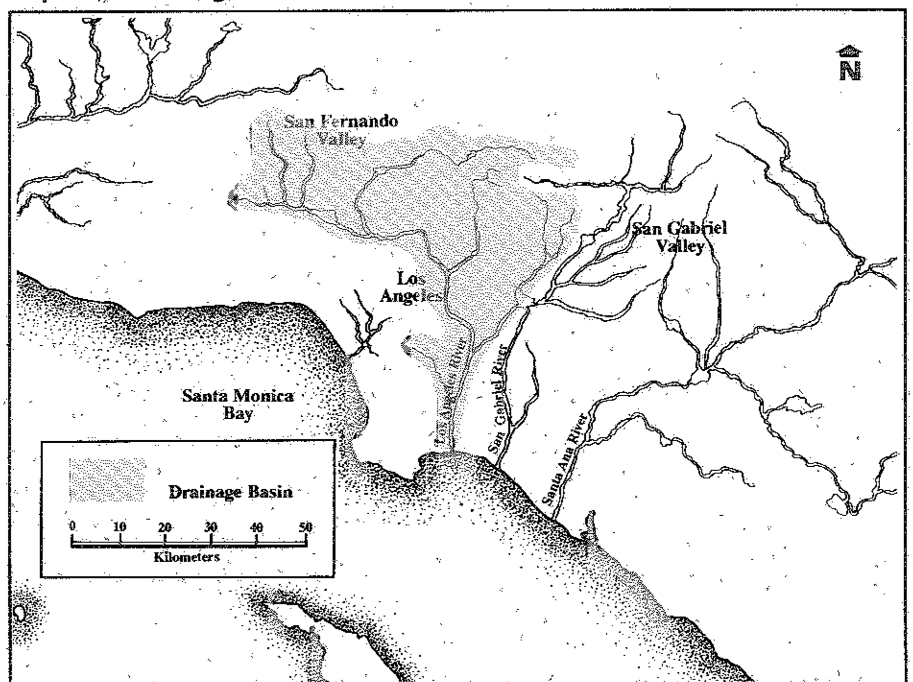
# Mass Emission Estimates for Selected Constituents from the Los Angeles River

The Los Angeles River is the largest single source of gauged runoff to the Southern California Bight (SCB). It originates in the Santa Susana and Santa Monica mountains in the western part of the San Fernando Valley (Figure 1). It also receives runoff from the San Gabriel and Santa Monica mountains. The Los Angeles River enters the ocean in San Pedro Bay, but historically it has changed course several times and entered the ocean as far north as Ballona Creek and as far south as the San Gabriel River. About 40% of the Los Angeles River basin (2,155 km$^2$) is upland catchments with elevations up to 2100 m and 60% is low foothills, valley floor, and coastal plain (Brownlie and Taylor 1981). Slightly less than 60% of the river basin was classified in 1982 as urban and suburban, 40% as native vegetation, and 1% as agriculture (Department of Water Resources 1984).

For its size, the Los Angeles River has the most extensive system of controls of any river in the world including check dams, debris basins, flood control and storage reservoirs, flood control basins, and percolation basins. All of the river is channelized below the upland catchments. The Rio Hondo, which joins the river 15 km above the tidal prism, can be manipulated to transfer water from the upper San Gabriel River watershed to the Los Angeles River (Brownlie and Taylor 1981).

There are few published estimates of the mass of contaminants delivered to the ocean by the Los Angeles River. The contaminants come from a combination of upstream activities, industrial and municipal discharges, and surface runoff. The objectives of this study were to measure the concentration of selected constituents in samples collected from the Los Angeles River during storms and low flows, and to estimate the annual loads delivered to the ocean.

**Figure 1.**
Map of the Los Angeles River basin.




## Materials and Methods

Water samples were collected from the Willow Street bridge near the mouth of the Los Angeles River in Long Beach between September 1986 and April 1988. The concrete-lined channel is 120 m wide at the top, 90 m wide at the bottom, and about 7 m deep. At low flow, the river occupies a channel 8.5 m wide and 0.3 m deep in the center of the main channel. Flow measurements were obtained from the Los

**Figure 2.**
Flow duration curve for the Los Angeles River for modified water years (September to August) 1971-72, 1986-87, and 1987-88. Data are mean daily volume and flow rate. (Note 5m³/s is approximately 114 mgd).

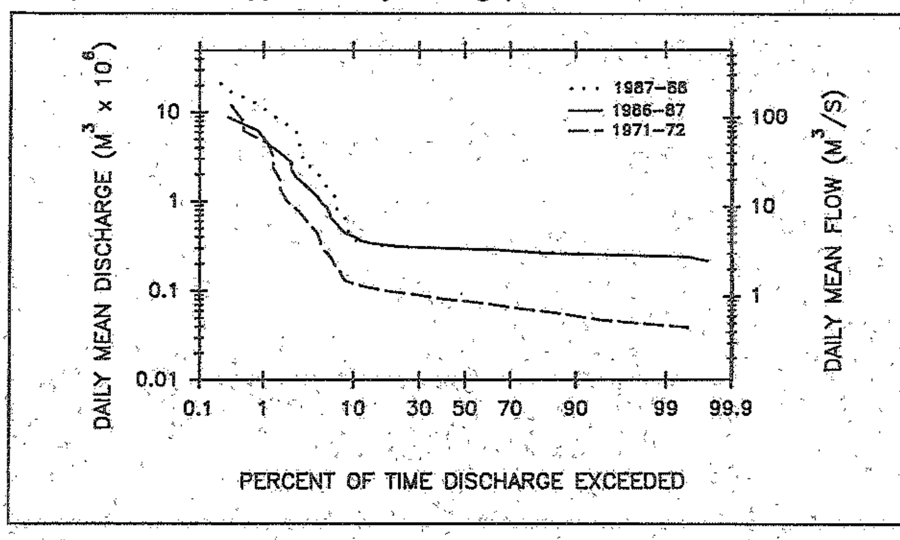
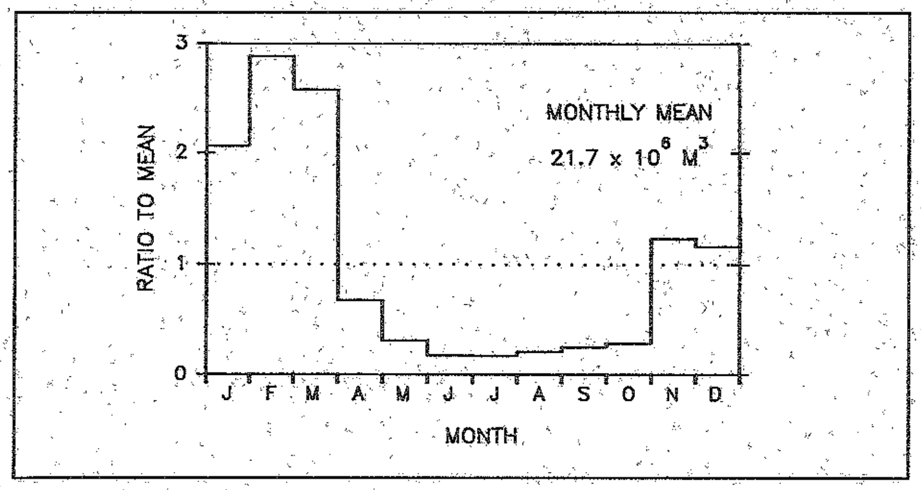



**Figure 3.**
Los Angeles River flow regime. Data are the ratio of mean monthly flow to mean annual flow for the study years (September 1986 to August 1988).



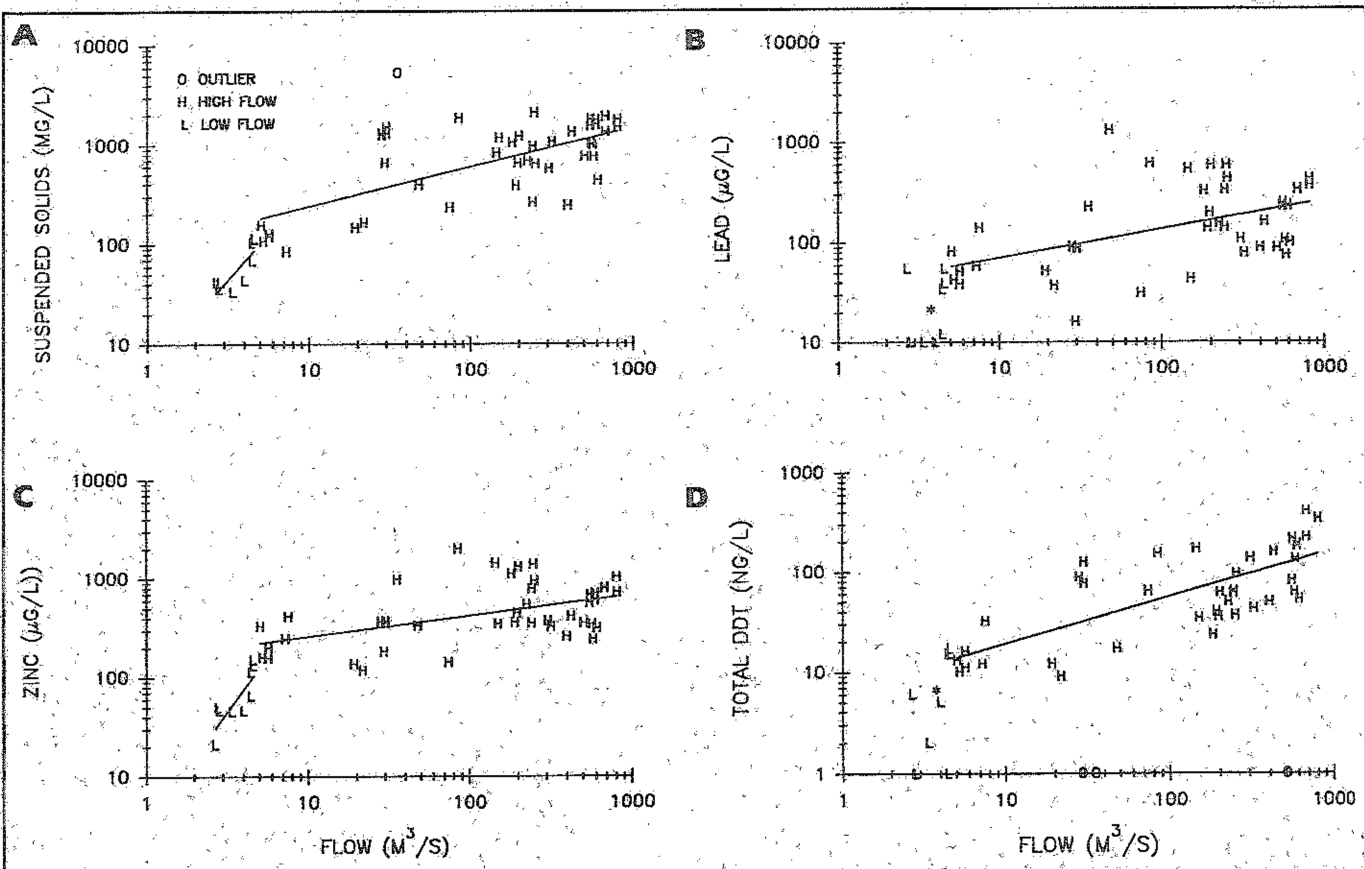

Angeles Department of Public Works which maintains an automatic flow gauging station 1500 m upstream from the bridge. The gauge measures flow from 2,110 km² of urban and rural landscape. Annual rainfall data for Los Angeles were obtained from the National Weather Service data base.

The sampler consisted of a short piece of weighted pipe containing an acid-washed 4-l sampling bottle. Stabilizing fins attached to the pipe kept the bottle oriented into the flow when submerged, but caused the bottle to rotate upright when the sampler was removed from the river. The sampler was lowered to the river by hand from a small davit attached to the bridge.

About 10 samples were collected per storm on rising and declining flows. During low to moderate flows, the sampler was lowered and raised through the water column. During high flows, the velocity of the river required us to slack the lowering line to keep the sampler submerged. We had less control over the sampler and probably did not sample throughout the water column. It took about one minute to collect a sample. Two samples were collected at each sampling time. The samples were analyzed for suspended solids, cadmium, chromium, copper, nickel, lead, zinc, total DDT, and total PCB. The analytical methods are presented in Appendix 1.

The load of a particular constituent in a river is the total mass of the constituent passing the point of measurement over some period of time. The loads of selected constituents transported by the Los Angeles River were estimated by two methods: a ratio estimator and a rating curve. Both methods are based on the relation between river flow and constituent concentrations. The ratio estimator is a flow-weighted mean constituent concentration that is multiplied by the average daily flow to estimate the daily load. The rating curve is an empirical regression of constituent concentration versus river discharge. The rating curve predicts concentrations from average daily flows; the two numbers are multiplied to obtain the daily load. In both methods, daily loads are summed to estimate the annual load. Concentration data were stratified by flow to reduce skewness and variability. The inflexion point on the flow duration curve was selected as the cutoff between low and high flow days (Figure 2). This corresponded to an average daily discharge of 5 m³/s for the recent

**Figure 4.**
Log-log plot of the concentration of suspended solids, lead, zinc, and total DDT versus instantaneous flow for Los Angeles River samples collected from September 1986 to April 1988. Data are stratified into high (H) and low (L) flows; regressions used for the rating curve estimates are shown for each stratum. In strata where regressions were not significant, means (*) were substituted. Outliers (O) were deleted from the final regression.



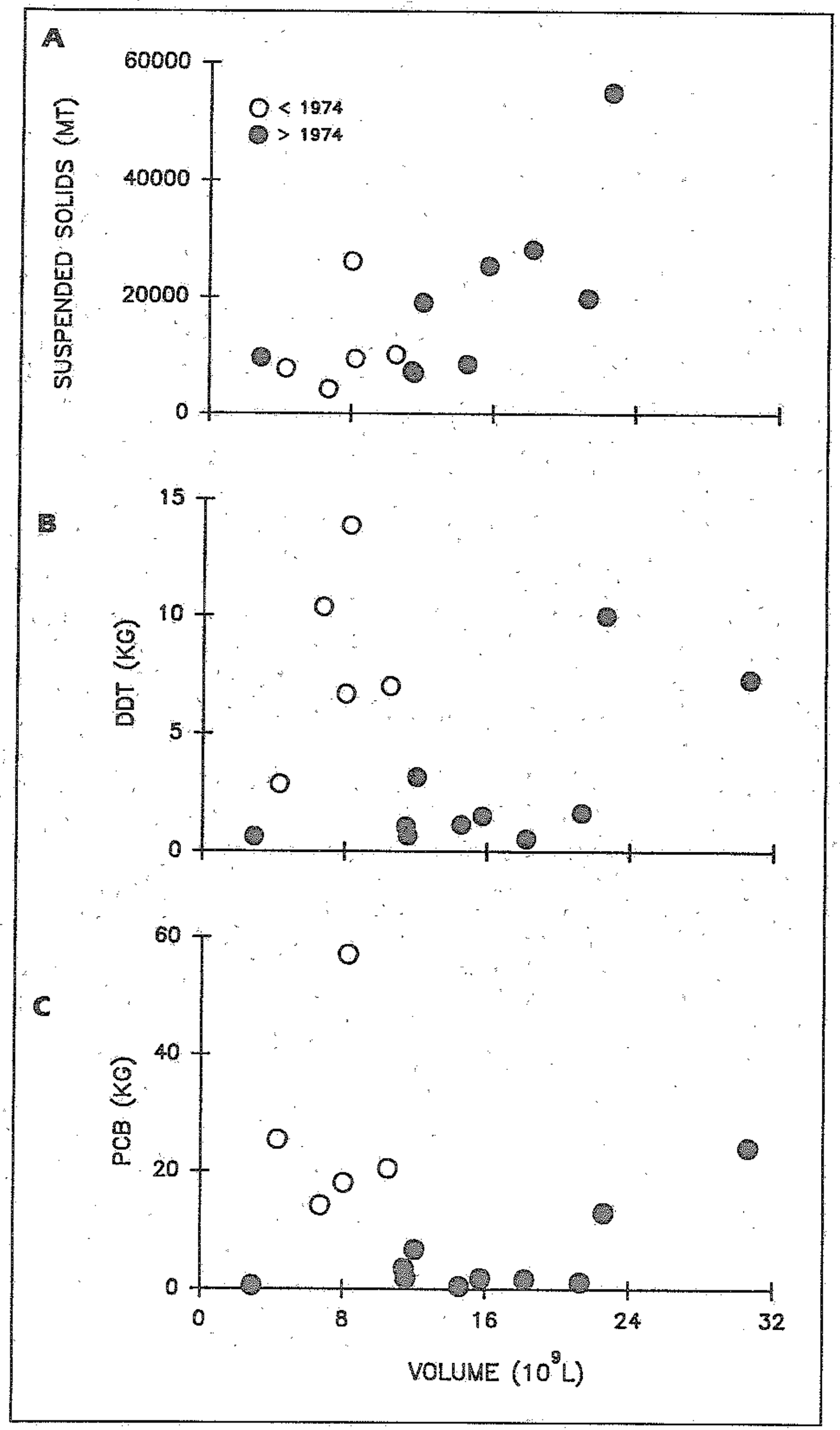

data and 2 m³/s for the historical data. Load estimation techniques are presented in Appendix 2.

At various times from 1971 through 1985, SCCWRP collected runoff samples from the Los Angeles River. We compiled constituent concentration data, instantaneous flow at the time of sampling, and daily mean flow. The original concentration data were obtained from laboratory notebooks archived at SCCWRP. Annual mass emissions were estimated for water year 1971-72 from data for 1971 through 1973 (SCCWRP 1973). The historical and recent data were used to estimate mass emissions for individual storms from 1971 through 1988 (SCCWRP 1973, Young *et al.* 1980). Annual and storm loads were estimated by the same methods that were applied to the recent data. The reader should bear in mind that analytical methods have changed over the past two decades.

## Results

During the first study year (September 1986 through August 1987), rainfall in Los Angeles was 19.5 cm and discharge from the Los Angeles River was $156 \times 10^6$ m³. During the second study year (September 1987 through August 1988), rainfall was 31.7 cm and discharge from the river was $217 \times 10^6$ m³. Most of the discharge from the river occurred between January and March (Figure 3). High flow days (mean daily flow >5 m³/s) occurred 8% of the time during 1986-87 and accounted for 39% of the annual discharge (Figure 2). High flow days occurred 9% of the time during 1987-88 and accounted for 57% of the annual discharge. Peak river discharge during the study (687 m³/s) was about 20% of the all-time peak discharge

**Figure 5.**
Estimated mass emissions of suspended solids, total DDT, and total PCB from the Los Angeles River during 15 storms from December 1971 to January 1988. Estimates for individual storms were calculated from flow-weighted mean concentrations of each constituent for each storm.




(>3,650 $m^3/s$, February 1980).

Fifty-four samples were collected during storms and low flows. Discharge from the Los Angeles River during the six sampled storms ranged from 2.9 x $10^6$ $m^3$ to 21.3 x $10^6$ $m^3$ (mean = 12.9 x $10^6$ $m^3$). Except for cadmium, the concentrations of all constituents measured in the Los Angeles River were positively correlated with river flow and suspended solids (Table 1).

The empirical relationship between flow rate and concentration changed from low to high flow regimes for most constituents (Figure 4). Regressions of log concentration on log flow were not significant for nickel, lead, total DDT, and total PCB at low flow, and for cadmium at high flow. Except for cadmium, 70-95% of the estimated annual constituent loads were discharged during high flow days (Table 2). One-third to one-half of the estimated annual load of cadmium went out during high flow days.

Total high flow volume increased 104% from 1986-87 to 1987-88. Consequently, the mass of solids and contaminants discharged during high flow days more than doubled and the proportion discharged during high flow days increased in 1987-88 (Table 2). Total low flow volume and the mass loading of solids and contaminants during low flow days were similar in both years.

Annual mass loading estimates of most constituents were higher for the ratio method than for the rating curve (Table 2). Estimates for suspended solids were 65-105% greater; estimates for copper, lead, and zinc were 30-70% greater; estimates of total DDT and total PCB were 70-185% greater. Annual mass loading estimates of cadmium, chromium, and nickel were similar between the two methods.

## Discussion

### River Discharge and Load Estimates

Discharge from the Los Angeles River comprises surface runoff, groundwater runoff, storage releases, and point source discharges. During the first study year, rainfall in Los Angeles was 48% below its long-term average (37.5 cm for the past 112 yr) and river discharge was 18% below its long-term average (189 x $10^6$ $m^3$ for the past 60 yr). During the second year, rainfall was 15% below average and discharge was 15% above average. In both years, the Los Angeles River contributed 33% of the total gauged discharge to the SCB.

From the first year to the second, rainfall in Los Angeles increased 63% and discharge from the Los Angeles River increased 39%. Low flow volume was similar in both years, but high flow volume and the estimated constituent loads doubled. This is not surprising because the concentration of all constituents except cadmium were positively correlated with flow and suspended solids.

Effluents from water reclamation plants compose a significant portion of the discharge from the Los Angeles River. On average, the Los Angeles-Glendale, Tillman, and Burbank water reclamation plants discharged 196,200 $m^3$/d (52 mgd) in 1986-87 and 239,900 $m^3$/d (63 mgd) in 1987-88 of sand-filtered, secondary effluent into the river. These effluents constituted 69% of low flow, 9% of high flow, and 45% of total river discharge in the first study year; and 85% of low flow, 6% of high flow, and 39% of total river discharge in the second study year. Except for cadmium and nickel, the combined mass emissions from the plants accounted for less than 30% of the estimated loads delivered to the ocean by the Los Angeles River (Table 3).

There are few published estimates of mass inputs to the SCB from the Los Angeles River. Brownlie and Taylor (1981) calculated that the Los Angeles and San Gabriel rivers delivered 315,000 mt of sand to the SCB each year after urbanization and 950,000 mt/year before urbanization. The Los Angeles River is 56.4% of the combined area; assuming equal sand delivery per unit area, the river would deliver 178,000 mt/yr on average to the SCB. Eganhouse and Kaplan (1982) calculated that the Los Angeles River delivered 150,000 mt of suspended solids to the SCB annually from 1960 to 1975 when mean annual river discharge was 198 x $10^6$ $m^3$ and mean rainfall was 36 cm. These estimates are similar to the ratio method estimate for suspended solids in 1987-88 (155,000 mt), a year of below average rainfall (32 cm).

**Table 1.**
**Spearman rank correlation coefficients ($r_s$) among constituents measured in runoff samples collected from the Los Angeles River at Willow Street in Long Beach between September 1986 and April 1988. N=54 except for suspended solids where N=53; *=significant at p<0.05; **=significant at p<0.01.**

| | Discharge | Suspended solids |
|---|---|---|
| Suspended solids | .720** | — |
| Cadmium | -.154 | .061 |
| Chromium | .507** | .787** |
| Copper | .659** | .829** |
| Nickel | .481** | .813** |
| Lead | .691** | .736** |
| Zinc | .671** | .845** |
| Total DDT[a] | .764** | .697** |
| Total PCB[b] | .492** | .408** |

[a]Sum of *o-p'* and *p-p'* isomers of DDT, DDD, and DDE
[b]Sum of Aroclors 1242 and 1254

## Historical Comparisons

Flow-weighted mean constituent concentrations were compared between the present study and data collected in the early 1970s (Table 4). The concentrations of lead, DDT, and PCB have declined at high and low flows. The concentrations of suspended solids, chromium, and nickel have declined at low flow. Interpretation of the changes is confounded by the fact that the effluents of three water reclamation plants that now constitute 70-80% of river discharge at low flow, did not exist in the early 1970s. Their impact on river discharge is evident in the upward shift of the flow duration curve and its inflexion point from 1971-72 to 1986-88 (Figure 2).

The declines in flow-weighted concentrations at low flow could be due to dilution by treatment plant effluents. After subtracting out the mass contributed by the three reclamation plants, the estimated concentration of suspended solids in the river was 216 mg/l in 1986-87 and 424 mg/l in 1987-88. Both estimates are within the confidence limits of the concentration of suspended solids in 1971-72. Comparisons of flow weighted mean concentrations are more appropriate at high flow when treatment plant effluents made up less than 10% of river volume.

The estimated mass loads of suspended solids and chlorinated hydrocarbons discharged during storms during the past two decades is further evidence for the declines (Figure 5). Suspended solids emissions are positively correlated with storm discharge volume for the entire period (Spearman rank $r_s$=0.560, $p<0.05$). Emissions of DDT ($r_s$= -0.018, $p>0.50$) and PCB ($r_s$= -0.218, $p>0.20$) are not; however, DDT and PCB emissions are correlated ($r_s$=0.767, $p<0.001$).

| | Ratio Estimator | | | |
|---|---|---|---|---|
| | 1986-87 | | 1987-88 | |
| Flow | High | Low | High | Low |
| Number of days | 28 | 337 | 32 | 334 |
| Volume (x $10^6$ $m^3$) | 60.7 | 95.8 | 124.0 | 93.3 |
| Suspended solids (mt[a]) | 72,437 | 6,799 | 148,011 | 6,627 |
| Cadmium (mt) | 0.20 | 0.40 | 0.41 | 0.39 |
| Chromium (mt) | 2.6 | 1.1 | 5.3 | 1.0 |
| Copper (mt) | 8.4 | 1.6 | 17.1 | 1.6 |
| Nickel (mt) | 3.0 | 1.2 | 6.1 | 1.2 |
| Lead (mt) | 14.7 | 2.2 | 30.0 | 2.1 |
| Zinc (mt) | 37.5 | 7.8 | 76.6 | 7.6 |
| DDT (kg[b]) | 9.6 | 1.0 | 19.8 | 1.0 |
| PCB (kg[c]) | 18.8 | 1.9 | 38.4 | 1.9 |

[a] mt=metric tons
[b] Sum of *o-p'* and *p-p'* isomers of DDT, DDD, and DDE
[c] Sum of Aroclors 1242 and 1254

**Table 3.**

**Estimated combined inputs to the Los Angeles River from the Los Angeles-Glendale, Tillman, and Burbank water reclamation plants in 1986-87 and 1987-88 (September to August). Concentrations of DDT and PCB were below detection limits.**

| | 1986-87 | 1987-88 |
|---|---|---|
| Volume (x $10^9$ l) | 70.7 | 85.7 |
| Suspended solids (mt[a]) | 188 | 247 |
| Cadmium (mt) | 1.1 | 0.72 |
| Chromium (mt) | 1.1 | 0.45 |
| Copper (mt) | 2.2 | 2.3 |
| Nickel (mt) | 6.7 | 3.1 |
| Lead (mt) | 2.3 | 2.3 |
| Zinc (mt) | 4.5 | 5.4 |

[a] mt=metric tons

| Rating Curve | | | |
|---|---|---|---|
| 1986-87 | | 1987-88 | |
| High | Low | High | Low |
| 28 | 337 | 32 | 334 |
| 60.7 | 95.8 | 124.0 | 93.3 |
| 33,807 | 4,907 | 89,409 | 4,560 |
| 0.22 | 0.87 | 0.45 | 0.85 |
| 2.1 | 0.9 | 4.9 | 0.8 |
| 5.1 | 1.9 | 12.2 | 1.8 |
| 2.3 | 1.3 | 5.3 | 1.2 |
| 9.1 | 2.1 | 22.5 | 2.0 |
| 25.4 | 5.2 | 59.5 | 4.8 |
| 3.1 | 0.6 | 8.5 | 0.6 |
| 7.6 | 1.9 | 21.8 | 1.9 |

**Table 2. (Left)**
Annual mass loading estimates for the Los Angeles River by the ratio estimator and rating curve techniques. Mean daily flows between September 1 and August 31 were stratified at 5 $m^3/s$. The number of days and volume are presented for each stratum. All estimates are wet weight except suspended solids, which is dry weight.

**Table 4. (Below)**
Flow-weighted mean concentrations and approximate 95% confidence intervals (in parentheses) of selected constituents in runoff samples collected from the Los Angeles River in 1971-72 (SCCWRP 1973) and 1986-88. Flows were stratified at 2 $m^3/s$ for 1971-72 and 5 $m^3/s$ for 1986-88 based on flow duration curves. Approximate confidence intervals were determined by bootstrap sampling original data 100 times (Efron 1982). In 1971-72, high flow discharge was 68.2 x $10^6$ $m^3$ in 27 days and low flow discharge was 27.4 x $10^6$ $m^3$ in 339 days.

| | High flow | | Low flow | |
|---|---|---|---|---|
| | 1971-72 | 1986-88 | 1971-72 | 1986-88 |
| Suspended solids (mg/l) | 1358 (1024-1764) | 1194 (942-1372) | 337 (139-586) | 71 (45-92) |
| Cadmium (µg/l) | 10.1 (3.8-16.5) | 3.3 (2.6-4.1) | 8.2 (2.3-15.2) | 4.2 (3.3-4.8) |
| Chromium (µg/l) | 78 (29-134) | 43 (37-51) | 119 (48-182) | 11 (3-17) |
| Copper (µg/l) | 130 (39-239) | 138 (115-161) | 74 (15-157) | 17 (13-21) |
| Nickel (µg/l) | 70 (31-112) | 49 (39-57) | 49 (19-91) | 13 (12-15) |
| Lead (µg/l) | 1076 (358-1805) | 242 (192-291) | 477 (80-992) | 23 (7-44) |
| Zinc (µg/l) | 1606 (482-2251) | 618 (530-721) | 597 (57-1354) | 81 (47-115) |
| Total DDT[a] (µg/l) | 1.13 (0.70-1.57) | 0.16 (0.10-0.21) | 0.25 (0.07-0.48) | 0.01 (<0.01-0.01) |
| Total PCB[b] (µg/l) | 3.93 (1.56-6.60) | 0.31 (0.16-0.45) | 1.85 (0.17-3.84) | 0.02 (<0.01-0.05) |

[a]Sum of *o-p'* and *p-p'* isomers of DDT, DDD, and DDE
[b]Sum of Aroclors 1242 and 1254

The declines in lead, DDT, and PCB are real. Increased regulation and source control have reduced the amount that reaches the ocean via runoff.

## River and Municipal Wastewater Mass Emissions

During the present study, annual mass loading estimates of cadmium, copper, lead, zinc, and total DDT were comparable between the Los Angeles River and Los Angeles County Joint Water Pollution Control Plant (JWPCP) (Table 5). Given the uncertainties in the load estimates for the Los Angeles River, mass emission estimates within a factor of two were considered similar. Annual mass emission estimates of chromium and nickel were greater for JWPCP. Annual mass emission estimates of suspended solids and PCBs were greater for the Los Angeles River.

These comparisons are not rigorous and over-interpretation should be avoided. For example, the composition of suspended solids differs between the two sources. Effluent particles collected from JWPCP in May 1990 averaged 41.3% total organic carbon (sd=1.5, n=2) and 4.8% nitrogen (sd=0.3) for a C:N ratio of 8.5 (sd=0.2). Suspended sediment samples collected from the Los Angeles River during a January 1990 storm averaged 9.2% total organic carbon (sd=3.5, n=24) and 0.8% nitrogen (sd=0.3) for a C:N ratio of 11.7 (sd=1.5) (SCCWRP, unpublished data). The bioavailability of contaminants adsorbed to suspended sediments in runoff and wastewater particles in effluent are likely to differ. Furthermore, discharge from the Los Angeles River and effluent from JWPCP enter the marine ecosystem in different habitats and probably have different fates.

Improved municipal wastewater treatment practices and source control have reduced the mass emission of contaminants to the SCB over the past two decades (Schafer 1989). Source control may have also reduced the mass loading of lead and chlorinated hydrocarbons to the SCB via surface runoff. In the 1970s, municipal wastewaters were the source of an order of magnitude more contaminants than surface runoff (SCCWRP 1973, Young *et al.* 1980). Today their relative contributions are comparable; in wetter years, their relative contributions may be reversed.

## Conclusions

The adequacy of the sampling device and the accuracy of flow measurements and constituent concentrations were not addressed in this study, but are clearly important. During storms, flow rates in the Los Angeles River can change by two orders of magnitude in less than one hour. Obtaining depth-integrated samples at high flows is difficult. Since most of the contaminants are discharged during high flows, sampling bias can effect load estimates. In this study, we assumed that flow measurements and constituent concentrations were measured without error. Based on SCCWRP laboratory

**Table 5.**
Estimates of annual mass emissions from the Los Angeles River (LAR) for 1986-87 and 1987-88. Ratio ($L_r$) and rating curve ($L_r$) estimates are based on mean daily flow from September 1 to August 31. Estimates for the Los Angeles River during 1971-72 are based on data collected between 1971 and 1973 (SCCWRP 1973). Mass emissions from Los Angeles County Joint Water Pollution Control Plant (JWPCP) are for calendar years 1971, 1987, and 1988 (SCCWRP 1973, 1987, 1989). All estimates are in wet weight except suspended solids, which is dry weight.

| | 1986-87 | | |
|---|---|---|---|
| | LAR-$L_r$ | LAR-$L_f$ | JWPCP |
| Volume (x10$^6$ m$^3$) | 156 | 156 | 506 |
| Suspended solids (mt[a]) | 38,714 | 79,236 | 36,912 |
| Cadmium (mt) | 1.09 | 0.60 | 1.01 |
| Chromium (mt) | 3.0 | 3.7 | 26.3 |
| Copper (mt) | 7.0 | 10.0 | 21.2 |
| Nickel (mt) | 3.6 | 4.2 | 25.8 |
| Lead (mt) | 11.2 | 16.9 | 23.3 |
| Zinc (mt) | 30.6 | 45.3 | 60.7 |
| Total DDT (kg[b]) | 3.7 | 10.6 | 30.3 |
| Total PCB (kg[c]) | 9.5 | 20.7 | <50 |

[a] mt=metric tons
[b] Sum of *o-p'* and *p-p'* isomers of DDT, DDD, and DDE
[c] Sum of Aroclors 1242 and 1254

QA/QC procedures, this assumption is warranted for constituent concentrations. The accuracy of flow measurements is unknown.

Accurate load estimates also require sampling strategies that produce precise estimates (minimum variance) and estimators that are unbiased. The precision and bias of load estimates depend on sampling frequency, sampling stratification, and calculation method (e.g., Richards and Hollaway 1987, Young *et al.* 1988). River loads are best estimated by frequently measuring contaminant concentrations. Where this is impractical, simulations can be used to assess the accuracy and precision of various estimation methods and sampling strategies (Ferguson 1987). For example, suspended solids are correlated with particle-associated contaminants. Data from a preliminary study with frequent measurements of suspended solids at low and high flows could be modelled to determine the best sampling design and estimation method for trace contaminants that are time consuming and costly to quantify. ■

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| 1987-88 | | | 1971-72 | | |
|---|---|---|---|---|---|
| LAR-$L_r$ | LAR-$L_f$ | JWPCP | LAR-$L_r$ | LAR-$L_f$ | JWPCP |
| 217 | 217 | 518 | 96 | 96 | 513 |
| 93,969 | 154,638 | 36,364 | 163,250 | 96,800 | 169,140 |
| 1.30 | 0.80 | 1.56 | 1.23 | 0.90 | 15 |
| 5.7 | 6.3 | 18.7 | 6.2 | 8.9 | 441 |
| 14.0 | 18.7 | 19.2 | 7.6 | 11.6 | 287 |
| 6.5 | 7.3 | 26.5 | 6.6 | 6.2 | 123 |
| 24.5 | 32.1 | 18.7 | 88 | 92 | 128 |
| 64.3 | 84.2 | 72.7 | 124 | 128 | 1,230 |
| 9.1 | 20.8 | 20.8 | 78 | 84 | 21,526 |
| 23.7 | 40.3 | <50 | 187 | 300 | 5,997 |

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## Appendix 1.
### Analytical Methods.

Two 4-l water samples were collected at each sampling time. The bottles and their contents were swirled and divided among a 1-l acid-washed polyethylene bottle for analyses of trace metals, an identical container for analysis of suspended solids, and a 4-l acid-washed glass bottle for analyses of total DDT, and total PCB. Samples for suspended solids and trace metal analyses were refrigerated at 5°C until analyzed. One hundred milliliters of *n*-hexane was added to the sample for trace organic analyses. Samples that could not be extracted immediately were poisoned with $HgCl_2$.

Samples collected for trace organic analyses were extracted with 100 ml of chloroform three times in succession and the extracts were combined. Approximately half of the extract was transferred into a tared flask and the chloroform was removed by rotoevaporation. The flask was desiccated for 24 hr and then resuspended in *n*-hexane. The extract was cleaned on activated Florisil (750°C for 4 hr) and analyzed for selected chlorinated hydrocarbons on a Varian 4600 high resolution gas chromatograph equipped with an electron capture detector.

Samples collected for trace metal analyses were prepared by evaporating a 500 ml aliquot to approximately 10 ml on a hot plate. Twenty milliliters of nitric acid were added and the sample volume was reduced to 2-5 ml. Finally, 20 ml of hydrochloric acid were added and the sample was evaporated almost to dryness. The digest was rinsed and filtered through Whatman No. 40 filter paper using distilled water and the final volume was adjusted to 20 ml. Metals were determined by aspiration into the flame on a Varian AA6 Atomic Absorption Spectrophotometer.

Suspended solids were determined by filtering a 10 to 100 ml aliquot through a Whatman GF/C filter. The filters plus solids were dried at 105°C for 24 hr, cooled, and weighed.

## Appendix 2.
### Load Estimates.

The load of a particular constituent in a river is defined as the total mass of the constituent passing the point of measurement over some period of time. The instantaneous transport rate (mass/time) of a constituent—the product of its concentration $C$ (mass/volume) and river flow rate $Q$ (volume/time) — is relatively easy to estimate. However, longer term loads are generally of more interest. Problems arise in estimating long-term loads because flows are usually monitored continuously or at short intervals, while river samples are collected much less frequently. Loads of selected constituents transported in the Los Angeles River were estimated by two methods: ratio estimator and rating curve. Measurement errors in $Q$ and $C$ were assumed to be negligible.

The flow-weighted ratio estimator is based on the relationship between flows and loads (Equation 1 in Table 6) where $L_f$ is the constituent load, $Q$ is the mean period flow, $T$ is the total time in the period, $c_i$ is the $i$th concentration, and $q_i$ is the corresponding flow rate. [The flow-weighted mean concentration for the period is given by Equation 2 (Table 6).] This method assumes that flows are continuously monitored, mean flow can be determined accurately, concentrations are related to flows, and the underlying distributions are approximately normal.

The rating curve method uses the empirical relationship between constituent concentration and river discharge to estimate concentrations for flows not sampled (Equation 3 in Table 6). $C_i$ is an estimate of the mean concentration in log units when river discharge is $Q_i$ in log units; $a$ and $b$ are fitted constants estimated by ordinary least squares regression. This method assumes that the relationship between log concentration and log flow is linear, errors are random and additive, the $C_i$'s at any $Q_i$ are log normally distributed with homogeneous variances, and measurement errors in the $Q_i$'s are negligible. The antilog (Equation 4 in Table 6) estimates the geometric mean $C$ at each $Q$. The total load for the period is given by Equation 5 (Table 6) where $m$ is the number of intervals for which discharge rates are known and $\delta t$ is the time interval between discharge measurements. However, the geometric mean estimate of $C_i$ is biased downward. The bias-corrected estimate of the total load is given by Equation 6 (Table 6) where $s$ is the standard error of the least squares estimate of $C_i$ in log units (Ferguson 1986, 1987). Plots of residuals were examined for each constituent and outliers were subjectively eliminated from the final regression. If the slope of the log-linear relationship was not significantly different from zero, the arithmetic mean constituent concentration was substituted for $C_i$ in (6) and no correction factor was applied.

The distributions of $Q$ and $C$ for the Los Angeles River were generally positively skewed and spanned up to three orders of magnitude. The greatest range of measurements in both flows and concentrations occurred during storm events that occurred sporadically, but contributed significantly to annual runoff volume and contaminant loads. To reduce skewness and variability, concentration data were stratified by flow. The

**Table 6.**
**Equations used to estimate loads. See text in Appendix 2 for explanation.**

$$L_f = Q\,T\,\frac{\sum_{i=1}^{n} c_i q_i}{\sum_{i=1}^{n} q_i} \qquad (1)$$

$$\frac{\sum c_i q_i}{\sum q_i} \qquad (2)$$

$$\log_{10} \hat{C}_i = a + b \log_{10} Q_i \qquad (3)$$

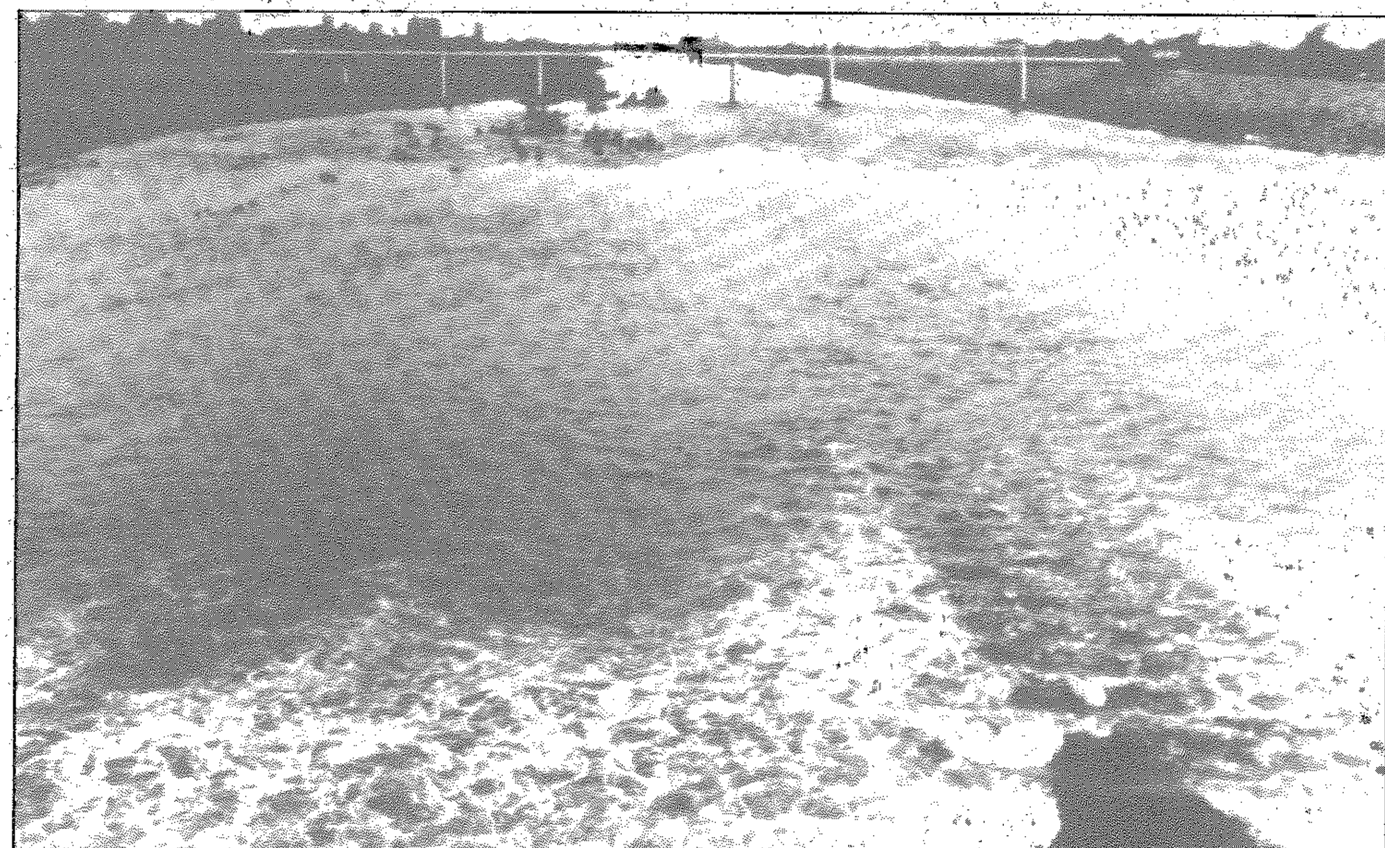
$$\hat{C}_i = 10^a Q_i^b \qquad (4)$$

$$\sum_{i=1}^{m} \hat{C}_i Q_i \,\delta t \qquad (5)$$

$$L_r = \sum_{i=1}^{m} \hat{C}_i Q_i \,\delta t \exp(2.651 s^2) \qquad (6)$$

inflexion point on the flow duration curve was selected as the cutoff between low and high flow days (Figure 2); this corresponded to an average daily discharge of 5 $m^3/s$ for the recent data and 2 $m^3/s$ for the historical data. Stratification reduced the residual sum of squares of the rating curve method by an average of 18% over the unstratified case for the recent data; no improvement was obtained for the historic data. $L_f$ and $L_r$ were estimated for each stratum and the estimates were summed to obtain annual loads. Contaminant data from the two years were pooled to increase the sample size in each stratum.

Differences in load estimates between the ratio method and the rating curve are due to several factors. The ratio method weights concentrations by flows and emphasizes high flows and high concentrations; the assumptions are generally met by the data. The rating curve estimates constituent concentrations for a given daily flow and is more sensitive to flow intensity; the assumptions are more restrictive and probably were not met by the data. Both methods suffer from sampling that did not cover the range of observed flows, a high proportion of samples of some constituents with non-detectable masses, and small sample sizes. Since the "true load" of any of the constituents measured is unknown, it is not possible to determine which estimation method is more accurate.



**Storm water runoff in the Los Angeles River.**