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ORGANOCHLORINE PESTICIDES IN THE ATMOSPHERE

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The problems introduced by the pollution of our atmospheric environment have been concerned largely with those pollutants the effects and presence of which are readily demonstrated, for example, smog, sulphur dioxide, sooty materials and dusts. More recently, attention has been directed to the polynuclear hydrocarbons[1-3], although their presence in air is by no means solely of modern origin.

Recent publications have given evidence for the presence of some organochlorine pesticides in rainwater[4,5]. It has been suggested[5] that the minute traces found arose from the 'scrubbing' action of the falling rain on the air through which it passed, in a manner analogous to the collection of the inorganic constituents of rainwater[6]. The present work describes the experiments which have been carried out to ascertain the extent to which these organochlorine compounds are present in the atmosphere.

Pesticidal compounds may enter the atmospheric environment in several ways and in various physical states. Direct drift from spraying operations will contribute particulate or globular matter at concentrations which are likely to vary inversely as the distance from the site of application, such effects being mainly local but possibly appreciable in extent. It has been shown[7,8] that several organochlorine insecticides volatilize from treated soils, thus adding a slow, long-term contribution. Effluents and vapours from industrial processes, such as pesticide manufacture or moth-proofing of garments, may also contribute, while further quantities may accrue from the use of domestic aerosol insecticides and thermal vaporizers, and the dust from treated clothing and carpets.

Wheatley and Hardman[4] examined rainwater for traces of pesticides in order to try to account for residues found in soil from untreated plots of land. The amounts which they found were insufficient to account for more than a very small proportion of the pesticides present in such soil. Although the concentration of these compounds in air is lower by a factor in the range of 10–100 than that in rainwater, the vastly greater volumes of air may render this contribution of greater significance. As well as the normal, constantly changing contact between air and soil, the mass of air in surface soil may alter by up to 5 per cent owing to diurnal variations in temperature. Pesticides may thus be absorbed by the soil acting as a gas-solid chromatographic 'column' as well as by direct surface adsorption mechanisms. Assuming a tendency to equilibrium, treated soils will lose pesticides while untreated plots will gain them.

Preliminary experiments to illustrate the presence of pesticides in air were carried out by using a small portable constant-rate air-sampler which was used to suck air through a hexane trap. Although this method gave a total sample of only about 180 l. of air per power-canister, gas-liquid chromatography showed the presence of traces of BHC, DDT, DDE, TDE and dieldrin in samples taken in central London and its suburbs. Dieldrin alone was observed in a sample taken in Norfolk, while Aberystwyth air gave no detectable amounts of pesticide at this sample size. It was clear from these preliminary observations that an analytical problem existed and that larger samples would be required before reliable data could be obtained. Accordingly, an electrically operated vacuum pump capable of drawing 15 l. of air per min for long periods of time was brought into use. At this rate of flow hexane was too volatile, but dimethylformamide proved to be a suitable, non-volatile extractant. Examination of the separate contents of a sequential train of four solvent traps showed that nearly all the pesticide content was retained in the first vessel. Attempts have also been made to ascertain whether the pesticides present were in the vapour state or in association with the particulate matter of the air. Interposing bacteriological membrane filters (pore size 0·22 μ) between the air inlet and the solvent trap showed that variable proportions of the pesticides were retained on the filter. The amount retained, however, tended to reach an equilibrium value, indicating that the compounds were volatilizing again from the filter into the air stream. Similar effects have been observed with some polynuclear hydrocarbons[3]. Thus, although the use of membrane filters offers a simple qualitative test for pesticides in air, quantitative results can only be obtained by solvent scrubbing procedures.

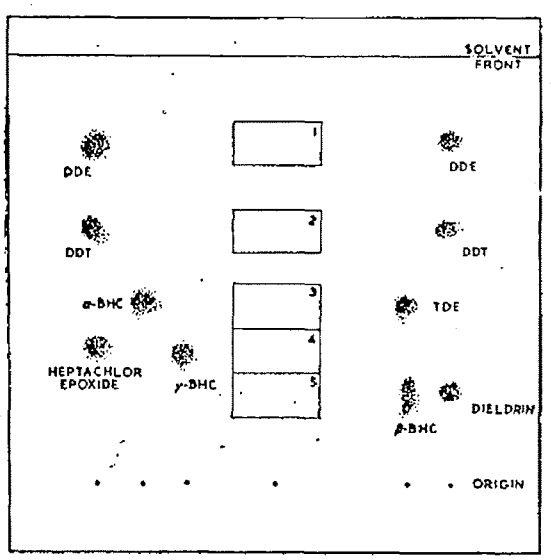


Fig. 1. Thin-layer chromatoplate

Metropolitan air was sampled by suction at about 15 l./min through 100 ml. of dimethylformamide contained in a Drechsel bottle fitted with a coarse sinter at the inlet to the solvent to ensure adequate diffusion. Dispersion of the solvent in 500 ml. of 5 per cent sodium sulphate solution followed by hexane extraction yielded a clean solution which, after evaporation to small bulk, was applied to a 250 μ silica-gel chromatoplate. This was developed with hexane : acetone, 99 + 1, for 35 min and appropriate fractions eluted with hexane[10] for examination by gas-liquid chromatography on both silicone and 'Apiezon' columns with electron-capture detection[11].

Fig. 1 shows the positions on the thin-layer plate of the more important organochlorine pesticides and indicates the areas containing the residues which were re-

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moved for examination. Figs. 2–4 illustrate gas-chromatograph traces obtained from some of these areas; peaks corresponding to known pesticidal materials are marked—the other peaks have not been positively identified as yet. The appearance of a peak at the appropriate retention time on two chromatographic columns of differing polarity on injecting the eluate from the chromatoplate area of correct R_F value for the compound concerned has been taken as evidence of the identity of the compounds. Table 1 lists the quantities of pesticides found on examination of 8,000 l. of air taken on the roof of Cornwall House in August, 1965. The presence of alpha-BHC, gamma-BHC, dieldrin (HEOD), *pp'*-DDE, *pp'*-TDE and *pp'*-DDT was confirmed as already described; substantial agreement between quantitative results on both columns confirmed the absence of any appreciable amount of interfering non-pesticidal material of similar retention time.

Table 1. Organochlorine Pesticides found in London Air

Compound	R_F range of chromatoplate area	Concentration found (parts per 10^{12} w/w) by gas-liquid chromatography on (a) Silicone E.301 – (b) 'Apiezon *L*'
		(a) (b)
Alpha-BHC	0·37–0·48	1 1
Gamma-BHC	0·27–0·36	5 11
Dieldrin (HEOD)	0·17–0·26	18 21
pp'-DDE	0·75–0·84	4 7
pp'-DDT	0·54–0·64	3 3
pp'-TDE	0·37–0·48	3 3

Silica-gel chromatoplate developed with hexane : acetone, 99 + 1.
Silicone column: 1·2 per cent silicone *E.301* plus 0·12 per cent 'Epikote 1001' on 'Silanized Chromosorb *G*' (70–80 mesh) at 158° C; nitrogen carrier gas, 100 ml./min.
'Apiezon' column: 8 per cent 'Apiezon *L*' plus 0·8 per cent 'Epikote 1001' on 'Celite 545' (100–120 mesh) at 180° C; nitrogen carrier gas, 100 ml./min

Great care must be taken in the interpretation of the gas-liquid chromatograms obtained from air samples. Even after the thin-layer separation process used, each fraction from the plate contained several peaks of unidentified materials showing electron-capturing properties. Some of the short-retention time peaks (Fig. 3) corresponding to section 2 of the chromatoplate (R_F 0·54–0·66) have been tentatively identified as the polynuclear hydrocarbons acenaphthylene (R_F 0·57), anthracene (0·67), fluoranthene (0·57) and fluorene (0·70). Retention times on both columns confirmed these identities; these substances are known to be among the polynuclear hydrocarbon ingredients of atmospheric dusts[2,13].

The three peaks of longest retention times obtained from section 1 of the chromatoplate (Fig. 2) would seem to result from compounds the behaviour of which on the plate and on each column is identical with that shown by the compounds giving the first three of a series of unidentified peaks often found in chromatograms of extracts from

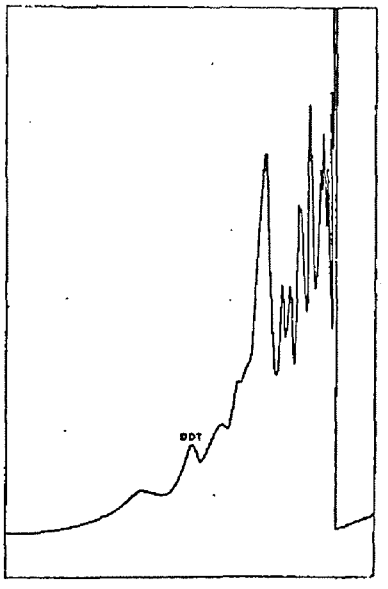


Fig. 3. Gas-liquid chromatogram from section 2 of the thin-layer chromatoplate

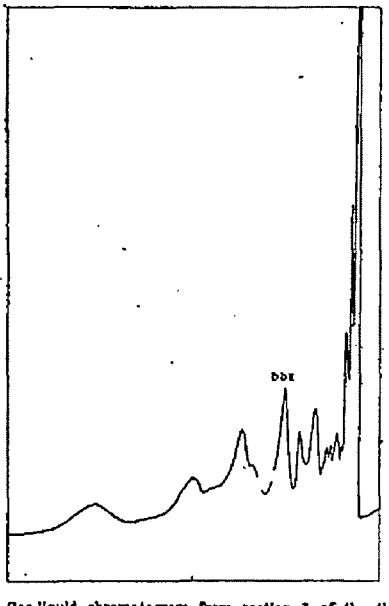


Fig. 2. Gas-liquid chromatogram from section 1 of the thin-layer chromatoplate

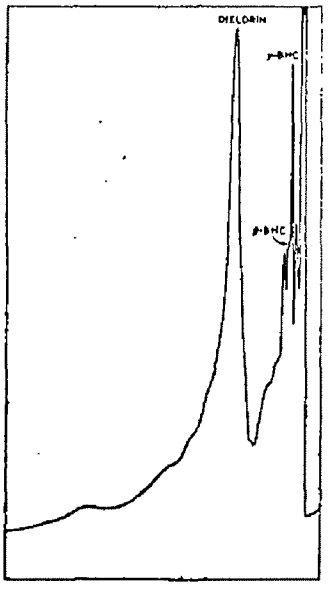


Fig. 4. Gas-liquid chromatogram from section 5 of the thin-layer chromatoplate

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the tissue and eggs of some predatory birds. Their concentrations relative to each other in these two sample sources are also closely similar. Total chlorine determinations on avian tissue samples have indicated that these compounds contain chlorine, and because they are only found in samples containing appreciable residues they are probably breakdown products of organochlorine pesticides.

The evidence presented here and from rainwater examination[4,5] indicates the general occurrence in the atmosphere of minute traces of some of the persistent organochlorine pesticides. Such compounds have also been found in samples of air taken during the spraying season in American peach-orchard districts[12]. The concentrations of these residues are so low that it is necessary to work almost at the limit of sensitivity of the detection systems at present in use. For this reason, scrupulous care is necessary in order to avoid contamination at each manipulative stage, from the initial apparatus preparation to the final injection on to the gas chromatograph. Blank experiments must be performed at each stage and on all materials used. Particular care is required to exclude laboratory dust, for it is found that it is frequently a carrier of interfering electron-capturing materials.

Although the levels concerned are extremely low, these indications of the presence in air of organochlorine pesticides call for further and more detailed investigation. Confirmation of the identity of these residues by other methods such as infra-red spectroscopy or mass spectrometry would also be desirable, although far larger samples would be required in order to obtain sufficient material in a suitably pure state. It would also be of interest to compare the levels found in London with those found in other parts of the country; seasonal variation and correlation with other indices of atmospheric pollution would also be worth investigation. In these ways it may be possible to obtain some indication as to whether the pesticides derive from within the shores of the British Isles or from further afield.

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