

Interim Report R&D Project 015

Atmospheric Inputs of Pollutants to
Surface Waters

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ATMOSPHERIC INPUTS OF POLLUTANTS TO SURFACE WATERS
Interim report on trace organics in atmospheric deposition

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EXECUTIVE SUMMARY

Data from atmospheric sampling carried out this year are presented. A novel GC-MS (multiple ion detection) method was developed to analyse the 21 organic contaminants selected for further study in the final year of the project. The majority of sampling this year has been focused on the Hartland Point sampling station since this site is vital to establishing background levels of pollutants. Initial results show that PAHs and a few persistent organochlorine contaminants are present in atmospheric samples taken at Hartland Point at levels similar to those measured at the other sampling sites. However, at present there are only a few results for Hartland Point and accurate quantitative comparison between data collected from other sampling sites may not be meaningful.

KEY WORDS

Atmospheric deposition, wet deposition, dry deposition, bulk deposition, surface waters, organic contaminants, PAHs, PCBs, organochlorine pesticides, phenols

1. INTRODUCTION

Work carried out at WRc in the last four years has established that a number of priority pollutants (including organochlorine pesticide residues, PCBs and PAHs) are regularly present at varying levels in both wet and dry atmospheric deposition at several sites in the UK. The analytical data compiled during the project has been used to assess the likely concentrations in surface waters which may be contributed from atmospheric deposition using a simple model catchment. This 'worst case' model suggested that mean concentrations of phenols may be several $\mu\text{g l}^{-1}$ in a receiving river water, but of more interest was the indication that the mean levels of lindane (a Red List chemical) may be about 30 ng l^{-1} . The latter concentration is a significant proportion of the EQS set for surface waters (100 ng l^{-1}) and exceeds the level set for coastal marine waters (20 ng l^{-1}). Hence the contribution from this source could be significant in terms of achieving EQS levels and setting discharge consents.

Further work was needed on assessing the significance of atmospheric deposition in order to take account of potential attenuation of pollutants during transport to surface waters. In addition, it was necessary to try to estimate the relative importance of background levels of pollutants (i.e. those transported large distances) compared with local emissions (i.e. those picked up by passage of air masses over industrialised areas) and this required further sampling and analysis at the Hartland Point site. A one year extension to the project was therefore proposed to cover this work.

After consultation with the NRA, a list of 21 priority pollutants have been selected from the existing list of determinands for detailed study in the final year of the project (see Table 1.1).

Table 1.1 Potential pollutants comprising the range of compounds for assessment of significance

Class	Compound	Potential attenuation	Priority status
PAH	Naphthalene	Volatilisation/biodegradation	2
	Fluorene	Sorption/biodegradation	2
	Phenanthrene	Sorption/biodegradation	2
	Pyrene	Sorption/biodegradation	2
	Fluoranthene	Sorption/biodegradation	2
PAK	Fluoren-9-one	-	-
OCI	α -HCH	Sorption/hydrolysis	1
	β -HCH	Sorption/hydrolysis	1
	γ -HCH	Sorption/hydrolysis	1
	Endosulphan	Hydrolysis	1
	Aldrin	Sorption/slow biodegradation	1
	Endrin	Sorption/slow biodegradation	1
	Dieldrin	Sorption/slow biodegradation	1
	p,p'-DDT	Sorption/slow biodegradation	1
	Hexachlorobenzene	Sorption/slow biodegradation	1
PCB	28	Sorption/biodegradation	1
	52	Sorption/biodegradation	1
	118	Sorption/slow biodegradation	1
	138	Sorption/slow biodegradation	1
Phenols	Phenol	Biodegradation	-
	Pentachlorophenol	Sorption/photolysis/biodegradation	1

2. EXPERIMENTAL

2.1 Sampling

The sampling methodology employed in the course of this work has been fully described in previous reports (Watts and Welch 1988, Watts *et al.* 1989, Smith and Sowray 1990, Smith and Watts 1992). Details of the samples collected this year are given in Tables 2.1 - 2.2.

It was decided that sampling and analysis effort should be focused on the Hartland Point sampling station in the final year of the contract, since this site is vital to establishing background levels of pollutants. Unfortunately, the automatic wet/dry sampler, which had been left installed at the lighthouse at Hartland Point some time ago, was not in working order on returning to the site in early March. Therefore, it was decided to continue taking dry deposition samples with the high volume sampler and replace the automatic wet/dry sampler with a bulk deposition sampler. Unlike the High Muffles sampling station, there is nobody regularly visiting the site to keep a check on the bulk deposition sampler between visits by WRC personnel. Thus, there is a possibility that the sample bottle in the sampler will overflow, if several large rain events occur between sampling trips.

Table 2.1 Details of dry deposition samples collected using a high volume air sampler at Hartland Point and High Muffles

	HP-1	Sample*		HM-3
		HP-2	HP-3	
Date of sampling (start)	4.3.93	14.5.93	15.5.93	29.3.93
Sampling time (hours:mins)	17:35	23:45	23:51	21:20
Flow rate ($l\ min^{-1}$)				
Initial	850	700	700	800
Final	850	650	700	770
Volume sampled (m^3)	897	962	1002	1005
Air temperature ($^{\circ}C$)				
Maximum	5	10	12	9
Minimum	-2	1	1	1
Wind direction	NW	SW	SW	S/SW

* HP = Hartland Point, HM = High Muffles

Table 2.2 Details of bulk deposition samples collected at Hartland Point and High Muffles

Sample N ^o	Date of sampling (start)	Sampling time (days)	Volume collected (litres)
Hartland Point			
HP-1	5.3.93	70	2.40*
HP-2	16.5.93	25	1.68
High Muffles			
HM-47	31.3.93	7	2.30
HM-48	14.4.93	14	2.26
HM-49	28.4.93	21	2.40

* The sample bottle had overflowed before collection.

2.2 Analytical methodology

Full details of analytical methodology have been given in previous reports (Watts and Welch 1988, Watts *et al.* 1989, Smith and Sowray 1990, Smith and Watts 1992). The sample extraction procedures used in the final year of the project are similar to those previously described, however, there are a few modifications which require explanation. Also, a new GC-MS method is described which was developed to quantify the 21 organics selected for study.

2.2.1 Sample extraction

Bulk deposition samples

Bulk deposition samples were spiked with a mixture of deuterium labelled standards immediately after collection. The compounds spiked into the samples and amount spiked per component are listed in Table 2.3.

Table 2.3 Internal standards spiking mixture

Compound	Amount spiked (μg)
d_8 -naphthalene	5.0
d_{10} -phenanthrene	5.0
d_{10} -pyrene	5.0
d_{10} -fluoranthene	5.0
d_5 -phenol	5.0
$^{13}\text{C}_6$ -pentachlorophenol	5.0
$^{13}\text{C}_8\text{d}_6$ -lindane	1.0
$^{13}\text{C}_4$ -dieldrin	1.0

The sample volume was measured using a 2-litre measuring cylinder and then the sample was carefully transferred to a 2-litre glass separating funnel. The sample bottle was washed out with a small volume of dichloromethane which was also transferred to the separating funnel. Sodium chloride (approximately 20 g) was dissolved in the sample to improve the extraction efficiency by 'salting out' the more water soluble determinands and to reduce the formation of stable emulsions. The sample was then extracted with dichloromethane (1 x 100 ml, then 2 x 50 ml aliquots) by vigorous shaking in the separating funnel. The solvent layer was separated off and filtered through pre-extracted glass wool to break up emulsions. The extract was dried by freezing out water (-20 °C overnight) and concentrated to 1 ml using a Zymark Turbovap. The concentrated extracts were then carefully exchanged into 1 ml of decane under a stream of dry nitrogen gas.

The 1 ml decane extracts were divided into two 500 μl portions. One portion was methylated with freshly prepared ethereal diazomethane to facilitate quantification of the phenols. The extract and approximately 1 ml of diazomethane were shaken together in a vial and left for five minutes. Excess diazomethane was removed under a stream of dry nitrogen gas.

Dry deposition samples

The glass fibre filters and polyurethane foam plugs (PUFs) were spiked on site with a mixture of deuterium labelled internal standards immediately after sampling (see Table 2.3).

Immediately after returning to the laboratory, glass fibre filters and PUFs were Soxhlet extracted with dichloromethane (250 ml) for a minimum of 16 hours. The solvent was then concentrated to 1 ml using a Zymark Turbovap. Glass fibre filters were cut into small pieces to facilitate solvent extraction. Fine white particles of polyurethane were present in the PUF extracts and were separated from the supernatant by centrifugation at 3000 rpm. The concentrated extracts were then carefully exchanged into 1 ml of decane under a stream of dry nitrogen gas.

The 1 ml decane extracts were then divided and methylated as described above.

2.2.2 GC-MS analysis

GC-MS analysis was carried out using a Hewlett Packard 5890 GC equipped with a cool on-column injector and a Hewlett Packard autosampler model number 7673A. The GC was connected to a VG Trio-1 MS via a heated direct interface. The MS was operated with either a dedicated electron impact (EI) source in positive ion mode or a dedicated chemical ionisation (CI) source in negative ion mode. The methylated portions were analysed by positive ion EI-MS and non-methylated portions by negative ion CI-MS (see Tables 2.4 and 2.5).

The following operating conditions were employed:

- GC conditions:

Column -	DB 1701, 60 m, 0.32 mm ID, 0.25 μ m film thickness	
Column temperature -	150 °C held for four minutes 150-280 °C at 4 °C/min ramp, held for 20 minutes	
Injection volume -	1 μ l	
- MS conditions:

	EI	CI
Filament trap current, μ amps	150	350
Electron energy, eV	70	70
Source temperature, °C	200	200

Tuning and mass calibration for both +EI and -CI was carried out using heptacosyl (perfluorotributylheptacosamine) which was bled into the source via a heated septum inlet.

- MID conditions:

	EI	CI
Sampling time, ms	80	80
Stabilization time, ms	20	20
MS peak width, amu	1	1

4. Materials

Helium (Research Grade, 99.99%, supplied by BOC Ltd) was used as a carrier gas at a flow rate of 1 ml min⁻¹.

Methane (Research Grade, 99.99%, supplied by BOC Ltd) was used as the CI reagent gas at a gas line pressure of 8 psi (it was not possible to measure the source pressure on the Trio-1).

Acetone, decane and cyclohexane (glass distilled grade, supplied by Rathburns).

Stock Standard Solutions were made up in acetone at a concentration of $100 \mu\text{g ml}^{-1}$ for the compounds shown in Tables 2.4 and 2.5. GC-MS calibration standards were made up in decane.

Table 2.4 GC-MS Multiple Ion Detection (MID) method using +EI mode

Peak	Compound	Relative reference peak	Ions monitored m/z	Retention time (min)
1	d ₅ -phenol	-	113	5.80
2	phenol	1	108	5.85
3	d ₈ -naphthalene	-	108, 136	6.26
4	naphthalene	3	102, 128	6.29
5	fluorene	3	165, 166	13.63
6	hexachlorobenzene	7	284, 286	16.83
7	pentachlorophenol	7	265, 280	17.08
8	¹³ C ₆ -pentachlorophenol	-	271, 286	17.14
9	fluoren-9-one	9	152, 180	17.56
10	d ₁₀ -phenanthrene	-	160, 188	18.56
11	phenanthrene	9	152, 178	18.74
12	PCB-C28	9	186, 256	21.97
13	PCB-C52	9	220, 292	22.57
14	d ₁₀ -fluoranthene	-	108, 212	25.67
15	fluoranthene	13	101, 202	25.79
16	pyrene	13	101, 202	27.07

Table 2.5 GC-MS Multiple Ion Detection (MID) method using -CI mode

Peak	Compound	Relative reference peak	Ions monitored m/z	Retention time (min)
1	α -hexachlorocyclohexane	2	71, 73	16.31
2	$^{13}\text{C}_6\text{d}_6$ -lindane	-	71, 73	17.74
3	β -hexachlorocyclohexane	2	71, 73	17.75
4	lindane	2	71, 73	17.95
6	aldrin	8	235, 237	23.66
7	α -endosulfan	8	240, 242	27.16
8	$^{13}\text{C}_4$ -dieldrin	-	239, 241	28.42
9	dieldrin	8	235, 237	28.43
10	endrin	8	238, 272	29.41
11	β -Endosulfan	8	240, 242	29.91
12	PCB-C118	8	324, 326	30.02
13	PCB-C138	8	360, 362	32.24

5. Quantification

Calibration was achieved using standard solutions and the compounds of interest were quantified against the appropriate stable isotope labelled internal standard.

3. RESULTS AND DISCUSSION

Table 3.1 Organic contaminants identified in high volume air samples from Hartland Point and High Muffles
Concentrations in pg m^{-3}

Compound	HP-1		HP-2		HP-3		HM-3	
	P	V	P	V	P	V	P	V
naphthalene	610	770	nd	nd	nd	nd	870	2200
fluorene	420	1100	nd	1700	nd	1300	900	1800
fluoren-9-one	280	420	nd	280	nd	140	380	720
phenanthrene	160	1200	nd	4000	nd	2700	270	2000
fluoranthene	260	320	nd	190	nd	200	420	500
pyrene	300	230	nd	310	nd	300	410	390
α -HCH	nd	78	nd	83	nd	90	nd	120
β -HCH	nd	89	nd	nd	nd	nd	nd	nd
lindane	nd	130	nd	83	nd	320	5	1100
α -endosulphan	nd	nd	nd	nd	nd	nd	nd	160
PCB C118	nd	nd	nd	nd	nd	nd	320	1100
β -endosulphan	nd	nd	nd	nd	nd	nd	nd	nd
p,p-DDT	nd	nd	nd	nd	360	nd	nd	400
PCB C138	nd	nd	nd	nd	nd	nd	350	1000

A range of polycyclic aromatic hydrocarbons (PAHs) were identified in the high volume air samples taken at the Hartland Point sampling station. Interestingly, the measured concentrations of PAHs were not significantly lower than the measured concentrations at the other sampling sites. However, it should be noted that at present we only have a few results for Hartland Point and accurate quantitative comparison with the results from other sampling sites is not possible.

Previous work by Veety and Hites (1988) has shown that even very remote, pristine areas are subject to deposition of PAHs, which can be carried thousands of miles through the atmosphere. However, Windsor and Hites (1979) noted that PAH deposition decreases dramatically with distance from urban centres. For example, within 100 km of Boston, USA, the total PAH abundance in sediments (directly related to atmospheric deposition) decreased by three orders of magnitude to the same concentration observed in samples from remote locations. Therefore, it is not surprising that PAHs were found in samples taken from the Hartland Point sampling site and the levels found may represent UK background contamination.

Depending on meteorological conditions, PAHs could be transported from industrial areas in South Wales and/or the urban centres of Plymouth and Bristol. However, the wind direction measurements taken during high volume air sampling indicate that the air

flow was south westerly. It is probable that more detailed meteorological information is required to fully understand atmospheric transport processes.

Lindane and the alpha and beta isomers of hexachlorocyclohexane were also identified at levels similar to those found at other sites. Hexachlorocyclohexane is very persistent in the environment with an estimated atmospheric residence time, for lindane, of 17 weeks (Lewis and Lee 1976) and is therefore likely to be found even in remote locations.

The glass fibre filters used for samples HP-2(P) and HP-3(P) only collected a very low loading of air particulates (the filters were only slightly discoloured after sampling) and this may explain why very few contaminants were identified in these samples.

The concentrations of contaminants identified in the one High Muffles sample taken this year are all within the concentration range found in previous samples from this site.

It was surprising that phenol was not identified in any of the high volume air samples taken this year as it has always been present in previous samples at relatively high concentrations.

Table 3.2 Organic contaminants identified in bulk deposition samples from Hartland Point and High Muffles. Concentrations in ng l⁻¹

Compound	HP-1	HM-47	HM-48	HM-49
naphthalene	nd	nd	31	nd
fluoren-9-one	nd	87	nd	nd
phenanthrene	52	50	nd	40
fluoranthene	81	78	nd	67
pyrene	120	110	nd	100
lindane	31	100	190	160
p,p-DDT	81	nd	44	nd
PCB C138	83	nd	nd	nd

Although two bulk deposition samples have been taken from Hartland Point this year, at present only the first sample has been analysed and interpreted. Several organic contaminants were identified in this sample (see Table 3.2) and the concentrations measured are not significantly lower than levels found in samples from the other sites. However, more data is required before the results from Hartland Point can be quantitatively compared with the results from other sites. Nevertheless, it should be noted that only the more persistent contaminants were found to be present.

Three samples have been taken from the High Muffles site this year and the range and concentration of contaminants found in these samples are similar to those found in previous samples.

4. FUTURE WORK

4.1 Final report

The proposed layout of the final report is shown below:

1. INTRODUCTION

- 1.1 Sources of atmospheric inputs
- 1.2 Significance of atmospheric inputs
- 1.3 Previous work

2. EXPERIMENTAL

- 2.1 Sampling
 - 2.1.1 Sites
 - 2.1.2 Samplers (bulk, wet only, high volume)
- 2.2 Analysis
 - 2.2.1 Extraction
 - 2.2.2 GC-ECD
 - 2.2.3 GC-MS
 - 2.2.4 Compounds
- 2.3 Modelling
 - 2.3.1 Simplistic worst case
 - 2.3.2 Fugacity Level III

3. DISCUSSION

- 3.1 Sampling
 - 3.1.1 Influence of sampler types
 - 3.1.2 Influence of site location
 - 3.1.3 Influence of meteorology
- 3.2 Compounds identified
 - 3.2.1 Range/amounts of compounds
 - 3.2.2 Site relationship
 - 3.2.3 Priority compounds
- 3.3 Modelling
 - 3.3.1 Data collation (range, means etc.)
 - 3.3.2 Worst case calculations
 - 3.3.3 Incorporation of attenuation processes
- 3.4 Significance of atmospheric inputs for NRA
- 3.5 Guidance on monitoring inputs to a catchment

4. CONCLUSIONS

5. RECOMMENDATIONS

6. FUTURE WORK

REFERENCES

4.2 Ideas for further research

Although the work has not yet been completed it has already become evident that further work will be required to properly assess the impact of atmospheric deposition on surface waters. Two brief proposals for further research have been included in this section so that they can be given careful consideration by NRA (and/or DoE) well before the contract comes to an end. These proposals will be developed further in the final report (and/or other proposals included) after the conclusions of this year's work have been carefully considered.

4.2.1 Specific catchment study

A better understanding of the impact of atmospheric deposition on surface water quality could be obtained from an intensive study on atmospheric inputs to a well-defined, small catchment. A suitable catchment area (probably in a remote location) would be selected and sampling sites established to give representative coverage of the whole area. Samples would be obtained over several seasons to allow detailed calculations of the fluxes of priority pollutants to the catchment. Sampling and analysis of the surface water within the catchment would also be carried out. By using a mass balance approach, total budgets for selected contaminants could be constructed and the role of atmospheric deposition in the catchment accurately defined. This detailed study would also help to assess the modelling approach developed this year.

A more detailed sampling regime would make it possible 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. A limited amount of meteorological data (windspeed, wind direction and temperature) has been routinely obtained for samples collected to date. More detailed information, including rainfall, taken over several seasons would be required to fully evaluate the impact on a catchment.

4.2.2 Atmospheric transport of pesticides

Recent results have revealed that precipitation and dry deposition contains low levels of pesticides of the chlorinated hydrocarbon type. In addition, during the past few years scattered reports have appeared showing that some precipitation may be contaminated by other pesticides (e.g. organophosphorous insecticides) in unexpectedly high concentrations (tens of micrograms per litre).

Pesticides may be transported over large distances and deposited onto soil and surface water in areas remote from application. This represents a risk to the steadily increasing number of farmers who grow their crops without the use of pesticides. In addition wet and

dry deposition of pesticides may lead to contamination of surface water (drinking water basins) and under very unfavourable conditions may leach down to groundwater.

Sampling sites would be established in the UK equipped with automatic wet only samplers and/or bulk deposition samplers. These sites would be located in areas with pesticide application, in agricultural areas without pesticide application and in remote areas. In addition, wells, springs in remote areas, and drinking water basins, also in remote areas, would be monitored for pesticides.

This project would help to determine the relative significance of short versus long range transport of pesticides in terms of the impact on agricultural practices and water quality.

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