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Organochlorine Pesticides in Rainwater in the British Isles

PREVIOUS studies of the presence of the persistent organochlorine pesticides in the atmospheric environment of this country[1-3] have all indicated the need for more comprehensive surveys. The first of these studies by Wheatley and Hardman[1] was confined to rainwater collected in the rural area of Wellesbourne, in Warwickshire. Subsequent studies by the Laboratory of the Government Chemist were concerned with the examination of rainwater[2] and air[3] collected chiefly in the central London area. These three studies showed that, in the areas concerned, the atmospheric environment contained small amounts of BHC, dieldrin and DDT; rainwater collected in these areas contained concentrations of up to 400 parts/10^{12} of these compounds and their breakdown products. The higher levels for DDT found in London rainwater, compared with that from Wellesbourne, were attributed to London air having a higher content of particulate matter, chiefly carbon particles, for which DDT has an affinity. Dieldrin probably also shows this affinity but to a lesser extent.

The work reported here details the results of a more comprehensive study. Rainwater was collected continuously during 12 months at seven widely distributed sites in the British Isles (Fig. 1). These sites were chosen so as to present a variety of conditions and locations and were as follows: Camborne: a rural area outside the town of Camborne, about 40 km from Land's End in Cornwall; Eskdalemuir: a remote mountain area in southern Scotland about 80 km south of Edinburgh; Lerwick: a small town in the Shetland Islands north of Scotland; London: rainwater was collected on the roof of a building approximately 53 m high in central London; Maidstone: a large town in Kent in south-east England; Sheffield: rainwater was collected in the centre of Sheffield, a large industrial town in the Midlands; Wellesbourne: a small rural town in Warwickshire in the Midlands.

Camborne, Maidstone and Wellesbourne are in agricultural country; there is also a large fruit growing industry in the Maidstone area. Eskdalemuir and Lerwick are

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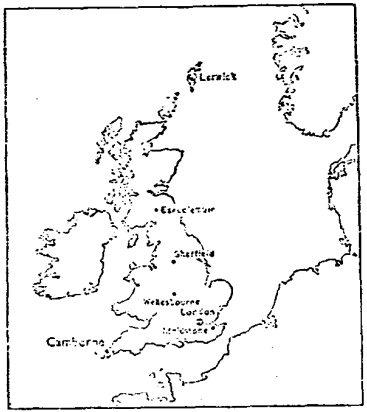

Fig. 1. Distribution of rainwater collecting sites in the British Isles.

both remote, sparsely populated areas with some sheep farming as a local activity.

At these sites, rainwater was usually collected in all-glass apparatus with amber coloured receiving vessels to reduce photochemical decomposition of the pesticides. In January, February and March, however, the glass receiving bottles were replaced by opaque lined polythene bottles to prevent loss of sample by fracture of the vessels caused by freezing of the contents.

The total precipitation collected in each 3 month period of a year at the seven sampling stations was analysed. The samples were extracted with hexane in the collecting vessels which were thoroughly washed out with the same solvent to ensure that no pesticide was retained in the vessels. The combined hexane solutions were dried over anhydrous sodium sulphate and passed through a column of prepared florisil (activated for 16 h at 250° C for 5 h, cooled and partially deactivated by the addition of 10 per cent of water). The eluates were then subjected to

thin-layer chromatography on silica gel plates using hexane as developing solvent[3]. Areas of the developed chromatoplate corresponding to areas of concentrically developed standard pesticide solutions were removed from the plates and eluted. These final eluates were then examined by gas-liquid chromatography using columns of silicone *GE SE 52* and 'Apiezon L' (ref. 4) and electron-capture detection. The identity of the more important of the compounds detected was confirmed by chemical and gas chromatographic techniques. The fractions containing pp'-DDT and pp'-TDE were hydrolysed to pp'-DDE and 1-chloro-2,2-di-(4-chlorophenyl)ethylene, respectively, and these products were estimated gas chromatographically. Dieldrin was converted to its brominated derivatives and these identified on the gas chromatograph[5]. Because of the low concentrations of these pesticide compounds in rainwater, extreme care had to be taken to avoid adventitious contamination at all stages of the analysis. Blank determinations were carried out but yielded no detectable residues. At two of the stations, London and Wellesbourne, duplicate collections were made for the first 6 months, at sites about 2 m apart. These duplicate samples were examined separately but yielded results which differed only within the range of the experimental error of the determinations. The limits of detection were about 2 parts/10^{12} for pp'-DDT and its breakdown products pp'-DDE and pp'-TDE but about 1 part/10^{12} for the other pesticide residues.

The results, expressed in parts/10^{12} of the rainwater collected, are set out in Table 1. They show the pesticide residues collected in each quarter and the mean value for the whole year for the individual sites. In addition, small amounts of beta-BHC and heptachlor epoxide were sometimes detected but these in no case exceeded 15 parts/10^{12}. No other organochlorine pesticides were detected but aldrin, chlordane, endosulfan, endrin and heptachlor would have been detected if present above their levels of detection, which are similar to those of the other pesticides. Small amounts of polychlorobiphenyl compounds were present in all samples but were not estimated.

At all the sampling sites, considerable variation was often shown in the pesticide concentrations for the different periods. This might be attributable, in part at least, to the seasonal variations in total rainfall in these areas. Nevertheless, the overall picture clearly indicates that at all the sites, throughout the year, rainwater contained alpha-BHC, gamma-BHC, dieldrin, pp'-DDT and its two primary toxic metabolites pp'-DDE and pp'-TDE; the concentrations of the individual compounds were of the order of parts/10^{11} or parts/10^{10}.

Comparison with the earlier reports[1,2] indicates that

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Table 1. ORGANOCHLORINE PESTICIDE RESIDUES IN RAINWATER COLLECTED BETWEEN AUGUST 1968 AND JULY 1969 (ng/l)

Collecting site	Period of collection	Alpha-BHC	Gamma-BHC	Dieldrin	pp'-DDE	pp'-TDE	pp'-DDT
Cambrin (Yorkshire)	Aug.–Oct.	15	20	4	30	15	5
	Nov.–Jan.	11	25	15	25	13	10
	Feb.–Apr.		20		25	11	10
	May–July	7	23	(6)	(27)	(13)	(8)
	(Mean 6)						
Eskdalemuir	Aug.–Oct.	15	15	9	15	12	12
	Nov.–Jan.	18	10	7	10	10	10
	Feb.–Apr.	14	13		10	8	8
	May–July	9	10	(4)	10	(10)	(10)
	(Mean 14)		(22)				
Lerwick (Shetland Islands)	Aug.–Oct.	13	35	10	13	18	15
	Nov.–Jan.	120	230		15		15
	Feb.–Apr.	40	100	11	20	7	10
	May–July		(131)	(11)	(20)	(7)	(13)
	(Mean 51)						
London, WC2	Aug.–Oct.	15, 31	56, 73	8, 6	36, 16	4, 4	40, 28
	Nov.–Jan.	30, 38	85	10	30	7	25
	Feb.–Apr.	10	150	13	19	(7)	(61)
	May–July		(104)	(10)	(23)		
	(Mean 39)						
Maidstone (Kent)	Aug.–Oct.	18	30	7	11	18	28
	Nov.–Jan.	17	115	9	14	9	15
	Feb.–Apr.	13	110	6	6	6	6
	May–July		(64)	(7)	(11)	(50)	(49)
	(Mean 35)						
Pontefract (Yorkshire)	Aug.–Oct.	40	40	12	13	10	40
	Nov.–Jan.	30	55	7	4		20
	Feb.–Apr.	12	110		3	(30)	(20)
	May–July	80	(52)	(9)	(23)		
	(Mean 41)						
Wellesbourne (Warwickshire)	Aug.–Oct.	10, 15	15, 18	4, 4	2, 3	2, 3	1, 10
	Nov.–Jan.	12, 12	40	3	3	3	5
	Feb.–Apr.	8	70		(7)	(3)	(10)
	May–July	50	(44)	1	8		8
	(Mean 22)						
	Limit of detection	1	1	1	1	1	1

a Sample contained dead insects.

the general concentrations at Wellesbourne and in London are now lower than they were. The fall in the dieldrin content may in part be a consequence of the abandonment of the large scale uses of aldrin and dieldrin that were previously approved in Britain. The effect of the substantial reduction in the amount of these two insecticides used in this country has already been noted in other contexts. For example, a reduction has taken place in the dieldrin content of human fat in the United Kingdom[6]; lower residues of dieldrin have also been found in home-produced foodstuffs[7].

Another factor which may have influenced the concentration of DDT compounds in London's atmosphere is the progressive reduction in the atmospheric pollution of the metropolis that has been taking place in recent years. The Warren Spring Laboratory[8] has shown the smoke content of London air to be declining at a steady rate under the influence of the Clean Air Act. Because DDT in the London atmosphere has been shown to be associated with the particulate content[2], a reduction of this form of pollution could lead to a corresponding reduction in DDT content.

Several studies, however, have indicated that the organochlorine pesticides are often transported long distances by winds and ocean currents. For example, although it was noted more than a century ago that dust seemed to be transported hundreds of miles out to sea from Africa[9], it has now been shown that dust and pesticides in trade winds reaching the Barbados had their origin in the African–European continent some 5,000 km away[10,11]. The blubber of penguins in the Antarctic has been found to contain a range of these pesticides derived from their principal food, the krill in the surrounding waters[12]. It is possible, as we have suggested, that usage and conditions in individual countries have some influence on the concentrations of these compounds in local atmospheric environments. It would, for example, be interesting to know whether endrin can be detected in the rainfall of those countries which use this compound extensively. These local variations, however, could not be expected to make large differences on a world-wide scale because of the ability of winds and ocean currents to distribute these compounds, eventually, over wide areas.

It seems logical to assume that these organochlorine pesticides now have a world-wide distribution. Certainly the present study gives credence to this view by demonstrating that they are present throughout the year in the atmospheric environment over the whole of the United Kingdom.

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