

Organochlorine Pesticides in UK Air

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Introduction

The UK government has initiated a programme to monitor persistent organic pollutants (POPs) in air in the UK as part of its commitment to the United Nations Economic Commission for Europe's (UNECE) POPs Protocol to the 1979 Geneva Convention on Long Range Transboundary Air Pollution. Sampling started in 1997 to monitor organochlorine pesticides, polychlorinated alkanes ("chlorinated paraffins") and brominated flame retardants. We present the results of 2 years of monitoring of air at 2 locations in the UK for organochlorine pesticides (OCPs) which are either included in the UNECE Protocol or have been identified as possible candidates for future inclusion and subsequent restriction on their production and use.

Name	Abbrevn.	Name	Abbrevn.
Hexachlorobenzene	HCB	a-chlordane	a-CHLOR
Pentachloronitrobenzene	PCNB	g-chlordane	g-CHLOR
Endosulfan	ENDO	cis-nonachlor	c-NON
alpha-hexachlorocyclohexane	a-HCH	trans-nonachlor	t-NON
beta-hexachlorocyclohexane	b-HCH	DDTs:	op-DDE
gamma-hexachlorocyclohexane	g-HCH		pp-DDE
Heptachlor	HEPT		op-DDD
Heptachlor epoxide isomer B	HEP-epB		pp-DDD
Heptachlor epoxide isomer A	HEP-epA		op-DDT
aldrin	ALDR		pp-DDT
dieldrin	DIEL		
endrin	ENDR		

Table 1: Pesticides monitored in UK air

Materials and Methods

Sampling: Two sites were chosen for monitoring: Stoke Ferry, located in an area of intensive arable agriculture in south eastern England, and Hazelrigg, located in a semi-rural location in north western England (see Figure 1). Graseby-Andersen model PM10 High Volume (Hi-Vol) samplers were used for sampling air, employing a glass fibre filter (GFF) and 2 polyurethane foam (PUF) to retain particulate and vapour phase POPs, respectively. The front PUF plug was spiked with 100 ng d-HCH as a sampling recovery spike: the mean recovery was 86 ± 23 % (N = 84). Samples were collected every 2 weeks in 1997-98 and every week in 1998-1999. The target air volume was 650m³. After sampling, the 2 PUF plugs and GFF were extracted in hexane for 12 hours.

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Following initial analysis (see below), individual samples were bulked to provide quarter-year samples and re-analysed for low level OCPs.

Organochlorine Pesticide Analysis: Sample extracts were cleaned and fractionated on an alumina/silica column eluted with 22 mL hexane and 20 mL dichloromethane. Fractions were then reduced and transferred to iso-octane for analysis by dual-column HRGC-ECD.



Figure 1: Location of sampling sites in the UK

Results and Discussion

HCB and HCHs: Of the pesticides monitored (see Table 1), only HCB, a-HCH and g-HCH were routinely detected in bi-weekly and weekly samples. There was some evidence that HCB was subject to breakthrough and loss from the sampling adsorbant during periods of elevated air temperatures (maximum temperature inside sampler body = 30°C). During these periods the mean breakthrough values calculated by $[\text{backPUF}]/[\text{frontPUF}+\text{backPUF}]$ for HCB, a-HCH and g-HCH, were 53 ± 1 , 17 ± 4 and 5 ± 2 %, respectively. Therefore, HCB is not considered further.

The distribution of HCHs over the sampling period are shown in Figure 2. The mean annual concentrations of a- and g-HCH (excluding spring peak, see below) at Stoke Ferry were 64 ± 36 and 940 ± 420 pg.m^{-3} , respectively. b-HCH was not detected in any samples. The corresponding values for Hazelrigg were 30 ± 13 and 220 ± 130 pg.m^{-3} , respectively. Turnbull (1) reported concentrations of g-HCH of 408 and 104 pg.m^{-3} for two areas in Southern England in 1987-90.

At both sites during the spring a large increase in g-HCH was indicated, attaining a maximum of 5900 pg.m^{-3} at Stoke Ferry. Granier and Chevreuil (2) also observed a seasonal cycle in g-HCH air concentrations, with higher values in the spring attributed to application to crops and in summer attributed to volatilisation from soil. Similarly, deposition of g-HCH in rain in Denmark and the Netherlands also shows a significant peak in April and elevated values in the summer compared to autumn and winter (3,4).

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The mean annual ratio of a-HCH to g-HCH at the 2 sites (0.07 and 0.15) is indicative of high g-HCH inputs (i.e. use of lindane) predominating. Technical HCH, which is now banned in many countries, contains the 2 isomers in the proportions of c.55-80% a-HCH and 8-15% g-HCH (5), which would result in a:g HCH ratios in the region of 4 - 10. This is typical of the range in a:g HCH ratios measured in Arctic air (6) which is subject to inputs from regions where technical HCH is still used

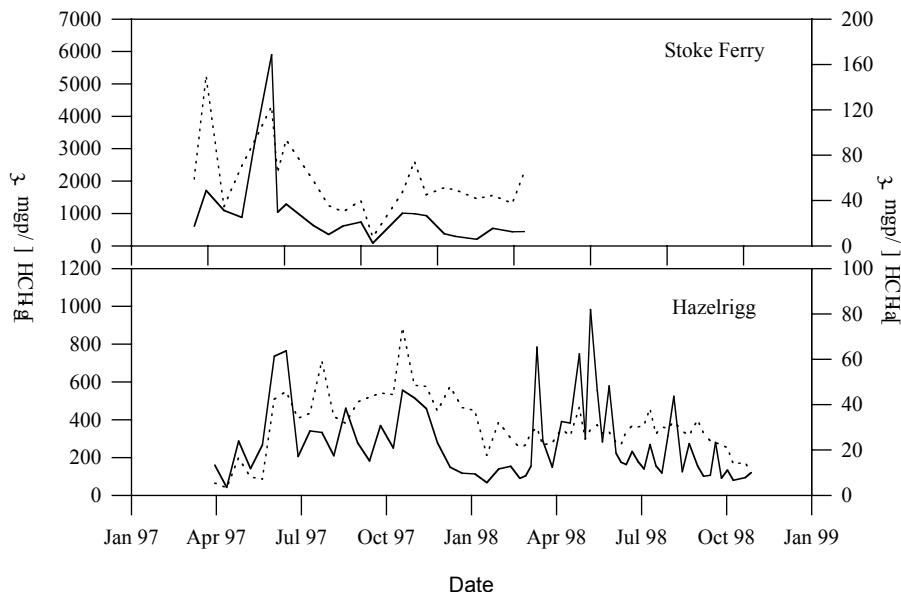


Figure 2: HCHs at Stoke Ferry and Hazelrigg. Solid line = g-HCH, dashed line = a-HCH

Other OCPs: Other OC pesticides detected in bulked UK air were pp-DDE, dieldrin and PCNB (the latter only at Stoke Ferry), all of which occurred at relatively low levels. This is consistent with the past usage of these pesticides in the UK. No other pesticides in Table 1 were detected.

The mean annual concentration of PCNB at Stoke Ferry was 9.2 pg.m^{-3} . Only one reference relating to PCNB in air was found in the literature. Thompson *et al.* (7) report semi-quantitative values of PCNB in the range of <10 to 1600 pg.m^{-3} with a mean value for samples above detection limit of 260 pg.m^{-3} ($N = 10$) for one location in western Canada.

Dieldrin and pp-DDE were detected at mean concentrations of 32 and 97 pg.m^{-3} at Stoke Ferry and 23 and 4.0 pg.m^{-3} at Hazelrigg. Dieldrin has been measured at concentrations of <1 - 210 pg.m^{-3} in North America (8) which is subject to inputs from remobilisation of soil residues from the southern USA, and also from Central America where dieldrin is used for termite control. The values for dieldrin reported for both sites in this study are in the middle of this range. Similar to this study, pp-DDE was the most abundant DDT component measured in air in southern Ontario, Canada, the Great Lakes region and in Antarctica (8,9,10).

Pesticide Levels and Usage in the UK: It is worthwhile to compare the levels of OC pesticides in the UK atmosphere with those of PCBs. The mean annual air concentration of PCB-153 (a hexachlorinated PCB with P_L of 3.5×10^{-4} Pa) at Hazelrigg is 1.7 pg.m^{-3} (11), whereas pp-DDT ($P_L = 1.35 \times 10^{-4}$) was recorded at below the detection limit of 1 pg.m^{-3} in this study at the same site. There is no recorded current use of DDT in the UK, and the total amount used in the UK since 1964 is estimated to be $1.1 \times 10^6 \text{ kg}$ (unpublished data, PUSG). Estimates of the single congener PCB-153 in total PCB sales in the UK for the period 1954-79 are $1.2 \times 10^6 \text{ kg}$ (12): i.e. similar in magnitude to total DDT use. However, in contrast to DDT, PCBs are still being emitted to the UK atmosphere from primary (point of use) as well as secondary (remobilisation) sources, and estimates of current PCB emissions to the UK atmosphere are of the order of $c.6 \times 10^3 \text{ kg.yr}^{-1}$ (13). The source of any DDTs in the UK atmosphere can be assumed to be solely from secondary sources: from remobilisation of residues from treated agricultural land or advection of air masses from outside the UK which contain DDTs.

Based on the pattern of use and the absolute amount of DDT used in the UK and a comparison with PCBs of similar physico-chemical properties and environmental behaviour, it is not unexpected that pp-DDT was not detected in the UK atmosphere at concentrations $> 1 \text{ pg.m}^{-3}$. This argument is equally applicable to the cyclodiene and chlordane pesticides, which were used at significantly lower amounts than DDT in the UK.

Acknowledgements

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References

1. Turnbull, A. (1997) in: Issues in Environmental Science and Technology, Vol.6 ed: Hester, R.E. and Harrison, R.M. Royal Society of Chemistry, London.
2. Granier, L.K. and Chevreuil, M. (1997) *Atmos. Env.* **31** : 3787-3802
3. Cleeman, M. *et al.* (1995) *Chemosphere* **30** : 2039-2049
4. van Jaarsvald, J.A. *et al.* (1997) *Atmos. Env.* **31** : 1011-1024
5. Li, Y-F. *et al.* (1996) *Environ. Sci. Technol.* **30** : 3525-3533
6. Oehme, M. *et al.* (1996) *Environ. Sci. Technol.* **30** : 2294-2304
7. Thompson, T.S. *et al.* (1997) *Bull. Environ. Contam. Toxicol.* **58** : 939-944
8. Hoff, R.M. *et al.* (1992) *Environ. Sci. Technol.* **26** : 266-275
9. Monosmith, C.L. and Hermanson, M.H. (1996) *Environ. Sci. Technol.* **30** : 3464-3472
10. Kallenborn, R. *et al.* (1998) *Sci. Tot. Env.* **220** : 167-180
11. Lee, R.G.M. and Jones, K.C. (1999) *Environ. Sci. Technol.* **33** : 705-712
12. Harrad, S.J. *et al.* (1994) *Environ. Poll.* **85** : 131-146
13. Dyke, P.H. and Stratford, J. (1998) *Organohalogen Compounds* **36** : 365-368