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Organochlorine Pesticides in the Atmospheric Environment

POLLUTION of the environment has long been a subject of public concern and much attention has been paid recently to the new ecological factors introduced by the wide agricultural usage of pesticidal chemicals. Contamination of soil and crops has often featured in environmental studies of these pesticides, but so far little attention has been given to atmospheric pollution, although, as long ago as 1961, Harris and Lichtenstein[1] showed that the loss by volatilization of aldrin, dieldrin, heptachlor and gamma-benzene hexachloride was a major factor in their disappearance from soils treated with these compounds. Later, in the United States, the President's Science Advisory Committee drew attention to the fact that inhalation of air contaminated with pesticides might present a hazard to man[2] and recommended that air should be continuously monitored for pesticide residue levels. In 1965, an Advisory Committee of the United States Food and Drug Administration referred to studies which showed the presence of up to 0·075 p.p.m. of dieldrin in total diets[3] and considered the possibility that half as much again could be absorbed from "air or other exposures".

Little practical work seems to have been undertaken to determine pesticide residues in the atmospheric environment, but in the United Kingdom, Wheatley and Hardman[4] recently reported indications of the presence of organochlorine insecticides in rain-water collected in an agricultural area at Wellesbourne in Warwickshire. Steps were therefore taken at this Laboratory to examine rain-water collected in the Metropolitan area.

Two collecting stations were set up in Central London, one being on the roof of the Laboratory of the Government Chemist in Lambeth, S.E.1, and approximately 20 m above ground-level. The other was set up, with the co-operation of the Meteorological Office, at the London Weather Centre's station on the roof of State House, High Holborn, W.C.1, some 53 m above ground-level and about 1·45 km distant from the other station, across the River Thames. At these two stations, rain was collected in all-glass apparatus, with amber-coloured receiving vessels to reduce the incidence of photochemical degradation[5]. Samples were removed monthly for examination.

The organochlorine pesticides in the water were determined by a gas-liquid chromatographic method using electron-capture detection and silicone and 'Aplezon' columns as described by de Faubert Maunder *et al.*[6]. The limits of detection by this method were 5 parts per million-million for the isomers of benzene hexachloride (BHC) and 10 parts per million-million for the other organochlorine pesticides in general use in the United Kingdom.

Table 1. ORGANOCHLORINE PESTICIDE RESIDUE LEVELS IN LONDON RAIN-WATER

(Parts per million-million)

Station—Cornwall House, London, S.E.1

Month 1965	α-BHC	β-BHC	γ-BHC	HEOD (dieldrin)	*pp'*-DDE	*pp'*-TDE	*pp'*-DDT
Feb.	40	90	90	50	70	—	400
Mar.	15	—	60	60	20	—	115
Apr.	30	—	80	50	—	—	300
May	20	65	70	95	—	—	190
June	30	—	55	25	—	15	70
July	25	—	40	10	15	85	85

Station—State House, High Holborn, London, W.C.1

Month 1965	Rain (mm)	α-BHC	β-BHC	γ-BHC	HEOD (dieldrin)	*pp'*-DDE	*pp'*-TDE	*pp'*-DDT
Mar.	33·4	10	—	20	20	—	—	—
Apr.	37·3	20	—	70	70	—	100	140
May	36·6	20	25	55	50	—	—	220
June	36·2	20	—	155	20	—	50	125
July	78·0	30	—	70	15	10	20	80

The results for the months of February to July 1965, expressed in parts per million-million, are given in Table 1. Because of the small amounts of rain collected and the low levels of the pesticides found, it was not possible to confirm the results obtained for the individual samples by an alternative technique. However, at the end of the 6 months, the combined residues from each station were examined by thin-layer chromatography on silica-gel plates with hexane : acetone, 99 : 1, as mobile phase.

The appropriate areas of the chromatoplates were eluted and the separate eluates individually re-injected on to the gas-liquid chromatograph in columns. In this way, the presence of dieldrin, *pp'*-DDT and the α- and γ-isomers of BHC was confirmed for both stations. The identity of the *pp'*-DDT from both stations was further confirmed by conversion to *pp'*-DDE by treatment with ethanolic potassium hydroxide[7]. The *pp'*-DDE formed by this reaction was identified and determined by gas-liquid chromatography.

Insufficient quantities of the residues were available to confirm the presence of β-BHC, *pp'*-TDE and *pp'*-DDE by alternative techniques or to make an infra-red study of any of the residues[8].

Some individual rain-water samples which had been taken between September 1964 and January 1965 at a number of other places in the British Isles were also examined. The collecting sites ranged from Stornaway in the Outer Hebrides to Camborne in Cornwall, and the samples showed residues of organochlorine pesticides in amounts similar to those found in London rain-water. Samples of snow collected in different suburban areas within 25 km of London gave similar results. The size of these other samples, and the low levels found, again precluded the application of any confirmatory technique to the individual samples, but by appropriate bulking of the residues it was possible to confirm, by thin-layer chromatography, the presence, in the rain-water

and in the snow, of dieldrin, *pp'*-DDT and the α- and γ-isomers of BHC.

The levels at which these pesticides have been detected are extremely low, near to the limits of sensitivity of the delicate electron-capture detection system used. Strict precautions were taken throughout to ensure that no fortuitous contamination of samples or extracts occurred within the Laboratory. Two samples taken from remote areas of Scotland during periods of heavy rainfall showed practically no residue content and these results suggest that adventitious contamination of samples in the Laboratory was negligible.

Present results suggest that the atmosphere carries, either as vapour or by occlusion on dust particles, small amounts of the organochlorine pesticides in common use in the United Kingdom and that they are 'scrubbed out' by rain and snow.

Work is now proceeding to determine the residue levels in air samples, and preliminary results show the presence of organochlorine pesticides in the range of 10–20 parts per million-million. Most of these residues appear to be associated with particulate matter. These experiments may eventually make it possible to determine the respiratory intake by man and to compare the result with his intake from certain foods of known pesticide-levels[8].

We thank the Director-General of the Meteorological Office for permission to quote from the London Weather Centre's records of the rainfall on the roof of State House.

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[1] Harris, C. R., and Lichtenstein, E. P., *J. Econ. Entomol.*, **54**, 1038 (1961).
[2] *Use of Pesticides, Rep. President's Sci. Advis. Comm.* (U.S. Government Printing Office, Washington, 1963).
[3] *Rep. Food and Drug Admin. Advis. Comm. appointed to Review Established Tolerances for Residues of Aldrin and Dieldrin on Raw Agricultural Commodities* (U.S. Government Printing Office, Washington, 1965).
[4] Wheatley, G. A., and Hardman, J. A., *Nature*, **207**, 486 (1965).
[5] Roburn, J., *Chem. and Ind.*, 1555 (1963).
[6] de Faubert Maunder, M. J., Egan, H., and Roburn, J., *Analyst*, **89**, 157 (1964).
[7] Hamence, J. H., Hall, P. S., and Caverly, D. J., *Analyst*, **90**, 649 (1965).
[8] Abbott, D. C., Crosby, N. T., and Thomson, J., *Proc. Soc. Anal. Chem. Cong.* (in the press).
[9] *Review of the Persistent Organochlorine Pesticides*, Appendix F (H.M.S.O., London, 1964).

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