

REPRINT

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HIGHLY URBANIZED SOUTHERN CALIFORNIA
TO THE ADJACENT MARINE ECOSYSTEM

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INTRODUCTION

The southern California coastal basin sustains one of the most rapidly growing urban complexes in the United States. Stretching more than 400 kilometers from Point Conception to the U.S.-Mexico border over an area of about 30,000 sq km (Figure 1), this basin is occupied by

approximately 11,000,000 persons, or about five percent of the nation's population. Most of its population growth has occurred in Los Angeles and Orange Counties, in a pattern that now is being repeated in Ventura County to the north and San Diego county to the south.

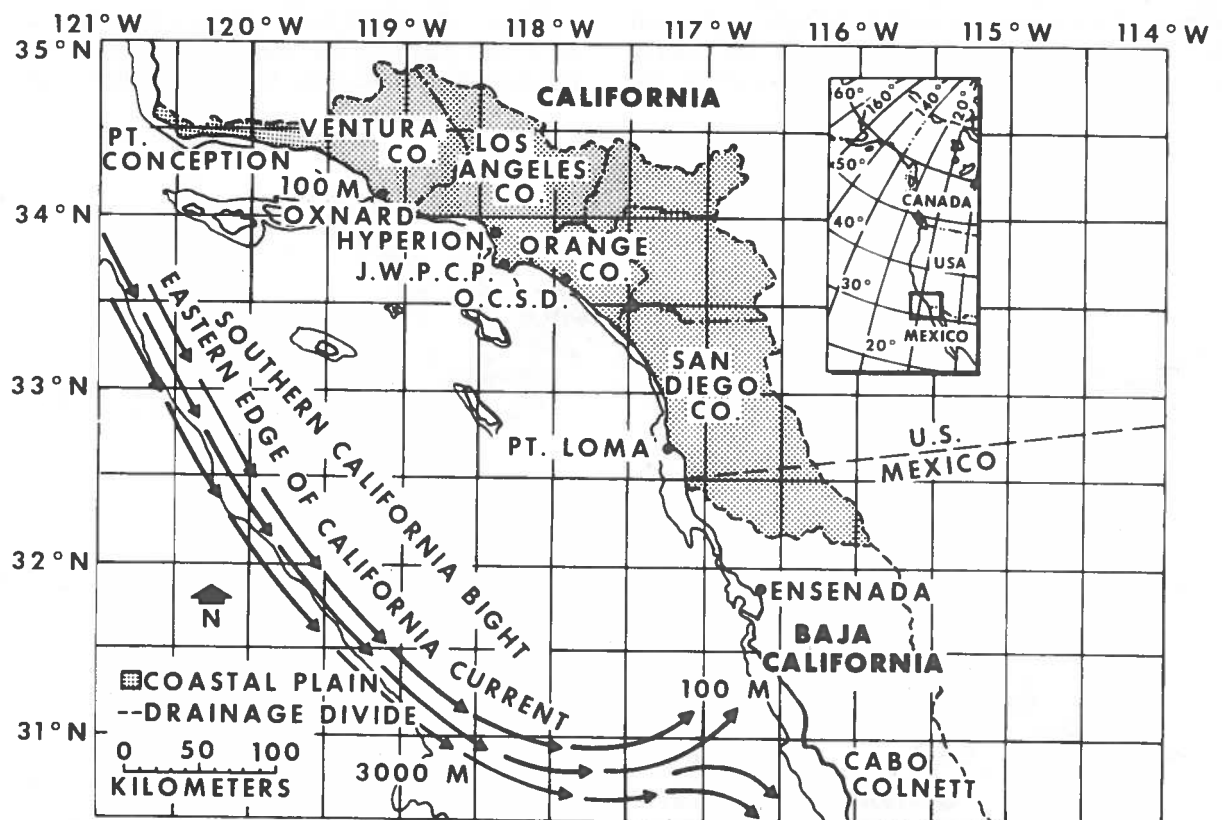


Figure 1. The coastal plain of southern California and the adjacent marine waters of the Southern California Bight.

The adjacent marine ecosystem of the Bight is a major recipient of the wastes produced in the highly urbanized coastal basin. In this paper we will discuss the present state of knowledge of the trace metal inputs to the

Figure 2 shows the locations of marine outfalls for municipal wastewaters (W), discrete industrial discharges (I), and cooling waters from power plants (P) in the Southern California Bight. Figure 2 also shows the major surface drainage channels along the southern California coast. Of these discrete sources, municipal wastewaters have received the most attention in the past.

At present approximately 1,000,000,000 gallons (1000 mgd) of treated municipal wastewaters are discharged daily through marine outfalls to the Southern California Bight. Most of this, 84 percent, receives primary treatment only. Three major municipal wastewater discharges to the Bight occur within about 30 km of Palos Verdes Peninsula (Figures 1 and 2). Located off this peninsula is the Joint Water Pollution



Control Plant (JWPCP) outfall system (average length: 1.5 miles) of Los Angeles County Sanitation Districts, the largest of the municipal wastewater discharges in the Bight (370 mgd). To the northwest in Santa Monica Bay lie the 5 mile effluent and 7 mile digested sludge outfalls (335 and 5 mgd, respectively) of the Hyperion Sewage Treatment Plant of the City of Los Angeles; to the southeast lie the old 1 mile and new 5 mile outfalls of Orange County Sanitation Districts (130 mgd). The City of San Diego (90 mgd) discharges through the Point Loma outfall (2 miles); the City of Oxnard (12 mgd) discharges approximately one mile off the Ventura County coast. Altogether these five major dischargers contribute approximately 95 percent of the municipal wastewaters discharged into the Southern California Bight. These discharges occur at depths of 50 to 100 meters, generally below the thermocline.

Trace metal monitoring programs by the major dischargers were established prior to, or during, 1971. This has enabled us to complete a reliable estimate of trace metal mass emission rates from municipal wastewater discharges to the Bight for 1971. Table 1 shows the 1971 average concentrations of ten trace metals: silver, cadmium, chromium, copper, mercury, nickel, lead, zinc, iron, and manganese as reported by the major dischargers.* It is to be noted that a variety of collecting, compositing, and analytical procedures were employed in the dischargers' routine monitoring

programs. Figure 3 shows, as an example, the monthly variation of zinc concentrations in wastewater discharge. These time variations are typical of those for the other metals studied, and illustrate that, while individual monthly values can vary from the year-long mean by a factor of two or occasionally three, order-of-magnitude deviations are uncommon.

In order to evaluate the intercomparability of these concentration values reported by the various laboratories, we conducted a short term trace metal survey in the summer of 1971. With the assistance of plant personnel, week-long composite samples at each of the five major treatment plants were collected. Grab samples were collected by the regular procedures at one or two hour intervals for seven consecutive days. Every day these samples were filtered by 0.45-micron filters, and the residues and filtrates were frozen along with the unfiltered replicates. At the end of the collection period the water samples were thawed and combined into weekly composites which were immediately refrozen. The filtrate composites and daily residues were analyzed by atomic absorption spectrometry at the University of California, San Diego.† Unfiltered composites were submitted to the treatment plant laboratories for trace metal determination.

The results of this survey indicated generally good agreement between those metal concentrations reported by the treatment plant laboratories and the University of

*The 1971 average concentrations of total suspended solids (mg/l) in the final effluents of these wastewater dischargers are: Oxnard - 80; Hyperion effluent - 73; Hyperion sludge - 3,000; JWPCP - 330; Terminal Island - 120; O.C.S.D. - 145; Pt. Loma - 110.

†This study was conducted in collaboration with J. Galloway, University of California, San Diego.

TABLE 1 AVERAGE CONCENTRATIONS OF TRACE METALS (mg/l) IN FINAL EFFLUENTS OF MUNICIPAL WASTEWATER DISCHARGERS, 1971

Discharger	mgd	Silver	Cad- mium	Cobalt*	Chro- mium	Copper	Mercury	Nickel	Lead	Zinc	Iron	Manga- nese	Remarks (note exceptions in footnotes)
W9 Oxnard	12												
	x	<.01	0.02	-	0.06	0.09	<.001	0.06	<.06	0.28	0.50	0.12	Avg. of Jan '71 &
	s _x	-	0.00		0.02	0.01	-	0.01	-	0.08	0.18	0.01	Mar '72 values
W10 Hyperion Effluent	335												
	x	0.002†	0.05	0.006	0.29	0.23	0.003	0.28	0.06	0.46	0.73	0.01†	Avg. of 12 monthly
	s _x	0.001	0.02	0.002	0.07	0.03	0.001	0.04	0.02	0.07	0.09	0.01	values
Sludge	5												
	x	0.03 †	0.23	0.03	2.1	12	0.10	2.6	0.51	16	47	1.6	Avg. of 12 monthly
	s _x	0.003	0.05	0.005	1.3	1.6	0.01	0.33	0.15	2.1	8.8	0.78	values
W11 JWPCP	371												
	x	0.02	0.03	-	0.86	0.56	0.001	0.24	0.25‡	2.4	9.9	0.13	Avg. of 12 monthly
	s _x	0.03	0.002		0.03	0.03	0.0001	0.01	0.04	0.11	0.63	0.01	values
W12 Terminal Island	8												
	x	0.002f	0.01	<.006	0.11	0.26	0.001	0.42	0.00	0.36	0.94	0.05	Avg. of Jan. & July
	s _x	0.00	0.01	.006	0.01	0.12	0.001	0.16	0.00	0.14	0.04	0.05	values
W16 Orange Co. San. Dist.	130												
	x	0.02	0.06	-	0.22	0.35	0.001 #	0.16	0.22	0.54	1.2	0.09	Avg. of Oct.-Dec.
	s _x	0.01	0.01		0.06	0.003	-	0.03	0.06	0.12	0.33	0.03	values
W24 Pt. Loma	90												
	x	-	0.02	-	0.15	0.16	<.001	0.06	0.10	0.18	-	-	Avg. of July-Sept.
	s _x		0.01		0.04	0.03	-	0.01	0.01	0.02			values

*All cobalt concentrations are averages of 24-hr composite samples collected 24 Aug. and 9 Sept. 70.

†Hyperion effluent and sludge silver concentrations are averages of 4 monthly values; effluent manganese concentration is average of 11 monthly values.

‡JWPCP lead concentration is average of 10 monthly values.

fTerminal Island silver concentration is average of Aug. and Sept. 71 values.

#Orange Co. mercury concentration is estimated from analysis of 22 grab samples, 15-21 Jun 72.

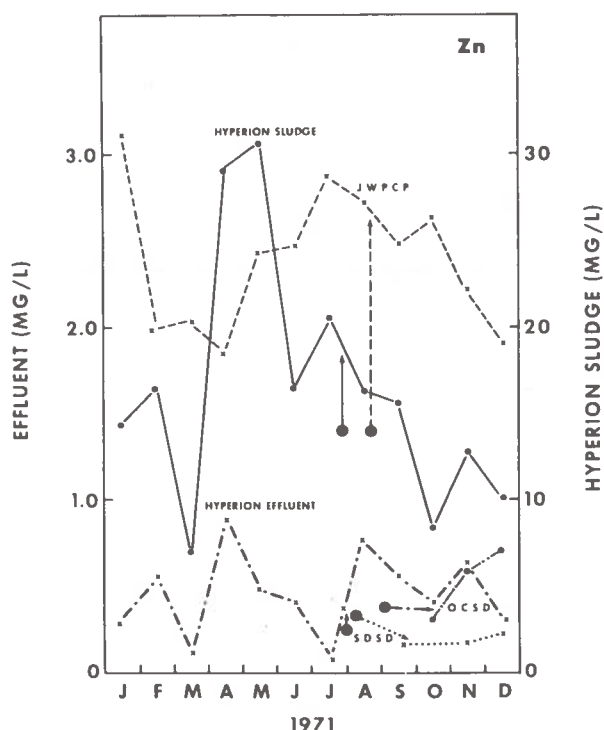


Figure 3. Concentrations of zinc observed during 1971 in municipal wastewaters of the major treatment plants along the southern California coast. Solid circles indicate concentrations measured in one-week composites of these wastewaters (2).

California, San Diego (2). The ratios of the two reported values usually were within a factor of two, and no trends were apparent. For those concentrations not reported by the treatment plants, comparisons between Galloway's data and the regular monitoring data for the closest collection period usually still showed a ratio of three or less. Figure 3 illustrates such comparisons for zinc.

Table 2 presents the percentages of trace metals that were found to be associated with the residue portions of the effluent samples. Although particles of smaller than 0.45-microns may be retained by the filter, the results do indicate a high degree of association between most of the metals and the wastewater solids. For silver, cadmium, chromium, copper, lead, zinc, and iron, 84 to 94 percent of the metals were associated with the residue. For cobalt, nickel, and manganese, these values range from 42 to 54 percent.

Although the data listed in Table 1 indicate considerable differences in average metal concentrations between the various wastewaters, the concentrations found on the wastewater particulates agreed much more closely, as is seen in Table 3. For example, the average 1971 metal concentrations (mg/l) in Hyperion effluent were generally 5 to 50 times lower than those in the digested sludge; however, on a particulate basis (mg/dry kg), the effluent concentrations in the composited effluent residue were generally only two to three times lower than those in the sludge residue. It is apparent that particulates play an important role in the wastewater transport of trace metals.

TABLE 2 PERCENT OF TRACE METAL RETAINED BY 0.45-MICRON FILTERS IN ONE-WEEK COMPOSITES OF FINAL EFFLUENT FROM MUNICIPAL WASTEWATER DISCHARGERS, SUMMER, 1971 (After Reference 2)

Discharger (data sampled)	Silver	Cad- mium	Cobalt	Chro- mium	Copper	Nickel	Lead	Zinc	Iron	Manga- nese
W9 Oxnard (8/15-8/21)	87	92	50	90	91	80	92	94	90	40
W10 Hyperion Effluent (7/26-8/1)	75	88	50	64	86	35	90	86	80	34
W11 JWPCP* (8/13-8/19)	95	95	72	95	96	45	97	91	91	60
W16 Orange County (8/27-9/2)	97	98	—	81	94	57	97	94	93	44
W24 Point Loma (8/1-8/7)	85	91	42	90	90	74	92	94	91	30
\bar{x}	88	93	54	84	91	58	94	92	89	42

*The average of 23 weekly composite values for 1971 from monitoring data of Los Angeles County Sanitation District indicates that approximately 90% of the total mercury in JWPCP final effluent was retained on a 0.8-micron filter.

TABLE 3 TRACE METAL CONCENTRATIONS (mg/dry kg) IN WASTEWATER PARTICULATES* AND NATURAL MARINE SEDIMENTS OFF SOUTHERN CALIFORNIA (After Reference 2)

	Silver	Cad- mium	Cobalt	Chro- mium	Copper	Nickel	Lead	Zinc	Iron	Manga- nese
W9 Oxnard	30	115	15	350	1000	145	300	1500	9000	140
W10 Hyperion Effluent	130	108	4	1440	1500	520	320	2300	5400	108
Sludge	265	180	23	3430	2500	670	1000	4820	13000	156
W11 JWPCP	32	65	8	1700	1120	220	570	4100	20000	150
W16 Orange County	40	245	—	1330	1850	220	920	2330	7000	120
W24 Point Loma	105	65	8	1000	1600	310	545	3000	10000	200
Natural Nearshore Marine Sediment	1.0	0.4	7.2	46	16	14	8.5	63	25000	320

* Residue after filtration through 0.45-micron Millipore filter.

Table 4 presents the estimated annual trace metal mass emission rates from municipal wastewater discharges to the Southern California Bight.* This estimate indicates that approximately 95 percent of the trace metals carried by municipal wastewaters into the Southern California Bight are discharged from a coastline approximately 70 km in length. From a broad-scale point of view, the trace metal inputs from municipal wastewater to the Bight may be considered as a semi-point source centered around the Palos Verdes Peninsula.

DISCRETE INDUSTRIAL DISCHARGES

In contrast to the case for municipal wastewaters, where a few major discharges contribute most of the waste input, the situation for discrete industrial discharges is much more complex. The types of industrial processes and reclamation steps, if any, employed can play a vital role in the total quantity of a particular trace metal that is released in the discharge.

irregardless of the volumetric flow rates. The first step in evaluating the importance of this source of trace metals to the Bight was to categorize the discharges in terms of the type of waste generated, the flow rate, and the location of the discharge. These data were obtained from the files of the local Regional Water Quality Control Boards, the state regulatory agencies for waste discharge into the waters of southern California.

Tabulations of such data for thermal cooling water and petroleum-related discharges along the coast are presented in Tables 5 and 6. No significant data on the concentration of trace metals in these discharges were located during the inventory compilation.†

One of the highly industrialized regions of the coast is the San Pedro Bay area. This is the site of Los Angeles-Long Beach Harbor, and is located just to the southeast of Palos Verdes Peninsula. In addition to the

*The corresponding input rate for total suspended solids is estimated to be 278,000 M tons/yr.

†An extensive analysis of the nature of thermal discharges to the Bight already has been presented elsewhere (3).

TABLE 4 TRACE METALS MASS EMISSION RATES (M tons/yr) FROM MUNICIPAL WASTEWATER DISCHARGERS TO THE SOUTHERN CALIFORNIA BIGHT, 1971

Discharger	Flow (mgd)	Silver	Cad- mium	Cobalt	Chro- mium	Copper	Mer- cury	Nickel	Lead	Zinc	Iron	Manga- nese
W9 Oxnard	12	—	0.3	—	1	1	—	1	—	4	8	2
W10 Hyperion Effluent	335	0.9	23	2.8	130	110	1.4	130	28	210	340	5
Sludge	5	0.2	2	0.2	10	80	0.7	18	4	110	320	11
W11 JWPCP	371	10	15	—	440	290	0.5	120	130	1220	5100	67
W12 Terminal Island	8	—	0.1	—	1	3	—	5	—	4	11	1
W16 Orange Co.	130	3.6	11	—	40	63	0.2	29	40	97	220	16
W24 Point Loma	90	—	2.5	—	19	20	0.1	8	12	22	—	—
TOTAL	950	15	54	3.0	640	570	2.9	310	210	1700	6000	100

TABLE 5 ANNUAL DISCHARGE OF COOLING WATER FROM THE MAJOR POWER GENERATING STATIONS ON THE SOUTHERN CALIFORNIA COAST

Generating station		Flow (10 ⁸ cu m/yr)
FOSSIL-FUEL		
L. A. Dept. of Water and Power		
P1	Harbor – Wilmington	1.1
P2	Haynes – Seal Beach	10.5
P3	Scattergood – Playa del Rey	2.5
	Subtotal	14.1
Southern California Edison Co.		
P4	Alamitos – Seal Beach	11.6
P5	El Segundo – El Segundo	5.0
P6	Huntington – Huntington Beach	6.5
P7	Long Beach – Long Beach	0.8
P8	Mandalay – Oxnard	3.2
P9	Redondo – Redondo Beach	9.8
P10	Ormond – Ormond Beach	10.2
	Subtotal	47.1
San Diego Gas and Electric Co.		
P11	Encino – Carlsbad	2.2
P12	Silver Gate – San Diego Bay	2.2
P13	South Bay – San Diego Bay	5.0
P14	Station "B" – San Diego Bay	0.9
	Subtotal	10.3
NUCLEAR		
P15	San Onofre – San Clemente	5.5
	TOTAL	77.0

extensive recreational, commercial and naval vessel activities there, San Pedro Bay receives more than 150 discrete industrial waste discharges, either directly into the bay or via storm drains (see Table 7). The combined flow rate of these discharges, excluding cooling waters from power plants, is about 100 mgd, or about 10 percent that of the combined municipal wastewater discharges to the Bight. Approximately 10,000 metric tons per year of suspended solids are carried into the bay; this is about 3 percent of the total figure for the combined municipal wastewaters. As for the coastal industrial discharges, no significant data on trace metal concentrations in industrial discharges to the bay were located. As is seen in the table, the combined flow rate for metallic industrial discharge (3.8 mgd) constitutes only about 4 percent of the total industrial discharge to the bay. However, the significance of this low percentage should not be over emphasized. The lack of any significant trace metal data in the public files for the industrial discharges described above represents a serious gap in the knowledge of trace metal inputs to the Southern California Bight.

SURFACE RUNOFF

There are 200 to 300 surface runoff discharge locations along the southern California coast. However, approximately 70 percent of the average annual flow is carried by 15 major streams during the storm runoff season. The normal annual precipitation in the southern California coastal basin averages approximately 40 cm (15 in.), and surface runoff from about 60 percent of the drainage area is regulated by dams and other flood control measures. The southern California coastal streams generally carry appreciable flow only during and shortly following the occasional rainstorms.

In an attempt to characterize the surface runoff in the southern California basin, five major watersheds were selected for study during the storm season of 1971 to 72. These were the Santa Clara River, Ballona Creek, the Los Angeles, Santa Ana, and San Luis Rey Rivers (Figure 2).

In light of the apparent association of trace constituents with particulates, a survey was made on the relationship between flow rate and concentration of suspended sediment in southern California storm runoff.

TABLE 6 DISCRETE INDUSTRIAL WASTE DISCHARGERS OF THE SOUTHERN CALIFORNIA COAST

	Discharger	Type of waste	Flow (mgd)
I1	Phillips Petroleum – Point Conception	Oil brine Tanker ballast	0.2
I2	Texaco, Inc. – San Augustin	Oil brine	0.2
I3	Getty Oil – Gaviota	Oil brine Tanker ballast	0.16
I4	Shell Oil – El Capitan	Oil brine Tanker ballast	0.2
I5	Signal Oil & Gas – Ellwood	Oil brine Tanker ballast	0.29
I6	Atlantic Richfield – Coal Oil Point	Oil brine	0.06
I7	Standard Oil – Summerland	Oil brine	0.4
I8	Standard Oil – Carpinteria	Oil brine Tanker ballast	0.4
I9	Atlantic Richfield – Rincon	Oil brine	0.01
I10	Atlantic Richfield – Rincon Island	Oil brine	0.04
I11	Western Oil & Dev. – Rincon	Oil brine	0.36
I12	Petrol Industries – Rincon	Oil brine	0.01
I13	Continental Oil – Rincon	Oil brine	0.49
I14	Norris Oil Co. – Rincon	Oil brine	0.05
I15	Phillips Petroleum – La Conchita	Oil brine	0.36
I16	Phillips Petroleum – Punta Garda	Oil brine	0.4
I17	Mobil Oil – Sea Cliff	Oil brine Tanker ballast	0.18
I18	Continental Oil – Pitas Point	Oil brine	0.27
I19	Continental Oil – Grubb Lease	Oil brine	0.75
I20	Getty Oil – Ventura	Oil brine Tanker ballast	0.06
I21	Standard Oil – McGrath Beach	Oil brine	0.14
I22	McDonnell Douglas Corp. – Venice	Cooling tower bleedoff	0.65
I23	Standard Oil – El Segundo	Cooling water Refinery wastes	72
I24	Standard Oil – Island Esther	Oil brine	1
I25	Union Oil – Platform Eva	Oil brine	0.02
I26	Signal Oil and Gas – Platform Emmy	Oil brine	0.08
I27	Signal Oil and Gas – Huntington Beach	Oil brine	0.6
I28	Standard Oil – Huntington Beach	Oil brine	0.8
I29	Gulf Oil – Huntington Beach	Oil line ballast	0.01

TABLE 7 COMBINED FLOW RATES (mgd) OF DISCRETE INDUSTRIAL WASTE DISCHARGERS IN THE SAN PEDRO BAY AREA

Discharge area	Oil field brine	Oil line and tanker ballast	Refinery & petrochemical	Metallic	Fish cannery	Miscellaneous chemical	Total
L. A. Harbor	0.43	0.82	28	2.0	9.6	5.6	47
Long Beach Harbor	24	5.7	—	0.03	—	3.8	34
Dominguez Channel	0.05	—	6.5	1.4	—	2.3	10
L. A. River Tidal Prism	5.9	—	1.1	—	—	—	7
Los Cerritos Channel	—	—	—	0.12	—	0.04	0.2
San Gabriel River Tidal Prism	3.4	—	—	0.19	—	—	3.6
TOTAL	34	6.5	36	3.8	9.6	12	102

Data were provided by the United States Geological Survey from studies conducted during January and February, 1969. Typical examples of the relationship that was found for this abnormally wet year are illustrated for the Santa Clara River and the Santa Ana River in Figures 4 and 5, respectively.

It is seen that, over the four day periods, peaks in the concentration of suspended sediment clearly correlate with peaks in the flow rate. The peak amplitudes often are roughly proportional; this relationship, where

applicable, has significant implications for programs aimed at the determination of mass emission rates of particulate-associated materials. For when the concentration (C_i) is proportional to the flow rate (F_i), e.g. $C_i = kF_i$, the transport rate (T) of the suspended substance increases as the square of the flow rate:

$$T = \sum_{i=1}^n C_i F_i = k \sum_{i=1}^n F_i^2 \quad (1)$$

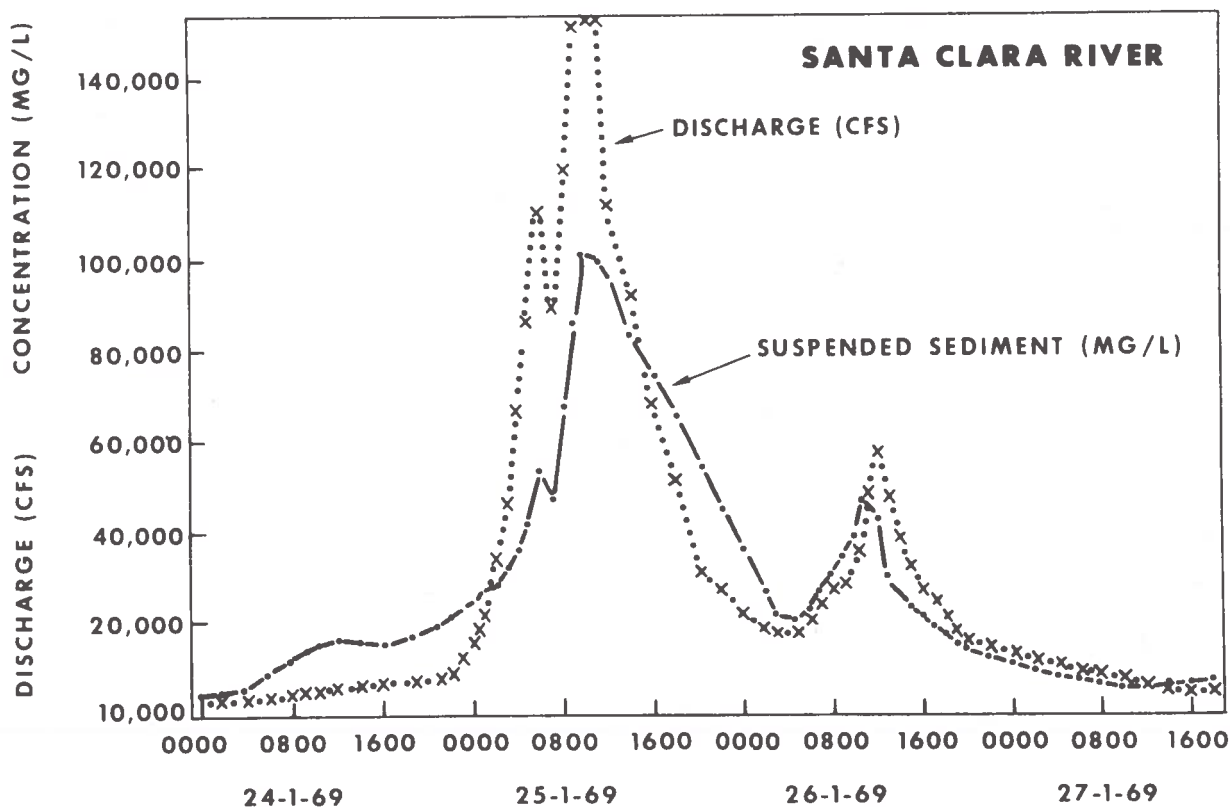


Figure 4. Comparison of discharge rate and suspended sediment concentration as a function of time in Santa Clara River storm runoff during January 24 to 27, 1969.

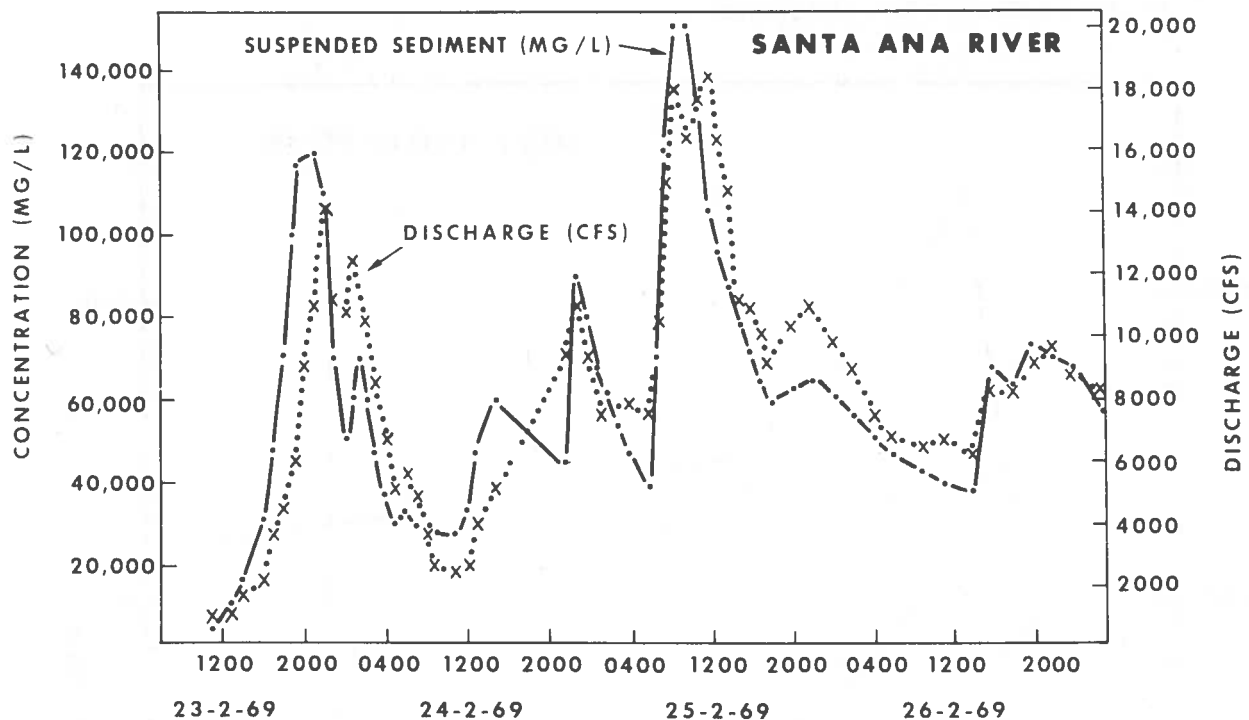


Figure 5. Comparison of discharge rate and suspended sediment concentration as a function of time in Santa Ana River storm runoff during February 23 to 26, 1969.

Under such conditions most of the transport of particulate-borne substances occurs during the period of peak flow. Sampling frequency therefore should be greater at these times to more accurately determine the total transport of the suspended material.

In order that representative samples of the storm runoff and its suspended sediments would be collected, a special depth-integrating sampler was constructed. This sampler was patterned after the United States Geological Survey suspended sediment pint sampler, but was enlarged to a one gallon capacity to provide sufficient sample for trace-level analyses. Other modifications also were made to decrease the chance of contamination; these will be reported in detail later. The collection stations were over the centers of the channels at bridges that were located as near to the coast as possible but above the tidal prism. As soon as possible after collection, generally within a few hours, the samples were taken to our laboratory where they were filtered through 0.45 micron filters. The filtrates and residues then were frozen until analyzed.

In this program, nine time series were obtained covering up to three storms in four channels. During periods of peak flow samples were collected at approximately two-hour intervals. The 1971 to 1972 period was an unusually dry year; all the channels did not flow at each storm, and no significant flow occurred in the San Luis Rey River and the southern streams during the year. Thus, the total surface runoff, estimated

to be 242×10^6 cu m, including both storm and dry weather flow, was approximately 43 percent of the long term average for the Bight. Of the 167×10^6 cu m of storm flow to the Bight, during the year, approximately 60 percent was covered in this sampling program.

Analyses of these samples were conducted at the California Institute of Technology (4). Concentrations of ten trace metals, the same as for municipal wastewaters, were measured in the runoff filtrates and residues. Where necessary, concentration of the samples with ion exchange resin was employed, followed by measurement using atomic absorption spectroscopy. A detailed analysis of the data, including a comparison of individual metal inputs from the various basin types, is still underway, and, along with a description of analytical procedures will be reported later (4).

An example of the results for the total concentrations of silver, copper, and lead in storm runoff from Los Angeles River is presented in Figure 6, along with the flow rate and concentration of suspended sediment. These data illustrate the general correlation of peak values for flow rate, and silt and metal concentrations that was observed during this study. Calculations of mass emission rates for the ten metals studied were made from such concentration and flow rate data. Table 8 lists the estimates obtained to date for metal inputs to the Bight from runoff during water year 1971 to 72.* Also listed are the average values for percent of trace metal associated with particulates in the runoff samples. In

*The corresponding input of suspended sediment (silt) to the Bight is estimated to be 274,000 M tons/yr.

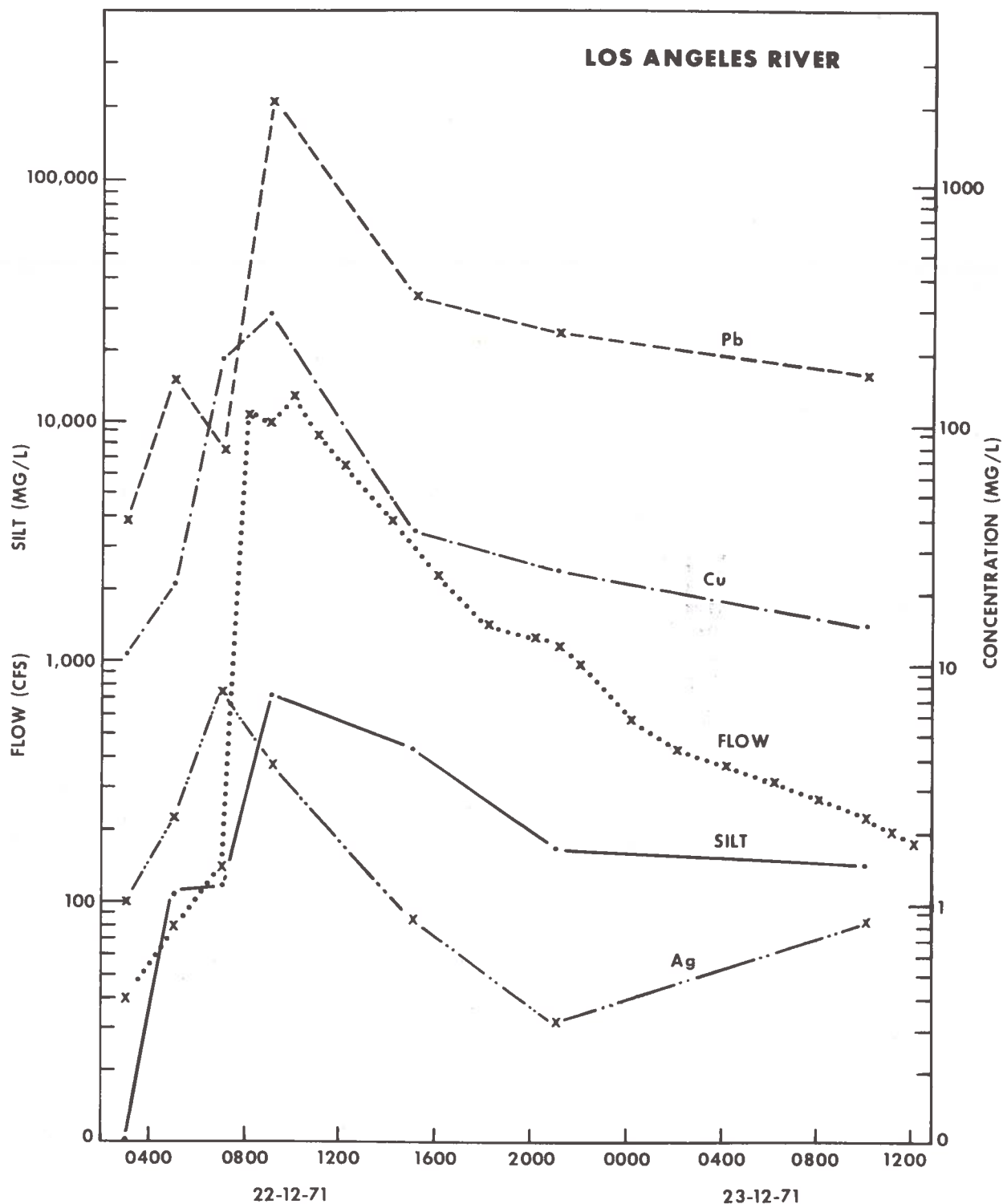


Figure 6. Concentrations of three trace metals and suspended sediment (silt) in the discharge (flow) of Los Angeles River during December 22 to 23, 1971.

general, these input rates were considerably lower than those for municipal wastewaters during 1971. For example, surface runoff inputs during the year

constituted the following percentages of the 1972 municipal wastewater inputs of metals to the Bight: silver, 6.7 percent; cadmium, 1.9 percent; chromium, 3.8

TABLE 8 ESTIMATED TRACE METAL MASS EMISSION RATES (M tons/yr) FROM SURFACE RUNOFF TO THE SOUTHERN CALIFORNIA BIGHT, 1971–72

Metal	Mass emission rate	% particulate*
Silver	1.1	74
Cadmium	1.2	78
Cobalt	5.3	75
Chromium	25	82
Copper	18	59
Mercury	0.06	—
Nickel	17	63
Lead	90	89
Zinc	100	74
Iron	26000	99
Manganese	180	72

*Percent of metal retained by 0.45-micron filter.

percent; copper, 3.2 percent; mercury, 3.3 percent; nickel, 5.5 percent; zinc, 5.9 percent. Only for lead (43 percent), cobalt (170 percent), iron (430 percent), and manganese (180 percent) were the runoff inputs relatively important.

DIFFUSE SOURCES

In addition to the discrete or point sources of pollutants which have been discussed previously, there are a number of potentially significant pollutants whose sources to the Bight are distributed widely and thus are much more difficult to quantitate. Four such pollutant sources are vessel antifouling paint and fuel consumption, ocean dumping, airborne inputs, and advective transport by the California current. Although these source categories have not been investigated thoroughly, preliminary analyses were conducted to provide a rough estimate of possible importance of these sources and to assist in establishing priorities for future studies. The following data on inputs from diffuse sources are order-of-magnitude estimates only and are presented here primarily to provide guidance for future studies.

VESSEL BODY PROTECTIVE MEASURES AND FUEL CONSUMPTION

The Southern California Bight harbors a large number of recreational, commercial, and naval vessels. Losses of bottom antifouling paint and anticorrosive anodes and spent fuel residues may represent important sources of trace pollutants to the marine environment.

To investigate the magnitude of these potential sources of pollutants, a preliminary survey of recreational vessel activity was undertaken. The two major objectives of this investigation were to inventory the recreational craft in each of the fourteen major

marinas between Santa Barbara and San Diego, and to obtain preliminary information on the consumption, and presumed release to the Bight, of certain materials such as antifouling paint, sacrificial zinc anodes, and leaded fuel in one of the largest recreational vessel facilities, Marina del Rey in Los Angeles. Estimates of the quantities of trace metals used in bottom paints and in spent fuel in Marina del Rey could be extrapolated to estimate annual marina-related input of these metals to the Bight.

Antifouling Paints and Primers

The largest drydock in Marina del Rey, Windward Yacht and Repair, was studied to obtain an estimate of the use of antifouling paints. Of the 5,500 recreation craft in the marina, nearly 1,200 are hauled out and painted annually. Fifty to 60 gallons of antifouling paint are applied weekly; the old paint is removed and washed through a storm drain into the marina. Thus, this drydock uses approximately 2,860 gallons of antifouling paint annually, which corresponds to about 2.4 gallons per boat. Based on this analysis, it is estimated that approximately 13,000 gallons of antifouling paint are applied annually to the recreational craft moored in Marina del Rey. Assuming that vessel activity in the marina is typical of recreation craft in the marinas of the Bight, and extrapolating this unit paint consumption, it is estimated that the annual antifouling paint requirement for the 34,850 recreation craft in the Bight area is approximately 84,000 gallons. A gallon of antifouling paint weighs about 8.6 kg, which results in an estimated total annual paint usage rate of approximately 720,000 kg for recreational craft.

In a recent study conducted by San Diego Regional Water Quality Control Board (5) Barry estimated that the annual paint usage for commercial and naval vessels at the major shipbuilding and repair facilities in San Diego Bay was approximately 30,000 gallons of antifouling paint (8.6 kg/gal), 23,000 gallons of red lead primer (5.2 kg/gal), and 10,000 gallons of zinc chromate primer (4.1 kg/gal). It is estimated that, at the most, 10 percent of the paints or coatings removed by sand blasting of commercial and naval vessels is lost to the bay water. The bulk of the sand and coating residues is disposed of in land fills.

Comparable information for other major harbor facilities, such as the Los Angeles-Long Beach Harbor, is not yet available. If one assumes that San Diego Bay practices are representative of commercial and naval vessels generally, then the annual loss of antifouling paints and primers to the Bight is estimated to be as follows: Antifouling paint, 52,000 kg; red lead primer, 24,000 kg; zinc primer, 8,200 kg.

Estimation of the concentrations of trace constituents in antifouling paints and primers is difficult; however, the results from the Marina del Rey survey indicate that antifouling paints typically contain between 35 to 78

TABLE 9 ESTIMATED TRACE METAL COMPOSITION OF ANTIFOULING PAINT AND PRIMERS

Type	Trace metal	Average concentration (%)
Antifouling paint	Copper	50
	Mercury	0.5*
	Arsenic	0.2†
Zinc chromate primer	Zinc	45
	Chromium	12
Read lead primer	Lead	25

* Assuming that mercury content of mercury paints is 5% and that mercury paints comprise 10% of total paint usage.

† Assuming that arsenic content of arsenic paints is 2% and that arsenic paints comprise 10% of total paint usage.

percent cuprous oxide (31 to 69 percent as copper). Although the use of mercury compounds in marine paint was banned recently by the U. S. Environmental Protection Agency, some paints containing about 7 percent mercury phenate and 3 percent yellow oxide of mercury and unspecified concentrations of arsenic are still being sold.

Based on Barry's report, it is estimated that antifouling paints contain, by weight, up to 67 percent cuprous oxide, 3.4 percent mercury phenate, 1.3 percent mercury oxide, and 1.7 percent phenarsazine chloride (zinc compound). In addition, primers, apparently used mostly on the larger commercial and naval vessels, may contain up to 45 percent zinc, 12 percent chromium (as zinc chromate), and 25 percent lead (red lead primer).

From the limited information available, estimates have been made of the average trace metal concentrations of antifouling paints and primers (Table 9). Using the foregoing estimated concentrations of trace metals, the annual input of such materials from these sources has been estimated and are reported in Table 10.

Zinc Anodes

The use of sacrificial anodes to control galvanic corrosion provides another source of trace metals to the Bight. Investigations at Marina del Rey indicate that about 90 percent of the sail and power craft harbored there employ zinc anodes to control galvanic corrosion. It is estimated that each boat uses approximately 4 to 5 kg of zinc per year for this purpose. Thus, it is estimated that about 160 metric tons of zinc per year are contributed to the Bight from the use of zinc anodes, most of which go into the marina harborage areas.

Data furnished by Bunker Hill, Inc., a major supplier of anode material, indicate that zinc anodes also contain approximately 0.05 percent cadmium, implying that approximately 0.1 metric tons per year of cadmium enter the Bight from this source.

It should be noted that the foregoing estimates do not consider the sacrificial anode contribution from commercial and naval vessels because of the lack of specific information on this source. Hence the estimates appear to be quite conservative.

TABLE 10 ESTIMATED TRACE METAL MASS EMISSION RATES (M tons/yr) FROM RECREATIONAL, COMMERCIAL AND NAVAL VESSELS TO THE SOUTHERN CALIFORNIA BIGHT*

Source	Gross tonnage	Arsenic	Cadmium	Chromium	Copper	Mercury	Lead	Zinc
Recreational vessels								
Antifouling paint	720	1.4	—	—	360	3.6	—	—
Zinc anode	160	—	0.1	—	—	—	—	160
Fuel	—	—	—	—	—	—	3.5	—
Commercial and naval Vessels†								
Antifouling paint	52	0.1	—	—	26	0.3	—	—
Zinc chromate primer	8.2	—	—	1	—	—	—	4.1
Red lead primer	24	—	—	—	—	—	6	—
TOTAL		1.5	0.1	1	390	3.9	9.5	160

* Excludes ocean dumping contributions.

† No estimates for gross tonnage of zinc anodes and fuel used.

Leaded Fuel

Union Oil Company, which operates the only fuel dock at Marina del Rey, reports its annual fuel sales of about 440,000 gallons of low-lead gasoline (containing 0.5 gm Pb/gallon) and 110,000 gallons of high octane gasoline (containing 3 gm Pb/gallon). Thus, the consumption of these fuels results in the release of about 0.55 metric tons of lead per year to the Bight from Marina del Rey fueled craft. If these fuel consumption and lead release data are applied to all recreational craft moored in the Marinas of the Southern California Bight, an input of lead to the Bight of approximately 3.5 metric tons per year is obtained.

Trace Material Mass Emission Rates

Table 10 presents a summary of the annual mass emission rates for trace metals reaching the Bight from selected sources associated with recreational, commercial, and naval vessel activity. It is recognized that some of the estimated inputs are crude; however, they represent the best information available. Moreover, it should be noted that the estimated vessel related mercury input of 4 metric tons per year is greater than the total input of mercury from treated municipal wastewater and surface runoff. The estimated vessel related input of copper (390 M tons/yr) is about two-thirds of the corresponding copper input to the Bight from municipal wastewater runoff.

OCEAN DUMPING

In an investigation of past ocean dumping practices, data on eight major types of wastes dumped from vessels into the Bight was reviewed. These were: (a) refinery wastes, (b) chemical wastes, (c) filter cake, (d) oil drilling wastes, (e) refuse and garbage, (f) radioactive wastes, (g) military explosives, and (h) miscellaneous types of wastes.

Figure 7 shows the location within the Southern California Bight of both active and inactive ocean dumping sites. Fourteen ocean dumping sites, which were approved either by the U. S. Army Corps of Engineers or by the California Regional Water Quality Control Boards, have been designated for waste dumping purposes since 1931. At present, dumping of various types of wastes at nine designated sites is prohibited by regulatory agencies, and disposal of military explosives at two other sites is still under moratorium issued by the Department of Navy in 1971.

Table 11 lists the major dumping sites, the total tonnage dumped during various periods, and the estimated present annual dumping rate for each type of waste.

Refinery Wastes

It is estimated that approximately 480,000 metric tons of petroleum refining wastes were dumped between 1946 and 1971, corresponding to an annual average of

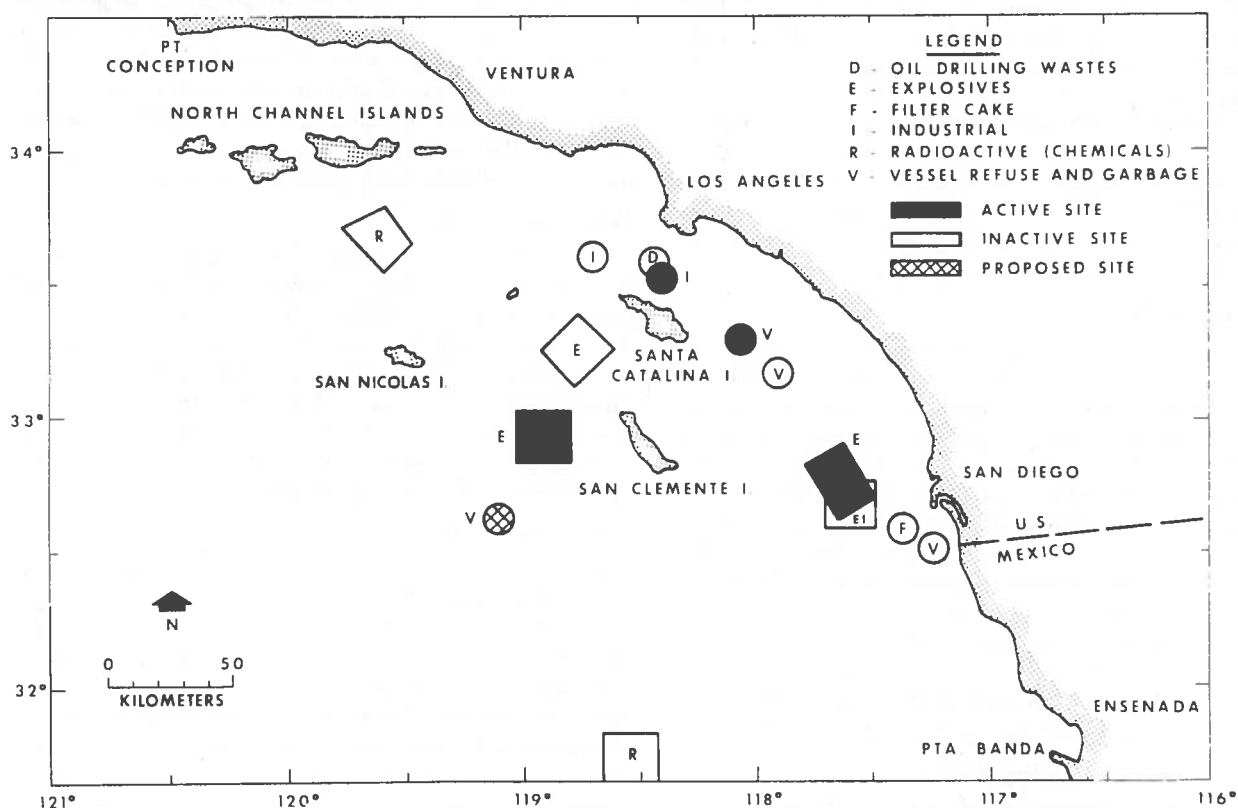


Figure 7. Locations of ocean dumping sites in the Southern California Bight.

TABLE 11 SUMMARY OF WASTES DUMPED INTO THE SOUTHERN CALIFORNIA BIGHT, 1931-71

Type of waste	Record period	Estimated total during record period (M tons)	Estimated present tonnage* (M tons/yr)
Refinery wastes	1946-71	480,000	1,800
Chemical wastes	1965-71	2,800	470
	1947-71	5,700	210
	1960-67	140	—
Filter cake	1969-70	320,000	—
Oil drilling wastes	1966-70	3,000,000	—
Refuse and garbage	1931-71	47,000	1,200
	1944-70	7,400	—
	1947-68	90,000	—
Radioactive wastes	1946-68	—	—
Military explosives	1945-70	—	—
Miscellaneous wastes	—	—	250

*Wastes for which no present tonnage estimate is given have been discontinued (military explosives by moratorium).

about 18,000 metric tons per year. However, the reported annual dumping rate has dropped to about 1,800 tons per year since 1968. The principal dumping site for refinery waste is in the San Pedro Channel. The specific composition of these refinery wastes are unavailable; however, they are believed to include spent caustic solutions, acid sludges, spent catalysts, petrochemical wastes, and chemical cleaning wastes. These materials surely must include trace metals, trace organics, and other potentially toxic substances, but quantitative information is not available.

Chemical Wastes

This type of industrial waste is dumped either in sealed containers or in bulk by tank barge, and includes waste material from aerospace, heat-treating, plating, film processing, chemical processing, and electronic manufacturing firms, industrial, medical, and academic laboratories, and military and other sources. Most of the recorded bulk tonnage, 210 metric tons/yr since 1947, is discharged approximately 15 km east of Catalina Island. Most of the containerized chemical wastes, 470 metric tons/yr since 1965, have been dumped in San Pedro Channel. Between 1960 and 1967, approximately 140 metric tons of chemical waste, sodium cyanide, were dumped in bulk 32 km west of Point Loma. However, such dumping there has been prohibited since 1967.

Filter Cake and Oil Drilling Wastes

Two types of relatively inert material, filter cake, 70 percent fixed and 30 percent volatile solids, and oil drilling wastes, similar to dredging spoils, were dumped to the Bight in large amounts for a short period. Filter

cake, consisting of about 50 percent perlite and 50 percent cellulose, is used in extraction of algin from kelp, and approximately 320,000 metric tons were dumped about 15 km west of Point Loma during 1969 and 1970. More than 3 million metric tons of oil drilling mud and cutting were dumped in the San Pedro Channel between 1966 and 1970. These two types of dumpings have been prohibited and discontinued since 1970.

Refuse and Garbage

Until recently, naval vessel refuse and garbage has been dumped into the Bight. Between 1947 and 1968, an estimated total of 90,000 metric tons were dumped in the vicinity of the Coronado Islands, and between 1944 and 1970 an estimated total of 7,400 metric tons were dumped 40 km southeast of Catalina Island. However, approximately 1,200 metric tons per year of refuse and garbage from commercial vessels is still being dumped approximately 16 km east of Catalina Island.

Other Types of Waste

Between 1945 and 1970, undetermined quantities of unspecified military explosives and toxic chemical ammunition have been dumped in several designated dumping sites in the Bight. Low-level radioactive wastes also have been dumped in the authorized locations during the period of 1946 to 1968. Dumping of military explosives and other wastes has been interrupted by a moratorium issued by the Navy in 1971. Dumping of radioactive wastes has been terminated since its prohibition in 1968.

Based on information furnished by H-10 Water Taxi Company, Los Angeles, approximately 250 metric tons

per year of undefined miscellaneous wastes are dumped in the Southern California Bight.

Trace Constituent Mass Emission Rates

Although there has been an attempt to quantify the distribution and amount of wastes in selected types dumped into the Bight, virtually nothing has been found in the public record regarding the concentration of specific pollutants in the wastes dumped. Thus, for pollutants such as trace metals, estimation of mass emission rates from this source is very difficult. Nevertheless, order-of-magnitude estimates of the probable upper limits of such mass emission rates have been attempted. It appears that only refinery and chemical wastes and some undefined miscellaneous wastes currently constitute any significant source of trace pollutants to the Bight. As shown in Table 11, it is estimated that approximately 1,800 metric tons per year of refinery waste and 1,000 metric tons per year of chemical and miscellaneous wastes were dumped into the Bight off Los Angeles and San Diego in 1971. It seems reasonable to assume that, on the average, these wastes would not contain more than 0.5 to 1 percent, by weight, of any one of the trace constituents being investigated by Southern California Coastal Water Research Project, with the exception of iron and zinc. It is likely that these wastes might contain up to 2 percent zinc and 10 percent iron. Owing to the value of mercury and silver, upper limits for their average concentrations are assumed to be an order-of-magnitude lower than the general level taken for most of the other metals. Based on these extremely rough assumptions, upper limit

estimates of present annual trace metal mass emission rates are presented in Table 12.

AERIAL FALLOUT

Limited data are available on aerial fallout rates of trace metals to the Bight. This source is difficult to quantitate for several reasons, including the high horizontal velocity compared to the vertical velocity of airborne particles, the diffuse nature of the source, the relatively high constituent gradients that may exist near the densely-populated areas, and the large area of the Bight.

Rainfall Washout

Several recent studies have provided some insight into this subject. Estimates of metal contributions from rain falling directly on the Bight (6), conducted on Catalina Island from September 1966 to January 1967, are shown in Table 13. The median metal concentration values were used, and an average annual rainfall rate of 40 cm (15 in) over a Bight area of 100,000 sq km was assumed. It should be noted that these data do not include the contribution of metals to the Bight from dry fallout.

The results of this rough estimate indicate, as seen in the summary Table 15, that the mass emission rate of lead from direct rainfall washout on the Bight is significantly higher than that from the discrete sources, municipal wastewater and surface runoff. The mass emission rates of nickel and iron from direct rainfall washout, on the contrary, are much lower than those from the discrete sources to the Bight. For copper,

TABLE 12 UPPER-LIMIT ESTIMATES OF TRACE METAL MASS EMISSION RATES TO THE SOUTHERN CALIFORNIA BIGHT FROM OCEAN DUMPING

Metal	Assumed maximum concentration (% by wt)	Est. max. mass emission rate* (M tons/yr)
Silver	0.05	1.5
Cadmium	0.5	14
Cobalt	0.5	14
Chromium	1	28
Copper	1	28
Mercury	0.05	1.5
Nickel	1	28
Lead	1	28
Zinc	2	56
Iron	10	280
Manganese	1	28

*Based on estimated 1971 dumping tonnage of 1800 M tons/yr of refinery wastes and 1000 M tons/yr of chemical and miscellaneous wastes.

TABLE 13 ESTIMATED TRACE METAL MASS EMISSION RATES FROM DIRECT RAINFALL ON THE SOUTHERN CALIFORNIA BIGHT

Metal	Median concentration* in rainwater ($\mu\text{g}/\ell$)	Mass emission rate (M tons/yr)
Copper	10	400
Mercury	0.2	8
Nickel	1	40
Lead	25	1000
Zinc	55	2200
Iron	1	40
Manganese	12	480

*From Reference 6.

mercury, zinc, and manganese, comparable amounts are contributed from rainfall washout and discrete sources.

Dry Fallout

It is possible that the contribution of particulate-borne materials to the Bight via dry fallout may exceed those due to direct rainfall washout. For example, the fallout rate of lead on dust particles ($24 \text{ mg Pb}/\text{m}^2\text{-yr}$) was about two to three times as large as that due to rainfall ($10 \text{ mg Pb}/\text{m}^2\text{-yr}$) (7). Isotopic analysis confirmed that this lead was not of soil origin, but that essentially all of it originated in the combustion of leaded gasoline. Extrapolation of the La Jolla fallout rates to the entire Bight yields annual lead input rates through dry and wet fallout of approximately 2,400 and 1,000 metric tons, respectively. It is interesting to note that the latter value is about the same as that obtained by extrapolating the Catalina Island rainfall data (6).

In 1968, approximately 23,000 metric tons of lead were combusted in gasoline in California (7). It is probable that at least half of this consumption occurred in southern California. Thus, approximately 10,000 metric tons of lead are released annually to the atmosphere in this area. The previous data suggest that as much as one-third of this amount may fall directly into the coastal waters, depending upon the degree to which fallout rates at La Jolla and Catalina Island are representative of fallout to the entire Bight.

ADVECTIVE TRANSPORT

At the regional scale considered here, a potentially significant but largely unevaluated source of trace metals transported into the Southern California Bight is the California current which carries seawater and associated constituents into the Bight (Figure 1). The complex flow pattern keeps the water in the Bight for some time, during which time various physical, chemical, and biological processes can occur. These processes may result in the retention of significant amounts of some constituents in the Bight. These processes may also

result in the removal of significant amounts of other constituents from the Bight in the advective flow from the Bight.

Mass Emission Rates

The surface area of the Bight has been estimated to be about $1 \times 10^{11} \text{ sq m}$. Assuming the mixed surface layer depth to be 50 m, the volume of the mixed layer of the Bight is computed to be $5 \times 10^{12} \text{ cu m}$. It has been shown that the mean residence time of water in the mixed layer is on the order of 3 months (1). Thus the advective flow rate of the California current is estimated to be approximately $2 \times 10^{13} \text{ cu m/yr}$.

Assuming that the trace metal concentrations reported for ocean waters are representative of California current waters, the mass transport rates of trace metals into the Bight by the California current are estimated to be as shown in Table 14. Although the role of the California

TABLE 14 ESTIMATED TRACE METAL MASS TRANSPORT RATES TO THE SOUTHERN CALIFORNIA BIGHT BY THE CALIFORNIA CURRENT

Metal	Concentration ($\mu\text{g}/\ell$)	Mass transport rate (M tons/yr)
Silver	0.3	6,000
Cadmium	0.1	2,000
Cobalt	0.4	8,000
Chromium	0.2	4,000
Copper	3	60,000
Mercury	0.03	600
Nickel	7	140,000
Lead	0.3	6,000
Zinc	10	200,000
Iron	3	60,000
Manganese	2	40,000

current as a source of trace metals to the Bight may be different from those of other sources, the estimated mass transport rates of most of the trace metals by advective transport far outweigh the mass emission rates from other sources. For example, the mass transport rate of mercury by the California current is estimated to be about 600 metric tons per year, which is about 30 times the amount of mass emission rates of mercury from all other sources to the Bight (8). However, for chromium, lead, and iron, the annual advective transport rates exceed the sum of the other, principally terrestrial inputs by only a few factors. At least for chromium and lead, whose terrestrial inputs are believed to be largely anthropogenic, these inputs appear to be a significant perturbation to the natural mass balance of metals in the Bight.

The circulation of marine waters off southern and Baja California is such that increased levels of trace constituents in the biota to the west and south of the densely populated southern California coastline may in fact be due to sources far to the north. For example, anomalously high levels of zinc-65 were found in the coastal mussel, *Mytilus californianus*, collected during 1963 to 64 from northern Baja California, where the California current sweeps eastward and impinges on this coast (9). The suggestion that this anomalous zinc-65 was being carried by the California current was further supported by increasing concentration of this radiometal in samples of the oceanic gooseneck barnacle, *Lepas anatifera*, collected toward the west off southern California. In contrast to zinc-65, the other two radiometals measured, cobalt-60 and manganese-54, did not show significant differences between the nearshore of La Jolla and California current specimens. The levels of these two nuclides also were approximately constant in *M. californianus* from both the southern California and Baja California stations. This argues

against nuclear fallout as the source of the anomalous zinc-65, and suggest that the Columbia River effluent, which carried approximately 55,000 pCi zinc-65 per month into the water off Washington and Oregon, was elevating zinc-65 concentrations in the marine biota 1,900 km to the south. Therefore, the dense population center off San Francisco, and the intense agricultural activity in the large central valley of California, both may be important source regions of runoff and airborne pollutants that are introduced into the California current north of Point Conception. Any such contaminants from the north could contribute to elevated levels in the marine biota to the west and south of southern California.

There is another important aspect of possible pollutant transport from the north. As the California current moves slowly down the coast of California, certain trace constituents introduced into the surface layer off Washington, Oregon, or northern California may be incorporated into the food web. If these substances are subject to trophic or feeding level concentration, higher levels might be expected in a specified organism caught off southern California, compared to levels observed in the same organism caught to the north. Ocean current advection from the north could play an important part in contributing to elevated levels of certain pollutants in the biota off southern and Baja California.

SUMMARY

In Table 15 we have summarized our estimates of trace metal annual mass emission rates to the Bight from the various sources for which sufficient data are available. Although the values are not all of comparable reliability, and several potentially important modes are not quantified at all, the summary does provide useful insight into which of the input modes studied are of

TABLE 15 ESTIMATED TRACE METAL MASS EMISSION RATES (M tons/yr) FROM VARIOUS SOURCES TO THE SOUTHERN CALIFORNIA BIGHT, 1971

Metal	1 Municipal wastewater	2 Surface runoff	3 Direct rainfall	4 Vessel* coating	5 Ocean dumping maxima	6 Sum of col. 1 through 5	7 Advective transport
Silver	15	1	—	—	2	18	6,000
Cadmium	54	1	—	0.1	14	69	2,000
Cobalt	3	5	—	—	14	22	8,000
Chromium	640	25	—	1	28	690	4,000
Copper	570	18	400	390	28	1,400	60,000
Mercury	3	0.1	8	4	2	17	600
Nickel	310	17	40	—	28	400	140,000
Lead	210	90	1,000	10	28	1,300	6,000
Zinc	1,700	100	2,200	160	56	4,200	200,000
Iron	6,000	26,000	40	—	280	32,000	60,000
Manganese	100	180	480	—	28	790	40,000

*Including vessel antifouling paints, primers, and spent fuel residues.

probable importance. For example, of the estimated input routes of locally derived copper and mercury, municipal wastewater discharge, vessel antifouling paint, and direct rainfall all appear to have about the same importance. For zinc, municipal wastewater and direct rainfall appear to predominate. In the case of lead, the surface runoff input is the same order as that of municipal wastewaters, but these sources probably contribute an order of magnitude less lead to the waters of the Bight than does aerial fallout. Cobalt, iron, and manganese are the only other trace metals studied that have surface runoff inputs of approximately the same importance as those of municipal wastewaters, and the inputs of these metals via both modes may be more dependent on natural than anthropogenic sources. However, for silver, cadmium, chromium, and nickel, present data suggest that municipal wastewater discharge to the Bight dominate all other locally-derived inputs. Clearly, more comprehensive and reliable information on the importance of wet and dry fallout, and of vessel-protective measures, are needed in the above comparison. Further, the lack of any reliable estimates of inputs of trace metals from direct industrial discharges represents a major deficiency in this mass balance attempt. Correction of these various deficiencies probably should assume a higher priority than improving our knowledge on the inputs from ocean dumping, as the present best estimates of probable maximum values suggest that only for cobalt does it appear likely that ocean dumping could represent the major local source. With the exception of chromium, lead, and iron, for each of the trace metals studied the sum, see column 6, Table 15, of all estimated yearly inputs emanating from the coastal plain of the Bight is one to two orders of magnitude below the estimated annual flux of the metal through the Bight via ocean current advection. Although this situation may be natural in the case of iron, the fact that local anthropogenic inputs of the other two metals are, to the first order comparable to that of gross advection suggests that chromium and lead transport from the urban areas may represent a specially important perturbation of the natural metals budget for the regional ecosystem. However, it is difficult to draw any very reliable conclusions from the comparison of local versus advective inputs until more is known about the net addition of metals to, or removal from, the Bight due to bottom sediment interactions and to ocean circulation. Further, the physical-chemical state of a metal advected into the Bight may be significantly different from that injected via a particular local input mode. In addition to better data on input rates of a particular trace metal to the Bight, much more needs to be learned about (a) the nature of the metal being transported to the local marine waters, (b) the changes that take place in the metal following introduction to these waters, and (c) the transport processes and eventual fate of the metal in the ocean ecosystem.

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