Deposition of Heavy Chlorinated Hydrocarbons from the Atmosphere

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ABSTRACT

A sensitive method for the measurement of deposition fluxes of volatile and aerosol chlorinated hydrocarbons (CHC) is presented. Fluxes of CHC ranging from 10^{-6} to 10^{-9} g m^{-2} day^{-1} for the 54% chlorine PCB mixture were measured at La Jolla, California (average: 3 X 10^{-7} g m^{-2} day^{-1}) during February, 1972. PCB fluxes are correlated with the component of the wind trajectory in the direction of Los Angeles weighted by the reciprocal of the wind speed. Chlorinated pesticide fluxes (DDT and dieldrin) are correlated with winds from agricultural areas inland from the measuring site.

INTRODUCTION

An understanding of the behavior of pollutants in the environment requires a knowledge of the amounts of material present in the atmosphere, in the soil and in the oceans and the rates at which pollutants are being transported between these reservoirs. The widespread occurrance of CHC in marine biota (GIAM, et al., 1973) prompted this investigation of the routes these chemicals take to enter the ocean. The approximate rates at which CHC enters the Pacific Ocean off Southern California via outfalls and runoff have have been measured (SCCWRP, 1973). After other possible sources, such as leaching of plasticizer from ship bottom paint, have been accounted for the most obvious remaining mechanism for pollutant entry is atmospheric fallout.

MEASUREMENT OF AEROSOL DEPOSITION FLUX

Sheets of glass having areas of 0.17 m^2 covered with a thin film of mineral oil were chosen as the deposition surface. If a mesh or screen is used as a fallout trap, an account must be made of the aerosol filtered from the air which would pass through the mesh (SODERGREN, 1972). A mixture of 20% pharmaceutical grade mineral oil in n-hexane was applied to the glass with an all-glass aspirator sprayer. Approximately 0.5 ml of oil was found to be sufficient. At the end of the sampling interval, the oil was removed from the glass with a Teflon (PTFE) squeegee and an eye dropper. Quantitative recovery from the surface was achieved by spraying and removing another layer of hexane-oil mixture.

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Mineral oil from the deposition plates was diluted slightly with n-hexane to reduce its viscosity and passed through a 5 mm dia. X 75 mm long column of active silica-gel to scavenge the chlorinated hydrocarbons. The scavenging adsorbent was prepared by rinsing Matheson, Coleman and Bell SX-144-6 silica-gel with 3 ml 1:1 (v/v) methanol/benzene solution per gram of adsorbent followed by drying in a Rotavapor and activation at 180° C for > 4 hours. (Temperatures higher than 180° C will result in a less active adsorbent.) The adsorbent was stored under hexane in a tightly stoppered flask and slurried into the columns (Pasteur pipettes with glass wool plugs) with this solvent. A vibrator was used to compact the adsorbent bed which contained about 1.7 g of silica-gel. One ml n-hexane per gram of adsorbent was passed through the column in order to remove the remaining mineral oil and 3 ml g^{-1} of 20% benzene in n-hexane was used to elute PCB and chlorinated pesticides. PCB was found to elute from the scavenging column after a total of 5 ml n-hexane and hexane/oil mixture have passed through the adsorbent bed. This elution behavior should be confirmed with each batch of adsorbent. The eluate was then concentrated under vacuum at room temperature to a suitable volume and analyzed by GLC with electron-capture detection. GLC columns packed with Supelco^{tm} 1.5% SP-2250 plus 1.95% SP-2401 were run at 195° C.

RESULTS

Deposition plates set out for two days captured residues equal to the sum of the contents of two plates, each of which were in place for only one of the consecutive days. Plates therefore retain full efficiency for at least two days. Clean glass plates were found to be only slightly less efficient than oiled plates.

The deposition fluxes were commonly in the range 10^{-6} to 10^{-8} g m^{-2} day^{-1} of individual chlorinated hydrocarbon compounds while the limit of detectability was less than 10^{-10} g m^{-2} day^{-1}. Measurements were made at the National Marine Fisheries, Fishery Oceanography Laboratory at La Jolla and duplicates of five 24 hour measurements were made from the Scripps Institution of Oceanography pier, about 1 km from the first station. The precision with which replicate flux measurements can be made is ± 5%. Fluxes at the two stations were within this tolerance showing that no point source of any of more than 30 chlorinated hydrocarbons apparent on the chromatograms was present in the immediate neighborhood of the sampling sites.

Wind velocity measurements were made at Montgomery Field, 10 km east of the sampling site. Montgomery Field is surrounded by level terrain for 10 km in all directions and in the direction of the prevailing wind, there are no irregularities greater than 150 meters high for over 50 km. Monthly mean wind for the month of February 1972 had a bearing of 323.4° while the monthly mean wind computed from data from the Synoptic Surface Meteorological Observations (SSMO) (U. S. NAVAL FLEET NUMERICAL WEATHER OFFICE, 1970) was 322.9°. The SSMO combine data from vessels in the region 31° to 34° North and from the coastline to 120° West. The coincidence

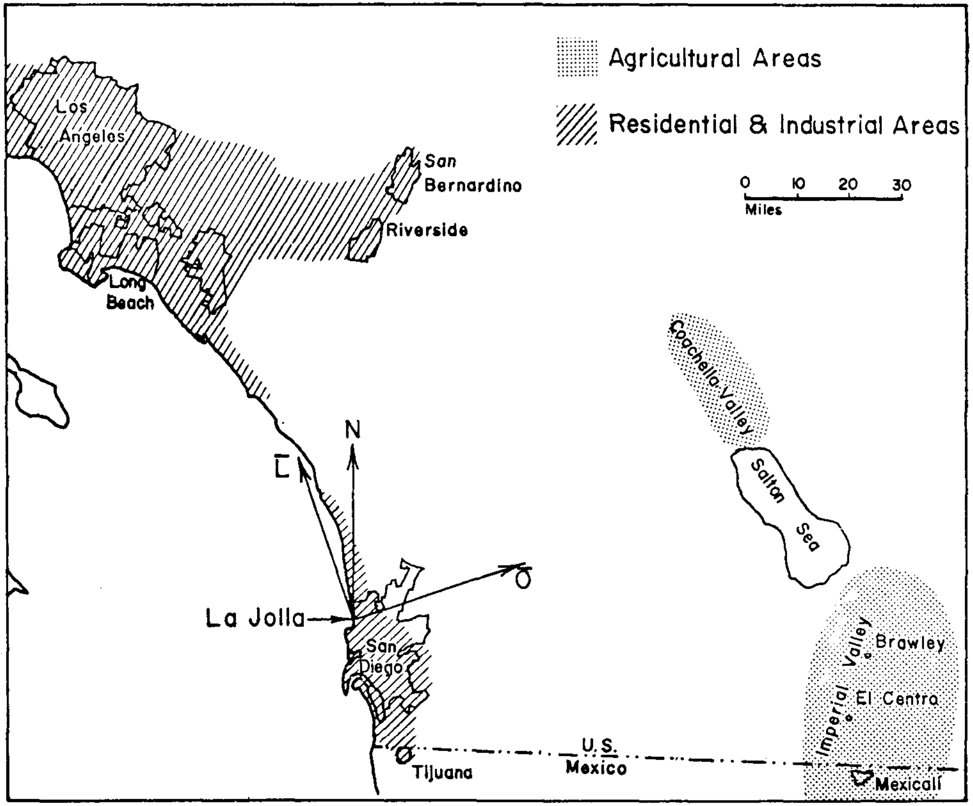

Figure 1. Locations of probable sources of chlorinated hydrocarbons in relation to the sampling location at La Jolla.

of our measured mean wind with the SSMO average shows that the wind field at our measuring site is free from systematic error attributable to local perturbing influences.

A striking feature of the CHC fluxes that were measured at La Jolla was a correlation between day-to-day changes of industrial CHC (PCB) and changes with opposite sign of agricultural CHC (DDT and dieldrin). (See measured fluxes in both parts of Fig. 2) The complimentary nature of PCB and pesticide deposition fluxes is consistent with an hypothesis which requires that the sources of the two classes of compounds be located in orthogonal directions from the flux measuring site. We therefore supposed that the most important source of pesticides is located inland (in the direction labeled $\bar{O}$ in Fig. 1) and that the pesticides are transported to the sampling site by Foehn winds or by high-level tropospheric offshore winds driven by the sea breeze effect. The most probable sources of PCB are the residential and industrial areas located primarily in the longshore direction (labeled $\bar{L}$) from La Jolla. Let $\bar{u}_i$ be the wind velocity (assumed constant) during the i^{th} hour so that with Δt = 1 hour

$$\bar{R}_h = \sum_{i=1}^{h} \bar{u}_i \Delta t$$

is the sum of directed distances which approximates the range traversed by a particle during (h) hours. The wind speed averaged over (h) hours is

$$[S]_h = \sqrt{\bar{R}_h \cdot \bar{R}_h} / h$$

With the assumption that the concentration of aerosol or volatile material in the air downstream from a source of CHC pollution is inversely proportional to the average wind speed, the variations of deposition flux with wind speed and direction (assuming sources of constant strength) was estimated thus:

$$\text{PCB Flux} = (1.0 \times 10^2 / [S]_h)(\bar{R} \cdot \bar{L})$$

$$\text{Pesticide Flux} = (2.0 \times 10^2 / [S]_h)(\bar{R} \cdot \bar{O})$$

$$\bar{O} \cdot \bar{L} = 0, \ \sqrt{\bar{L} \cdot \bar{L}} = \sqrt{\bar{O} \cdot \bar{O}} = 1$$

The results of these considerations with (h) = 48 hours are shown in Figure 2.

Identities of the various compounds detected in the fallout were confirmed by comparison with known standards using both the retention times exhibited in gas-liquid chromatography and retention volumes from liquid-solid chromatography on active silica-gel (McCLURE, 1972).

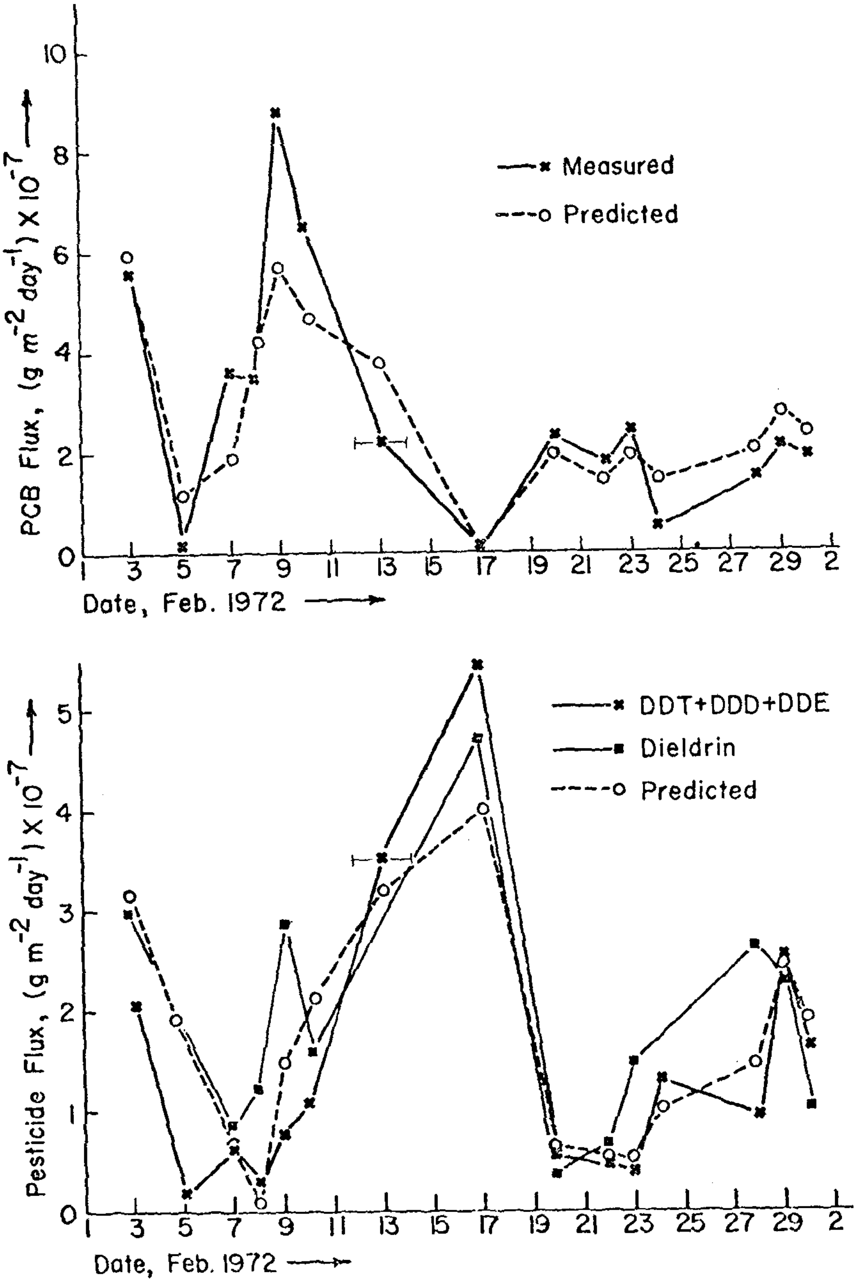

Figure 2. Fluxes of chlorinated hydrocarbons at La Jolla, Calif. during February, 1972 and predicted fluxes based upon a semi-empirical model and assumptions about the distribution of sources as shown in Fig. 1. A three-day sampling period was employed for the measurement shown at the 13th day. All other sampling periods were 24 hours long.

The EC-GLC peak labeled "N" and identified as 87.5% penta- and 12.5% hexa-chloro biphenyl by HIRWE, et al. (1974) was used to quantify Aroclor^{tm} 1254. Aroclor^{tm} (Monsanto Co., St. Louis, MO., USA) mixtures having 42%, 54% and 60% chlorine by weight were used as standards. Compounds from fallout matching the retention times of the 42% chlorine mixture were frequently apparent. However, fluxes listed in this work reflect only the 54% chlorine mixture since this was the principle constituent of the fallout. Very little of the 60% chlorine mixture was found to be present.

The weather in So. California during the first 4 days of February 1972 was characterized by light and variable winds followed on the 5th by the passage of a weak frontal system bringing light and intermittent rain. Local circulation was dominant through the 10th day which resulted in a smoggy condition and a large flux of PCB. Easterly winds (Foehn winds locally known as Santa Ana) from the 13th through the 17th reduced the PCB flux to below 10^{-9} g $m^{-2}day^{-1}$ and brought relatively larger amounts of pesticides from the agricultural areas to the east (Imperial and Coachella Valleys). During this period Dieldrin was evident at 3.0×10^{-7} g m^{-2} day^{-1}. Winds were moderate and variable in direction (prevailing from the northwest) throughout the remainder of the month.

DISCUSSION AND CONCLUSIONS

A three order of magnitude variation between highest and lowest measured fluxes indicates that aerosol transport of heavy chlorinated hydrocarbons in the troposphere is a mesoscale (hundreds of kilometers) rather than an hemispheric or global phenomenon. The correlation between measured fluxes and the component of the wind trajectory in the assumed direction of the source weighted by the reciprocal of the wind speed supports the hypothesis that the predominant source of aerosol PCB at La Jolla is in the Los Angeles metropolitan area.

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