Aerial Fallout of DDT in Southern California

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DDT and its metabolites are among the most serious contaminants yet identified in the marine environment (RISEBROUGH et al. 1967; DE LONG et al. 1973; MC DERMOTT et al. 1974). In past years, very large quantities of DDT wastes were released into the JWPCP* sewer system of the County Sanitation Districts of Los Angeles County (MAC GREGOR 1974). These wastes, apparently produced by Montrose Chemical Company (during the manufacture of this pesticide) were subsequently discharged via the JWPCP submarine outfalls off Palos Verdes Peninsula to the marine ecosystem of the Southern California Bight (Figure 1).

During the last 3 years we have investigated the input rates of DDT and other chlorinated hydrocarbons to the Bight via a number of different routes (YOUNG et al. 1974; RISEBROUGH et al. 1974). Here we report the results for one of the routes, dry aerial fallout. In view of the very low rainfall in southern California, approximately 30 cm/yr, dry aerial fallout dominates aerial inputs along this section of the Pacific Coast.

Utilizing a glass plate and mineral oil collection technique first developed by Dr. Vance McClure (National Marine Fisheries Service, La Jolla, 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.

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* Joint Water Pollution Control Plant
** July-September 1973 and March-June 1974

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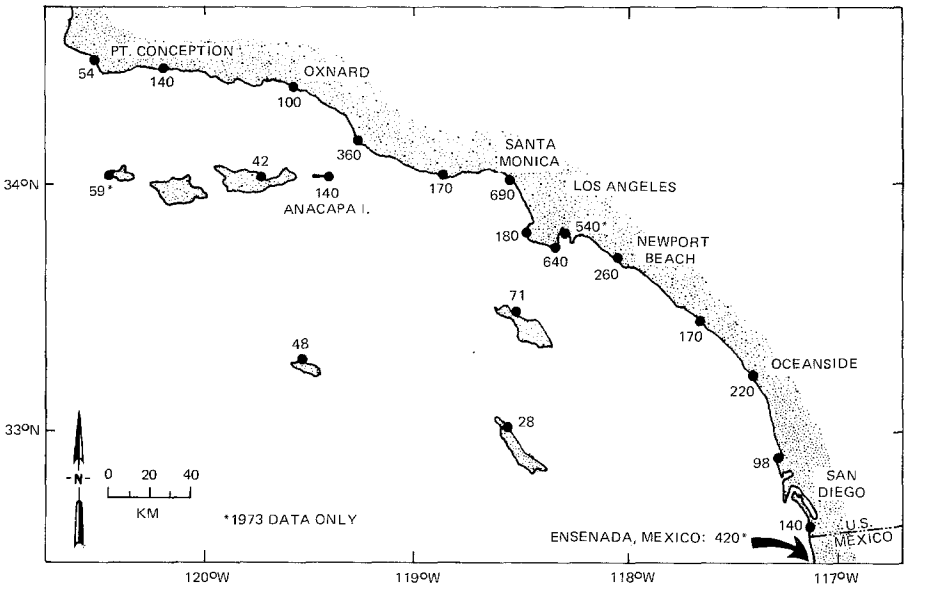

FIGURE 1. Average flux of total DDT (10^{-9} g/sq m/day) via dry aerial fallout collected in the Southern California Bight during 1973-74.

MATERIALS AND METHODS

The collection device for sampling dry aerial fallout was a piece of cleaned window glass (0.1 square meter) sprayed with a mixture of pharmaceutical mineral oil (Squibb brand) diluted by five parts pesticide-grade hexane. A pair of cleaned plates wrapped in aluminum foil were taken to the collection site, unwrapped, and placed on a horizontal surface above the ground. Generally this was the roof of a one-story structure located on or near the beach but removed from obstructions with large profiles which might cause excessive turbulence. Every effort was made to isolate the sampling plates from nearby painted surfaces, especially if the paint was flaking. If this was impossible, samples of the potentially contaminated material were taken for analysis.

Once the places were unwrapped and in place, they were sprayed with a very light coat of the diluted mineral oil using a TLC sprayer (Chromatosprayer brand). The criterion followed was to apply enough oil so that the plate would trap small particles but not larger objects such as insects and feathers. Usually, spraying from a distance of about 0.3 meter for a period of about 5 seconds was sufficient. After the hexane evaporated,

this left roughly 0.3 ml of oil on the plate.

At the end of the one week sampling period, a cleaned piece of teflon, cut with a straight edge, was used to scrape the mineral oil and fallout particles from the plate. The oil was transferred from the edge of the teflon strip to the inner rim of a pointed, graduated pyrex centrifuge tube. After several minutes of scraping, the plate was re-sprayed with diluted mineral oil and rescraped; this procedure was repeated for a third scraping. (Tests have indicated that this three-step process recovers more than 95% of the fallout material.) Then, the sample tube was covered with aluminum foil under a screw cap and returned to the laboratory. Before leaving the site the scraped sampling plates were re-sprayed to begin the next sampling period.

Aerial fallout samples were processed through a "clean-up column" before being analyzed by gas chromatography. The clean-up column was a disposable 5 ml pipet packed with specially prepared and activated silica gel. MCB Silica Gel (SX-144-6) 100-200 mesh was washed with a 1:1 solution of methanol/benzene. Three milliliters of solution were used per one gram of adsorbent. After rinsing, the silica gel was dried in a Rotovapor and activated at 180°C overnight and then stored under hexane. The column was packed by inserting a plug of silane treated glass wool, adding several mls of hexane and slurrying the silica gel with a pipet. Using the markings on the 5 ml pipet as a guide, adsorbent was added until the volume of the compacted bed was 1.7 ml $\pm$ 0.1 ml. A vibrator was held against the column briefly to compact the adsorbent.

The fallout samples came into the laboratory in centrifuge tubes containing up to 1 ml of mineral oil. The sides of the tube were washed down with enough hexane to bring the volume to 3 mls. The sample was then introduced into the column using a pipet to transfer it from the centrifuge tube. The initial elution was with 1.7 ml of hexane to remove the mineral oil from the column; this fraction was discarded. The DDT compounds were then eluted with 5.7 ml of 20% benzene/hexane. Dilutions of this fraction were made to appropriate volumes for analysis by electron capture gas chromatography.

RESULTS AND DISCUSSION

The results for p,p'-DDT, o,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 respective collection efficiency factors of 60, 64, 36 and 63 percent. The Wilcoxon

signed-rank test was used to determine if there was a statistically significant difference between the two seasonal values of total DDT fallout onto the Bight. None was demonstrated at the 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, we have observed that approximately three-quarters of the total DDT in ocean bottom sediments around the site of the JWPCP outfalls is made-up of p,p'-DDE and the principal components of the wastewaters discharged are p,p'-DDE and p,p'-DDD.

During the first seasonal collections a few weekly samples also were taken 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 our research had indicated that dry aerial fallout was a relatively important source of DDT compounds to the Bight, we conducted a fallout survey within the Los Angeles Basin to further investigate this finding.

Between 26 April and 24 May 1974, we sampled 24 basin 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 located in a suburb of Los Angeles. 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, the DDT constituents 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.

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. The values for total DDT are illustrated in Figure 2.

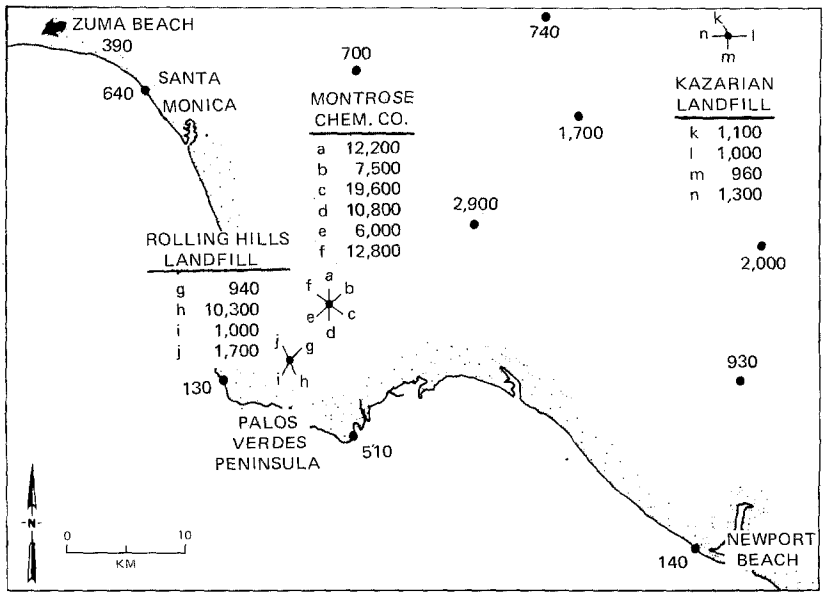

FIGURE 2. Median flux of total DDT (10^{-9} g/sq m/day) via dry aerial fallout collected in the Los Angeles Basin during 6 weeks of 1974.

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) was 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 (15 sites); median values for the two groups were 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, p,p'-DDT and o,p'-DDT together constituted the largest percentage of total measurable DDT at these 10 sites; median percentages for the two groups were 85 percent and 63 percent. This too 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 normalized the values against 1254 PCB, which is not manufactured by Montrose Chemical Co. Distinctively higher values for this ratio were 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 had a significantly higher flux than the other three sites. As this value was the median of six weekly values, and this site had the single highest weekly flux reported for the entire Basin study, it appears that the site represents a secondary source of DDT. However, the median flux for the four sites around the landfill ($1{,}400 \times 10^{-9}$ g DDT/sq m/day) is a more representative value for that region. Because the location of sampling sites and the high values at Montrose biased 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 3.0×10^{-6} g/l, which alone exceeded the level allowed by the State of California Water Quality Control Plan for Ocean Waters of California (STATE WATER RESOURCES CONTROL BOARD, 1972) for total identifiable chlorinated hydrocarbons in such wastewaters (2×10^{-6} g/l on a 50 percent occurrence basis). The corresponding mass emission rate for total DDT was 1.4 metric tons/yr. From the results of our two seasonal surveys, we estimate that a similar quantity (1.3 metric tons/yr) 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 control 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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