

Interim Report

R&D Project 015

**ATMOSPHERIC INPUTS OF POLLUTANTS TO
SURFACE WATERS**

**Interim report on trace organics in atmospheric
deposition**

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Interim report on trace organics in atmospheric deposition

D J Smith and C D Watts

Research Contractor:
WRc plc
Henley Road Medmenham
PO Box 16 Marlow
Buckinghamshire SL7 2HD

National Rivers Authority
Rivers House Waterside Drive
Almondsbury Bristol
Avon BS12 2UD

NRA Interim Report 015/4/T

National Rivers Authority
Rivers House Waterside Drive
Almondsbury Bristol
Avon BS12 2UD

Tel: 0454 624400
Fax: 0454 624409

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WRc plc
Henley Road Medmenham
PO Box 16 Marlow
Buckinghamshire SL7 2HD

Tel: 0491 571531
Fax: 0491 579094

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NRA Project Leader

The NRA's Project Leader for R&D Contract 015:

J Eastwood - Thames Region

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EXECUTIVE SUMMARY

There is increasing evidence that atmospheric deposition is a significant source of input of some organic compounds to surface water. However, little information is available on deposition of organic compounds in the UK. Previous NRA-funded work at WRc has demonstrated high levels of organics, including priority pollutants, in deposition at several sites in the UK. Over the past year this work has continued, examining a wider range of sampling sites and focusing on compounds of particular concern, such as PAH, PCB, organochlorine pesticides and phenols.

Significant amounts of a number of priority pollutants (including Red List substances) have been identified in both wet and dry deposition. Similarities in the data for different sites indicate that atmospheric deposition of such pollutants is a widespread and common phenomenon in the UK. Seasonal variations were evident, particularly among the PAH where increased combustion of fossil fuel during the winter appears to increase atmospheric concentrations of these compounds. Several contaminants (such as HCH and phenol) were highlighted by the data as being of particular concern with regard to potential impacts on surface water quality.

The results to date also point to the need to incorporate the effects of attenuation processes on the amounts of deposited contaminants which eventually enter surface water. This is essential to allow accurate predictions of the effects of atmospheric deposition on surface water quality. It is also clear that some atmospheric contamination is imported into the UK from distant sources and further investigation of this aspect is warranted.

KEY WORDS

Atmospheric Deposition, Fallout, Wet Deposition, Dry Deposition, Organic Contamination, PAH, Pesticide Residues, Atmospheric Fluxes

1. INTRODUCTION

The importance of the atmosphere as a sink, transport system and source of pollutants is becoming increasingly recognised (GESAMP 1989, Kurtz 1990, Oehme 1991, Ballschmiter and Wittlinger 1991). Organic contaminants can enter the atmosphere in a variety of ways, e.g. emission in stack and vehicle exhaust gases, volatisation from soil, vegetation and water, resuspension of particulate matter containing adsorbed contaminants, and subsequently be dispersed over a wide area. Due to the large volume of the atmosphere, the generally low levels of organic contaminants present there and the difficulties of measuring their concentrations, the view was long held that, once pollutants had entered the atmosphere, they were in effect permanently lost to the lithosphere and hydrosphere and no longer of concern. As techniques for collecting and analysing atmospheric samples have developed and improved, it has become evident that this is not necessarily the case. Organic compounds emitted to the atmosphere can return to the surface through several mechanisms, i.e. adsorption of vapour, settling of particles or washout of either vapours or particles in wet deposition (rain, snow, etc.) Ample evidence is now available that the amounts involved can be significant, and that deposition can occur a long way from the original source of the contaminants - in the case of a number of persistent organic pollutants (e.g. DDT, HCH, PCB) it is clear that atmospheric transport occurs on a global scale (Kurtz 1990, Ballschmiter and Wittlinger 1991, Oehme 1991).

A considerable amount of work has been carried out regarding atmospheric inputs of contaminants to the Great Lakes of North America. For some substances (e.g. PCB) this appears to be the major pathway by which the compounds enter the lake system and gives rise to significant concentrations in the water (Murphy and Rzeszutko 1977, Eisenreich *et al* 1981, Strachan 1988). In the UK, most work on atmospheric deposition of pollutants has focused on inorganic substances such as heavy metals, sulphate and nitrate, while the organic component of deposition has been largely neglected. Work in progress at WRc since 1987, however, has shown that both wet and dry deposition at several UK locations contain many organic compounds, including a large number of pollutants in quantities sufficient to warrant detailed study (Watts and Welch 1988, Watts *et al* 1989, Welch and Watts 1990, Smith and Sowray 1990). The pollutants identified have generally been similar in both type and quantity to those reported from comparable studies in other industrialised countries (e.g. Leuenberger *et al* 1985, Kawamura and Kaplan 1986, Bidleman *et al* 1987, Czuczwa *et al* 1987, Strachan 1988).

From the point of view of the NRA, the main concern is whether inputs of organic pollutants from the atmosphere are likely to have a significant impact on water quality. As discussed above, this is certainly the case for the Great Lakes. Preliminary calculations of atmospheric fluxes of pollutants to a model catchment (Watts *et al* 1989, Smith and Sowray 1990) have suggested that, in the UK also, certain compounds may well be of concern in this respect. The general lack of data on the organic composition of precipitation in the UK, together with inadequate knowledge of the effects of attenuation processes (e.g. adsorption, degradation) on fluxes of contaminants to surface water, make accurate predictions of the amount of organic contamination of water which will result from atmospheric deposition very difficult. It is also of interest to measure both the flux of atmospheric pollutants arising from UK sources (probably representing the bulk for most substances) and that which is 'imported' and which may have arisen from distant sources. The latter may account for a significant

proportion of certain compounds and, unlike the former, will not be amenable to any control measures implemented within the UK.

The work described in this report has addressed all the above problems by means of a sampling and analysis programme designed to obtain detailed quantitative data on organic contaminants present in various types of atmospheric deposition (rain, snow, vapour, dry particulate), collected at several geographically varied sites in the UK, including one believed to receive minimal inputs of pollutants from UK sources (Figure 1.1). In keeping with the strategic objectives of the NRA, analysis of samples and data has focused on compounds from UK and EC lists of priority pollutants (e.g. the Red List) and their potential impact on surface water quality.

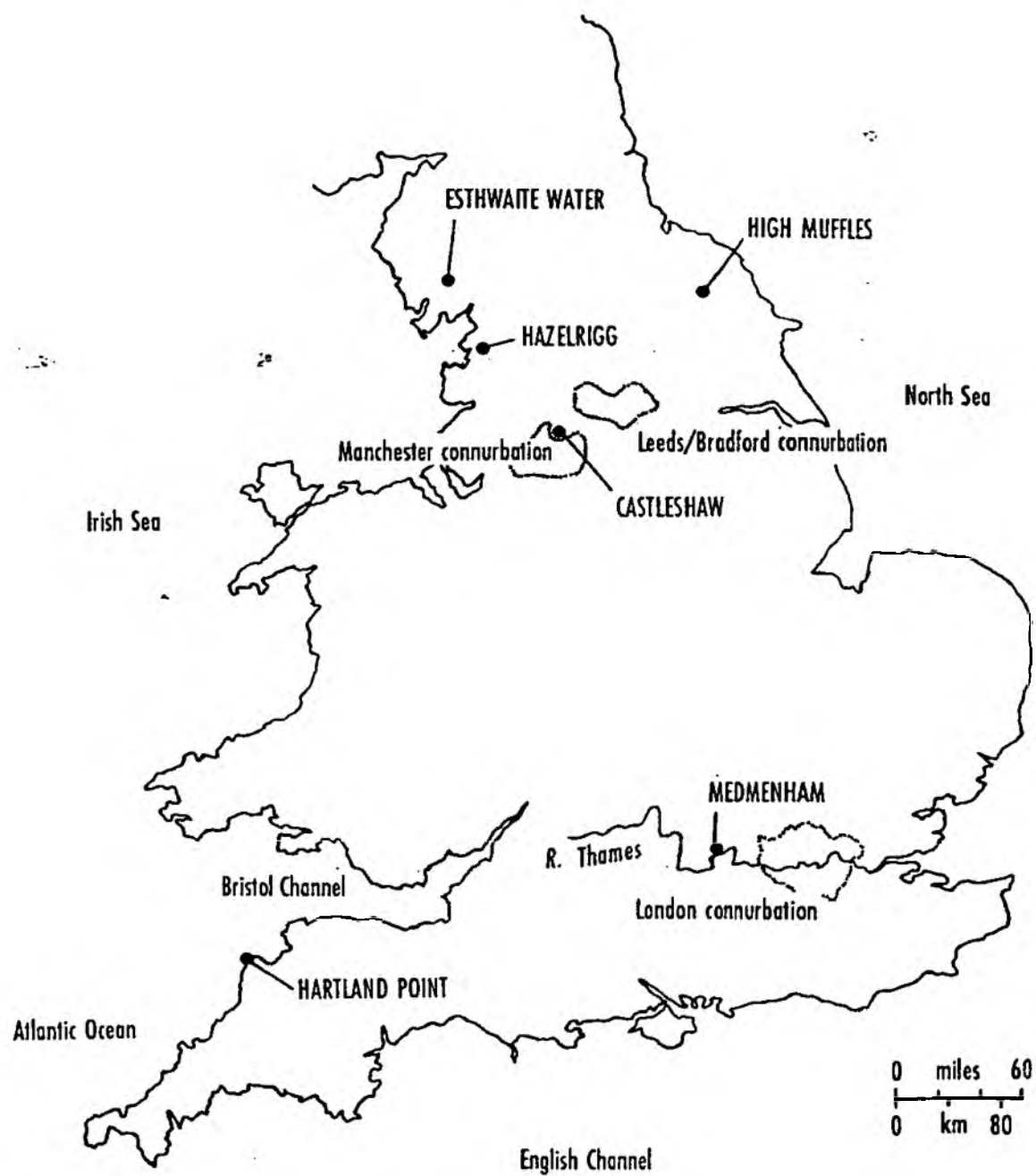


Figure 1.1 Map of England and Wales showing locations of sampling sites

2. PROJECT DESCRIPTION

It is now well established that a range of priority pollutants present in the atmosphere can be deposited onto surfaces in both wet and dry deposition, possibly after transport from sources a considerable distance away. Previous work in this project has demonstrated the presence of a complex array of organic compounds in atmospheric deposition at several sites in the UK, derived from both natural and anthropogenic sources. A number of these compounds are in UK and EC lists of priority pollutants (including the Red List). This is of concern to the NRA, as atmospheric deposition is an essentially uncontrolled source of contaminants which may ultimately end up in surface water, either by direct deposition to the water surface or via runoff from the catchment. Preliminary calculations have suggested that, for some pollutants at least, atmospheric inputs may be sufficiently large to give rise to significant concentrations in the receiving water.

The overall objective of this work is to use an array of specialised sampling equipment at several sites to determine the organic composition of atmospheric deposition in the UK, and assess the contribution of airborne pollutants to the organic content of surface waters. The phase of the work described in this report has broadened the geographical coverage of the sampling programme and obtained a considerable amount of additional quantitative data on the organic content of atmospheric deposition, while focusing specifically on several classes of priority pollutants (PAH, organochlorine pesticide residues, PCB and phenols).

3. METHOD

3.1 Sampling

3.1.1 Sample types

Several types of sample have been collected in the course of this work. Rainwater, high volume air samples and bulk deposition samples have been regularly collected since the beginning of the programme and have been fully described in previous reports (Watts and Welch 1988, Watts *et al* 1989, Smith and Sowray 1990). Details of the samples collected since the last report are given in Tables 3.1 - 3.3. In February 1991, a heavy snowfall occurred at the Medmenham sampling site (Section 3.1.2) and the opportunity was taken to collect samples of snow for analysis. Two samples were simultaneously collected by carefully scraping snow into stainless steel buckets, using stainless steel beakers. Care was taken not to include any soil or vegetation in the sample. Details of the samples are included in Table 3.1. Sample 1 was obtained from the top surface of the wet-only rainwater sampler at Medmenham, which was closed at the time (Watts and Welch 1988). Sample 2 was collected from an area of open grassland about 5 m east of Sample 1. The samples were covered with clean aluminium foil and allowed to thaw overnight at ambient temperature before analysis.

Table 3.1 Details of wet deposition samples collected at Medmenham, June 1990 to February 1991

	Sample Number	
	26	27
<hr/>		
A. Rainfall		
Date of sampling	18.6.90	3.9.90
Collection time (hrs:min)	2:30	0:40
Volume collected (l)	2.0	2.5
Air temperature (°C)		
Maximum	22	24
Minimum	21	20
Wind direction	W	-
Wind speed (m s ⁻¹)	1	0
<hr/>		
	Sample Number	
B. Snowfall	1	2
Date of sampling	8.2.91	8.2.91
Approximate area sampled (m ²)	0.5	0.5
Approximate depth of sampling (cm)	0 - 2	0 - 2
Volume of melted sample (l)	1.1	1.2
Wind speed (m s ⁻¹)	0	0

Table 3.2 Details of dry deposition samples collected using high volume air sampler at Medmenham, High Muffles and Hazelrigg, August 1990 to June 1991

	MD-20	MD-21	MD-22	Sample* MD-23	HM-2	HR-3
Date of sampling (start)	29.8.90	27.9.90	1.11.90	29.11.90	27.6.91	6.11.90
Sampling time (hours)	24	24	24	24	24	24
Flow rate (l min ⁻¹)						
Initial	725	725	725	750	750	750
Final	700	700	700	750	725	725
Volume sampled (m ³)	1026	1026	1026	1080	1062	1062
Air temperature (°C)						
Maximum	31	20	11	7	19	6
Minimum	4	-1	-1	0	8	-3
Wind direction	W	W	-	N	nr	NW
Wind speed (m s ⁻¹)	1	1	0	1	nr	2

Notes: * MD = Medmenham, HM = High Muffles, HR = Hazelrigg
nr = not recorded

Table 3.3 Details of bulk deposition samples collected at Medmenham and High Muffles, March 1990 to September 1991

Sample No.	Date of sampling (start)	Sampling time (days)	Volume collected (litres)
Medmenham (MD)			
12	16.4.90	84	2.0
13	9.7.90	42	2.0
14	20.8.90	44	1.8
15	3.10.90	28	1.7
16	18.1.91	41	2.0
17	28.2.91	41	2.0
18	10.4.91	64	2.0
19	13.6.91	18	2.0
20	1.7.91	45	1.8
High Muffles (HM)			
21	20.3.90	50	2.0
22	16.5.90	28	2.0
23	13.6.90	14	2.0
24	27.6.90	10	1.8
25	7.7.90	47	2.0
26	22.8.90	21	2.0
27	12.9.90	17	2.0
28	29.9.90	11	2.0
29	10.10.90	14	2.0
30	24.10.90	7	2.0
31	31.10.90	7	2.0
32	7.11.90	21	2.0
33	28.11.90	14	1.7
34	12.12.90	16	2.0
35	28.12.90	12	2.0
36	9.1.91	28	1.6
37	6.2.91	21	2.0
38	27.2.91	7	2.0
39	6.3.91	21	2.0
40	27.3.91	28	2.0
41	24.4.91	42	2.0
42	5.6.91	14	2.0
43	19.6.91	14	2.3
44	3.7.91	35	1.9
45	7.8.91	42	1.8
46	18.9.91	28	2.3

During the summer of this year, an automatic wet/dry deposition sampler, constructed by the University of Lancaster, was tested at WRC Medmenham. This equipment uses a precipitation sensor to control a motor which moves a stainless steel tray along the bed of the sampler. Under dry conditions the tray, which is filled with water, is exposed for the collection of dry deposition. When the sensor detects the onset of rain (or other wet deposition), the tray is moved under a cover and a stainless steel funnel, draining into a glass collecting bottle, is exposed to collect the wet deposition. When the sensor dries out again (assisted by an integral heater) the tray is again moved out into the open, simultaneously covering the funnel. A diagram of this equipment is shown in Figure 3.1. The sensitivity of the rain sensor can be adjusted to obtain (by trial and error) the optimum response threshold. Counters on the sampler record the number of events (i.e. the number of times the sensor was triggered) and the total time that the sampler has been in wet deposition mode. This sampler can be left in the field for extended periods, to automatically collect composite wet and dry deposition samples.

The dry deposition tray of the sampler has to contain a matrix of some sort to prevent resuspension and loss of deposited material. In this work, the tray has been filled with double distilled water. This was chosen as experience at the University of Lancaster (who have been operating these samplers for over a year), has indicated that water forms a simple and effective sampling matrix. After initial testing at Medmenham, the automatic sampler was installed at a sampling site at Hartland Point (Section 3.1.2). Few data are yet available from this site, but it is hoped that it will provide useful information on background concentrations of atmospheric pollutants reaching the UK.

Full details of all atmospheric deposition samples reported on here are given in Tables 3.1 - 3.3.

3.1.2 Sampling sites

The locations of the sampling sites referred to in this report are shown in Figure 1.1.

Three of these (Medmenham, High Muffles and Hazelrigg) have been described in previous reports (Watts and Welch 1988, Watts *et al* 1989, Smith and Sowray 1990). One conclusion from the last report (Smith and Sowray 1990) was that these three sites showed considerable similarity in terms of atmospheric organic deposition, as all three were significantly affected by inputs from urban/industrial areas. To try to gain an indication of the 'background' levels of pollutants, a site was sought where air which was essentially unaffected by such inputs could be sampled. This is not easy to find in a small, densely populated country. By its very nature, such a site is likely to be very isolated, with associated problems of access, power supply and logistics for regular visits to service the equipment. Several potential sites were investigated, and, after consultation with Trinity House, the site of the lighthouse at Hartland Point on the North Devon coast (OS Map Reference SS 230277) was selected as the most suitable (see Figure 1.1).

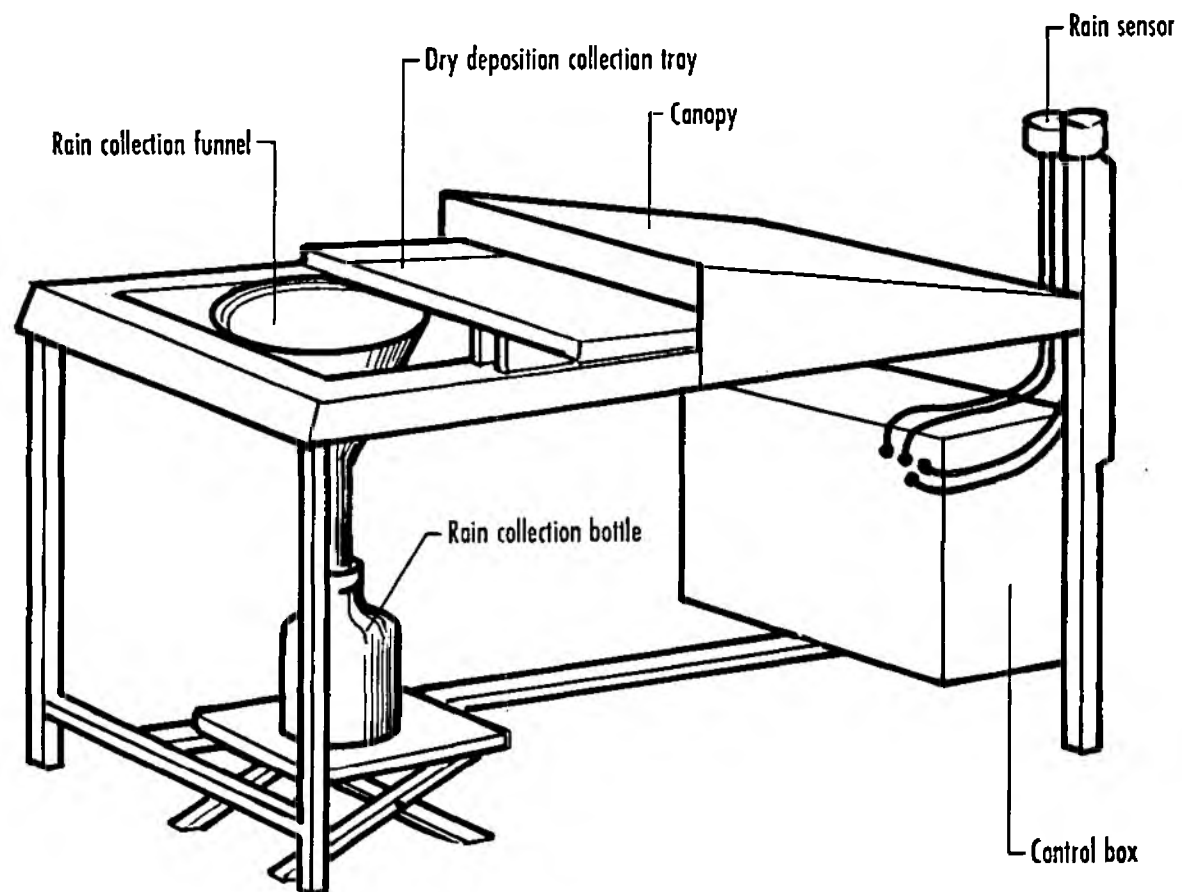


Figure 3.1 Diagram of automatic wet and dry deposition collector

This site offers reasonable access, a reliable power supply from the lighthouse, and is well removed from major sources of atmospheric pollution such as towns and major roads. In addition, the actual position chosen for the sampler - on the roof of a small storeroom at the base of the lighthouse tower - is secure from public access, and well sheltered on the landward side by high cliffs while being completely open on the seaward side (the direction of the prevailing winds). By this means, it is hoped to sample incoming air masses from the Atlantic Ocean which have received no significant inputs of pollutants for a considerable time, and should therefore be well mixed and provide a representative sample of 'global' background levels of air pollution in the Northern hemisphere.

As mentioned in the previous section, the University of Lancaster has been operating automatic wet/dry samplers since July 1990. This forms part of a CASE Studentship funded by this project, and some results from the work are presented in this report. Samplers have been operated at two sites in Northwest England, at Castleshaw, Lancashire (OS Map Reference SJ 997103) and at Esthwaite Water, Cumbria (OS Map Reference SD 357965) (see Figure 1.1). Both samplers are located beside a small body of water. Esthwaite Water is a small lake (area ca 1 km²) with several villages and small towns within a 20-mile radius. The site is considered to be semi-rural on the basis of concentrations of atmospheric total suspended particulates (TSP) measured during the summer of 1990 (17 - 38 $\mu\text{g m}^{-3}$). The sampler is located in a small fenced enclosure, somewhat sheltered by surrounding vegetation. At Castleshaw, the sampler is beside a small service reservoir belonging to North West Water, on Castleshaw Moor. The site is very open and exposed, but is nevertheless classed as urban (in terms of atmospheric deposition) due to the relatively high levels of atmospheric TSP (measured as 45 - 65 $\mu\text{g m}^{-3}$ during summer 1990). This is the result of the close proximity upwind of major urban and industrial conurbations, such as Oldham (six miles southwest), Rochdale (eight miles west) and Manchester (city centre twelve miles southwest). In addition, the M62 motorway runs only three miles north of the site.

3.2 Analytical methodology

Full details of analytical protocol have been given in previous reports (Watts and Welch 1988, Watts *et al* 1989, Smith and Sowray 1990). Briefly, all samples from Medmenham, High Muffles and Hazelrigg were extracted with dichloromethane and the extracts analysed by capillary gas chromatography (GC) and gas chromatography-mass spectrometry (GC-MS). Major components were identified and quantitative determinations of selected compounds made using a range of internal or external standards. Attention was focused mainly on the occurrence of certain groups of priority pollutants in the samples, namely those on the UK Red List plus polycyclic aromatic hydrocarbon (PAH).

Analysis of laboratory and field blanks was carried out as described in the previous report (Smith and Sowray 1990).

Samples from Esthwaite Water and Castleshaw were analysed at the Institute of Environmental and Biological Sciences, Lancaster University, for selected PAH. Samples were extracted with dichloromethane and the extracts analysed by HPLC using a silica-bonded C₁₈ phase eluted with acetonitrile/water. PAH were detected by UV fluorescence. Compounds of interest were identified and quantified by measurement of retention time and peak area, respectively, relative to a set of PAH standards, using a VG

Minichrom data system. Twelve PAH were routinely determined, although, under the conditions used, two pairs could not be adequately resolved and hence their combined concentrations were measured (Table 4.7).

4. RESULTS AND OBSERVATIONS

4.1 Wet deposition samples

4.1.1 Rainwater

Table 4.1 shows the results of analyses for a range of organic priority pollutants in five rainwater samples collected at Medmenham between June 1990 and February 1991. Details of these samples are given in Table 3.1.

**Table 4.1 Priority pollutants identified in rainwater samples from Medmenham.
Concentrations in ng l⁻¹**

Compound	Sample Number				
	23	24	25	26	27
A. Polycyclicaromatic hydrocarbons					
Naphthalene	10	Tr	Tr	Tr	10
Fluorene	nd	nd	Tr	nd	nd
Phenanthrene	nd	nd	30	Tr	Tr
Pyrene	nd	nd	Tr	Tr	Tr
Fluoranthene	nd	nd	Tr	Tr	Tr
B. Organochlorine compounds					
α-HCH	nd	39	nd	18	14
β-HCH	nd	nd	nd	19	nd
γ-HCH	47	nd	12	62	51
HCB	nd	56	nd	nd	nd
α-endosulfan	5	nd	nd	nd	nd
endrin	nd	nd	nd	6	nd
p,p'-DDT	nd	nd	nd	15	13
c-heptachlorepoide	nd	nd	nd	Tr	Tr
PCB-138	nd	nd	nd	nd	18
C. Phenols					
phenol	14	nd	250	4260	2010
chlorophenols	nd	nd	nd	133	123
dichlorophenols	7	nd	nd	nd	nd

Table 4.2 Compounds identified by GC-MS in samples of snow collected from Medmenham, February 1991

Compound	Approximate concentration* ($\mu\text{g l}^{-1}$ melted snow)
A. n-alkanes	
C ₂₀	1.0
C ₂₁	3.0
C ₂₂	2.5
C ₂₃	3.0
C ₂₄	2.0
C ₂₅	3.0
C ₂₆	1.0
C ₂₇	4.0
C ₂₈	0.5
C ₂₉	4.5
C ₃₀	0.5
C ₃₁	2.0
C ₃₂	0.2
C ₃₃	0.5
B. Polycyclic aromatic hydrocarbons	
Anthracene/phenanthrene	1.0
Pyrene	1.0
Fluoranthene	1.0
C. Others	
Methoxymethylbutane	80
Dimethoxymethylbutane (2 isomers)	30
Chloromethylbutane	30
Hexanol	5
Phenol	3
Tetradecanoic acid	1.5
Hexadecanoic acid	2.0
Phenylpentenone	4.0
9,10-Anthracenedione	0.5
Di-isobutylphthalate	4.0
Dibutylphthalate	3.0
Di-(ethylhexyl)-phthalate	4.0

Notes: * Concentrations given are estimated from preliminary results and should only be regarded as a rough guide to the relative amounts of the compounds present.

Small quantities (5 - 62 ng l⁻¹) of a few polycyclic aromatic hydrocarbons (PAH) and organochlorine pesticide residues were detected. A single PCB congener PCB-138) was identified in one sample. Phenol was present in four of the five samples at relatively high concentrations (14 - 381 ng l⁻¹) and a few chlorinated phenols were also identified.

4.1.2 Snow

In Table 4.2, data from GC-MS analysis of the two snow samples (Section 3.1.1) are presented. The chromatograms produced were very complex, and the amount of extractable organic matter present in the snow was clearly much greater than in the rain samples. Because of the complexity of the chromatograms and the high background produced on GC-MS analysis, only approximate quantification has been possible from the results so far. Both samples gave very similar results, and the concentrations given in Table 4.2 should only be regarded as giving an indication of the levels of compounds present in the snow. Major components were alkanes (including an unresolved complex mixture of branched/cyclic alkanes), phthalate esters, alkanolic acids and a series of methoxylated butanes. Only three PAH could be identified; however, it is possible that a number of others were present at lower levels, but could not be distinguished amongst the high background of unresolved compounds. This may also be the case for a variety of other pollutants (e.g. pesticide residues) and fractionation of the extract, to remove the alkane components, may assist in revealing them.

4.2 Dry deposition samples

A range of polycyclic aromatic hydrocarbons was identified in high volume air samples from Medmenham and High Muffles (Table 4.3). The highest concentrations were present in vapour phase samples, with naphthalene, alkylnaphthalenes (consisting mainly of several mono-, di- and trimethylnaphthalene isomers), phenanthrene, pyrene and fluoranthene generally being both the most abundant, and most commonly occurring, compounds. Compounds with a molecular weight greater than pyrene/fluoranthene were only occasionally detected, exclusively in the particulate phase samples. Sample MD-17 contained both the highest concentrations and greatest variety of PAH, which included a number which could not be unambiguously identified or quantified by GC-MS analysis due to the high background of ions present. In contrast, samples MD-19 and MD-20 contained only low levels of a few PAH. There is no clear distinction to be made between either the concentrations, nor distribution, of PAH present in the single sample from High Muffles compared to those from Medmenham.

Table 4.4 shows data for a range of chlorinated compounds and phenols in high volume air samples from Medmenham, High Muffles and Hazelrigg. Hexachlorocyclohexane (HCH) isomers (especially α -HCH and γ -HCH) were the most prominent of the pesticide residues present, appearing in every sample at relatively high levels. Hexachlorobenzene (HCB) also occurred in every sample, though generally at lower concentrations than HCH; all these compounds were associated primarily with the vapour phase of the air samples. In contrast, some other pesticide residues which were identified fairly regularly (e.g. DDT/DDE and heptachlor) were present predominantly in the particulates. An interesting case is trifluralin; this was identified in several Medmenham samples, generally at very low levels (ca 10 pg m⁻³) in the particulate phase. However, in one sample (MD-20) it was present in the vapour phase at 483 pg m⁻³.

Table 4.3 Polycyclicaromatic hydrocarbons in high volume air samples collected at Medmenham and High Muffles.
Concentrations in pg m^{-3} of sampled air

Compound	Sample*		MD-17		MD-18		MD-19		MD-20		HM-1	
	MD-16 P	V	P	V	P	V	P	V	P	V	P	V
Naphthalene	nd	200	nd	4480	nd	210	nd	10	nd	30	Tr	850
Alkyl naphthalenes	nd	400	nd	13 440	nd	1000	nd	80	nd	50	190	3000
Fluorene	nd	+	nd	1790	nd	300	nd	15	nd	nd	nd	+
Alkylfluorenes	nd	nd	nd	nd	nd	880	nd	50	nd	nd	nd	nd
Biphenyl	nd	nd	nd	2660	nd	170	nd	10	nd	nd	nd	nd
Acenaphthene	nd	nd	nd	900	nd	nd	nd	nd	nd	nd	nd	nd
Acenaphthylene	nd	nd	nd	2350	nd	nd	nd	nd	nd	nd	nd	nd
Phenanthrene	nd	300	nd	1950	Tr	690	Tr	40	Tr	5	240	3500
Anthracene	nd	200	nd	970	nd	nd	nd	nd	nd	+	250	5500
Alkylphenanthrenes/ anthracenes	nd	+	nd	+	nd	+	Tr	Tr	nd	nd	50	+
Pyrene	nd	50	500	2130	Tr	+	Tr	Tr	Tr	5	400	Tr
Fluoranthene	Tr	50	400	580	Tr	+	nd	nd	Tr	5	330	Tr
Alkylpyrenes/fluoranthenes	nd	Tr	900	+	nd	nd	nd	nd	nd	nd	+	nd
Benzo(ghi)fluoranthene	nd	nd	400	nd	nd	nd	nd	nd	nd	nd	nd	nd
Triphenylene	nd	nd	+	nd	nd	nd	nd	nd	nd	nd	nd	nd
Chrysene	nd	nd	+	nd	nd	nd	nd	nd	nd	nd	nd	nd
Naphthacene	nd	nd	+	nd	nd	nd	nd	nd	nd	nd	nd	nd
Benzpyrenes/fluoranthenes	nd	nd	+	nd	nd	nd	nd	nd	nd	nd	nd	nd
Unidentified (MW 228)	nd	nd	nd	nd	+	nd	nd	nd	nd	nd	+	nd
Unidentified (MW 242)	nd	nd	+	nd	nd	nd	nd	nd	nd	nd	nd	nd
Unidentified (MW 252)	nd	nd	+	nd	+	nd	nd	nd	nd	nd	+	nd
Unidentified (MW 254)	nd	nd	+	nd	nd	nd	nd	nd	nd	nd	nd	nd
Unidentified (MW 266)	nd	nd	+	nd	nd	nd	nd	nd	nd	nd	Tr	nd
Unidentified (MW 276)	nd	nd	+	nd	nd	nd	nd	nd	nd	nd	Tr	nd

Notes: * Details of samples are given in Table 3.2 and in the previous report (Smith and Sowray 1990).
MD = Medmenham, HM = High Muffles, P = particulate phase sample, V = vapour phase sample.
+ = Compound present, but could not be quantified due to interferences.
Tr = Trace component, i.e. compound present in amount too small for quantification.
nd = not detected.

Table 4.4 Organochlorine pesticides, polychlorinated biphenyls and phenols identified in high volume air samples from Medmenham, High Muffles and Hazelrigg. Concentrations in $\mu\text{g m}^{-3}$ of sampled air

Compound	MD-16		MD-18		Sample* MD-19		MD-20		MD-21		HM-1		HR-3	
	P	V	P	V	P	V	P	V	P	V	P	V	P	V
a-HCH	nd	44	6	100	nd	56	nd	134	nd	20	nd	96	nd	176
b-HCH	nd	nd	nd	nd	nd	22	nd	20	nd	23	nd	42	nd	22
g-HCH	nd	138	6	194	5	173	18	884	14	168	nd	296	7	199
Dieldrin	nd	14	14	nd	nd	23	nd	89	nd	nd	nd	16	nd	12
Endrin	nd	nd	nd	nd	15	nd	nd	nd	nd	14	16	nd	nd	nd
a-Endosulfan	nd	22	nd	13	nd	8	nd	36	nd	nd	nd	nd	nd	14
p,p'-DDT	nd	nd	19	nd	nd	nd	nd	nd	38	nd	21	nd	nd	nd
p,p'-DDE	nd	nd	9	nd	16	nd	nd	nd	nd	15	nd	nd	nd	nd
HCB	nd	23	nd	86	nd	20	nd	54	nd	18	nd	65	9	117
Heptachlor	nd	nd	nd	nd	20	nd	6	nd	21	nd	35	5	nd	nd
Heptachlor epoxide	nd	nd	nd	nd	nd	nd	12	5	nd	nd	nd	nd	nd	nd
Trifluralin	nd	nd	8	nd	8	nd	15	483	10	nd	nd	nd	nd	nd
PCB-28	nd	52	nd	nd	nd	nd	nd	nd	72	309	35	69	nd	nd
PCB-52	nd	53	nd	nd	72	nd	nd	nd	nd	27	nd	nd	nd	nd
PCB-118	nd	nd	nd	nd	nd	nd	nd	nd	60	nd	nd	nd	nd	nd
PCB-138	nd	nd	nd	nd	nd	nd	nd	nd	56	nd	nd	nd	nd	nd
Phenol	95	650	2680	17 000	2800	3900	1450	26 400	580	6900	2 400	2 100	850	35 000
Monochlorophenols	+	30	30	+	40	nd	80	+	54	+	40	nd	50	+
Dichlorophenols	nd	nd	nd	nd	nd	nd	70	+	nd	nd	nd	80	nd	nd
Trichlorophenols	nd	nd	nd	nd	nd	nd	nd	+	nd	nd	nd	nd	nd	nd

Notes: * Details of samples are given in Table 3.2 and in the previous report (Smith and Sowray 1990)
 MD = Medmenham, HM = High Muffles, HR = Hazelrigg, P = particulate phase sample, V = vapour phase sample
 + = compound present, but could not be quantified due to interferences
 nd = not detected

Phenol was present in all samples at relatively high concentrations (up to 35 ng m⁻³) and in both phases, though predominantly as vapour. Much smaller quantities of a few chlorinated phenols were also identified.

4.3 Bulk deposition samples

Tables 4.5 and 4.6 show the results of analyses of several bulk deposition samples from Medmenham and High Muffles for a range of UK priority pollutants. Some PAH were identified at concentrations up to 100 ng l⁻¹, with naphthalene being the most commonly occurring. The High Muffles samples tended to contain higher concentrations of all the PAH identified than did the Medmenham samples.

Small amounts of several pesticide residues were also found, with γ -HCH being both the most abundant and most commonly occurring. Two PCB congeners (PCB-28 and PCB-101) were occasionally detected, and the two Medmenham samples also contained phenol and (in one case) a monochlorophenol.

Table 4.5 Polycyclicaromatic hydrocarbons in bulk deposition samples collected at Medmenham and High Muffles.
Concentrations in ng l⁻¹

Compound	Sample*								
	MD-4	MD-7	MD-10	HM-5	HM-6	HM-17	HM-18	HM-19	HM-2
Naphthalene	Tr	Tr	nd	nd	20	Tr	10	10	10
Alkyl naphthalenes	nd	nd	nd	nd	nd	Tr	Tr	Tr	Tr
Phenanthrene	Tr	Tr	nd	50	+	nd	nd	50	20
Anthracene	nd	nd	nd	nd	nd	nd	nd	nd	10
Alkylphenanthrenes/ anthracenes	nd	nd	nd	100	nd	nd	nd	nd	nd
Pyrene	Tr	Tr	nd	100	+	nd	nd	Tr	nd
Fluoranthene	Tr	Tr	nd	50	+	nd	nd	Tr	nd
Benzpyrenes/fluoranthenes	nd	nd	nd	nd	20	nd	nd	nd	nd

Notes: * Details of samples are given in Table 3.3 and in the previous report (Smith and Sowray 1990).
MD = Medmenham, HM = High Muffles, P = particulate phase sample, V = vapour phase sample.
+ = compound present, but could not be quantified due to interferences.
Tr = trace component, i.e. compound present in amount too small for quantification.
nd = not detected.

Table 4.6 Organochlorine pesticides, polychlorinated biphenyls and phenols identified in bulk deposition samples from Medmenham and High Muffles. Concentrations in ng l⁻¹

Compound	MD-7	MD-9	Sample* HM-9	HM-12	HM-13	HM-16
a-HCH	4	nd	nd	nd	8	nd
b-HCH	10	nd	nd	nd	nd	nd
g-HCH	55	11	10	26	45	18
p,p'-DDT	nd	nd	nd	nd	12	nd
Trifluralin	nd	nd	nd	nd	10	4
PCB-28	nd	nd	nd	nd	nd	33
PCB-101	21	nd	nd	nd	99	nd
Phenol	63	27	nd	nd	nd	nd
Monochlorophenols	nd	15	nd	nd	nd	nd

Notes: * Details of samples are given in Table 3.3 and in the previous report (Smith and Sowray 1990).
MD = Medmenham
HM = High Muffles.
nd = not detected.

4.4 Samples from Esthwaite Water and Castleshaw

Samples of rainwater and dry deposition were obtained from automatic wet/dry deposition samplers (Section 3.1.1) at these sites, at approximately two-week intervals, between July 1990 and August 1991. These were analysed for the range of PAH shown in Table 4.7.

Table 4.7 Polycyclic aromatic hydrocarbons studied at Esthwaite Water and Castleshaw

PAH	Abbreviation
Acenaphthene/fluorene	ACE/FL
Phenanthrene	PHEN
Anthracene	ANT
Fluoranthene	FLR
Pyrene	PYR
Benz[a]anthracene/chrysene	BaCh
Benzo[b]fluoranthene	BbF
Benzo[k]fluoranthene	BkF
Benzo[a]pyrene	BaP
Dibenz[a,h]anthracene	DiB

The concentrations of these compounds determined in rainwater are depicted in Figure 4.1, on the basis of seasonal mean concentration of each PAH. The sampling periods and number of samples used to calculate the seasonal mean are as follows:

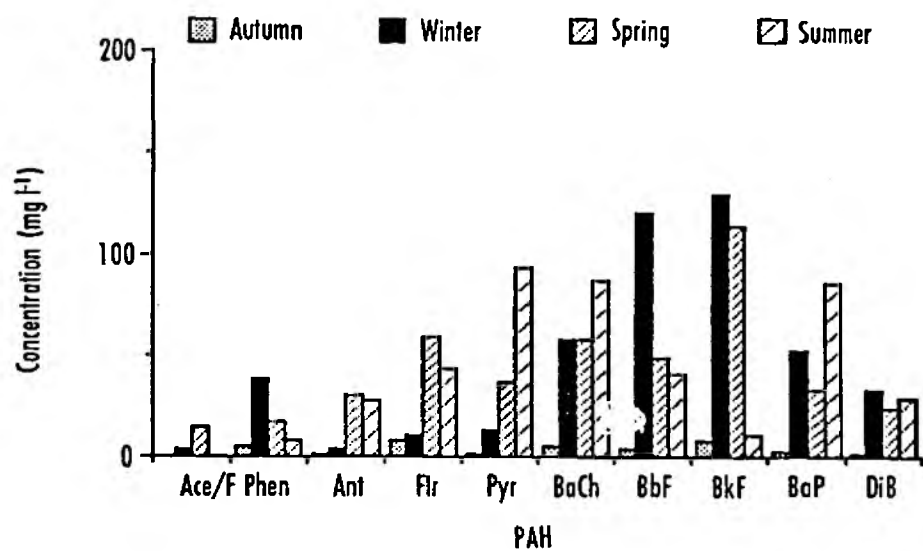
- Autumn: 12 September - 23 October 1990 (three samples);
- Winter: 6 December 1990 - 5 March 1991 (six samples);
- Spring: 5 March 1991 - 1 June 1991 (six samples);
- Summer: 17 July - 12 September 1990 and 1 June - 20 August 1991 (nine samples)

The overall distribution of PAH at both sites tended to be dominated by the higher molecular weight components, particularly benzo[b]fluoranthene, benzo[k]fluoranthene and benzo[a]pyrene, with PAH concentrations generally tending to be highest in winter and spring. These features are particularly marked at Esthwaite Water, where the concentrations of these three particular compounds in winter were about double those found at Castleshaw, although, overall, the PAH concentrations at both sites were fairly similar. The seasonal distribution of PAH was broadly the same at both sites, with relatively high concentrations in rainfall in winter and spring, and uniformly low concentrations in autumn. At Castleshaw, the concentrations of certain PAH showed a maximum in the summer.

Figure 4.2 shows data from dry deposition samples obtained from high volume air samplers run in parallel with the automatic wet/dry samplers at Esthwaite Water and Castleshaw. Total PAH concentrations in each particulate and vapour sample collected during the period July 1990 to July 1991 are shown. For most of that time, the PAH were present predominantly in the vapour phase; however, during the period December 1990 to February 1991, there was a clear shift in the phase distribution at both sites, with more PAH being present on particulates.

In general there is little difference between the PAH profiles through the year at the two sites, although concentrations tended to be slightly higher, overall, at Esthwaite Water. This was particularly true during December 1990 - January 1991 when both particulate and vapour phase concentrations at Esthwaite were double those at Castleshaw. In contrast, during July 1990 PAH were considerably more abundant at the Castleshaw site.

Castleshaw



Esthwaite Water

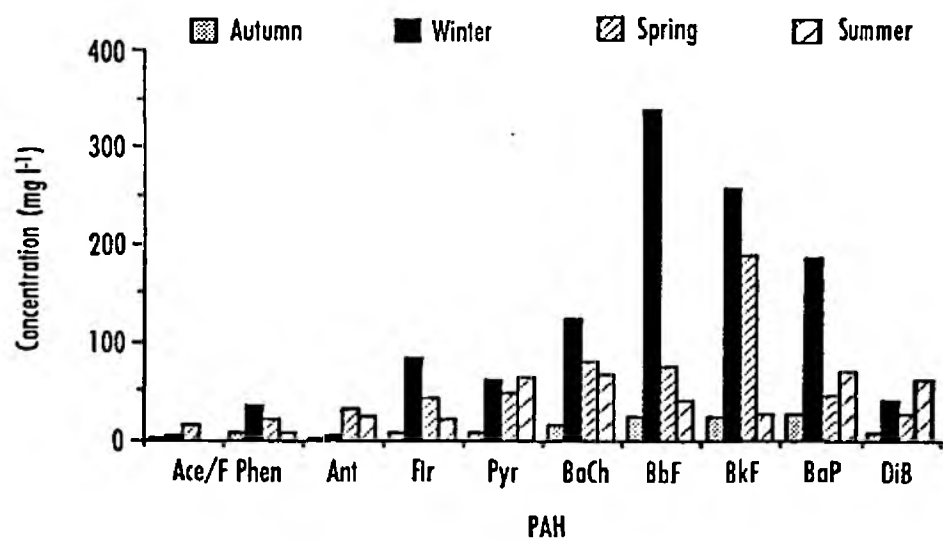
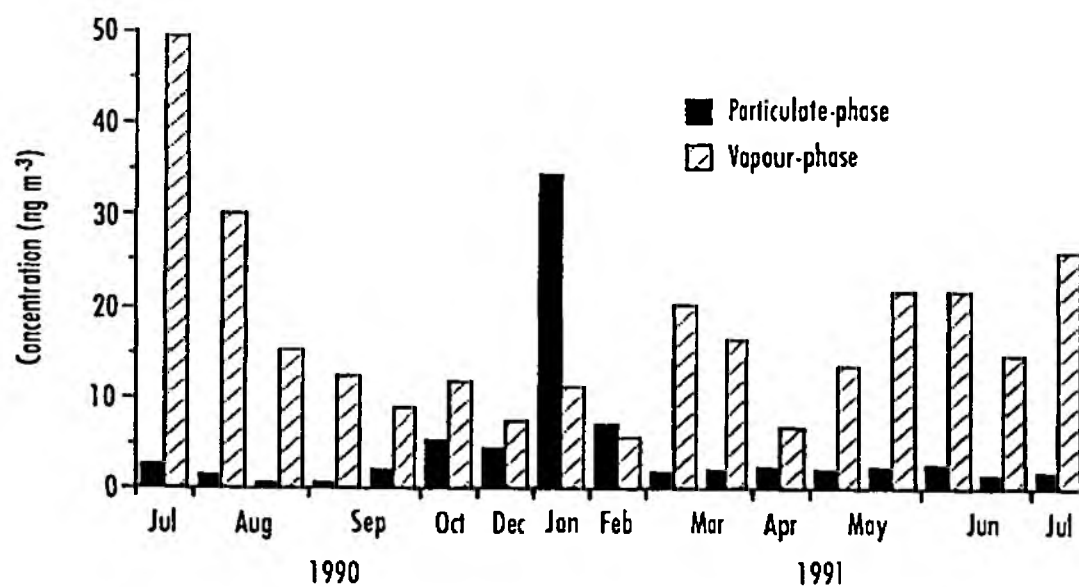


Figure 4.1 Seasonal mean concentrations of polycyclic aromatic hydrocarbons in rainwater from Castleshaw and Esthwaite Water. PAH are listed in Table 4.7

Castleshaw



Esthwaite Water

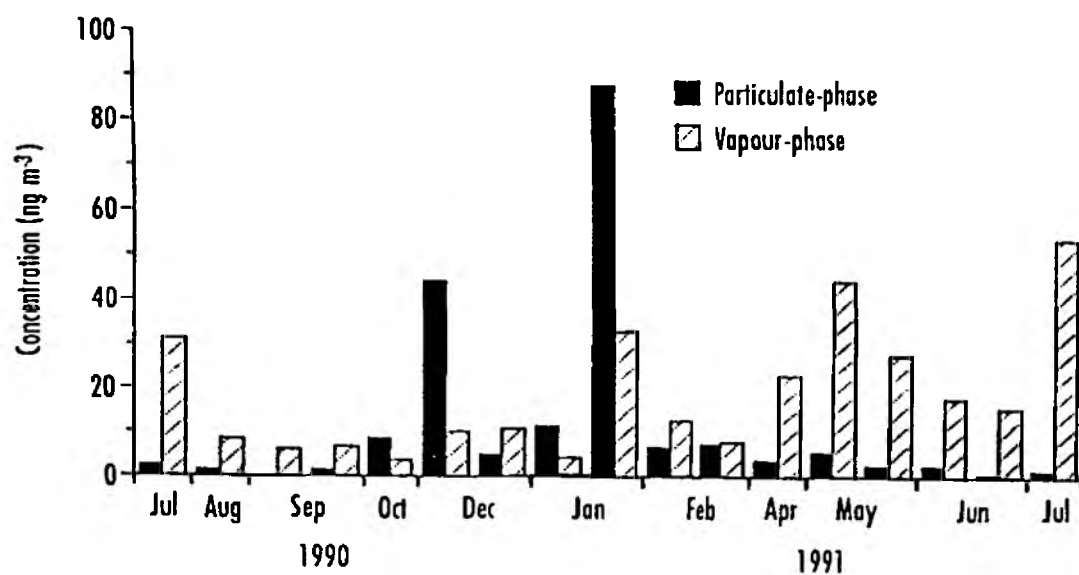


Figure 4.2 Concentrations of polycyclic aromatic hydrocarbons measured in high volume air samples from Castleshaw and Esthwaite Water, July 1990 - July 1991

5. ANALYSIS AND DISCUSSION

5.1 Polycyclic aromatic hydrocarbons

A range of PAH containing 2 - 5 rings was identified in the atmospheric samples, with the greatest variety occurring in the dry deposition (Tables 4.1 - 4.6). Relatively few were present in wet deposition and these tended to be the lower molecular weight, higher solubility compounds. The distributions present in rainwater and bulk deposition samples were generally similar in terms of both specific compounds present and concentrations. Comparisons between 'single event' rainwater samples and bulk deposition samples, however, are probably not very meaningful as the latter represent much longer collection periods and will also contain an element of dry deposition (although the efficiency of collection of dry deposition, especially from the vapour phase, is unlikely to be high due to the small collection area of the sampler and possibility of resuspension of deposited material). The main advantage of bulk deposition is the simplicity of collection, and its greatest value is in comparing different sampling sites and obtaining long term records from a site. Interestingly, the PAH in bulk deposition show no discernible seasonal trend, the samples in Table 4.5 representing collection periods during spring, summer and winter. This is in contrast to the dry deposition samples (discussed below) where higher PAH concentrations are evident in winter. There is no very clear distinction between the two sites (Medmenham and High Muffles) from which bulk deposition samples have been obtained in terms of PAH content, although slightly higher concentrations were generally measured in the High Muffles samples. In view of the low concentrations overall, however, this may not be significant. Unfortunately it has not been possible to obtain single event rain samples from High Muffles to compare with Medmenham.

A much wider range of PAH were identified in dry deposition samples from high volume air sampling (Table 4.3). These data show clearly that the lower molecular weight compounds such as naphthalene and phenanthrene occurred almost exclusively in the vapour phase, whereas the higher molecular weight compounds, such as chrysene and benzpyrene/fluoranthene were almost entirely associated with particulates. Intermediate between these are components such as pyrene and fluoranthene, which were present in both phases. These different phase associations are not unexpected when considering the volatility of the compounds. Volatility, and hence the tendency to exist in a gaseous state, decreases with increasing molecular weight. Similar behaviour has been recorded in other studies of atmospheric PAH (Albaiges *et al* 1991, Lioy and Daisey 1986).

The concentrations of PAH present in the air samples show a significant variation between seasons. Samples collected during summer (MD-16, MD-19 and MD-20) contained both fewer, and lower concentrations, than those collected during winter (MD-17 and HM-1). Sample MD-18, collected in spring, is intermediate between these in terms of amounts of PAH. These differences are probably related to different patterns of fossil fuel use between seasons, e.g. increased demand for heating in winter. It thus follows that any impact on surface water quality from atmospheric fallout may also vary from season to season, at least as far as combustion derived pollutants, such as PAH, are concerned. There will probably not, however, be a simple, direct relationship between air concentrations and surface water concentrations as many other seasonally variable factors will affect inputs to the water, such as amount of rainfall, temperature and type and amount of vegetation cover in the catchment.

Any attempts to predict the impact of atmospheric pollutants on surface water quality should take into account such variables and will therefore require data on local meteorological and geographical conditions as well as concentrations of pollutants in the air.

Only three PAH have so far been definitely identified in the samples of snow collected from Medmenham (Table 4.2), although further work on the complex mixture of compounds present in the total extracts may reveal others. These were also present in the other types of wet deposition, but at much lower concentrations. This suggests that snow may be more efficient than rain at removing PAH from the atmosphere, an observation which is supported by data from other studies (Kawamura and Kaplan 1986, McVeety and Hites 1988). This also has implications for possible impact on surface water quality, for example in areas of the UK where a high proportion of the spring inflow to rivers, lakes and reservoirs is derived from snowmelt.

5.2 Organochlorine compounds

The most widely occurring and abundant compound of this class in all types of deposition sample was hexachlorocyclohexane (HCH), of which the γ -isomer ('lindane') predominated (Tables 4.1, 4.4 and 4.6). HCH is globally distributed in the atmosphere (Kurtz 1990, Oehme 1991) being a widely used and persistent insecticide. It has frequently been reported as a major constituent of organochlorine pesticide residues in atmospheric samples (e.g. Ligocki *et al* 1985, Strachan 1988, Kurtz 1990, Ballschmiter and Wittlinger 1991). γ -HCH is the only Red List compound which has been identified (albeit at low levels, ca 4 ng l⁻¹) in rainwater from the 'background' site at Hartland Point (Section 3.1.2), suggesting that quantities of this substance are introduced to the UK in incoming airflow. Further data from this site is required, however, before the significance of this can be assessed. The predominance of γ -HCH in all samples suggests the main sources to have been applications of lindane, rather than technical HCH, as whereas the former is the pure (>98%) γ -isomer, the latter contains up to 70% of the α -isomer plus small amounts of the β -isomer (Kurtz 1990). In addition, photochemical reactions in the atmosphere are believed to convert γ -HCH to α -HCH (Kurtz 1990, Ballschmiter and Wittlinger 1991), which may well be the origin of at least some of the α -HCH in these samples.

Whatever the sources of HCH, it is one of the atmospheric pollutants which is of greatest significance in terms of potential impact on surface water quality. This is on account of, not only its relatively high abundance in the atmosphere and slow degradation, but also its relatively high water solubility (ca 7 mg l⁻¹ at 25°C) (Kidd and James 1991). In addition, other NRA-funded work at WRc has demonstrated that γ -HCH shows little tendency to partition from solution onto particles and hence, unlike some other pesticides such as DDT, will not so readily be removed from runoff by binding to soil particles. It occurs consistently, and at similar concentrations, at three widely separated sites throughout the year, suggesting that HCH (and particularly γ -HCH) is a widespread and persistent contaminant of the atmosphere over the UK. Other studies have indicated that washout in precipitation is an important removal mechanism for HCH from the atmosphere (Kurtz 1990), and its occurrence as the most regularly identified and abundant organochlorine pesticide residue in wet deposition samples in this work (Tables 4.1 and 4.6) supports this. It should therefore be considered as a priority target compound in more detailed studies of the impact of atmospheric organic pollutants on surface water.

A range of other organochlorine compounds, including pesticide residues and PCB, were present in the high volume air samples from all sites (Table 4.4) and a few of these also appeared in some wet deposition samples. Like HCH, hexachlorobenzene (HCB) was present in all vapour samples, but at lower levels. This compound, too, has been found to be a globally dispersed contaminant of the atmosphere (Kurtz 1990, Ballschmiter and Wittlinger 1991, Oehme 1991), and may also be of concern with regard to inputs to surface water. It has been detected in oceanic water at remote locations, where its presence is most likely the result of atmospheric deposition (GESAMP 1989).

Many of the organochlorine compounds found in the samples are on the UK Red List, and hence of particular concern. As well as HCH and HCB (discussed above), these include DDT, DDE, dieldrin, endrin, α -endosulfan, trifluralin and several PCB congeners. The presence of several of these, such as DDT (mainly associated with the particulate phase) and dieldrin, is of interest as these compounds have had no approved uses in the UK for many years. Apart from possible illegal use (which is likely to be very limited), several sources could explain their presence. These compounds have long environmental lifetimes and residues from historical use will continue to be dispersed in the environment (e.g. adsorbed on soil particles) for many years to come. Also, their use is still approved in some other countries (mostly outside Europe) and they could enter the UK atmosphere either indirectly from imported products, or directly via long range atmospheric transport (Kurtz 1990, Oehme 1991). Trifluralin is still approved for use as a pre-emergence herbicide, and it is notable that a relatively large amount was found in one particular air sample (MD-20) (Table 4.4). This probably reflects a local application at that time. Otherwise, it was only occasionally detected in very small amounts in air and bulk deposition samples.

5.3 Phenols

The presence of phenolic compounds in water used as a source of drinking water is of particular concern, as the process of chlorination during water treatment can produce chlorinated phenols which are known to give rise to major taste and odour problems in potable water. The relatively large quantities of phenol found in these atmospheric samples (Tables 4.1, 4.4 and 4.6) are therefore of interest. These levels are similar to those reported previously in this work (Watts *et al* 1989, Welch and Watts 1990), and to those found in rainwater samples from the USA (Leuenberger *et al* 1985, Kawamura and Kaplan 1986) and Switzerland (Czuczwa *et al* 1987). Phenol is a fairly volatile compound, which is emitted to the atmosphere from a variety of natural and anthropogenic sources, where it is present in relatively large amounts (as illustrated by the data in Table 4.4). It is also quite soluble in water, and hence is readily washed out of the atmosphere by rain. It could therefore enter surface water in significant amounts via surface runoff. Simple calculations for a model catchment carried out earlier in this work (Watts *et al* 1989, Smith and Sowray 1990) suggest that this process could give rise to levels in the receiving river of several micrograms per litre. These calculations made no allowance for attenuation processes, such as degradation or adsorption which would tend to reduce this level, as there is insufficient information on such processes available. Nevertheless, the concentrations of phenol found in air and rainwater samples suggest that atmospheric deposition could be a significant contributor of this compound to surface water.

It is notable that phenol was not detected, or only present at comparatively low levels, in the bulk deposition samples (Table 4.6). This was also true for two of the rainwater samples (23 and 24); however, in these cases, this may be due to the fact that collection of these particular samples did not commence until after the rain event had started. As phenol tends to be rapidly washed out of the atmosphere (Leuenberger *et al* 1985), it may be that much higher concentrations were present in the early rainfall which was not collected. This cannot apply to the bulk deposition samples, however. Those from High Muffles contained no detectable amounts of phenol, which may reflect a regional difference in atmospheric levels compared to Medmenham - the high volume air sample from High Muffles (HM-1 in Table 4.4) showed lower levels of phenol than most of those from Medmenham. However, the most likely reason is loss of phenol from the samples during their prolonged exposure to the environment. Phenol is both more volatile and less chemically stable than most of the other compounds identified in the samples, and significant amounts could have revolatilised and/or degraded between deposition and extraction of the samples. This illustrates the main inherent disadvantage of the bulk deposition technique and is one reason why it is difficult to compare such samples with single event air or rain samples.

Chlorophenols were present in some samples, in much smaller amounts than phenol. This is in agreement with previous reports of chlorophenols in rainwater (Leuenberger *et al* 1985).

5.4 Deposition of PAH at Castleshaw and Esthwaite Water

A study of PAH deposition at two sites in Northwest England (Section 3.1.2) has been carried out as a CASE Studentship funded by the NRA. Interpretation of the results is still under way and a full report of this study will be issued at a later date, however a brief summary of the main points will be presented here.

The distribution of PAH in rainwater was similar at both sites (Figure 4.1) with overall concentrations highest in winter and spring. This probably reflects higher inputs of PAH to the atmosphere during the colder months of the year due to increased burning of fossil fuel. The winter peak in concentrations was more pronounced at Esthwaite Water than at Castleshaw; the reasons for this are not clear. The relatively low concentrations found in autumn were not due to high rainfall producing more dilute samples, as calculations of the total flux of PAH show that this was lowest during autumn at both sites (Table 5.1).

Table 5.1 Mean seasonal atmospheric deposition fluxes of PAH to sampling sites at Castleshaw and Esthwaite Water. Fluxes of total PAH in $\text{ng m}^{-2} \text{hr}^{-1}$

	Autumn	Flux of total PAH		Summer	Annual
		Winter	Spring		
Castleshaw					
Wet deposition	4.3 (4.3)*	44.5	16.9	33.5	24.8 (24.8)*
Dry deposition	17.2 (74.7)*	84.3	32.1	16.3	37.5 (51.9)*
Total deposition	21.5 (79.0)*	128.8	49.1	49.9	62.3 (76.7)*
Esthwaite Water					
Wet deposition	3.6	65.4	33.1	47.6	37.4
Dry deposition	11.2	109.8	139.4	26.7	72.0
Total deposition	14.7	175.3	172.5	74.3	109.4

Notes: *Figures in parenthesis include the flux resulting from the stubble burning episode in September 1990 (Section 5.4)

Another factor which could have contributed to increased concentrations of PAH in winter rainfall is the fact that, during winter months, a high proportion of the atmospheric PAH are associated with particulates (Figure 4.2). Particulate-bound PAH may well be more efficiently scavenged by rain than unbound compounds, due to their hydrophobic nature and low water solubility.

Total fluxes of PAH to the two sites over the sampling periods have been calculated and are shown in Table 5.1. First, it is clear that the dry flux generally exceeds the wet flux, something which has been observed before (McVeety and Hites 1988). The exception to this, at both sites, was during the summer when the wet flux was greater. It is uncertain why this should be. The total flux of PAH was highest during the winter in both cases, and was generally greater at Esthwaite Water than Castleshaw.

During the period 15 - 25 September 1990 some stubble burning took place in the vicinity of the sampling site at Castleshaw. This was evidenced by the collection of large, sooty flakes in the dry deposition tray of the sampler, and a major quantitative and qualitative difference in the dry deposition PAH collected during this period compared to the average for the

autumn. The stubble burning clearly contributed a considerable extra input of PAH compared to normal inputs, as is illustrated in Table 5.1 where PAH fluxes both including and excluding the affected sample are quoted. When the stubble burning contribution is included, the dry deposition flux for the autumn is more than quadrupled. This suggests that isolated events such as stubble burning, which release large amounts of atmospheric pollutants in a short time and over a small area, could have a major impact on the quality of local water resources (e.g. reservoirs) if a significant amount of the pollution deposited in the catchment is transported to the water. It is therefore possible that such eventualities may need to be considered in water quality management programmes.

This study was designed primarily to evaluate the amount of PAH which was being deposited from the atmosphere directly into a body of water. For Castleshaw reservoir (Section 3.1.2), this can be estimated by a simple calculation. The measured total average annual flux of PAH at the site, (excluding the effect of the stubble burning episode), was $62.3 \text{ ng m}^{-2} \text{ h}^{-1}$ (Table 5.1). Over the surface area of the reservoir ($400\,000 \text{ m}^2$) this amounts to an average of 24.9 mg h^{-1} of PAH being deposited. To gauge the overall impact of PAH deposited from the atmosphere on the water quality in the reservoir, this must be added to other inputs derived from PAH deposited in the catchment area and washed into the reservoir. These are much more difficult to evaluate due to the difficulties in extrapolating data from a single sample point to a very much larger area, and the uncertainties surrounding the degree of attenuation which PAH levels will undergo following deposition and during subsequent transport to the reservoir. If the streams feeding the reservoir are assumed to contain between $10 - 200 \text{ ng l}^{-1}$ of PAH (which is a reasonable range of concentrations for semi-urban water courses), then, from the known volumes of water entering the reservoir, inputs of PAH in feeder streams will amount to ca $3 - 60 \text{ mg h}^{-1}$. Of course, not all of these are necessarily derived from atmospheric fallout. The important point is that the calculated flux of atmospheric PAH directly to the reservoir (ca 25 mg h^{-1}) is likely to form a significant proportion of the total flux entering the reservoir. The overall input of PAH from atmospheric deposition (including that entering via runoff) is therefore likely to be even more significant. This all supports the case for including atmospheric inputs when considering the sources of surface water contamination.

6. CONCLUSIONS

1. The atmosphere over the UK contains significant amounts of a wide range of organic pollutants (e.g. PAH, organochlorine pesticide residues, PCB, phenols), many of which also appear in wet deposition (rain and snow). The results are generally in good agreement with published data from comparable studies in other countries, suggesting that local atmospheric inputs of organic contaminants may be similar throughout the industrialised world.
2. Analysis has been carried out of deposition samples from widely separated inland sites, collected at different times throughout the year. Similarities, both qualitative and quantitative, between the contaminants deposited at the different sites support the concept of a common flux of atmospheric pollutants to the ground throughout a developed country such as the UK. Seasonal differences were apparent amongst some compound classes, especially PAH where increased fluxes during winter reflect increased combustion of fossil fuel which is a major source of these pyrolytic products.
3. Atmospheric inputs of several pollutants, especially HCH and phenol, have considerable potential for adversely affecting the quality of surface waters in the UK. More information on attenuation processes affecting these compounds between deposition and entry into surface water bodies is required in order to quantify the likely impact.
4. Localised atmospheric pollution created by isolated events such as stubble burning could have a significant impact on local water resources.

7. RECOMMENDATIONS

The work covered by this report has clearly demonstrated the potential of atmospheric deposition to contribute inputs of organic contaminants to surface water, and highlighted a number of substances of particular concern in this respect. The work has also shown up some specific aspects where more information is needed in order to properly assess the impact of atmospheric deposition. The most important of these are:

- to evaluate the relative importance of contributions, to levels of atmospheric organic pollutants, from UK sources (which are, in principle, amenable to control) and 'global' background contamination (which is outside the scope of UK legislation);
- to relate the amount and type of atmospheric deposition within a catchment to local meteorological and seasonal variations, and assess how these will affect its impact on water quality;
- to assess the influence of attenuation processes on deposited compounds in order to allow a realistic calculation of the amounts of compounds entering water bodies in runoff.

The sampling site at Hartland Point was established specifically to provide information on background levels of contamination by sampling deposition free from any significant inputs from UK sources. This has just started to yield useful data, and continued sampling at this site over different seasons would provide a vital baseline against which the contaminants deposited at other sites can be set. Sampling at the other sites should also be continued and analysis of samples widened to include other specific groups of priority pollutants, such as triazine herbicides and organophosphorus insecticides.

To address the second point will require correlation of measured deposition with meteorological and other data specific to the sampling locality. A limited amount of such data (windspeed, wind direction and temperature) has been routinely obtained for samples collected to date. More detailed information, including rainfall, is required over several seasons to fully evaluate the impact on a catchment. Such information should be obtainable from both the Esthwaite Water and Castleshaw sites used in this work and one or both of these would be employed in a continuation of the work.

The incorporation of attenuation processes into calculations of inputs to surface water is highly problematical, due to the paucity of data on such processes. Nevertheless, they are of such importance that any realistic attempt to predict the impact of atmospheric deposition of pollutants on surface water quality must take them into account. The general lack of relevant data and the huge resources needed to generate appropriate data means that an approach based mainly on theoretical considerations will be needed. For each of a number of selected chemicals, the key attenuation processes (e.g. adsorption to soil, degradation) will be identified by considering the physico-chemical properties of the compound together with any available environmental fate data. Relevant information for a particular catchment (e.g. area, soil type, prevailing meteorology) will be collected. These data sets will then be combined to provide an assessment of how much of a particular pollutant will be deposited in the catchment and how much of this is likely to enter surface water bodies, for a given set

of conditions. This will then allow calculation of the resultant concentration in the water arising from atmospheric deposition. This can be compared with the EQO for a number of priority pollutants to determine whether or not atmospheric deposition should be considered an important pathway for surface water contamination.

A better understanding of the impact of atmospheric deposition on surface water quality could also be obtained from an intensive study of a whole catchment. A suitable catchment area would be selected and sampling sites established to give representative coverage of the whole area. Samples would be obtained regularly over several seasons to allow detailed calculations of the fluxes of priority pollutants to the catchment. Analysis would also be carried out of surface water within the catchment and of other identifiable sources of the pollutants. By this means, total budgets for selected compounds could be constructed and the role of atmospheric deposition in that particular catchment accurately defined.

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