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DDT IN MARINE PLANKTON AND FISH IN THE CALIFORNIA CURRENT

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DDT residues have entered all compartments of the world ecosystem due to their mobility, environmental stability, and their affinity for biological materials (Risebrough, *et al.*, 1968; Risebrough, 1969). Due to estuarine, air, and sewage transport of these contaminants to the oceans and their subsequent fixation into organisms and sedimenting particles, one would expect an eventual net transfer and accumulation of these materials in oceanic ecosystems (Wurster, 1969).

DDT residues, especially the compound p, p'-DDE, must have remarkable resistance to physical and biological degradation because of their abundance in the environment (Risebrough, *et al.*, 1970). A measure of the persistence of these compounds in the environment is the half life, or the time required for half of the originally present DDT to disappear. These estimates range from 10 to 15 years in the soil of forests and agricultural plots (Edwards, 1966; Nash and Woolson, 1967). "Disappearance" in this context does not necessarily imply degradation to non-toxic derivatives of DDT; movement of the DDT from the site of application must be considered. DDT is highly mobile when it is in contact with water (Bowman, *et al.*, 1964). This facilitated evaporation has been referred to as "codistillation." Recent estimates (Lloyd-Jones, 1971) indicate that half of the DDT applied to crops may eventually evaporate; a specific rate of 3×10^{-3}g cm^{-2} hr^{-1} at 20°C has been calculated.

Because of latent vaporization of the DDT residues from the site of application, as well as other causes of movement, such half life estimates are likely to be minima. An additional cause of global dispersal of DDT residues is atmospheric transport of DDT which becomes dispersed during aerial application. Hindin (1970) in a careful study of an agricultural study plot, estimated that 35% of released DDT never reached crop height. In an earlier study of forest soil, Woodwell (1961) indicated that over half of the released DDT did not actually reach the ground.

Latent movements of DDT residues from sites of application also occur via movement of particles with adsorbed DDT in run-off water (Peterle, 1970), and wind-borne dust (Cohen and Pinkerton, 1966). DDT residues in rainwater are present in quite high concentrations (Tarrant and Tatton, 1968), indicating that rain will remove much of the burden of DDT residues from the atmosphere, where it is present as aerosol and adsorbate on dust.

These processes require a certain amount of time to effect a transfer of DDT residues from terrestrial areas to the ocean. Evidence gathered from a series of DDT residue analyses of net phytoplankton samples collected in Monterey Bay, California from 1955 to 1969 (Cox, 1970a) suggests an approximately threefold increase in DDT residue concentrations. Considering the minimum environmental half life estimates of ten to fifteen years and the latency factor inherent in the transport of DDT residues to the ocean, it is not surprising that DDT residues in these phytoplankton samples increased despite a twofold decrease in domestic usage over the period 1959 to 1969.

Smith, *et al.* (1970) analyzed available data on DDT concentrations in river systems, dust and rainwater, and concluded that atmospheric transport was the greatest factor contributing to DDT residues in the surface mixed layer of the world's oceans. Their calculations of river input yielded a maximum annual input of 3.8×10^3 metric tons, and it was felt that even this figure was probably too high. Rainwater DDT residue concentrations and annual rainfall statistics yielded a value of 2.4×10^4 metric tons, almost an order of magnitude greater than the maximum estimate for runoff water.

An alternative procedure for calculation of DDT input to the ocean is to combine estimates of DDT residue concentrations in dust collected over the ocean and figures for sedimentation rates of the dust. Risebrough, *et al.*, (1968, thus computed the input to the Atlantic Ocean between the equator and 30° N at 0.6 metric tons annually and compared this to an estimated input of 1.9 metric tons per year from the San Joaquin River drainage. Goldberg and Griffin (1970) made further measurements of DDT residue concentrations in dust over the Bay of Bengal and found concentrations of 7.3 to 135×10^{-8}g with a mean of 32×10^{-8}g DDT residues/g of dust (compared to 4.1×10^{-8}g DDT residues/g of dust collected at Barbados). They calculated an input of six metric tons annually. These estimates of pesticides in dust are minimal estimates because of the inability of the dust traps to collect small particles, *ca.* 1μ and less, which may constitute the majority of the adsorptive interface present in airborne particulate material (Delany, *et al.*, 1967).

The foregoing discussion has emphasized exogenous measures of DDT residue inputs. Another way to assess this input is to measure DDT residues in the organic particulate material of the ocean.

Prevailing levels of DDT residues in phytoplankton material collected by a net in Monterey Bay are about 3×10^{-5}g DDT residues/g carbon (Cox, 1970a).

Using estimates of standing crop density given by Mullin and Brooks (1970), and Holm-Hansen (1969), the total DDT content of an area of about 100 km by 600 km extending from San Diego to Monterey Bay, California (hereafter referred to as the described area) was estimated at about 1–10 metric tons. The larger figure is more likely because of negative bias in standing crop estimations and because the DDT concentration value quoted above is a minimum value since it was determined for very high standing crop densities.

Extractions of whole seawater from a number of transects through the described area yielded DDT residue concentrations of whole seawater in this area of about 5×10^{-6}g/m^3, accounting for the extraction efficiency of the procedure. Assuming a depth of 50 m in the mixed layer of the described area, a total of 15 metric tons is yielded as an estimate of the DDT residues present. Much of the material included in the net tow material described above was excluded from these raw water extractions (chain-forming diatoms, larger detritus, *etc.*), so it is not unreasonable to lump this amount with the one reported above for an estimate of *ca.* 25 metric tons existing at one time in the phytoplankton, detritus, and water of the surface waters of the described area.

Fish, primarily the northern anchovy *Engraulis mordax,* account for about 3 metric tons in the described area, assuming a mean concentration of one part per million DDT residues and the values for fish tonnage of the area quoted by Baxter (1967). Estimates of zooplankton standing crop (Lasker, 1970) used with an assumed concentration of 0.25 parts per million yield another 3 metric tons. This brings the total estimate to 31 metric tons of DDT residues for the area.

In the southern California area especially, input of DDT residues from sewage effluent is considerable. In May, 1970, estimates of the input of the sewage outfall at Whites Point in Los Angeles amounted to 146 metric tons per year, authough it dropped to 36.5 metric tons after partial control of the manufacturing disposal of DDT into the sewage system. Clearly this input is of sufficient magnitude to account for a large share of the DDT residues estimated to be present in the surface waters of the described area. However, it is not known what fraction of this effluent is effectively transported to and dispersed in the water above the pycnocline (the outfall at Whites Point is below the pycnocline).

Risebrough, *et al.* (1968) estimated that the dust samples collected at the Scripps pier in La Jolla, California contained 10^3 times more pesticide than the Barbados samples, despite the prevailing landward winds, and attributed this high concentration to ". . . an unknown admixture of air from neighboring agricultural area." They estimated a mean concentration of 1.8×10^{-5}g total pesticides/g of dust. DDT residues represent the principal component of this figure; if the same sedimentation rates apply to the described area as to the tropical Atlantic, the estimated input must be at least 0.7 metric tons annually. This amount is a minimum estimate since particulate fallout in the described area is most likely greater than that over the tropical Atlantic: moreover, the aforementioned negative bias in the collection techniques suggests the actual value is higher. Thus atmospheric fallout must be a quantitatively important factor for DDT residue input in the described area, along with runoff and sewage. Spatial patterns in DDT analyses of whole seawater collected on transects inside and outside of the described area are discussed in further detail by Cox (1971a).

Not accounting for runoff, the estimate of 31 metric tons of DDT in the described area may be attributed to inputs from sewage and airborne particles. A more accurate assessment of the magnitudes of the annual inputs from each of the three mentioned sources would allow computation of a turnover rate in the surface waters of the described area. Of equal importance is the description of the processes involved in the movement of these residues into and through pelagic food chains.

Fig. 1 schematically depicts the sources of DDT residues in the coastal environment and outlines some of the distributional possibilities once the residues have entered seawater. Before attempting to discuss the various transfer steps and the consequences of this schematic model, it is necessary to establish a few basic points:

(1) DDT residues entering the ocean via any of the indicated sources is mostly sorbed to the particulate material carried with the influx (Freed, 1970; Peterle, 1970).

(2) This binding is reversible, so when contact of the particle is made with biological material of high lipid content, there is a chance that the associated DDT residues will pass into the fatty material, in which it is highly soluble. In Fig. 1, we may consider material "soluble" if it is available for uptake by organisms.

(3) Once DDT has entered the lipid phase of a biological system, it is likely to remain chemically stable (Risebrough, *et al.*, 1970) and to stay there. Once it is in lipid, its movements are bound to be influenced almost entirely by phase equilibria rather than adsorption equilibria. For example, loss of DDT can be mediated by phase partitioning of DDT in the blood of an organism into the lipids of undigested remains of material in the digestive tract. This can be inferred from the data of Macek, *et al.* (1970) for freshwater fish.

(4) Sorption of DDT residues to particulate material changes in intensity with the nature of the substratum, so that interchange between the physical system and the biological one may be due to a difference in the adsorption energy coefficients of the two substrata (Weber and Gould, 1966).

The first step in entry to the food chain is uptake by organic particulate material. Initial studies of this step showed that phytoplankton cells had great concentrating capacity (Cox, 1970b), but the generality of the partition coefficients, as they were expressed,

became dubious because it appeared in the analyses of the net tow material that the density of cells or particles did not greatly affect the amount of DDT residues taken up per unit volume of water (Cox, 1970a). The observation admitted two distinct possibilities: (1) a phase partition mechanism determined uptake, and in each instance the nearly total amount of available residues ("dissolved") were taken up in the lipids of the phytoplankton and other particles, or (2) uptake was determined by adsorption equilibria, but the concentrations were such that the liquid-solid adsorption equilibrium was still on the linear part of the curve (where there are still many available adsorption sites on the substratum), where almost all of the DDT is adsorbed. The only way to distinguish between these possibilities is to attempt to saturate the system. If phase partitioning is the case, it would take more "available" DDT to saturate the system, since DDT is soluble in lipids by as much as 50% by weight (*e.g.* in corn oil). Later experiments (Cox, 1971a) showed that, in the presence of abundant, available ^{14}C-DDT, algal cells took up a constant amount per cell. This supports the adsorption hypothesis for *Dunaliella salina*, the species tested. In diatoms, the situation might be different because of the large oil inclusions often found in the cells.

Zooplankton (including various larval forms of fish) are likely to obtain some of their body residues of DDT by direct uptake from water. Cox (1971b) describes the results of uptake studies with a common euphausiid shrimp of the California coastal waters. The results are consistent with a two step uptake process: adsorption, then diffusion into lipid. It appeared that most of the DDT taken up during short term experiments would be lost when the ambient concentration was lowered, suggesting an easily reversible adsorption equilibrium. Direct uptake from water may be more important for the smaller zooplankton.

Uptake from food was shown to be an adequate explanation for the natural levels of DDT residues in the study organism. Uptake can be explained by bulk assimilation of lipids; loss of DDT in body is probably due to the process described in item (3) above, or to release of gametes (Cox, 1971c).

Fish in most environments probably do not acquire much of their body's DDT residues by uptake from water (Macek and Korn, 1970; Macek, 1970). Originally, it was assumed that uptake via gill surfaces was the principal mechanism by which fish acquired DDT residues (Holden, 1966). This is a reasonable explanation in instances of areas receiving direct or heavy indirect input of DDT (Edwards, 1970). One observation which has been made about fish in freshwater or marine environments is that DDT residues continue to accumulate with age (Reinert, 1970; Macek and Korn, 1970; Cox, 1970c). A study of DDT residues in *Engraulis mordax*, an important planktotrophic fish of the described area, suggests some of the basic mechanisms expected to control the acquisition and loss of DDT residues by fish (Cox, 1971c).

An examination of Fig. 1 leads to the idea that DDT residues, once they have entered the biological system, will eventually be transferred away from the

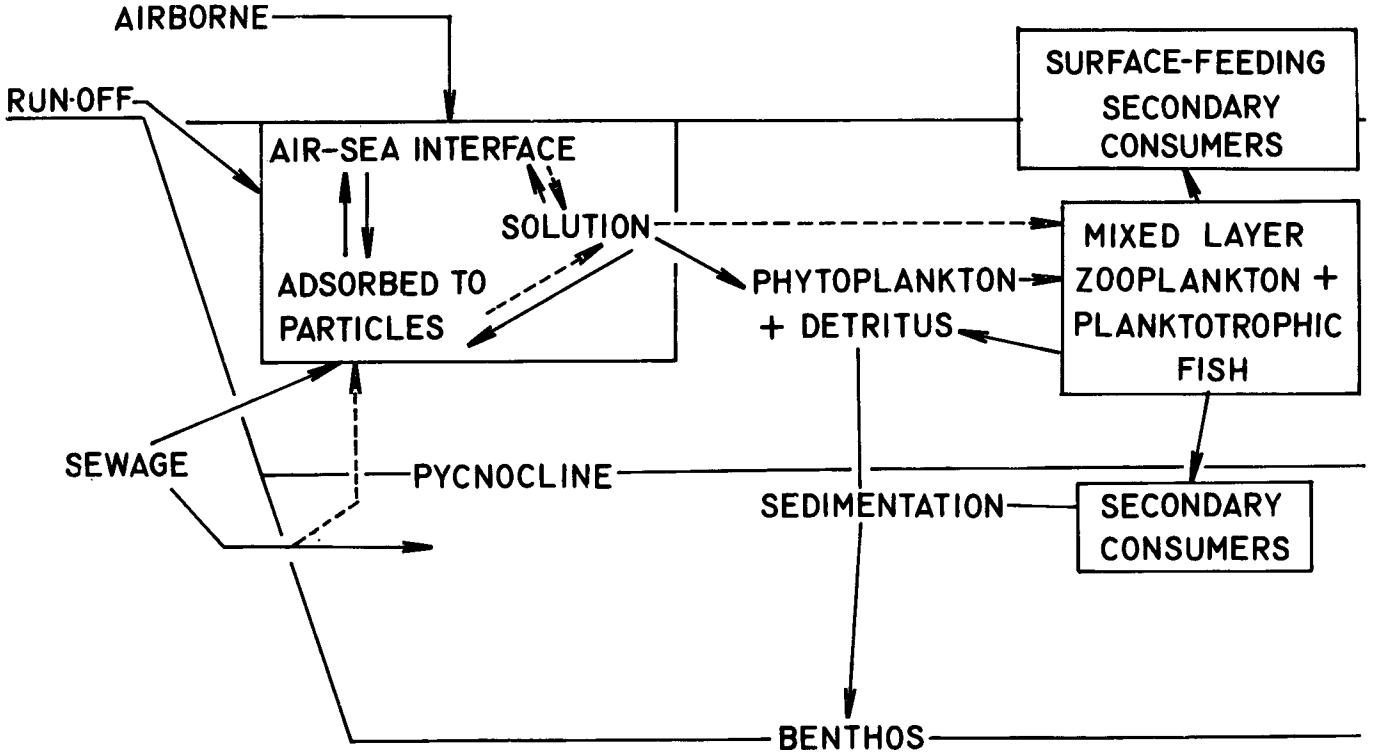

FIGURE 1. Flow chart depicting the fate and distribution of DDT residues in a populated coastal environment.

first compartment of planktotrophic fish and surface dwelling zooplankton by three routes: (1) by being eaten by avian, mammalian, or piscine predators, all of which will remain in association with surface layers, (2) by the sedimentation of detritus produced by this compartment, (3) or through consumption by vertically migrating predators from mid-depths. Some algal cells themselves will fall out of the surface layers. Although many possibilities exist for trophic re-

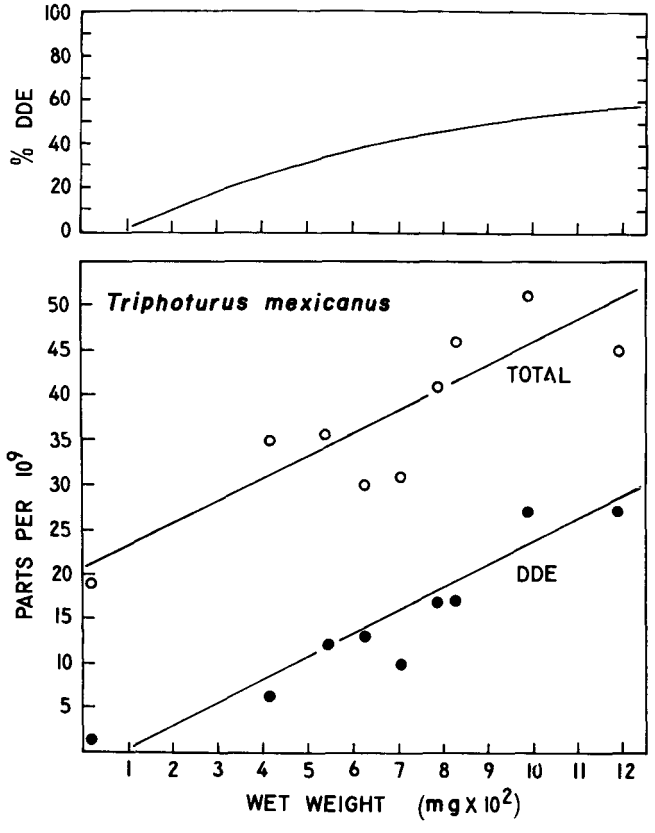

FIGURE 2. DDT residue concentration as a function of wet weight in the fish *Triphoturus mexicanus*, from the Gulf of California (Cox, 1970c). Upper curve is derived by measuring the differences between the regression lines in the lower plot.

cycling of DDT residues in the surface layers, ultimately the bulk of these residues will be transported away by highly mobile, surface feeding predators, or will sink to the benthos after death. Decay of the surface feeding predators will ultimately lead to some sedimentation of their DDT residues. On this basis, a net transport of DDT to oceanic sediments can be predicted.

One of the consequences of the incorporation of DDT into animal lipid is that it is relatively stable there and will tend to remain in association with lipid according to the mechanism stated in item (3) in a previous paragraph. As DDT stays in contact with biological materials, the amount which is converted to DDE apparently increases. Fig. 2 shows a DDE accumulation function derived from the analysis of *Triphoturus mexicanus* (Cox, 1970c). Risebrough, *et al.* (1970) postulated that the high DDE concentrations in oceanic predators reflected the residence time in biological materials occasioned by the multiple trophic transfers leading to consumption by high order predators.

On this basis, one would expect DDE to be accumulating in the benthos, since it is the final compartment of the system, and since its DDT residues may be expected to have resided in pelagic biological systems for a certain time before sedimentation.

Since the trophic relationships, the distribution and sedimentation rates of organic particulate material, and the actual biomass content of pelagic ecosystems are still imperfectly understood, we cannot expect a greater level of understanding of the distribution and movement of DDT residues in this system. The foregoing discussion has dealt with findings which allow use of our present knowledge of pelagic ecosystems for prediction of these distributions and movements. The examples studied, however, are far from being representative of the whole pelagic ecosystem and much more investigation is required. DDT and its metabolites are the most ubiquitous man-made substances known; while we still do not understand the complete range of their toxic effects, they are worthy of our continued attention on the basis of their global abundance alone.

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