COASTAL WATER RESEARCH PROJECT

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INPUTS OF DDT AND PCB

With the support of the U.S. Environmental Protection Agency, we have continued our investigation of the input rates of chlorinated hydrocarbons into the waters off southern California. The main routes are municipal wastewaters, surface runoff, aerial fallout, direct industrial discharge, antifouling paint application, and ocean current advection. During the past year, we have concentrated our efforts on quantifying the inputs via the first four routes.

One of the principal goals of this research has been to determine the concentrations and emissions of chlorinated hydrocarbon contaminants from the major municipal wastewaters discharged to the Bight. During the 2 years of the study, we have analyzed a number of 1-week effluent composites from each of southern California's six largest outfall systems, which account for approximately 95 percent of the submarine discharge of such wastewaters. Detailed intercalibration programs on split samples have been conducted with laboratories at the University of California and the University of Washington, and at the major sanitation districts responsible for routine monitoring.

One of our major conclusions from these intercalibrations is that the determinations of DDT compounds in Joint Water Pollution Control Plant (JWPCP) final effluent (once the dominant source of chlorinated hydrocarbons) made by the County Sanitation Districts of Los Angeles County have been in good agreement (±20 percent) with those of the other laboratories since the beginning of that monitoring effort in 1971. This is important in light of the fact that the JWPCP annual mass emission rate decreased from approximately 22,000 kg in 1971 (a mean effluent concentration of 42 µg/l) to 1,400 kg in 1974 (a mean concentration of 3.0 µg/l): Because of the rapid changes, occasional surveys by outside laboratories such as ours could provide only a coarse evaluation of the effect of control efforts in reducing coastal inputs that have been dominated by this discharge. The agreement between the DDT determinations of the other major sanitation agencies and those of outside

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laboratories was not as good, but the DDT levels in these effluents were generally quite low (less than 0.3 μg/l, except for Hyperion's 7-mile sludge, which was an order-of-magnitude higher). The only other chlorinated hydrocarbon pesticide we have observed in local wastewaters is Dieldrin; typical concentrations now appear to be on the order of 0.1 μg/l or lower.

The situation for the polychlorinated biphenyls is less satisfactory. These industrial materials often are a complex mixture of synthetic organic compounds that are difficult to identify and quantify by gas chromatography. For 1254 PCB, which has an average 54 percent chlorination, some degree of agreement on analytical data is now being reached between the outside laboratories and the monitoring agencies. However, major discrepancies still exist, and these must be resolved before confidence can be placed in this part of the effluent monitoring programs. The most significant recent finding is that 1242 PCB appears to be the dominant known polychlorinated biphenyl in most of the local municipal wastewaters. Effluent levels of 1242 PCB range from 0.1 to 8.0 μg/l, and Hyperion sludge contains 70 μg/l.

In contrast to DDT compounds, PCB's are widely discharged from submarine outfalls along the southern California coast. A comparison of estimated 1974 mass emission rates for total DDT and PCB compounds in the major municipal wastewaters to the Bight is given in Table 1. This comparison shows that approximately 90 percent of the DDT compounds released with municipal wastewaters during 1974 came from the JWPCP discharge off Palos Verdes Peninsula, in spite of the fact that control efforts instituted by the Los Angeles County Sanitation Districts in 1970 resulted in a 93 percent decrease in DDT waste emissions between 1971

Table 1. Estimated 1974 annual mass emission rates of total DDT and total PCB discharged to the Bight via major municipal wastewaters.

Discharger	Flow (mgd)	Total DDT (kg/yr)	Total PCB (kg/yr)
Oxnard, Ventura County	10	4	8
Hyperion, Santa Monica Bay			
5-mile effluent	340	56	160
7-mile sludge	5	17	790
Total	350	73	950
JWPCP, Palos Verdes Peninsula	350	1,440	1,300
Orange County Sanitation Districts, Orange County	170	54	2,100
Point Loma, San Diego	100	14	1,100
Total, Southern California Bight	980	1,600	5,500

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Table 2. Estimated 1972-73 annual mass emission rates of chlorinated hydrocarbons carried into southern California coastal waters via storm and dry weather runoff.

Type	Volume (10^6 cu m)	Total DDT (kg/yr)	Dieldrin (kg/yr)	PCB 1254 (kg/yr)
Storm	574	313 – 318	61.6	241 – 274
Dry Weather	127	7.1 – 7.2	4.9	7.3 – 7.8
Total	701	320 – 325	66.5	248 – 282
Dry Weather	18.1%	2.2%	7.4%	2.6 – 3.1%

and 1974. Emission of PCB compounds via these sources was much more uniform off Los Angeles, Orange, and San Diego Counties; the highest mass emission rate estimate (2,100 kg/yr, off Newport Beach) was only about two times the lowest (950 kg/yr, into Santa Monica Bay). PCB's now constitute the major chlorinated hydrocarbon contaminant found in municipal wastewaters discharged to the Bight, amounting to approximately three and one-half times the input of DDT compounds (5,500 vs. 1,600 kg/yr, respectively). Other chlorinated pesticide inputs via this route appear to be relatively minor; Dieldrin is the only other pesticide we have observed, and its estimated 1974 mass emission rate from municipal wastewaters appears to be less than 100 kg/yr.

Because pesticides are often widely dispersed following application in the field, surface runoff is generally assumed to be one of the dominant modes of chlorinated hydrocarbon transport to the sea. To determine the importance of such inputs in southern California during Water Year 1971-72, we conducted an intensive sampling of storm runoff in four major channels flowing into the Bight. During the following year, we limited our efforts to one of the largest of these channels, sampling the Los Angeles River over four storm periods. We also conducted two seasonal samplings of dry weather flow from ten channels widely spaced throughout the Bight.

On the basis of very satisfactory agreement obtained between Los Angeles River storm runoff results for the 2 years, we have used the 1971-72 flow-weighted mean concentrations in storm runoff to obtain Bight-wide mass emission rates for Water Year 1972-73. The results for this year, which was not unusually wet or dry, are summarized in Table 2. These data indicate that, although dry weather flow from the coastal plain constituted approximately 20 percent of the total surface runoff during 1972-73, it accounted for only about 3 percent of the mass emissions of chlorinated hydrocarbons

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via this route. Thus, most of the surface transport of these synthetic organic contaminants to the sea takes place during the few stormy days of the year that occur in southern California.

In addition to surface runoff, aerial fallout is a potentially-important mode for transport of chlorinated hydrocarbons to coastal waters. A technique of collecting dry fallout particles on glass plates sprayed with a hexane/mineral oil mixture has been used to determine the amount of aerial inputs to the Southern California Bight. Details of this fallout survey are presented in the following article. Our studies of chlorinated hydrocarbon inputs to the Southern California Bight via six routes during 1973-74 have produced the results summarized in Table 3. This summary indicates that submarine discharge of municipal wastewaters is still the largest known source of chlorinated hydrocarbons entering the marine ecosystem from the coastal plain. Although there has been a dramatic decrease in the DDT contribution of this wastewater during the last 3 years, it is still seen to be about one-half the total coastal input, excluding ocean current advection. However, the data indicate that aerial fallout is also an important route of entry for DDT and that surface runoff appears to be of secondary importance.

Municipal wastewaters are also the dominant known source of polychlorinated biphenyls. Of the 5,500 kg estimated to have been discharged via these wastewaters during 1974, approximately 80 percent was characterized as 1242 PCB and 20 percent as 1254 PCB. All of the large municipal systems make a significant contribution to this total, and it is important that more reliable monitoring data for PCB's be obtained in the future.

Table 3. Estimated annual mass emission rates of chlorinated hydrocarbons via six routes to the Southern California Bight.

Route	Year	Total DDT (kg/yr)	Dieldrin (kg/yr)	Total PCB (kg/yr)
Municipal Wastewater	1974	1,600*	80	5,550
Direct Industrial Discharge (San Pedro Bay)	1973	20	5	50
Antifouling Paint	1973	<1	<1	<1
Surface Runoff	1973	320	70	≤800**
Aerial Fallout	1973-74	1,300	—	1,500†
Ocean Currents	1973	7,000	—	4,000†

*90 percent from JWPCP.
**1,284 PCB: 300 kg/yr.
†1254 PCB only.

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Only 1254 PCB was detected in the aerial fallout samples, and a preliminary estimate of this input is about 1,500 kg/yr. We do not yet have a corresponding value for the lighter polychlorinated biphenyls such as 1242 PCB. However, it appears that surface runoff contains more 1242 than 1254 PCB; thus, the aerial fallout contribution of the lighter polychlorinated biphenyls may also be significant.

Surface runoff carries almost the same amounts of total DDT and 1254 PCB to the coastal waters (about 300 kg/yr, each). Thus, preliminary estimates for the aerial fallout inputs of these contaminants (1,300 and 1,500 kg/yr, respectively) are in good agreement with the relative amounts found in runoff.

An investigation of the importance of vessel antifouling paints as a potential source of chlorinated hydrocarbons (particularly PCB's) has demonstrated that, by 1973, this was a completely insignificant mode of input, although it may have been an important source in the past.

Our survey of approximately 40 industrial effluents being discharged directly into San Pedro and San Diego Harbors has produced no evidence that such discharges presently constitute a significant source of chlorinated hydrocarbons to the local marine waters.

In conclusion, it appears that inputs of PCB compounds to the Southern California Bight from the adjacent coastal plain are several times larger than those of DDT compounds. In contrast to DDT, the major PCB inputs are broadly distributed along the coast; thus, it may be considerably more difficult to obtain significant reductions in the quantities of PCB reaching the local marine ecosystem.

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AERIAL FALLOUT OF DDT

The comparison of chlorinated hydrocarbon inputs presented in the previous article indicates that, during 1973 and 1974, aerial fallout contributed almost as much DDT and its residues to the coastal ecosystem as did municipal wastewater, the largest single source of the pesticide. In light of the decreasing concentrations of DDT in the municipal effluents, it appears that aerial transport will be the dominant input route of the future. Thus, with the support of the U.S. Environmental Protection Agency, we have investigated the fallout rates of chlorinated hydrocarbons onto the Bight in considerable detail over the last 2 years.

Utilizing a glass plate and mineral oil collection technique first developed by Dr. Vance McClure (National Marine Fisheries Service, Tiburon, California), approximately 1,000 samples were taken in replicate 1-week collections made during two 13-week periods at 14 coastal stations and 6 island stations between Point Conception and the U.S./Mexico border. These samples have yielded a large body of data on several DDT compounds in dry aerial fallout, at levels free of apparent chromatographic interferences or significant contributions from analytical blanks.

The results for p,p,'-DDT, and p,p'-DDE (plus p,p'-DDD for the second survey) have been converted to estimated mean daily fluxes (10^{-9} g/sq m/day) for each sampling, applying a collection efficiency factor of 50 percent. The Wilcoxon signed-rank test was used to determine if there was any statistically significant difference between the two seasonal values of total DDT fallout onto the Bight. None was demonstrated at 95 percent confidence level; therefore, the weekly data for the individual components were averaged over the entire 26-week collection period. Figure 1 presents the resultant mean for total DDT. The average ratio of p,p'-DDT to o,p'-DDT observed in the Bight was 2.5 to 1, and these two isomers constituted approximately 70 percent of the "total" measurable flux of DDT compounds onto the Bight. In contrast, p,p'-DDE is the principal component

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observed in JWPCP wastewater and in the ocean bottom sediments around the site of this major discharge: Approximately three-quarters of the total DDT is made up of p,p'-DDE in the surface sediment samples.

Northern Baja California is often used as a control zone in Project studies; thus, during the first seasonal collection, a few weekly samples also were taken by student volunteers at the Institution for Oceanographic Investigations, Universidad Autonoma de Baja California, in Ensenada, Mexico. The results indicated that one of the highest coastal flux values for total DDT observed in the Bight during summer 1973 occurred at Ensenada. This is an agricultural region of the Baja California peninsula, and these higher fallout values appear to reflect greater or more recent local usage of DDT than to the north.

One of the most striking results of this Bight-wide survey was that, with the exception of the Ensenada results, the total DDT fallout values generally increased toward Los Angeles. This was surprising, as the major agricultural areas of the coastal plain lie to the north and south of this highly-urbanized region. Because the results of this research had indicated that dry aerial fallout was a relatively important source of DDT compounds to the Bight, the project conducted its own fallout survey within the Los Angeles Basin to further investigate this finding.

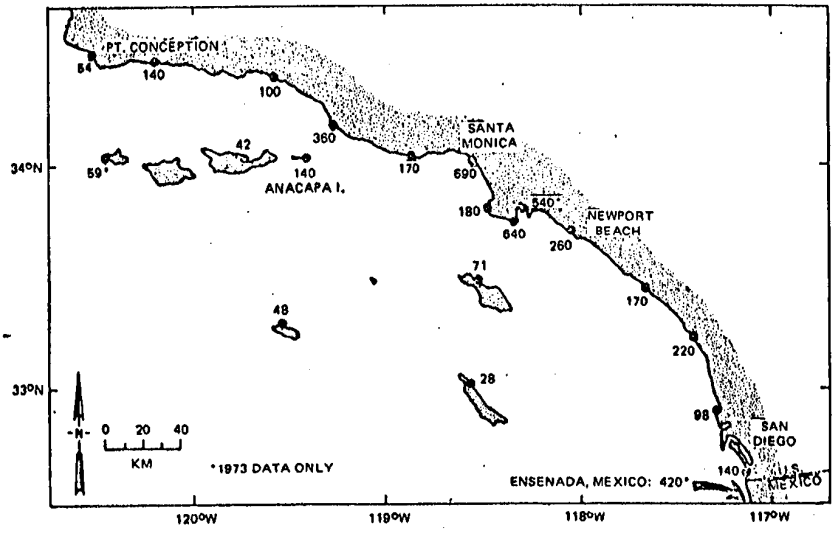

Figure 1. Average flux of total DDT (10^{-9} g/sq m/day) in dry aerial fallout, 1973-1974.

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Between 26 April and 24 May 1974, we sampled 24 stations during 4 successive weeks. Because of the past history of dramatic DDT pollution of the Bight, apparently as a result of waste discharges from Montrose Chemical Company, four stations were established within a few blocks of this industrial plant in the city of Torrance. Four sites also were established around the sanitary landfill in Rolling Hills Estates on the Palos Verdes Peninsula, operated by the County Sanitation Districts of Los Angeles County. It is reported that this landfill received DDT wastes from the Montrose plant up until about 1972. In addition, four sites were established around a private sanitary landfill owned by Ben K. Kazarian and located near the city of West Covina where the Montrose wastes are now taken.

In this survey, both the DDT constituents and 1254 PCB were clearly identified at levels at least an order of magnitude above those found in process blanks. The results showed two regions of relatively high DDT fallout, located in the vicinity of the Montrose plant and the Rolling Hills sanitary landfill. The highest of the values in each region generally occurred at the south or southeast stations. As the prevailing coastal winds are from the northwest, this suggests two separate sources. Wind data for the interior of the Basin are being analyzed to further investigate this subject.

In light of the large gradients in DDT fallout rates that were observed, and the implications regarding the sources, the survey was repeated during 2 weeks in September 1974; two additional stations were included in the pattern around the Montrose plant. The September DDT data were similar to those of the previous spring and indicate little seasonal effect.

The occurrence of an occasional anomalous value can strongly bias a small-sample mean, so for this basin study, we assumed the median of the six weekly values to be most representative of the fallout flux at a given station. These values for total DDT and 1254 PCB are illustrated in Figures 2 and 3, respectively.

The data presented above indicate an apparent relationship between the DDT fallout distribution and the location of a major manufacturing facility and one of its past waste disposal sites. However, the level of DDT in the dry aerial fallout around the present disposal site (the Kazarian landfill) is not any higher than levels at other Basin stations. As the two principal constituents of the pesticide itself are p,p'-DDT and o,p'-DDT, we examined these two products of the manufacturing process in greater detail. We found a considerably larger value for the ratio of p,p'-DDT to o,p'-DDT around the two regions of highest fallout (10 sites) than in the rest of the Basin

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(15 sites); median values for the two groups are 5.0 and 3.2, respectively. This ratio may be an indication of the relative "freshness" of the DDT constituents collected on our fallout plates. Similarly, the para and ortho isomers together constitute the largest percentage of total measurable DDT at these 10 sites; median percentages for the two groups are 85 percent and 63 percent. This too

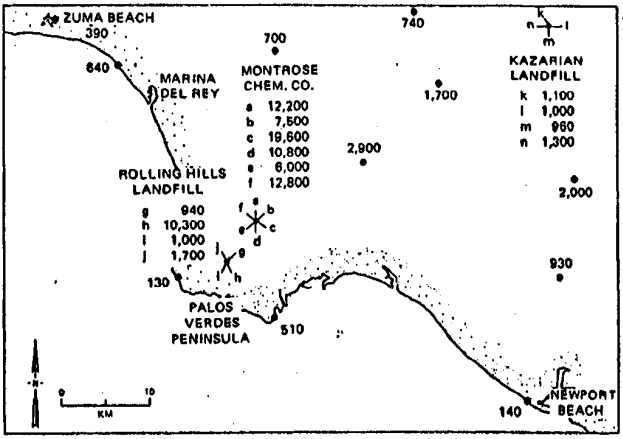

Figure 2. Median flux of total DDT (10^{-9} g/sq m/day) in dry aerial fallout collected during 6 weeks of 1974.

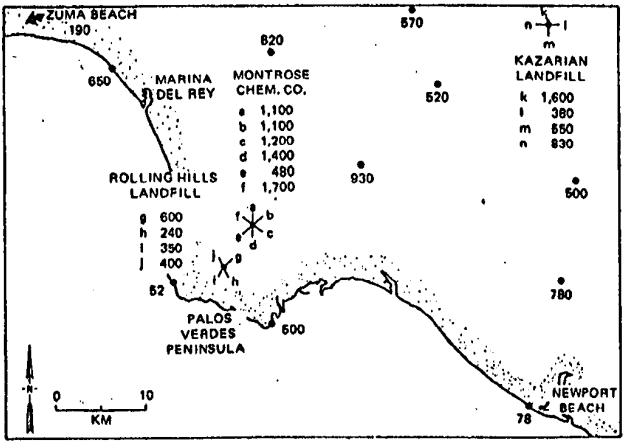

Figure 3. Median flux of 1254 PCB (10^{-9} g/sq m/day) in dry aerial fallout collected during 6 weeks of 1974.

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may be related to effects of "weathering." Finally, to determine if the relatively high DDT fallout values around the manufacturing plant and its past waste depository could be due merely to higher deposition of particulates, we have normalized the values against 1254 PCB, which is not manufactured by Montrose Chemical Co. Distinctively higher values for this ratio are observed around the plant and the Rolling Hills landfill (median: 6.0) than in the rest of the basin (median: 1.2). Thus, it appears that the gradients in DDT fallout values we have observed do indicate two regions that are potentially important sources of DDT compounds to the Los Angeles Basin and the adjacent Southern California Bight.

Two methods were used to calculate the amount of total DDT falling onto the basin annually. The first involved a strict linear interpolation between data points. For those stations where there were two or more sampling sites, the median flux was used to represent the station. It should be noted that in the case of the Rolling Hills landfill, one site has a significantly higher flux than the other three sites. As this value is the median of six weekly values, and this site had the highest weekly flux reported for the entire Basin study, it appears that the site represents a secondary source of DDT. However, the median flux of $1{,}400 \times 10^{-9}$ g DDT/sq m/day is a more representative value for that station. Because the location of sampling sites and the high values at Montrose bias the fallout estimate of 2.2 metric tons/yr derived from our contours, we consider this to be an upper limit. The median flux for the entire Basin, 930×10^{-9} g/sq m/day, was used to estimate a lower limit. The fallout estimate calculated using this value is 0.5 metric tons/yr, resulting in an estimated range of 0.5 to 2.2 metric tons/yr.

One of the most important aspects of these findings is that there still may be a significant release of DDT wastes to the southern California environment from the manufacture of this pesticide in Los Angeles County, even though the discharge of liquid wastes to the County sewer system has been stopped. During 1974, the average level of total DDT in JWPCP final effluent was 3.0 μg/l, which alone exceeds the level allowed by the California State Water Resources Control Board "Ocean Plan" (2 μg/l on a 50 percent occurrence basis) for total identifiable chlorinated hydrocarbons in such wastewaters. The corresponding mass emission rate for total DDT was 1,400 kg/yr. We have estimated that a similar quantity (1,300 kg) of DDT compounds fell onto the coastal waters annually during 1973-74. A significant fraction of this material may have emanated from DDT wastes produced during manufacture of the pesticide in Los Angeles County, either directly from the plant or from its original land waste disposal site. Thus, a unified con-

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trol plan to reduce marine inputs of this pollutant would require that attention also be paid to these potential sources of DDT to the atmosphere in Los Angeles Basin.

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