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ABSTRACT

Rates of polychlorinated biphenyl (PCB) transport via several routes to the coastal waters off southern California have been quantified. Submarine discharge of municipal wastewater was the single largest source, contributing 5,400 kg of these synthetic organics in 1974. However, inputs via this route appear to be decreasing, as the corresponding estimate for 1971 exceeded 19,000 kg. One result of this continuing discharge is that bottom sediments around the largest outfalls contain up to 10 ppm PCB. Aerial fallout also appears to be an important source; the estimated deposition rate of 1254 PCB onto the coastal waters during 1973-74 was 1,800 kg/yr--highest inputs were measured off Los Angeles. This region also contributed the most PCB in surface runoff, although less than 800 kg were discharged annually during 1972-73 via storm and dry-weather flow. Direct industrial discharges to San Pedro and San Diego Harbors did not appear to be a major PCB source, totaling less than 250 kg/yr. Although antifouling paints may have been an important source in the past, present inputs are negligible. Despite high levels measured in three major harbors, we found no evidence of significant PCB transport from these harbors to the adjacent coastal waters.

CONTENTS

INTRODUCTION

Polychlorinated biphenyls (PCB's) have been used for more than 4 decades in a wide variety of industrial products (Jensen 1970; Jay 1970). Within the last 10 years, the problem of environmental contamination by these synthetic organic compounds has become a subject of increasing concern (Risebrough 1968; Kuratsune et al. 1972; de Long et al. 1973). In this memorandum, we report the results obtained to date on the routes by which PCB's enter one coastal marine ecosystem, the Southern California Bight (Figure 1), and the rates at which inputs occur.

The coastal plain of southern California is inhabited by approximately 11 million people--about 5 percent of the nation's population. The wide variety of activities occurring here provides ample opportunity for contamination of the adjacent marine ecosystem (Young et al. 1973). Submarine discharge of municipal (domestic and industrial) wastewaters, which constitute the major input of freshwater to the Bight, is one potential source of such contamination. Another is the runoff of surface waters, composed of both storm and dry-weather flow, via numerous channels on the plain. A third is deposition of contaminants directly onto the sea surface from the relatively polluted atmosphere of this region. A fourth potentially important source of contaminants is industrial effluent discharged directly into nearshore marine waters, principally within San Pedro and San Diego Harbors. The vessel antifouling paints used in the harbors and the numerous other anchorages located along the coast of the Bight are a fifth source of pollution. A sixth is the flushing of accumulated contaminants from these harbors and marinas to the coastal waters. Finally, contaminants from other regions lying to the north may be transported into this ecosystem via the California Current, which flows through the Bight (Young and Folsom 1973).

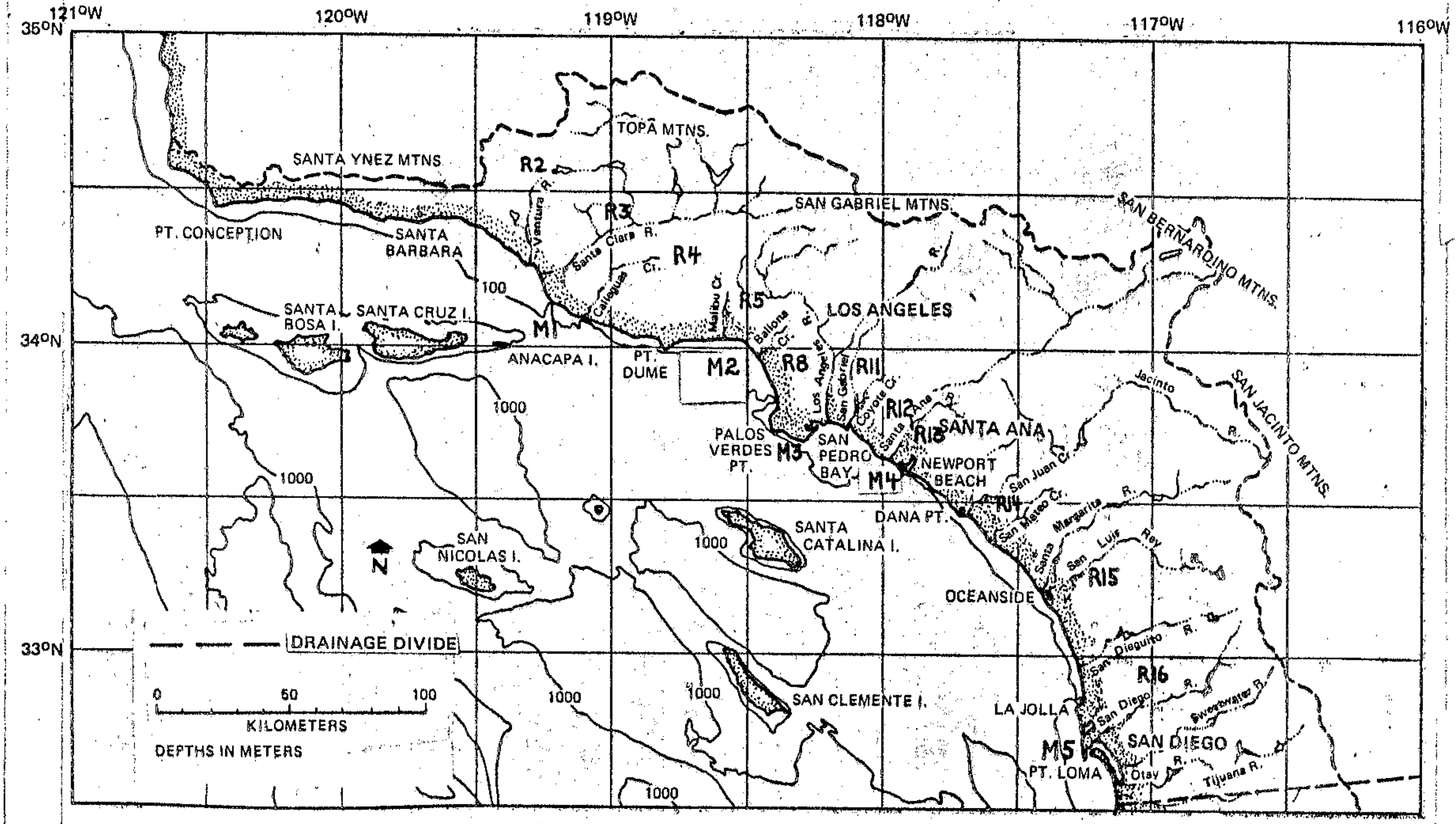

Figure 1. The Southern California Bight. Major submarine discharges of municipal wastewaters indicated are M1, Oxnard City; M2, Hyperion, Los Angeles City; M3, JWPCP, Los Angeles County; M4, Orange County; and M5 San Diego City. Names of the major drainage basins shown (R2 through R16) are listed in Table 4. San Pedro Harbor is located in San Pedro Bay.

MUNICIPAL WASTEWATERS

Every day, over 1 billion gallons (approximately 4×10^9 l) of municipal wastewaters are discharged from submarine outfalls to the Southern California Bight (Southern California Coastal Water Research Project 1973). Almost 95 percent of these wastewaters are released by five major treatment plants, whose locations are shown on Figure 1. By sampling these five plants, we have been able to obtain a reasonably representative picture of PCB inputs to the Bight via this route.

Once or twice a year since 1972, the Coastal Water Project has obtained 1-week samples of effluent from each plant. During the week, three to six grab samples of final effluent were collected daily in cleaned glass jars and refrigerated; at the end of the week, these samples were composited and extracted. Details of our laboratory procedures are presented in Appendix A.

Because of the significant analytical uncertainties associated with identification and quantification of different PCB mixtures in wastewaters, we have devoted considerable effort to intercalibration. Several replicate pairs of samples were usually obtained during each 1-week collection period to permit intercalibration exchanges with the laboratories of the treatment plants, other government agencies, and universities. During 1973, replicate pairs of composited JWPCP* wastewaters were analyzed by the Project, by Dr. R. Risebrough and B. de Lappe at Bodega Marine Laboratory (University of California, Berkeley), by Dr. S. Pavlou at the University of Washington, and by the County Sanitation Districts of Los Angeles County. The following year, 1-week composite replicates from each of the five major treatment plants were analyzed at the Project and Bodega laboratories; each effluent was also analyzed at the laboratory of the plant from which it was taken. The results are presented in Appendix B. The Project, Bodega, and University of Washington laboratories obtained quite consistent results, with PCB concentrations usually agreeing within a factor of 2.

Thus, we have combined the appropriate results obtained during 1972-75 and estimated representative effluent concentrations and annual mass emission rates for 1242 PCB and 1254 PCB (these two

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*Joint Water Pollution Control Plant, the treatment plant of the County Sanitation Districts of Los Angeles County.

mixtures,* which average 42 percent and 54 percent chlorination by weight, respectively, are the most common types of polychlorinated biphenyls characterized in samples taken in the Bight). The data presented in Table 1 and summarized below indicate that, since 1971, there has been a significant decrease in the amount of PCB's discharged through these outfall systems.

Year	1242 PCB (kg/yr)	1254 PCB (kg/yr)	Total PCB (kg/yr)
1972	>19,200	>250	>19,400
1973	>1,900	1,500	>3,400
1974	4,300	1,100	5,400
1975	1,900	700	2,600

Although the data for the earlier years are incomplete, one of the principal causes of this decrease appears to be reductions in PCB concentrations in the effluent of the largest discharger, the JWPCP, whose outfalls are located off the Palos Verdes Peninsula. (Monitoring data from the County Sanitation Districts of Los Angeles County also suggest at least an order-of-magnitude reduction in total PCB levels over this period.) Most of this PCB input is best characterized as 1242 PCB.

The municipal wastewater discharges have resulted in obvious contamination of the bottom sediments around the larger outfall systems. Figure 2 illustrates concentrations of total PCB measured in surface sediments (0 to 2 cm) collected in 1971 by box corer around the Hyperion outfalls in Santa Monica Bay. Figure 3 shows vertical profiles of total PCB obtained from 1971 box corer samples collected off Palos Verdes Peninsula near the major diffuser and at two stations downcurrent of this diffuser. Figure 4 illustrates total PCB concentrations measured in surface sediment samples collected around the 8-km Orange County outfall off Newport Beach in 1975, 4 years after this outfall became operational. (Individual 1242 and 1254 PCB concentrations in sediments from around these three outfall systems are available from the Project.)

Maximum concentrations of PCB measured near the 7-mi. Hyperion outfall (the sludge line) and the JWPCP outfalls were similar, on the order of 10 ppm (mg/dry kg). However, within a few kilometers of the Hyperion sludge discharge, which is at the head of Santa Monica Canyon, the surface sediment concentrations of PCB had fallen to about 0.2 ppm. On the Palos Verdes Peninsula, large vertical gradients were observed in the upper 20 cm of sediments collected within a few kilometers of the JWPCP diffusers; values fell by one to two orders of magnitude over that distance. We previously calculated that, in 1972, the upper 30 cm of bottom sediments in a 50-sq-km area of this discharge zone contained approximately 200 metric tons of DDT and its

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*Mixtures with gas chromatographic profiles that most closely resemble those of Aroclor 1242 and Aroclor 1254, respectively.

Table 1. Representative PCB concentrations and mass emission rates from major municipal wastewater discharges to the Southern California Bight, 1972-75.

Discharger	Total Suspended Solids (mg/l)	Flow (mgd)	1242 PCB Concentration (μg/l)	1242 PCB Mass Emission Rate (kg/yr)	1254 PCB Concentration (μg/l)	1254 PCB Mass Emission Rate (kg/yr)
1972						
JWPCP	290	350	24	11,600	ND	-
Hyperion						
Effluent	90	330	ND	-	0.3	140
Sludge	7,670	4.6	280	1,780	ND	-
Orange Co.	150	150	28	5,800	ND	-
Point Loma	140	95	ND	-	0.9	120
Oxnard	70	10	ND	-	0.2	3
Total		940		>19,180		>260
1973						
JWPCP	260	360	3.9	1,930	1.6	790
Hyperion						
Effluent	80	340	ND	-	0.38	180
Sludge	7,500	4.8	ND	-	26	170
Orange Co.	150	150	ND	-	1.4	290
Point Loma	160	100	ND	-	0.48	70
Oxnard	130	10	ND	-	0.35	6
Total		965		>1,930		1,510
1974						
JWPCP	280	350	1.9	910	0.76	360
Hyperion						
Effluent	80	340	0.11	50	0.24	110
Sludge	7,300	4.7	72	470	50	320
Orange Co.	110	170	8.0	1,890	0.89	210
Point Loma	140	100	6.6	950	0.74	110
Oxnard	170	10	0.1	1	0.24	3
Total		975		4,270		1,110
1975*						
JWPCP			0.6	290	0.52	250
Hyperion						
Effluent			0.06	30	0.18	80
Sludge			34	220	28	180
Orange Co.			5.2	1,230	0.63	150
Point Loma			1.1	160	0.39	60
Oxnard			0.03	0.4	0.16	2
Total				1,930		720

*1974 flow values (mgd) used for calculations of 1975 mass emission rates.

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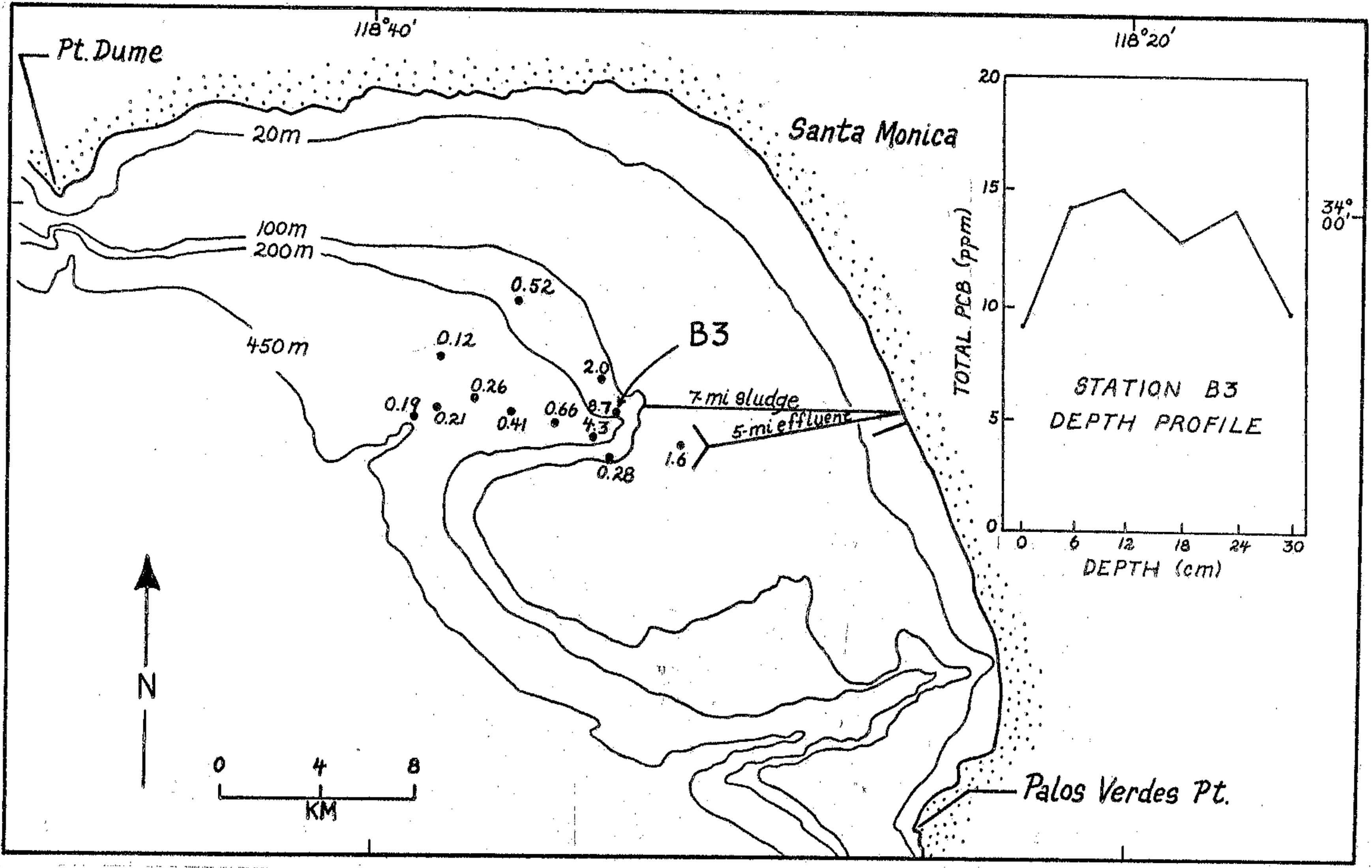

Figure 2. Concentrations of total PCB (mg/dry kg) measured in the top 2 cm of bottom sediments collected during July 1971 off the Hyperion submarine outfalls in Santa Monica Bay.

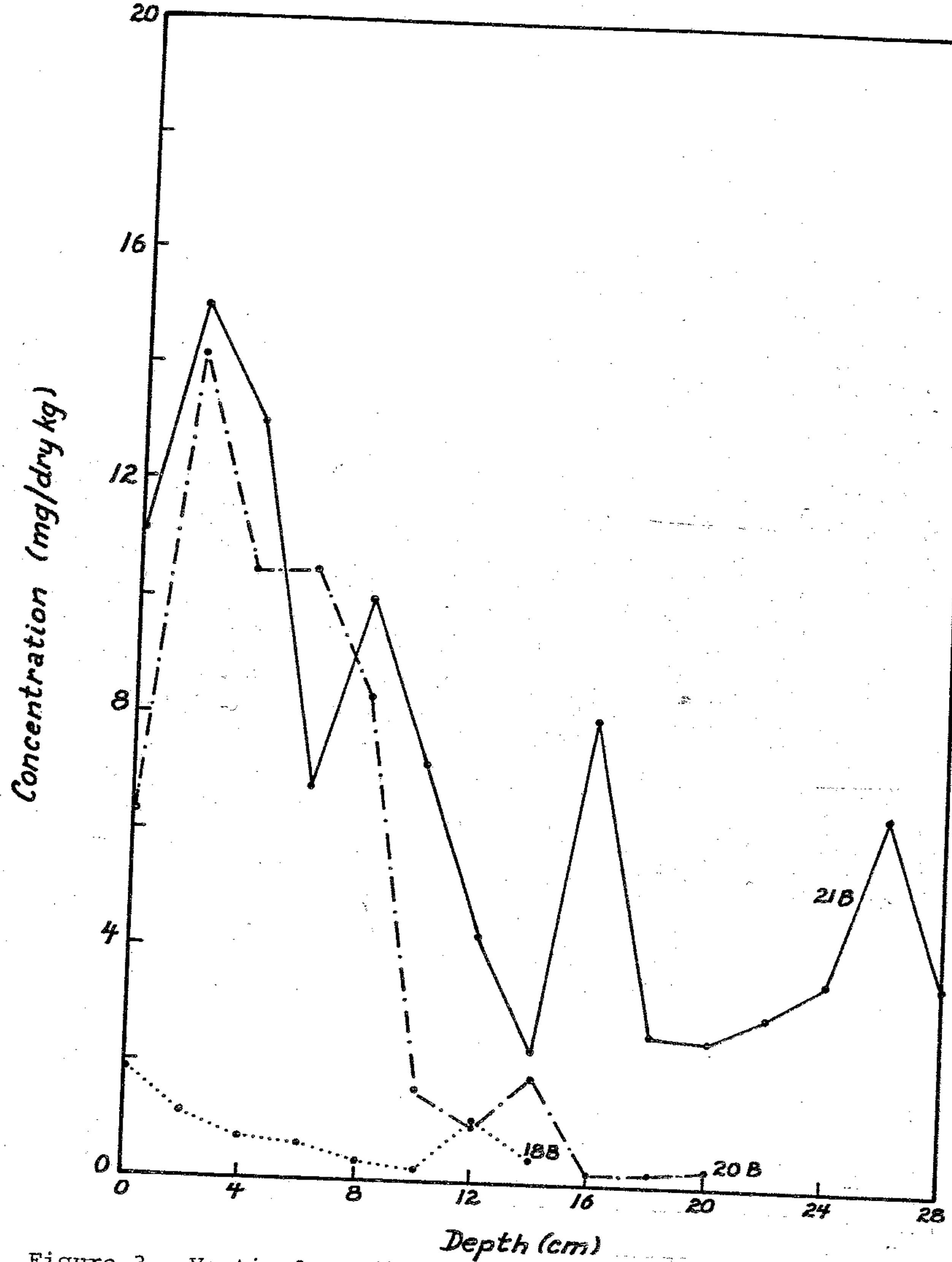

Figure 3. Vertical profiles of total PCB concentrations in bottom sediments, Palos Verdes shelf, July 1971. Stations 20B, 21B, and 18B are located near the 60-m depth contour, 0, 1.5, and 7 km northwest of the JWPCP "wye" outfall diffuser, respectively.

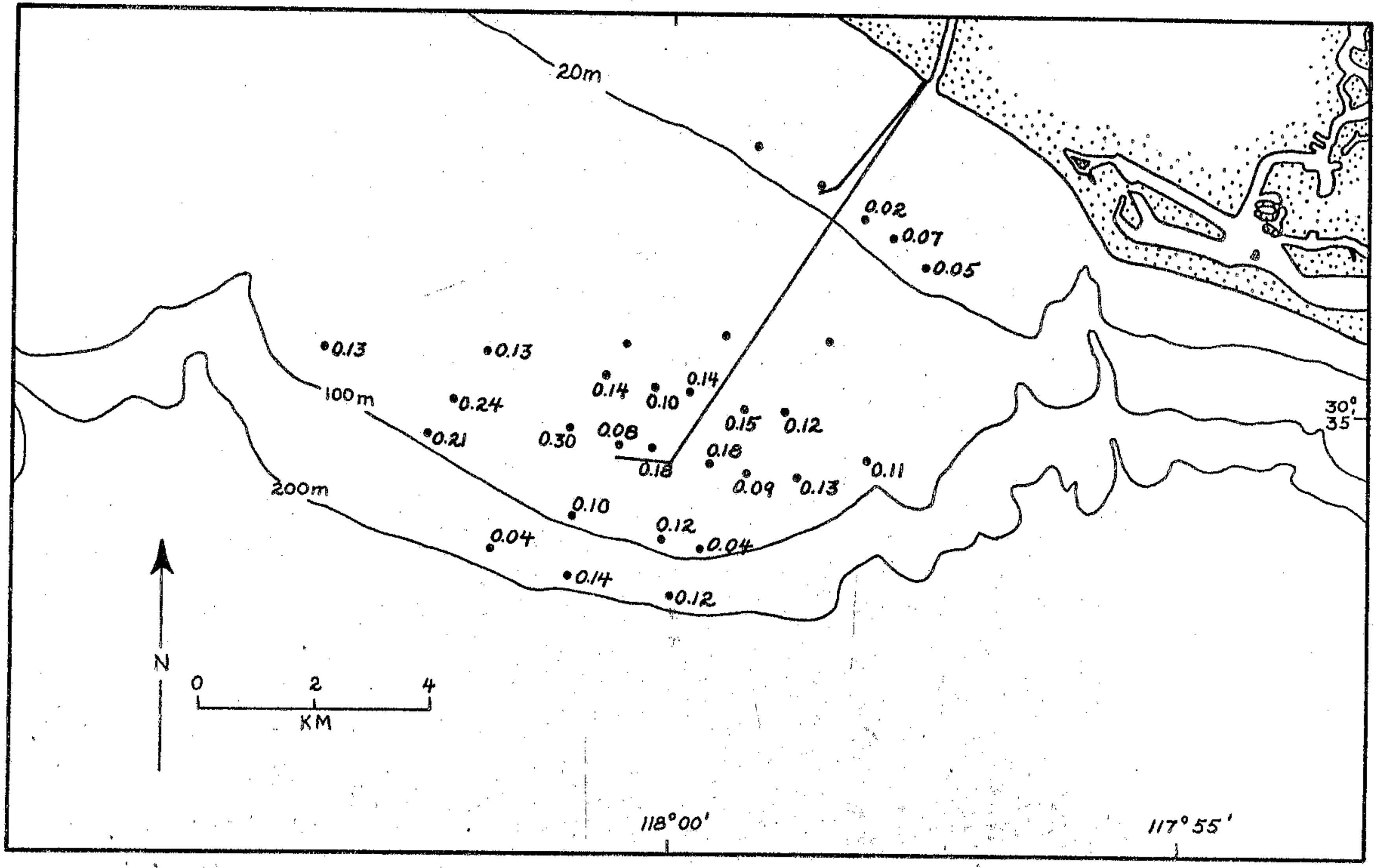

Figure 4. Concentrations of total PCB (mg/dry kg) measured in the top 2 cm of bottom sediments collected near the Orange County outfalls, July 1975.

residues (McDermott et al. 1974); we believe this estimate to be within 25 percent of the actual value. Although we have much fewer data on the distribution of PCB in these sediments, extrapolation of our present information and use of observed PCB-to-DDT ratios suggests that the load of 1254 PCB in these sediments is on the order of 6 metric tons.

Surface sediments around the Orange County 8-km outfall did not exhibit large gradients of total PCB; the median value was 0.1 ppm, with values ranging from 0.04 to 0.3 ppm. Similar concentrations were measured 6 months after discharge commenced in 1971, indicating little buildup of PCB's in these sediments since then. However, the 1975 samples were characterized by unusually distinct gas chromatographic profiles of 1242 PCB. This is consistent with the relatively high 1242/1254 PCB ratios (9 and 8, respectively) measured in 1974 and 1975 composites of Orange County final effluent (Table 1). In comparison, typical ratios of 1242/1254 PCB in Hyperion and JWPCP emissions averaged about 1.5 during this period.

SURFACE RUNOFF

In Water Year 1971-72, we conducted a detailed survey of chlorinated hydrocarbon inputs to the Southern California Bight via storm runoff. During the major storms of the year, time series of depth-integrated samples were collected in an all-metal sampler near the mouths of four major drainage channels--the Santa Clara River, Ballona Creek, the Los Angeles River, and the Santa Ana River (Figure 1). Analyses of the preserved samples were conducted by Dr. R. Risebrough and B. de Lappe at Bodega Marine Laboratory.

The following year, we resurveyed one of these channels on a limited basis. Los Angeles River runoff was sampled during four storms and analyzed in our laboratory. Subsequently, two seasonal collections of dry-weather flow were made from channels located throughout the Bight. The analysis procedures used in both cases are described in Appendix A.

Final hydrographic data for both water years were then obtained from local flood control districts and the U.S. Geological Survey. Figure 5 illustrates the pattern often observed--a correlation between concentrations of chlorinated hydrocarbons and suspended solids and rate of flow. In the case of the storm data, flow-weighted mean concentrations of the chlorinated hydrocarbons were calculated as the most representative characterization of the results, because the concentrations usually vary greatly during any given storm. For the dry-weather flow, values from the two seasonal collections were averaged for each channel or region.

Table 2 presents final flow-weighted mean PCB concentrations in 1971-72 storm runoff in the four channels sampled. In Table 3, we list flow-weighted mean PCB concentrations for the four Los Angeles River storm flows sampled in 1972-73 and compare the yearly averages for this channel with those for 1971-72. To aid in the comparison, we also list corresponding results for total DDT and Dieldrin.

In light of the variation in concentrations during any given storm, and the fact that two water years and two laboratories were involved, the agreement between the flow-weighted means is

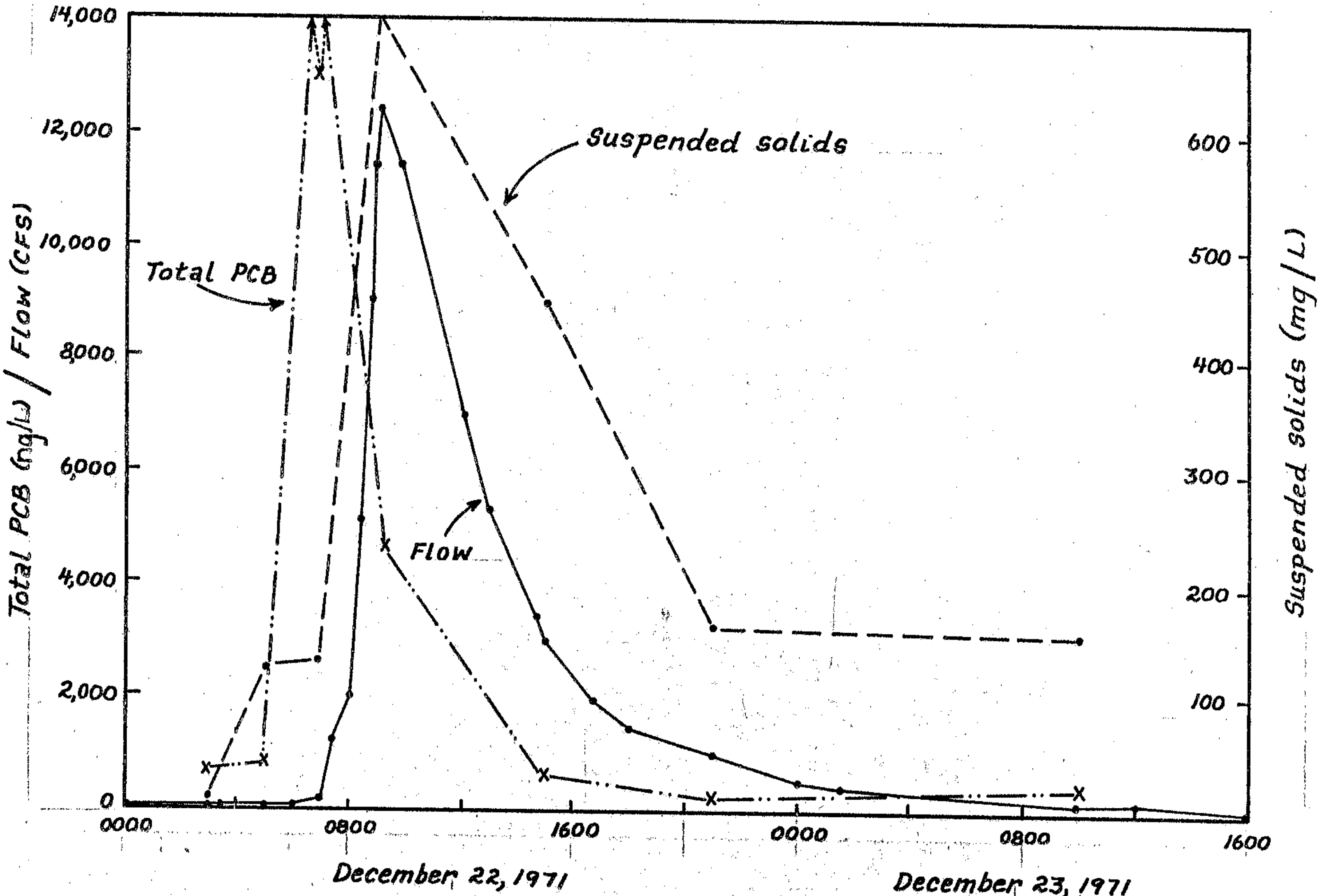

Figure 5. Concentrations of total PCB (ng/l) and suspended solids (mg/l) and discharge rate (cu ft/sec) measured in Los Angeles River storm runoff during December 1971.

Table 2. Flow-weighted mean concentrations (µg/l) of PCB in storm runoff via major channels in southern California, 1971-72.

Basin No.[1]	Channel	Volume[2] (10^6 cu m)	1242 PCB	1254 PCB	Total PCB
R-3	Santa Clara	9.0	0-0.13	0-0.16	0-0.29
R-8	Ballona	2.6	0-0.43	0.47	0.47-0.90
R-10	Los Angeles	9.0	1.2-1.9	0.9-1.1	2.1-3.0
R-13	Santa Ana	1.0	ND	0.11-0.23	0.11-0.23

1. Drainage basins shown on Figure 1.
2. Accumulated storm flow from which samples were obtained for chlorinated hydrocarbon analysis.

Table 3. Flow-weighted mean concentrations (µg/l) of chlorinated hydrocarbons in Los Angeles River storm runoff, 1971-73.

Date	Total DDT	Dieldrin	1242 PCB	1254 PCB	Total PCB
4-7 Dec 72	0.66	0.12	0-1.1	0.51	0.5-1.6
27 Feb to 1 Mar 73	1.5	0.16	0-3.2	1.0	1.0-4.2
6-9 Mar 73	0.78	0.16	0-1.0	0.83	0.8-1.8
11-12 Mar 73	0.60	0.08	0-2.6	0.71	0.7-3.3
Average Blank	<0.004	<0.001	<0.002	<0.001	<0.003
Averages					
1972-73	0.92	0.14	0-1.9	0.77	0.8-2.7
1971-72	0.93	0.16	1.2-1.9	0.9-1.1	2.1-3.0

remarkably good. The 1972-73 means for each constituent in each storm flow agree within about a factor of 2, and the means for the successive years obtained from the Bodega and Project measurements are even closer (e.g., total DDT: 0.93 vs. 0.92 ppb; Dieldrin: 0.16 vs. 0.14 ppb; 1254 PCB: 0.92 to 1.10 vs. 0.77 ppb). The greatest discrepancy results from the fact that our 1242 PCB values were often quantified only as upper limits. Thus, in obtaining a range for total PCB, the lower limit was taken as zero. As a result, our average lower limit for total PCB (0.77 ppb) is several times lower than the 2.16-ppb value obtained from the 1971-72 Bodega data. However, the upper limit estimates of the two laboratories for total PCB are in good agreement (3.0 vs. 2.7 ppb, respectively).

Because of this general agreement, we concluded that the results from the 1971-72 Bight-wide storm runoff survey could be safely extrapolated to the following year, on the basis of relative

Table 4. Estimated PCB mass emission rates via storm runoff into the Bight, 1972-73.[1]

Basin No.	Channel	Volume (10^6 cu m)	1242 PCB Mean Concentration (µg/l)	1242 PCB Mass Emission Rate (kg/yr)	1254 PCB Mean Concentration (µg/l)	1254 PCB Mass Emission Rate (kg/yr)	Total PCB Mean Concentration (µg/l)	Total PCB Mass Emission Rate (kg/yr)
R-2	Ventura R.[2]	45.3		0-5.9		0-7.2		0-13
R-3	Santa Clara R.	93.4	0-0.13	0-12	0-0.16	0-15	0-0.29	0-27
R-4	Calleguas Cr.[2]	13.1		0-1.7		0-2.1		0-3.8
R-5	Malibu Cr.[2]	26.9		0-3.5		0-4.3		0-7.8
R-6	Topanga Cr.[2]	6.5		0-0.8		0-1.0		0-1.8
R-7	Sawtelle-Westwood Ch.[3]	11.6		0-5.0		5.4		5.4-10
R-8	Ballona Cr.	48.3	0-0.43	0-21	0.47	23	0.47-0.90	23-44
R-9	Dominguez Ch.[3]	15.7		0-6.8		7.4		7.4-14
R-10	Los Angeles R.	199	0-1.8	0-380	0.77	150	0.77-2.7	150-530
R-11	San Gabriel R.[4]	33.7		0-64		26		26-90
R-12	Coyote Cr.[3]	48.1		0-21		23		23-44
R-13	Santa Ana R.	16.7	ND	-	0.11-0.23	1.8-3.8	0.11-0.23	1.8-3.8
R-14	San Juan Cr.[5]	6.0		-		0.7-1.4		0.7-1.4
R-15	San Luis Rey[5]	4.9		-		0.5-1.1		0.5-1.1
R-16	San Diego R.[5]	5.1		-		0.6-1.2		0.6-1.2
	All Areas	574		0-520		240-270		240-790

1. Basins shown on Figure 1. 1972-73 storm runoff concentrations used in calculations for the Los Angeles River; 1971-72 concentrations used in calculations for all other channels.
2. PCB concentrations estimated using data for Santa Clara River.
3. PCB concentrations estimated using data for Ballona Creek.
4. PCB concentrations estimated using data for the Los Angeles River.
5. PCB concentrations estimated using data for the Santa Ana River.

Table 5. Estimated PCB mass emission rates via dry-weather surface runoff into the Bight, 1972-73.

Basin No.[1]	Channel	Volume (10^6 cu m)	1242 PCB Mean Concentration (µg/l)	1242 PCB Mass Emission Rate (kg/yr)	1254 PCB Mean Concentration (µg/l)	1254 PCB Mass Emission Rate (kg/yr)	Total PCB Mean Concentration (µg/l)	Total PCB Mass Emission Rate (kg/yr)
R-1	Arroyo Grande/ Santa Ynez R.		0-0.04		0.02		0.02-0.06	
R-2	Ventura R.	13.2	0-0.04	0-0.53	0.02	0.26	0.02-0.06	0.3-0.8
R-3	Santa Clara R.[2]	0.1		0-0.004		0.002		0.002-0.006
R-4	Calleguas Cr.[2]	6.4		0-0.26		0.13		0.1-0.4
R-5	Malibu Cr.[2]	4.7		0-0.19		0.09		0.1-0.3
R-6	Topanga Cr.[2]	1.2		0-0.05		0.02		0.02-0.07
R-7	Sawtelle-Westwood Ch.[3]	3.1		-		0.12-0.19		0.1-0.2
R-8	Ballona Cr.	11.0	-[5]	-	0.04-0.06	0.44-0.66	0.04-0.06	0.4-0.7
R-9	Dominguez Ch.[3]	1.8		-		0.07-0.11		0.07-0.11
R-10	Los Angeles R.	26.7	0-0.78	21	0.12	3.2	0.12-0.90	3.2-24
R-11	San Gabriel R.	36.9	0-0.09	0-3.3	0.05	1.8	0.05-0.14	1.8-5.1
R-12	Coyote Cr.	5.8	0-0.06	0-0.35	0.08	0.46	0.08-0.14	0.5-0.8
R-13	Santa Ana R.[4]	0	0-0.40	-	0.03	-	0.03-0.43	0
R-14	San Juan Cr.	2.4	0-0.02	0-0.05	0.01	0.02	0.01-0.03	0.02-0.07
R-15	San Luis Rey	6.6	0-0.57	0-3.8	0.01	0.07	0.01-0.58	0.1-3.8
R-16	San Diego R.	7.1	0-0.62	0-4.4	0.08	0.57	0.08-0.70	0.6-5.0
	All Areas	127		0-34		7-8		7-42

1. Basins shown on Figure 1.
2. PCB concentrations estimated using the average of measurements for the Arroyo Grande, Santa Ynez, and Ventura Rivers.
3. PCB concentrations estimated using data for Ballona Creek.
4. PCB concentrations estimated using the average of measurements for San Juan Creek, San Luis Rey, and San Diego River.
5. Anomalously high values (53 and 2.5 µg/l) not included in calculations.

Table 6. Estimated 1972-73 mass emission rates of PCB via storm and dry-weather runoff to the Bight.

Type	Volume (10^6 cu m)	PCB (kg/yr) 1242	1254	Total
Storm	574	0-520	240-270	240-790
Dry Weather	127	0-30	7-8	7-40
Total	700	0-550	250-280	250-830
% Dry Weather	18	2	7	3-5

flow rates. The resulting 1972-73 mass emission rates are presented in Table 4.

During spring and fall of 1973, dry-weather flow from 12 channels throughout the Bight was collected and analyzed. These data have been combined to yield average concentrations for dry-weather flow in those regions for which the 1972-73 volumes of nonstorm waters are known (Table 5). Using the dry-weather runoff volumes for the channels indicated, and average dry-weather concentrations for the corresponding drainage basins, we calculated the estimated mass emission rates of chlorinated hydrocarbons to the Bight via dry-weather flow in Water Year 1972-73; these results are also presented in Table 5.

These flow data show that the Los Angeles River carried an order of magnitude more PCB's via storm runoff than any other channel. Further, the estimated input of 1254 PCB in storm runoff from the major channels in the Los Angeles Basin (Drainage Basins R-7 through R-12, Figure 1) was 235 kg, constituting 86 to 98 percent of the estimated total storm runoff input of this contaminant to the Bight. These channels also carried more than 80 percent of the dry-weather input of 1254 PCB.

A comparison of mass emission rates for all areas via the dry-weather and storm runoff for Water Year 1972-73 is presented in Table 6. This summary illustrates that, although dry-weather flow constituted almost 20 percent of the total surface runoff volume during the year, it carried only about 5 percent of the measurable PCB's. Thus, it appears that storm runoff is the dominant mode of surface runoff inputs of this synthetic organic to the Bight, and that the Los Angeles Basin is the principal source region.

AERIAL FALLOUT

It is difficult to determine the amounts of contaminants deposited from the air directly into the ocean's mixed layer because of the problems in positioning samplers at an adequate number of stations throughout the study area. Fortunately, the Southern California Bight contains a number of islands, which we used as stations in an aerial fallout study.

In the study, we used a collection technique developed by V. McClure (National Marine Fisheries Service, La Jolla). This technique involves a clean glass plate, which is sprayed with a 5:1 mixture of hexane and mineral oil and exposed to fallout for a specified period. The miniral oil is then collected with a teflon scraper and analyzed according to the procedure described in Appendix A.

In our studies, we exposed replicate plates 0.1 sq m in area for about 1 week at an elevation of about 4 m on structures at 13 coastal and 5 island stations between Point Conception and the U.S./Mexico border. Two 13-week surveys were conducted in summer 1973 and spring 1974, and a 3-week survey was conducted during fall 1974. To ensure high recovery of the exposed mineral oil sample, we sprayed and scraped each collection plate three times in succession. In addition, detailed tests (described in Appendix C) were conducted to determine the collection efficiency of this technique. Although fallout rates of 1242 PCB were not obtainable, apparently because of poor retention of this relatively volatile mixture, the collection efficiency for 1254 PCB over a 1-week exposure was estimated at about 50 percent. In most cases, blanks were a negligible fraction of sample concentrations.

During the first two surveys, net flux values for 1254 PCB generally ranged between 50 and 150 ng/sq m/day; values at certain coastal stations at the edge of the Los Angeles Basin were higher. During the third survey, however, values were higher by a factor of 2, on the average. The fall and winter seasons in southern California are characterized by desert (Santa Ana) winds, which occur periodically and transport the polluted air of the Basin out over the Bight.

In an effort to estimate the annual aerial input of 1254 PCB to the Bight, we have used the median flux value measured at each sampling site during each of the three surveys to calculate

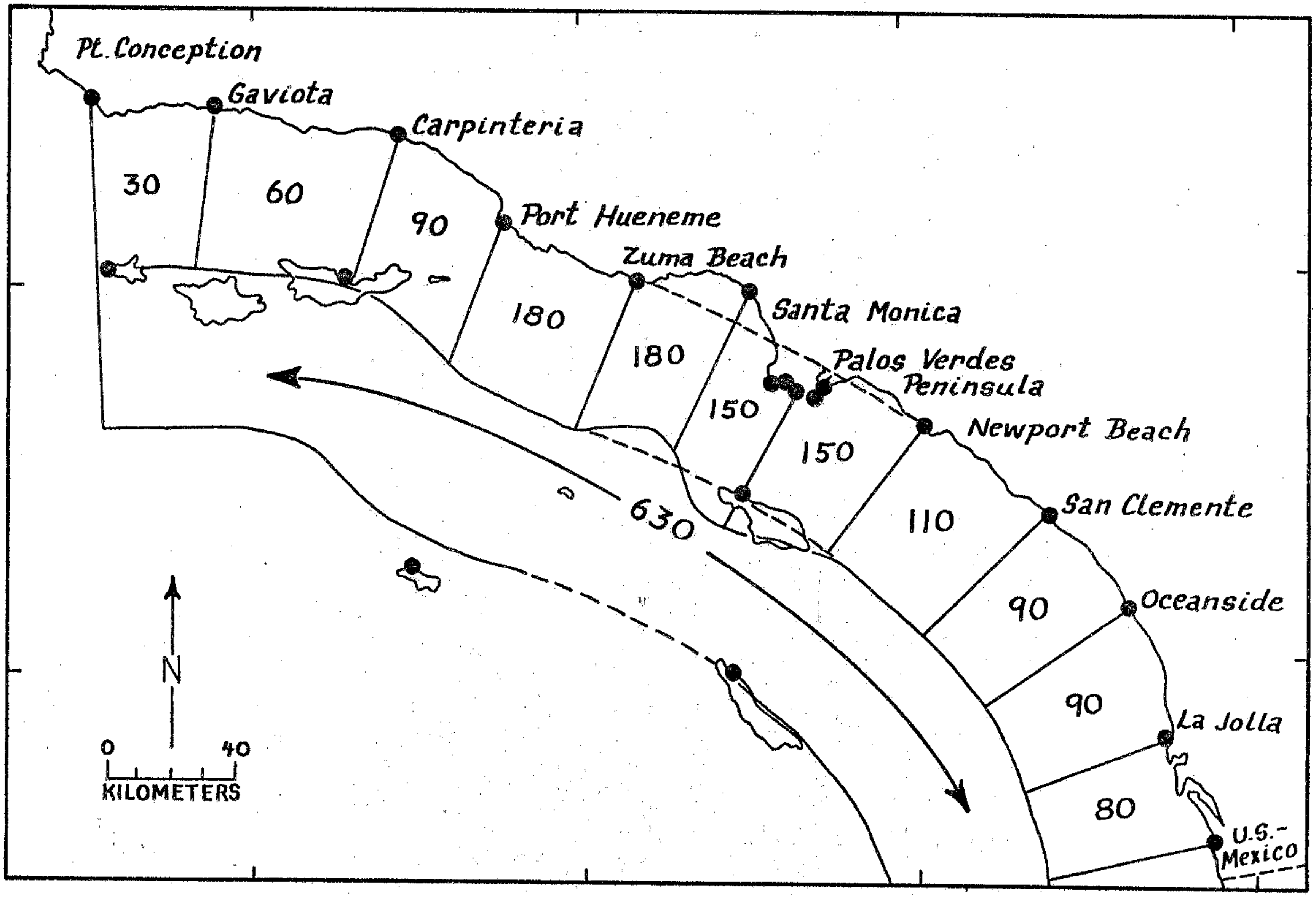

Figure 6. Estimated annual input of 1254 PCB (kg/yr) to sectors of the Southern California Bight via dry aerial fallout during 1973-74.

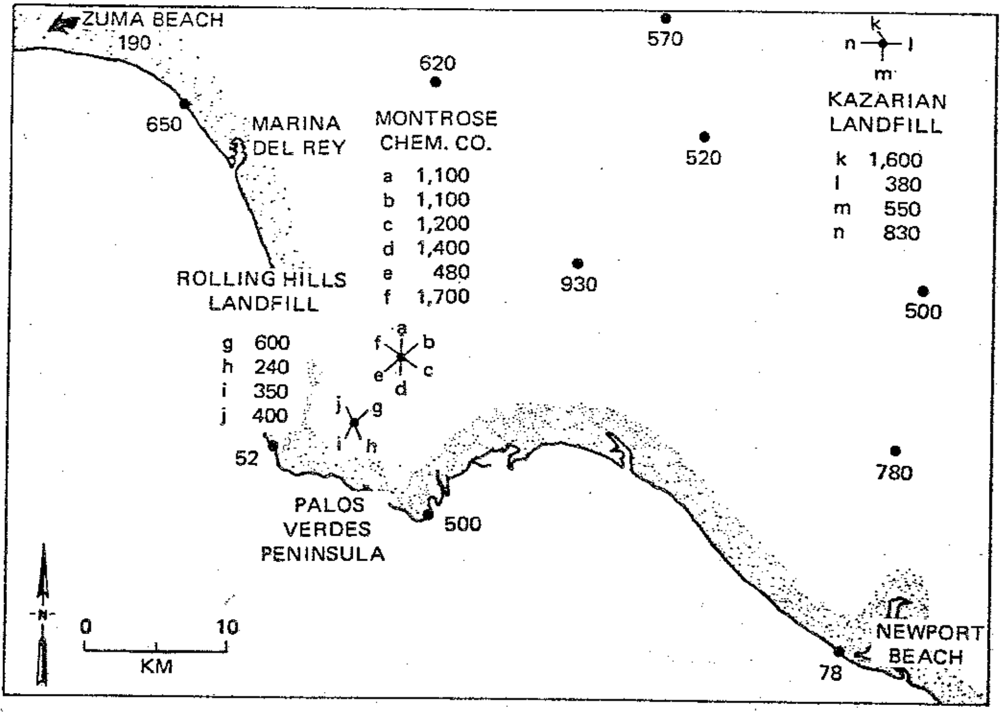

Figure 7. Median flux of 1254 PCB (ng/sq m/day) in dry aerial fallout collected during 6 weeks of 1974.

seasonal input values for the sectors shown in Figure 6. These sectors comprise an inner and an outer coastal zone, each almost 500 km in length and 50 km in width. (There were few stations in the outer zone; thus the input estimates for this area are considerably less reliable than those for the inner zone.) The resulting estimates for input rates of 1254 PCB in spring, summer, and fall were 1,400, 1430, and 2,700 kg/yr, respectively. Giving equal weight to each seasonal survey resulted in an estimated annual input of about 1,800 kg/yr 1254 PCB to the study area via dry aerial fallout. (Rainfall is so infrequent in this region that its overall effect is judged to be negligible.)

The estimated annual aerial inputs of 1254 PCB to the individual sectors of the study area are shown in Figure 6. Highest values (each over 100 kg/yr) occurred in the five sectors off Los Angeles and Orange Counties (centering around the Palos Verdes Peninsula). This portion of the coastal plain of southern California is most affected by air pollution. The three sectors between Zuma Beach and Newport Beach (100 km by 50 km), which account for only about 10 percent of the 50,000-sq-km study area, received approximately 25 percent of the total measured PCB input. Thus, we find a pattern similar to that for surface runoff: The central basin area appears to be the single most important source of 1254 PCB transported via the atmosphere to the waters of the Bight.

To investigate this region further, collection plates were exposed at 25 stations in the Los Angeles Basin during spring and fall of 1974 for a total of six 1-week periods. Although the study was designed to locate potential point sources of DDT compounds, it also provided an interesting comparison to the Bight-wide PCB survey described above. Figure 7 presents the median flux value for 1254 PCB measured at each station. Most of the interior values agreed within about a factor of 2, and no dominant point source was located. However, these Basin values typically were an order of magnitude greater than those found to the north and south along the coast or at the island stations in the Bight.

DIRECT INDUSTRIAL DISCHARGE

Most of the industrial discharges directly to marine waters off southern California occur in San Pedro and San Diego Harbors. These harbors also receive a wide variety of industrial effluents. Thus, we were able to study a number of different types of industrial effluents under similar conditions by surveying the two harbors.

More than 20 discharges from the Los Angeles and Long Beach sectors of San Pedro Harbor, and approximately 10 discharges into San Diego harbor, have been investigated. To ensure representative samples, we enlisted the assistance of the government agencies holding jurisdiction over the various discharge areas to be sampled. In October 1973, field personnel of the Los Angeles Bureau of Sanitation provided composites of four hourly collections of effluents at 12 discharge sites in the Los Angeles Harbor. Access to discharge sites on Dominguez Channel in Long Beach Harbor was provided by the Los Angeles County Flood Control District, and similar composites of 10 additional industrial effluents were obtained there by Project personnel. During August 1974, the major industrial discharges into San Diego Harbor were also sampled in this manner, with the assistance of the San Diego Regional Water Quality Control Board.

The industrial effluents were extracted and analyzed for identifiable chlorinated hydrocarbons, using the techniques used for municipal wastewaters and surface runoff (Appendix A). Results for individual discharges into Los Angeles Harbor are presented in Appendix D. Estimates for overall industrial inputs of 1254 PCB to San Pedro Harbor (1254 PCB was the only PCB mixture detected there) were obtained by calculating corresponding flow-weighted concentrations in three types of effluents--power plant cooling water, fish cannery wastes, and "other industrial" discharges (these categories were selected because of the relatively high flows of the power plant discharges and the relatively high DDT concentrations in cannery wastes). The flow-weighted concentrations were then multiplied by the reported total flows of each of the three classes of industrial wastewaters into San Pedro Harbor to obtain estimates of annual mass emission rates. The values are presented in Table 7. Corresponding data for San Diego Harbor are given in Table 8.

Clearly, there are uncertainties involved in extrapolating the results of analyses of industrial effluent composites collected in a short time period to unsampled discharges and to an entire

Table 7. Flow-weighted mean concentrations and estimated 1973 mass emission rates of 1254 PCB in industrial discharges to San Pedro Harbor.

Discharge Type	Total Flow (mgd)	Concentration (µg/l)	Mass Emission Rate (kg/yr)
Power plant cooling water	1,020	0.01	14
Fish cannery wastes	15	0.09	2
Other industrial wastes	250	0.10	35
Total			50

Table 8. Flow-weighted mean concentrations and estimated 1974 mass emission rates of PCB in industrial discharges to San Diego Harbor.

		1242 PCB		1254 PCB	
Discharge Type	Total Flow (mgd)	Concentration (µg/l)	Mass Emission Rate (kg/yr)	Concentration (µg/l)	Mass Emission Rate (kg/yr)
Cooling waters	757	<0.03	<30	0.01	10
Brine waters	0.5	<0.01	<0.01	0.05	0.03
Flume waters	2.8	<0.02	<0.07	0.01	0.05
Total			<30		10

year. Unfortunately, the kind of assistance provided by municipal wastewater treatment plant personnel in obtaining reliable week-long composites upon request is not yet available from industrial dischargers. Provision for access to such samples as a requirement for discharge would greatly enhance independent quantification of pollutant inputs. Nevertheless, these data provide no indication of significant releases of PCB's to the harbors from the industrial effluents studied. However, the fact that shipyard-related discharges into Los Angeles Harbor had the highest 1254 PCB concentrations of the industrial discharges surveyed (Appendix D) is consistent with our observations that highest levels of this contaminant in harbor mussels occurred in regions of greatest vessel activity (Young et al. 1975a; McDermott et al. 1975).

VESSEL ANTIFOULING PAINT

In 1973, the Project surveyed most of the drydock or haulout facilities serving naval, commercial, or recreational vessels in San Pedro and San Diego Harbors, as well as those serving recreational vessels in Newport Harbor and Marine del Rey, the two largest small-craft anchorages in the Bight (Young et al. 1974). Our objective was to obtain a representative picture of antifouling paint usage in southern California. We obtained samples of the approximately 40 brands of antifouling paint most commonly used at these facilities, as well as data on the number of craft in each harbor and the quantities of these paints applied annually. Procedures are described in Appendix A; resultant PCB concentrations are listed in Appendix D.

The survey of antifouling paint application indicated that about 75 percent of the boats in the marinas investigated were painted once a year and that, on the average, approximately 4 liters of paint were used per boat. On the basis of this relationship and small craft inventories obtained from harbor masters, we estimated the use of antifouling paints in the 12 major marinas or harbors in the Bight; the results are presented in Table 9 (estimated quantities of antifouling paint applied annually to commercial and naval vessels in these anchorages are included in the estimates).

1242 PCB or 1254 PCB were detected in only 7 of the 28 wet paint samples analyzed (Appendix D). Levels were generally on the order of 1 mg/l or below; two samples had total PCB concentrations of approximately 40 mg/l. (Neglecting inequality signatures, median values for 1242 and 1254 PCB were 0.3 mg/l and 0.7 mg/l, respectively.) When we combined these median values with the estimated quantities of antifouling paint applied annually to recreational, commerical, and naval vessels in marinas and harbors of the Bight, we obtained the estimated upper limits for PCB annual usage at each of the southern California anchorages (Table 9).

Sixteen samples of antifouling paint scrapings collected from drydock facilities were also analyzed. Most of the PCB concentrations measured were less than 20 ppm. However, four samples yielded total PCB concentrations of 270, 3,300, 56,000, and 150,000 ppm, respectively. Furthermore, the two highest concentrations of 1254 PCB that we found in the dried samples (approxi-

Table 9. Estimated annual rate of application of PCB's (via antifouling paint) to recreational, commercial, and naval vessels at the major marinas and harbors of the Bight, 1973.

Basin No.*	Harbor	Paint Applied** (l/yr)	PCB's Applied (g/yr) 1242	PCB's Applied (g/yr) 1254
R-1	Santa Barbara	2,300	0.7	1.6
R-2	Ventura	2,800	0.8	2.0
R-4	Oxnard	2,800	0.8	2.0
R-8	Marine del Rey	16,700	5.0	12
R-8	Redondo-King	4,200	1.3	3.0
R-10	San Pedro	141,000	42	98
R-11	Huntington	9,700	2.9	6.8
R-13	Newport	24,200	7.3	17
R-14	Dana Point	1,700	0.5	1.2
R-15	Oceanside	1,700	0.5	1.2
R-16	Mission Bay	4,500	1.4	3.2
R-16	San Diego	84,000	25	58
	Total	295,000	88	206

*Harbor located near this basin, which is shown on Figure 1.
**The values for San Pedro and San Diego Harbors include estimates for commerical and naval vessels (116,000 and 73,000 l/yr for the two harbors, respectively).

mately 5 and 15 percent on a dry weight basis) correspond with an observation by Dr. V. McClure,* who found that a paint chip collected in a zooplankton trawl in 1970 contained approximately 10 percent PCB. Polychlorinated biphenyls are reported to have been used extensively as a plasticizer in paints before such use was banned in this country in 1971.

The data in Table 9 indicate that approximately 300,000 liters of antifouling paints are applied to vessels annually throughout the Bight. Our survey revealed that, on the average, the density of antifouling paints used in southern California is about 1.5 dry kg/l. Therefore, if such paints did contain 10 percent PCB in the past, an application rate of 300,000 l/yr would correspond to a PCB usage of 45,000 kg/yr.

Antifouling paints are designed to slough off with time, and an estimated 5 to 10 percent of the old paint removed from vessel bottoms is believed to be carried back to the harbor

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*National Marine Fisheries Service, La Jolla, personal communication.

waters (Barry 1972). Thus, although the actual PCB concentrations in paints used in southern California before the ban are not known, and despite the fact that an uncertain fraction of such materials are actually released to the water, these observations point to the possible importance of antifouling paints in the past as a source of PCB's to the coastal marine environment. As mentioned in the previous section, we have observed that the highest levels of PCB's found in harbor mussels occur in regions of greatest vessel activity. For example, the whole soft tissues of mussels collected near vessel bottom scraping and repainting yards in Newport and San Diego Harbors contained approximately 20 times as much PCB's as did those from mussels taken at nearby coastal sites (Young and Heesen 1974; McDermott et al. 1975).

HARBOR FLUSHING

In view of the relatively high levels of PCB contamination found in San Pedro, Newport, and San Diego Harbors, we attempted to determine if any significant levels of PCB's could be detected in the waters moving from these harbors into the open ocean during periods of peak tidal flow. In the fall of 1974, we surveyed concentrations of these chlorinated hydrocarbons in surface seawater flowing through the mouths of the three harbors. The samples were collected in a cleaned stainless steel bucket from the bow of a small boat heading slowly into the current. Replicate 40-liter samples were collected over a semidiurnal period (five collections in approximately 12 hours) on the day when the greatest tidal difference of the month occurred. Current meter readings at midchannel and middepth also were obtained over the collection period. These samples were concentrated on board the vessel by passing the seawater through polyurethane foam plugs in stainless steel columns at a rate of approximately 250 ml/min. The columns were then wrapped in aluminum foil and returned to the Project's laboratory for analysis (Appendix A). This procedure was developed by B. de Lappe and Dr. R. Risebrough,* who have found it to be as efficient as batch extraction of chlorinated hydrocarbons from seawater.

Figure 8 illustrates the results obtained from the San Diego Harbor survey; net concentrations of 1254 PCB for the replicate samples of each collection period are plotted against tidal flow (Young et al. 1975b). Although there is some evidence of increased PCB concentrations near the time of tide reversal, when the greatest influence of "back harbor" water would occur near the harbor mouth, the measured concentrations were extremely low, at the part-per-trillion level (pptr: ng/l).

We combined individual sample concentrations for each harbor with the corresponding volume of seawater that flowed during the 3-hour period beginning 1.5 hours before each sampling to obtain the amount of PCB's that was transported. The sum of these individual mass transports was divided by the total flow, disregarding direction, for the entire 12-hour period to obtain the flow-weighted mean concentrations for the three harbors. Resultant values for San Pedro and San Diego Harbors were 1.5 and

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*Bodega Marine Laboratory, personal communication.

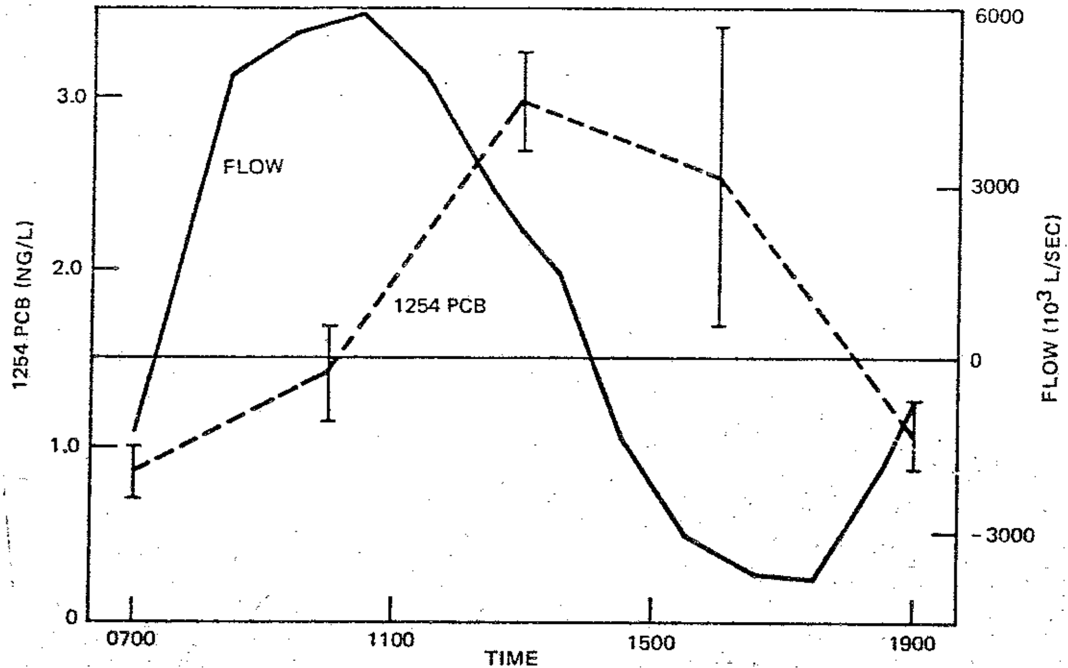

Figure 8. Concentrations of 1254 PCB in surface seawater collected over a semidiurnal tidal cycle at the mouth of San Diego Harbor, 12 November 1974. Positive flow represents outflowing water; negative, inflowing. Vertical bars indicate individual replicate values.

1.8 pptr; for Newport Harbor, the value was significantly greater (19 pptr). There was a major storm a few days prior to the Newport sampling, and it is possible that the large quantities of "terrestrial detritus" that washed through the harbor mouth during the sampling period caused the higher PCB values measured there.

By combining the measured concentrations with tidal flow values obtained from the current meter measurements and channel geometries, we obtained estimates for maximum net transport of 1254 PCB from the harbors to the adjacent coastal ecosystem. Because of the extremely low concentrations observed, none of the values exceeded 50 kg/yr when extrapolated to an annual basis. Thus, these pilot seawater surveys have provided no indication that any of the three harbors is now a significant source of polychlorinated biphenyls to the coastal marine ecosystem.

OCEAN CURRENT ADVECTION

As a part of this inputs study, we attempted to estimate the quantities of measurable chlorinated hydrocarbons in surface seawater annually flowing through the Southern California Bight. In October 1973, we sampled surface seawater at seven stations along a north/south transect (120°35'W) at the northwestern edge of the Bight. The transect began off Point Conception and ended approximately 300 km west of Oceanside. Circulation patterns (Jones 1971) indicated that the transect chosen should have intersected California Current water flowing into the Bight.

Replicate 40-liter samples were collected in a stainless steel bucket, which was lowered from the bow of a research vessel that was slowly underway. Immediately upon collection, the replicate samples were passed through polyurethane foam columns in the manner described in the previous section; they were subsequently taken to Bodega Marine Laboratory for analysis. The results,

Table 10. Chlorinated hydrocarbon concentrations (ng/l) in surface seawater collected along the northwestern edge of the Southern California Bight, September 1973.

Station Number	Position	p,p'-DDE	p,p'-DDT	1254 PCB*
1	120°35'W, 34°26'N	0.12 0.10	0.37 0.32	0.27
2	120°35'W, 34°18'N	0.09 0.07	0.35 0.27	0.36
3	120°35'W, 34°10'N	0.12 0.13	0.79 0.82	0.49
4	120°35'W, 34°02'N	0.10 0.13	0.51 0.75	0.46
5	120°35'W, 33°54'N	0.08 0.09	0.46 0.53	0.44
6	120°35'W, 33°34'N	0.13 0.08	1.3 0.79	0.49
7	120°35'W, 33°14'N	0.06 0.06	0.47 0.53	0.38

*Replicates were combined prior to analysis for PCB's.

listed in Table 10, indicate average concentrations for total DDT and 1254 PCB of 0.7 and 0.4 pptr, respectively.

These data may be used to obtain rough estimates of the quantity of these synthetic organics carried into the Bight via ocean current advection. Taking the length of the Bight as 500 km and the width influenced by the coast as 100 km, the effective study area is 5 x 10^{10} sq m. Assuming the mixed surface layer to be 50 m, the volume of the mixed layer is 2.5 x 10^{12} cu m. It has been shown that the mean residence time of water in this mixed layer is on the order of 3 months (Jones 1971). Thus, the estimated advective flow rate of California Current water through the Southern California Bight is 10^{13} cu m/yr, equal to 10^{16} l/yr. Corresponding estimates for advective flux rates of measurable DDT and 1254 PCB compounds are 7,000 and 4,000 kg/yr, respectively.

CONCLUSIONS

The results of the Project's 1972-74 study of the sources and input rates of polychlorinated biphenyls to the marine waters off southern California are summarized in Table 11. These data indicate that, in recent years, municipal wastewaters have been the dominant source of PCB's to this coastal marine ecosystem. In 1974, more than 5 metric tons of this synthetic organic material were discharged via the five major treatment plants in the Bight. Although the quantity of 1242 PCB transported through the Bight via ocean currents has not yet been estimated, the fact that the 1254 PCB values for municipal wastewaters and ocean currents were of the same order of magnitude testify to the importance of the wastewater input route.

Aerial fallout is the other important route by which PCB's enter the waters of the Bight. The 1973-74 estimate of 1,800 kg for 1254 PCB exceeded the 1974 input from municipal wastewaters (1,100 kg). We do not yet know the importance of the 1242 PCB input via aerial fallout; however, the fact that PCB levels in municipal wastewater are continuing to decrease suggests that aerial transport of these contaminants may become the dominant input mode in the future.

Table 11. Inputs of PCB's to the Southern California Bight.

Route	Year	PCB's (kg/yr) 1242	1254	Total
Municipal wastewater	1974	4,300	1,100	5,400
Surface runoff	1972-73	≤550	250	≤800
Aerial fallout	1973-74	-	1,800	-
Industrial discharges	1973-74	<180*	60	<250
Antifouling paint	1973	<1	<1	<1
Harbor flushing**	1974	-	<150	-
Ocean currents	1973	-	4,000	-

*Assuming that the maximum 1242/1254 PCB ratio (3:1) found in San Diego Harbor also applies to San Pedro Harbor industial discharges.
**San Pedro, Newport, and San Diego Harbors.

Finally, these studies have demonstrated that, in southern California, surface runoff is only a secondary PCB source, while contributions from industrial discharges and antifouling paint use in the major harbors appears to be insignificant. Although intertidal mussels in these harbors had an order of magnitude more PCB in their soft tissues than did nearby coastal specimens, we found no evidence that harbor flushing constitutes a significant source of polychlorinated biphenyls to the coastal marine ecosystem.

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Appendix A

PROCEDURES FOR CHLORINATED HYDROCARBON ANALYSIS USED IN THE COASTAL WATER PROJECT LABORATORY

All glassware used for chlorinated hydrocarbon analysis is washed with soap and water. The glassware is then heated in a kiln at 535°C for 4 hours to volatilize any compounds that might interfere with the analysis from its surfaces. All solvents used in the analysis are pesticide quality.

MUNICIPAL AND INDUSTRIAL WASTEWATERS AND SURFACE RUNOFF

The samples, which are preserved in 75 ml/l of 15 percent (by volume) diethyl ether in hexane, are placed in a graduated cylinder and measured and then transfered to a separatory funnel (500-ml, or 2-liter for larger samples) equipped with a teflon stopcock. The separatory funnel is shaken for 2 minutes and the layers are allowed to separate. The aqueous layer is drained into a beaker, and the organic layer is placed in a round-bottomed flask; the aqueous layer is then returned to the separatory funnel and covered with 6 percent diethyl ether in hexane. The separatory funnel is again shaken for 2 minutes; the resulting organic layer is combined with the first organic layer in the round-bottomed flask. The aqueous portion is then extracted a third time with pure hexane. The flask with the organic layers is then attached to a Rotovapor (Rinco Instrument Co., Inc., Greenville, Ill.), and the volume is reduced to about 25 ml. The extracts are cleaned on a Florisil column before injection into a gas chromatograph.

Since 1974, the municipal wastewater extracts have routinely been split and one-half "saponified" in the manner described later in this appendix. If necessary, other water sample extracts are also saponified.

PAINT

Most wet paint samples are extracted using a separatory funnel. A measured volume of the paint is pipetted into a 500-ml separatory funnel containing 100 ml of 15 percent diethyl ether in hexane (by volume). If the paint seems to disperse easily when dropped into the ether/hexane mixture, the separatory funnel method of extraction is employed. On the other hand, if the wet paint sample forms a seemingly nonpermeable drop or plastic-like string, the samples are extracted using the Soxhlet method.

Separatory Funnel Method

The separatory funnel containing the ether/hexane mixture and the sample is shaken for 2 minutes. The sample is then allowed to settle to the bottom of the separatory funnel, and the extract is carefully decanted into a round-bottomed flask. This procedure is repeated two times, first with the addition of 100 ml 6 percent diethyl ether in hexane and then with the addition of 100 ml of hexane. In both cases, the settled extract is decanted into the round-bottomed flask. The flask is then attached to the Rotovapor and reduced to a volume suitable for a Florisil cleanup.

Soxhlet Extraction Method

This method is used on dry paint samples and on wet paints that do not disperse easily when dropped into an ether/hexane mixture (the wet paint to be Soxhlet-extracted is first spread on aluminum foil and dried).

Before a sample is extracted, the thimbles and hexane are added to the Soxhlet extraction apparatus, and the hexane is refluxed for a period of 2 hours to clean the apparatus. The rinse hexane is then removed and replaced with clean hexane, and the samples are weighed into the cleaned thimbles. The Soxhlets are then refluxed for an 18-hour period, and the extracts are concentrated in a Rotovapor to a volume suitable for Florisil cleanup.

AERIAL FALLOUT

Aerial fallout samples are first processed through a "cleanup" column before being analyzed by gas chromatography. The column consists of a disposable 5-ml pipet (8 mm OD, 6 mm ID), which is packed with specially prepared and activated silica gel. (MCB Silica Gel (SX-144-6), 100/200 mesh, is used. The gel is washed with a 1:1 solution of methanol benzene; 3-ml of solution are used per 1 g of adsorbent. After rinsing, the silica gel is dried in a Rotovapor and activated at 180°C overnight--it is then stored under hexane until use.)

The column is packed by inserting a plug of silane-treated glass wool, adding several milliliters of hexane, and slurrying the silica gel with a pipet. Using the markings on the 5-ml pipet as a guide, adsorbent is added until the volume of the compacted bed is 1.7 ml ± 0.1 ml. A vibrator is then held against the column briefly to compact the adsorbent.

The fallout samples come into the laboratory in centrifuge tubes containing up to 1 ml of mineral oil. The sides of the tube are first washed down with enough hexane to bring the volume to 3 ml. The sample is then transfered from the centrifuge tube to the column using a pipet. An initial elution of

1.7 ml hexane is used to remove the mineral oil from the column; this fraction is discarded. The column is then eluted with 5.7 ml of 20 percent benzene in hexane (by volume), followed by 6 ml of benzene. The first fraction elutes the PCB and DDT compounds, and the sedond fraction elutes Dieldrin. For the fall 1974 survey, the first fraction was split, and one-half was saponified for PCB determination.

SEAWATER

Chlorinated hydrocarbons are concentrated from the seawater samples on polyurethane foam contained in stainless steel columns. The columns are 33 cm long, 6.4 cm OD, and 6.0 cm ID. Stainless steel cross-hairs are welded into the column 23 cm from the end to prevent the plugs from passing through the column under vacuum. The polyurethane plugs (Stock No. 2064, United Foam Company, Los Angeles, Calif.) are 6.4 cm in diameter and 6.4 cm thick. The columns are cleaned before use with a wash of 500 ml of acetone, followed by 500 ml hexane. The hexane wash is then tested for impurities by gas chromatography. Just prior to sampling, the column is primed with 250 ml of ethyl alcohol.

The water samples collected from the sea surface are transfered to 4-liter glass beakers aboard ship and immediately passed through the column at a flow rate of 250 ml/min. until 40 liters of water have passed through the column. The excess water is removed from the columns by swinging them; they are then wrapped in aluminum foil and transported to the laboratory.

In the laboratory, the samples are extracted by eluting with 500 ml of acetone followed by 500 ml of hexane. The plugs are squeezed with a glass rod to remove the last portion of solvent. The solvent is then transfered to a 2-liter separatory funnel, and 500 ml of deionized water is added to the separatory funnel. The separatory funnel is shaken for 2 minutes, and the layers are allowed to separate; the organic layer is then transfered to a round-bottomed flask and concentrated to about 50 ml with a Rotovapor.

The sample is next put through a cleanup column. The column packing is made by mixing 17 g of Celite (J.T. Baker Co., E406) with 5 ml of concentrated sulfuric acid and 5 ml of fuming (30 percent free SO_3) sulfuric acid (J.T. Baker Co., 9705) in a beaker with a glass stirring rod; the packing is then covered with hexane. The mixture is packed into a Buckner funnel with fritted glass of medium porosity with a diameter of 7.6 cm and tamped down; the excess solvent is removed with an aspirator. The sample is then placed on the column, where it passes through into a receiving flask. Next, the column is eluted with 75 ml of hexane. When the hexane has passed, another 75 ml portion of hexane is passed through the column. The column is then taken to dryness with the aspirator to remove the last portion of hexane. Half the sample is saponified for PCB determination. the sample fractions are then injected into the gas chromatograph.

SEDIMENTS

A sample is first dried in an oven at about 60°C. A Soxhlet extraction apparatus is used for the extraction. The dried sediment sample is weighed into a cellulose thimble and placed into the Soxhlet apparatus. The Soxhlet flask is charged with 200 ml of hexane, and the extraction is run for an 18-hour period. The extract is then cleaned up using a Florisil column, concentrated, and injected into the gas chromatograph.

MUSSEL TISSUES

The whole soft tissues of mussels are first homogenized into a paste. About 10 g of each homogenate is weighed into a 150-ml beaker. The homogenate is then covered with 20 ml of acetonitrile and ground with a high-speed blender for about 1 minute or until all pieces of the sample have been thoroughly ground. The blades of the blender are then rinsed twice with 20 ml of acetonitrile, and the rinse is added to the beaker containing the sample. The acetonitrile is then decanted and filtered through filter paper into a 500-ml separatory funnel with a ground-glass stopper. The sample is rinsed three times with 20 ml of acetonitrile and the rinse decanted and filtered into the 500-ml separatory funnel with the other acetonitrile fraction. Fifty milliliters of hexane is added to the funnel, and it is shaken vigorously for a period of 1 minute. The two layers are allowed to separate (the hexane layer is less dense than the acetonitrile layer). The acetonitrile layer is then drained through the stopcock into a 400-ml beaker, and the hexane layer is emptied into a 250-ml flask. The acetronitrile fraction is returned to the separatory funnel and extracted two more times with 50 ml of hexane. The hexane extracts are all combined into the 250-ml flask and concentrated to about 50 ml with the Rotovapor. The samples are cleaned up on a Florisil column prior to concentration and injection.

SAPONIFICATION (DEHYDROHALOGONATION)

A sample extract (reduced in volume to about 40 ml) is measured into a 250-ml Erlenmeyer flask equipped with a standard tapper ground-glass joint. Five grams of KOH are dissolved in water and diluted to 50 ml with ethanol. This mixture is added to the Erlenmeyer. The sample is then fitted with a three-ball Snyder condenser, and the mixture is placed on a steam table and refluxed for 30 minutes after it begins to boil.

The contents of the Erlenmeyer are placed in a 500-ml separatory funnel along with 100 ml of deionized water and 50-ml of hexane. The separatory funnel is then shaken for 5 minutes and the layers allowed to separate. The lower aqueous layer is discarded, and the organic layer is washed with two 100-ml portions of water. The saponified sample is then concentrated and injected into the gas chromatograph.

FLORISIL CLEANUP

Activation of the Florisil (MCB, FX284) is carried out at 705°C using a pottery kiln. The Florisil is placed in 250-ml covered crucibles in the kiln and baked for 4 hours after the kiln reaches equilibrium temperature. The activated Florisil is stored under hexane until use.

To clean a sample, 8 cm of the slurried-activated Florisil is added to the cleanup chromatographic columns (25 mm OD, 22 mm ID, and 400 mm in length, with sealed-in, coarse porosity fritted disc; Kontes Glass Co., Vineland, N.J.), and 1 cm of anhydrous sodium sulfate is added over the Florisil. Samples are concentrated to a volume of approximately 50 ml and added to the Florisil column. The column is eluted with 45 ml of 6 percent diethyl ether in hexane. If Dieldrin is also to be measured, the receiving flask is changed and the column is eluted again with 100 ml of 15 percent diethyl ether in hexane.

INSTRUMENTATION AND QUANTITATION

Samples are injected into a Tracor MT-220 gas chromatograph equipped with a ^{63}Ni detector. The glass column used is 1.8 m long, 6 mm OD, and 4 mm ID and packed with 11 percent mixed-phase OV-17 and QF-1 on 80/100 mesh Gas Chrom Q (prepared by Applied Science Laboratories, Inc., State College, Penn.). The carrier gas is prepurified nitrogen with a flow rate of 80 ml/min. The injector, column, and detector temperatures are 225, 205, and 285°C, respectively. The components are identified by retention time and quantitated by comparing the peak heights of the samples with the peak heights of standards.

Appendix B

PCB'S IN MUNICIPAL WASTEWATERS: A LABORATORY INTERCALIBRATION PROGRAM

The tables of this appendix give the values for PCB's in split samples of municipal wastewater effluent analyzed in the Project's laboratory and those at Bodega Marine Laboratory (Dr. R. Risebrough and B. de Lappe), the University of Washington (Dr. S. Pavlou), and four of the five major municipal wastewater treatment plants in southern California (Oxnard City Treatment Plant did not have this analytical capability in 1974, when most of the work was done).

Tables B-1 and B-2 give values for May 1973 and 1974 samples of JWPCP final effluent. Tables B-3 through B-5 give results from 1974 analyses of effluents from Hyperion, Orange County and Point Loma Treatment Plants, respectively.

Table B-1. PCB concentrations (µg/l) measured by four laboratories in split samples of JWPCP final effluent collected prior to discharge 4-10 May 1973.

	1242 PCB			1254 PCB			Total PCB		
Laboratory	R-1	R-2	Avg.	R-1	R-2	Avg.	R-1	R-2	Avg.
Coastal Water Project	3.7	4.1	3.9	1.4	1.6	1.5	5.1	5.7	5.4
Bodega Marine	3.5	3.3	3.4	ND	ND	ND	3.5	3.3	3.4
Univ. of Washington	4.2	4.1	4.2	1.9	1.8	1.8	6.1	5.9	6.0
L.A. County Sanitation Districts	0.8	-	0.8	0.4	-	0.4	1.2	-	1.2

Table B-2. PCB concentrations (µg/l) measured by three laboratories in split samples of JWPCP final effluent collected prior to discharge 17-24 May 1974.

	1242 PCB			1254 PCB			Total PCB		
Laboratory	R-1	R-2	Avg.	R-1	R-2	Avg.	R-1	R-2	Avg.
Coastal Water Project	1.9	1.9	1.9	1.3	1.3	1.3	3.2	3.2	3.2
Bodega Marine	3.1	3.3	3.2	0.7	0.7	0.7	3.8	4.0	3.9
L.A. County Sanitation Districts	<0.01	-	<0.01	0.6	-	0.6	0.6	-	0.6

Table B-3. PCB concentrations (µg/l) measured by three laboratories in split samples of Hyperion 7-mile outfall sludge collected prior to discharge 5-11 June 1974.

	1242 PCB			1254 PCB			Total PCB		
Laboratory	R-1	R-2	Avg.	R-1	R-2	Avg.	R-1	R-2	Avg.
Coastal Water Project	27	24	26	11	14	12	38	38	38
Bodega Marine	46	52	49	16	15	16	62	67	64
Hyperion	<0.1	<0.1	<0.1	ND	ND	ND	<0.1	<0.1	<0.1

Table B-4. PCB concentrations (μg/l) measured by three laboratories in split samples of Orange County final effluent prior to discharge, 18-24 May 1974.

Laboratory	1242 PCB			1254 PCB			Total PCB		
	R-1	R-2	Avg.	R-1	R-2	Avg.	R-1	R-2	Avg.
Coastal Water Project	10.3	10.8	10.6	1.4	1.5	1.4	11.7	10.3	12.0
Bodega Marine	11.0	13.0	12.0	0.8	0.8	0.8	11.8	13.8	12.8
Orange County Sanitation Districts	7.0*	12.1*	9.6*	ND	ND	ND	7.0	12.1	9.6

*Quantified as 1248 PCB.

Table B-5. PCB concentrations (μg/l) measured by three laboratories in split samples of Point Loma final effluent collected prior to discharge, 18-24 May 1974.

Laboratory	1242 PCB			1254 PCB			Total PCB		
	R-1	R-2	Avg.	R-1	R-2	Avg.	R-1	R-2	Avg.
Coastal Water Project	9.1	8.8	9.0	0.8	0.6	0.7	9.9	9.4	9.6
Bodega Marine	11.0*	8.9*	10.0*	0.4	0.4	0.4	11.4	9.3	10.4
Point Loma Treatment Plant	ND	-	ND	ND	-	ND	ND	-	ND

*Identified as 1016 PCB.

Appendix C

SPECIAL STUDIES: AERIAL FALLOUT COLLECTION

EFFICIENCY OF GLASS PLATE COLLECTION METHOD

In April 1974, we conducted a detailed series of experiments in an effort to estimate the collection efficiency of the glass plate system for sampling chlorinated hydrocarbons in dry aerial fallout. Fourteen plates were sprayed with mineral oil and exposed over a period of 8 days on the roof of a private home near the coast of Santa Monica Bay, far from any known point source of contamination. The plates were divided into four groups. The samples were removed from three of the plates daily; these were then repositioned. A second set of three plates was sampled and repositioned every other day. A third set of four plates was sampled and repositioned on the fourth day, and the remaining four plates were sampled on the eighth day.

Five chlorinated hydrocarbons were identified in these samples: p,p'-DDT, o,o'-DDT, p,p'-DDE, p,p'-DDD, and 1254 PCB. In Table C-1, average values for the total quantity of each of these compounds accumulated over the 8 days are given as a function of collection frequency.

These data indicated that collection efficiency decreased with duration of plate exposure. To determine if this loss of efficiency was a linear porcess that we could correct for by linear recovery factors, we calculated corresponding regression lines and their correlation coefficients (Table C-2). Most of the results were statistically significant at greater than the 95 percent confidence level; p,p'-DDE and p,p'-DDD results were significant at the 94 percent level. Because our fallout samplers are generally exposed for 1 week before the sample is collected, the collection efficiency factor for a given constituent was taken as the ratio of the best-fit cumulative value for a 7-day exposure to the extrapolated value for a zero-day exposure. Standard 7-day collection efficiencies (and their 95 percent confidence intervals) calculated from these data are listed in Table C-3. We normalized our fallout survey results to standard weeks (Monday through Sunday) and divided by 7 to obtain an estimated average daily flux at a given station for that week. The flux values then were corrected by the efficiency factors shown in Table C-3.

Table C-1. Cumulative average quantities (ng) of chlorinated hydrocarbons measured over an 8-day period (3-11 April 1974) on four sets of collection plates sampled at different frequencies.

Collection Frequency	3-5 Apr	3-7 Apr	3-9 Apr	3-11 Apr
p,p'-DDT				
1-day	190	300	384	540
2-day	158	263	345	509
4-day	-	235	-	454
8-day	-	-	-	312
o,p'-DDT				
1-day	52	90	121	181
2-day	46	81	114	172
4-day	-	68	-	166
8-day	-	-	-	110
p,p'-DDE				
1-day	29	64	91	134
2-day	17	48	63	94
4-day	-	37	-	74
8-day	-	-	-	39
p,p'-DDD				
1-day	28	62	104	180
2-day	23	46	81	157
4-day	-	51	-	163
8-day	-	-	-	104
1254 PCB				
1-day	60	140	218	401
2-day	46	90	161	352
4-day	-	104	-	327
8-day	-	-	-	195

Table C-2. Correlation coefficients for 8-day collection series of chlorinated hydrocarbons in dry aerial fallout.

Constituent	Correlation Coefficient*
p,p'-DDT	-0.99
o,p'-DDT	-0.97
p,p'-DDE	-0.94
p,p'-DDD	-0.94
1254 PCB	-0.98

*For the two degrees of freedom applicable here, correlation coefficients of ±0.95 and ±0.99 correspond to the 95 and 99 percent confidence limits, respectively.

Table C-3. Dry aerial fallout 7-day collection efficiencies with 95 percent confidence intervals.

Fallout Constituent	Collection Efficiency (%)	Confidence Interval
p,p'-DDT	60	56-64
o,p'-DDT	64	50-82
p,p'-DDE	36	11-81
p,p'-DDD	63	42-92
1254 PCB	54	43-66

Recently, we have conducted experiments to determine if additional recovery could be accomplished by collecting at a lower temperature. A nonoiled aluminum pan sampler resting on a block of dry ice was exposed for 2 to 3 days next to our regular oil-on-glass collection plate. The ratios of the quantities of total DDT and 1254 PCB collected by the cooled pan and the uncooled, oiled plate are summarized below:

Test No.	Ratio, Cooled to Uncooled, Total DDT	Ratio, Cooled to Uncooled, 1254 PCB
1	1.27	1.24
2	0.86	0.71
3	0.98	1.03
Average	1.04	0.99

These preliminary results suggest that the oil-on-glass collection system used in our studies does provide a representative picture of the fallout rate of these chlorinated hydrocarbons onto the Bight. However, the volatility of certain constituents does interfere with the efficiency of this collection system, as described below.

VOLATILITY STUDY

At the beginning of the fallout sampling program, several experiments on the retention of various chlorinated hydrocarbons by the glass plate collectors were conducted. The results of these experiments, such as the one described just above, indicated that, for the compounds with relatively low molecular weights (such as p,p'-DDE, Dieldrin, and 1242 PCB), the flux values obtained from daily collections were considerably larger than the values obtained for weekly collections. This suggested significant losses of the lighter compounds through volatilization or some other process, such as decomposition via ultraviolet radiation. Thus, we investigated this phenomenon further.

Two compounds of interest with low recovery were Dieldrin and Aroclor 1242; 0.1 mg of each compound was added to 10 ml of a 17 percent mineral oil in hexane solution (by volume). The

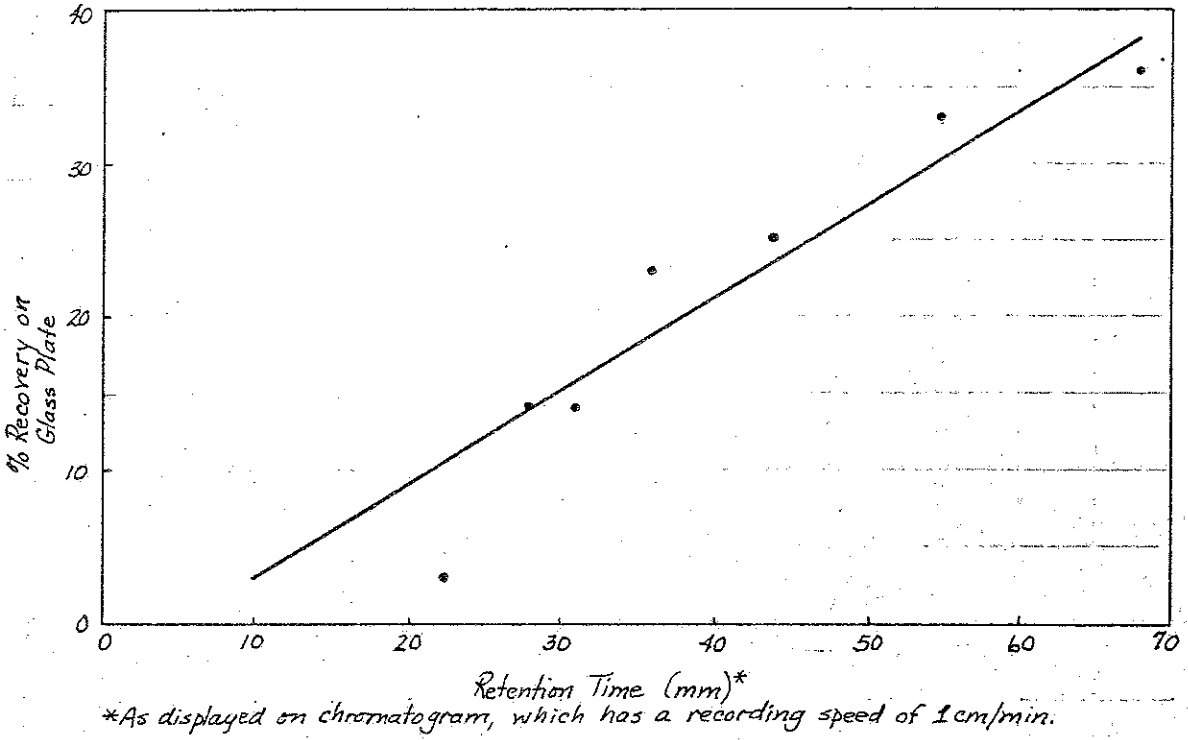

Figure C-1. Recovery of Aroclor 1242 from spiked glass plate.

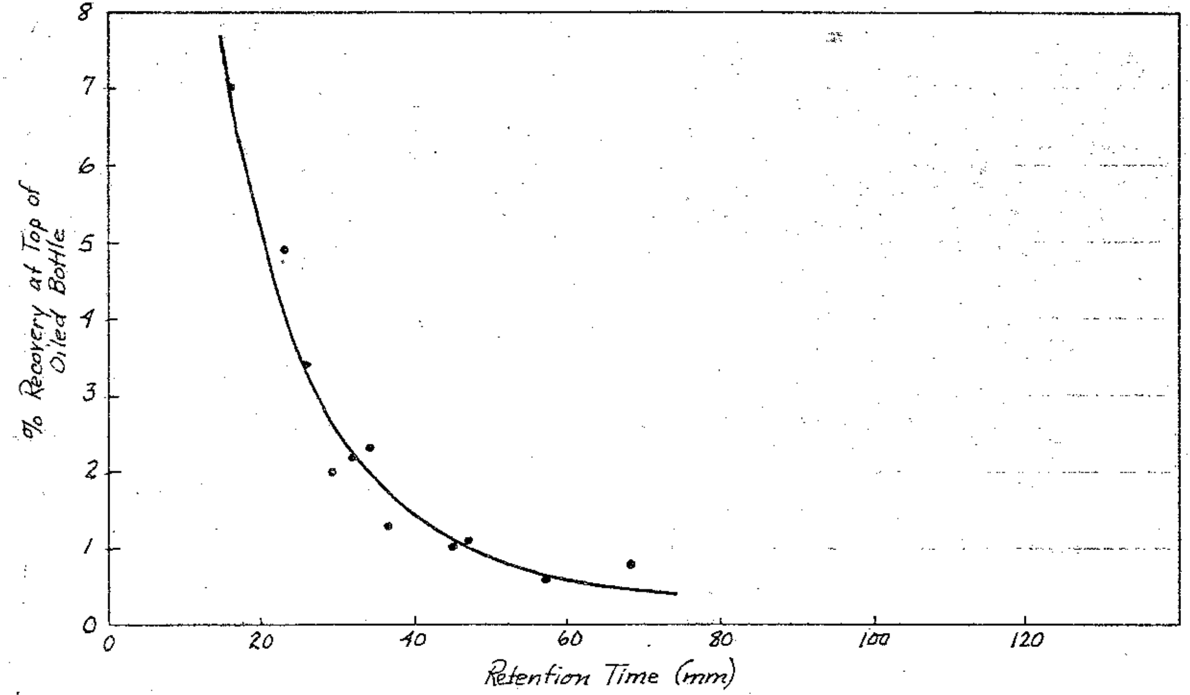

Figure C-2. Recovery of PCB's (Aroclors 1242 and 1254) from top of oil-spiked glass jug.

mixtures were placed on fallout sampling plates and allowed to stand for a period of 4 days on the Project's roof. The results of the experiment for 1242 PCB are illustrated in Figure C-1. The low recovery and the linear relationship between retention time and percent recovery suggest that the problem with detection of Aroclor 1242 in fallout is one of volatility. The recovery from the sample spike with Dieldrin was 26 percent--the problem with this substance also seems to be one of volatility. It should be noted that 0.1 mg is an especially heavy spike. The chromatograms essentially show only the compounds that were spiked and not any decomposition peaks. This would suggest that decomposition by ultraviolet radiation is unlikely.

In another experiment, Aroclor 1242 Standard was added to mineral oil and hexane. This mixture was then placed in a 1-gallon glass jug that had been previously sprayed with mineral oil and hexane. The hexane was allowed to evaporate, and the jug was sealed with a cap lined with aluminum foil; the jug was then placed on the Project's roof for a period of 6 days, after which the jug was cut about 5 cm from the bottom, the top half was rinsed with hexane, and the sample was analyzed. The results of this experiment are illustrated in Figure C-2. These data indicate that recovery from the upper section of the jug increases with decreasing retention time.

One problem with the second experiment was that the mineral oil seemed to be trapping the PCB's, as the oil was about 0.5 cm thick in the bottom of the jug. To more closely model the fallout sampling field conditions, the amount of oil was reduced in a third experiment. Both Aroclor 1242 and 1254 were utilized as spikes to get a wider range of molecular weights. Again, a 1-gallon glass jug was used for the experiment. The jug was sprayed lightly with a mineral oil/hexane mixture, and the PCB spike in hexane was added. The hexane was allowed to evaporate, and the jug was sealed with an aluminum-foil-lined cap and placed on the Project's roof. After 6 days, the jug was cut about 5 cm above the bottom, and each section was analyzed. The results (Figure C-3) indicate that compounds with relatively low molecular weights, such as Dieldrin and 1242 PCB, are not adequately captured and retained by the glass plate collectors coated with mineral oil. We are now attempting to develop an improved sampling procedure that will overcome these limitations.

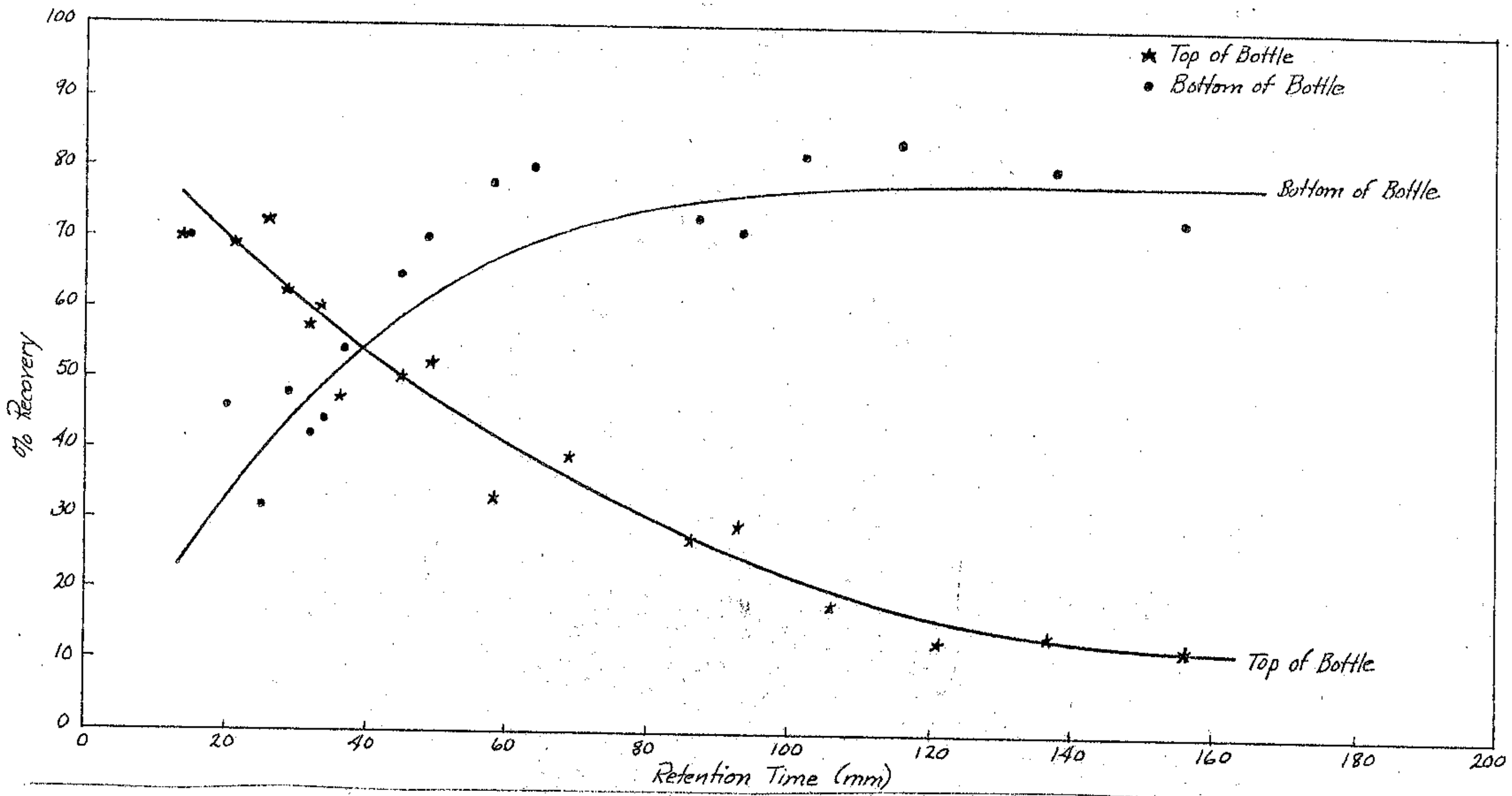

Figure C-3. Recovery of PCB's (Aroclors 1242 and 1254) from hexane-spiked glass jug.

Appendix D

PCB'S IN INDUSTRIAL DISCHARGES AND ANTIFOULING PAINTS

Table D-1 lists the concentrations of chlorinated hydrocarbons measured in 4-hour composites of industrial effluents discharged directly into the Los Angeles Harbor. Wastewaters from shipyards contained the highest concentrations of 1254 PCB (the only polychlorinated biphenyl identified in this survey). The highest levels of DDT compounds were found in fish cannery wastes.

Table D-2 presents the results of our survey of PCB levels in vessel antifouling paints presently used in anchorages of the Bight. Total DDT was not quantified, but upper-limit values generally were an order of magnitude below those for PCB.

Table D-1. Concentrations (μg/l) of chlorinated hydrocarbons in industrial discharge, Los Angeles Harbor, October 1973.

Type of Discharge	Flow (mgd)	Total DDT	Diel-drin	1254 PCB
Fish Cannery				
Waste No. 1	5.55	0.49	0.016	0.05
Waste No. 2	3.20	0.10	0.002	0.17
Retort Discharge	0.12	0.007	0.001	0.02
Shipyard				
Cooling Water No. 1	0.04	0.003	0.012	0.65
Cooling Water No. 2	0.43	0.001	0.001	0.01
Oil Tanker Cleandown	0.25	0.18	-	2.10
Ship Ballast No. 1	0.04	-	0.010	1.52
Ship Ballast No. 2	0.29	-	0.024	0.02
Oil Refinery Cooling Water	0.02	0.002	0.001	0.02
Power Plant Cooling Water	257	0.002	0.001	0.01
Chemical Plant, Combined Processes	5.51	0.002	0.002	0.03
Blank		<0.002	<0.002	<0.004

Table D-2. Polychlorinated biphenyl concentrations in antifouling paints used in southern California.

		PCB (mg/L)	
Code	Brand and Type	1242	1254
RECREATIONAL			
	Brolite Z-Spar		
P23	2000	<0.06	<0.16
P48	Multitox	<0.05	1.6
P34	Colortox	-	0.29
P53	Killer (B-90)	<0.3	<0.6
P37	A-1316 (1969)	<0.4	<1.2
	Woolsey		
P24	Vinelast (Blue)	<0.3	<1.0
P39	Vinelast (Red)	<0.1	<0.3
	International		
P28	Inter-lux 62	<0.2	<0.6
P26	Bottomkote 69	<0.4	<1.1
P20	Vinyl-lux	<0.03	<0.07
P19	Tri-lux	<0.3	<1.0
P18	Copper-lux	<0.06	<0.15
	Pettit		
P25	Unepoxy	<0.01	<0.03
P51	Trinidad 75 (red)	<0.09	<0.2
P31	Pacific Special	1.7	1.2
	Mariner's		
P2	1034 Lido	<0.3	<0.6
	Singapore		
P32	696 Blue	<0.4	<1.2
	Devoe-Reynolds		
P30	Navicote	<84	<220
P63	Triple C	12.0	28.0
COMMERCIAL			
	Devoe-Reynolds		
P54	Super Tropical	18	23
P58	3407	<0.005	<0.023
P59	213	<0.92	<0.29
P64	Hot Plastic	1.30	3.00
P55	Cold Plastic 105	<1.6	<4.0
	Amarcoat		
P62	Emeron 67	1.20	2.80
	Proline		
P57	1080	<0.17	<0.72
NAVY			
	Devoe-Reynolds		
P60	121/63	<0.1	<0.4
P61	129/63	<0.1	<0.4