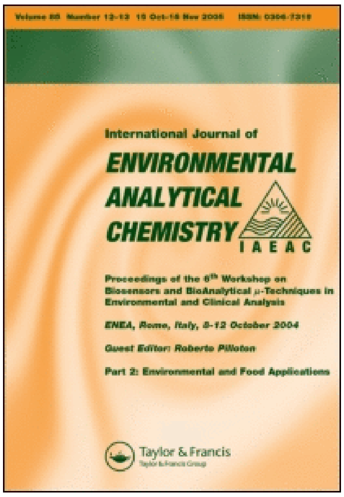

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

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To cite this Article Welch, D. I. and Watts, C. D.(1990) 'Collection and Identification of Trace Organic Compounds in Atmospheric Deposition from a Semi-Rural Site in the U.K.', International Journal of Environmental Analytical Chemistry, 38: 2, 185 — 198

To link to this Article: DOI: 10.1080/03067319008026926

URL: http://dx.doi.org/10.1080/03067319008026926

Intern. J. Environ. Anal. Chem., Vol. 38, pp. 185–198
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COLLECTION AND IDENTIFICATION OF TRACE ORGANIC COMPOUNDS IN ATMOSPHERIC DEPOSITION FROM A SEMI-RURAL SITE IN THE U.K.

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The collection of rainwater, aerosol and vapour samples at a semi-rural site in the UK was achieved using a PTFE-lined wet-only rainfall collector and a high-volume filter/adsorption trap air sampler, respectively. Analysis of atmospheric deposition revealed the presence of several hundred compounds, many of which were of anthropogenic origin, e.g.: PAH, phenols and alkylbenzenes. Amounts of compounds varied from low nanograms to tens of micrograms per litre in rainwater samples and from low picograms to high nanograms per cubic metre in aerosols. Phenolic compounds were the most abundant group of organics identified in rainwater and were present at total concentrations of $>20\,\mu g\,l^{-1}$ in some of the samples analysed. In the high-volume air samples most anthropogenic compounds were detected in the adsorbent rather than the filter extract. Seasonal variations in the PAH content of the adsorbent extracts were observed. The presence of siloxanes in the air samples was thought to be the result of contamination.

KEY WORDS Trace organic compounds, rainwater, aerosol vapour samples, PAH, phenols, alkylbenzenes, gas chromatography, mass spectrometry.

INTRODUCTION

The presence of organic compounds in surface water is important to the water industry since some organics are potential toxins[1] or precursors in the formation of toxins[2] and may also cause taste and odour problems[3] in derived potable water supplies. Previous studies[4] have shown that precipitation can result in significant inputs of organic carbon to large water surfaces close to urban areas. At present little information is available in the UK as to the nature and extent of organic pollutants contributed by atmospheric deposition to surface waters. Such information would be valuable to the water industry in the future determination of control strategies for organic contaminants in drinking water sources and supplies.

Control strategies are required for certain organics e.g. alkylbenzenes, PCB's and chlorinated pesticides in order that the water industry can satisfy its legal obligations to meet environmental quality standards and drinking water quality directives issued by the EEC.[5]

The deposition characteristics and behaviour of organic compounds are related to their physico-chemical properties and the forms in which they are emitted.

Predictive modelling which attempts to describe the passage of an organic compound from the atmosphere to a surface water, requires information on the partitioning between aqueous, vapour and particulate phases in order to determine the deposition velocities and fluxes of selected organic species. Sampling methodology of atmospheric deposition is therefore designed to distinguish between dissolved, vapour and particulate fractions. To this end rainfall is commonly collected on a wet-only event basis[6] and airborne organics using a high-volume air sampler employing a filter-adsorbent system.[7]

A research programme was initiated at the Water Research Centre (WRc) with the overall objective of making an assessment of the contribution of airborne organic pollutants to the organic content of UK surface waters. This paper describes the sampling equipment, collection site, analytical methodology and preliminary results obtained. It is intended that a remote rural site will also be instrumented in order to see whether the results obtained at the Medmenham site are representative of other areas of the UK.

EXPERIMENTAL

Sampling

A sampling site was selected adjacent to the WRc Laboratory at Medmenham (OS ref SU 805838), which is situated in the Thames Valley between the small towns of Marlow and Henley-on-Thames. Because of the close proximity (3–4 miles) of these towns, the site can be classed as "semi-rural". It is well removed from local point and line source emissions (e.g. domestic fires, car parks and roads) and tall obstructions (e.g. buildings and tall trees). Existing vegetation was manually cleared and a layer of coarse gravel laid to give an area of approximately $10\,m^2$.

Rainwater samples (1 to 5 l) were collected on an event basis using an approximately $1\,m^2$ area collector consisting of a PTFE collection surface held 1.5m above the ground in an aluminium casing, draining to a glass bottle. The sampler was covered with a lid during dry periods and this was manually opened at the start of a rain event and closed at the end or when a sufficient sample was collected.

In anticipation of a rain event, the collection surface was rigorously cleaned by sequential washing with tapwater, isopropanol, dichloromethane and deionised, activated carbon treated water. Blank samples were obtained by slowly pouring deionised, activated carbon treated water (5 l) over the collection surface. The ambient temperature was recorded at the start and end of sample collection and the depth of rainfall was measured during the period of sample collection using a standard Meteorological Office rain gauge.

Aerosol and vapour phase samples were collected using a high volume 750 l min: Hi Vol) air sampler (University of Lancaster) consisting of a sealed aluminium casing supporting a glass fibre filter paper (Whatman EPM 2000) and polyurethane foam (PUF) plug (10 cm diameter, 5 cm thickness, density

0.0234 g cm^{-3}) adsorption train. Flow rate was measured using a flow meter (IGU/1 Platon Flow Control Ltd, Basingstoke, Hants) at the start and finish of the sampling period. Prior to sampling, the glass fibre filters were cleaned by heating them at 450 °C, in a muffle furnace, overnight. The polyurethane foam plugs were Soxhlet extracted in dichloromethane for 48 hours. The glass fibre filter was spiked with 1 μl of a mixture of deuterium labelled standards at a concentration of 100 ng μl^{-1} per component prior to sample collection. The compounds spiked were: d_3 – 1,1,1-trichloroethane, d_6-benzene, d_5-chlorobenzene, d_{10}-p-xylene, d_5-phenol, d_8-naphthalene, d_{34}-hexadecane and d_{10}-phenanthrene. After the sampling period of 24 hours the filter and PUF were carefully removed and wrapped in solvent washed aluminium foil for transportation to the laboratory.

Extraction

Blank and rainwater were filtered through glass wool and spiked with the above deuterium labelled standards mixture to a concentration of 100 ng l^{-1} per component. Dichloromethane (50 ml per litre of sample) was added and the mixture acidified (to pH 2) with concentrated hydrochloric acid. The samples and solvent were stirred vigorously overnight and the solvent layer then separated off. Concentration of the solvent (to about 1 ml) was performed using a Kuderna-Danish apparatus with macro-Snyder column, with further concentration under a stream of dry nitrogen.

Glass fibre filters and PUF's were Soxhlet extracted with dichloromethane (250 ml) for 16 h and the solvent extract concentrated as described above. Glass fibre filters were cut into small pieces to facilitate solvent extraction.

Gas Chromatography (GC)

GC was carried out on a 60 m DB1 bonded phase fused-silica capillary column (J & W Scientific) of 0.25 μ film thickness and 0.25 mm internal diameter installed in a Carlo-Erba gas chromatograph. Injection was performed via a splitless injector, the column oven temperature maintained at 50 °C for 3 minutes and then linearly increased at 8 °C min^{-1} to a final temperature of 300 °C. Detection was by a flame ionisation detector (FID) maintained at 330 °C.

Gas Chromatography-Mass Spectrometry (GC-MS)

GC-MS was carried out on a Hewlett Packard 5710A gas chromatograph directly coupled to a VG Analytical 7070E double focussing mass spectrometer. The gas chromatograph was fitted with an OCI-2 on-column injector (SGE) and a fused silica capillary column (DB-1; 60 m × 0.32 mm; 0.25 μ film thickness; J & W Scientific). Data acquisition and processing were performed by a Super-Incos datasystem (Finnigan MAT, UK) with mass calibration using perfluorokerosene.

Table 1 Details of rainwater samples

Sample no	*Date*	*Collection time (hrs)*	*Amount (l)*	*Rainfall (mm)*	*Temperature °C*	
					Initial	*Final*
1	26.02.87	2	5	3	5	5
2	26.02.87	2	2	2	5	5
3	01.04.87	8	3	2.8	9	11
4	07.04.87	2½	>6[a]	8	8	9
5	07.04.87	2½	3	2.8	9	12
6	14.05.87	2½	3	2.8	8	11
7	20.10.87	2¾	5	5.1	9.5	10
8	20.10.87	1¼	6	6	10	10
9	15.12.87	4½	3.2	3.2	3	3

[a] Overflow of sampling bottle occurred

Table 2 Details of high-volume air samples

Sample no.	*Date*	*Flow rate ($l\,min^{-1}$)*	*Sampling period (hrs)*	*Temperature °C*	
				Min	*Max*
1F 1P	30.09.87	700	24	0	19
2F 2P	20.10.89	750	24	9	14
3F 3P	02.12.87	750	24	0	5
4F 4P	15.12.87	775	24	1	5
5F 5P	12.01.88	750	24	2	6
6F 6P	08.03.88	750	24	0	13
7F 7P	20.04.88	775	24	5	20
8F 8P	24.05.88	725	24	8	21
9F 9P	14.06.88	700	24	10	29

All mass spectra were obtained under electron impact (EI) conditions using 70 eV electron energy, 200 μA trap current and 6 kV accelerating voltage. The mass spectrometer was continuously scanned over the mass range 20–700 μ at 0.5 sec decade^{-1} with a dynamic resolution of about 2000 m/Δm.

RESULTS AND DISCUSSION

Details of the nine rainwater and high-volume (Hi Vol) air samples collected are given in Tables 1 and 2. Rainwater samples 1 and 2 were collected during the same event using a stainless steel collection surface prior to the interception area being replaced by PTFE. The collection efficiency of the PTFE surface was approximately 100% compared to the standard Meteorological Office rain gauge. Air samples 2 and 5 were collected immediately after rain events 8 and 9.

Rainwater Extracts

A typical capillary GC chromatogram obtained for one of the rainwater extracts (from sample number 5) is shown in Figure 1a. This clearly shows the complexity of the extracts obtained which consist of mixtures of several hundred compounds. The GC-MS total ion current (TIC) chromatograms (Figure 1b) obtained for the same extracts were similar to the GC-FID chromatograms. Examination of the mass spectral data showed that many of the individual peaks in the chromatograms actually consisted of two or more components, thus underlining the complexities of the mixtures present.

More than two hundred organic compounds were identified in the rainwater extracts and the types of compounds that were consistently present (observed in two or more extracts) in all atmospheric samples are listed in Table 3. A wide range of compound classes are apparent, ranging in polarity from alkanes to fatty acids. Many of the compounds are biogenic in origin e.g. the fatty acids (C_{12} and C_{19}) which are components of microbial and plant lipids.[8,9] Other compounds may have mixed biogenic and anthropogenic sources, e.g. alkylphenols which have known industrial ambient emission sources[10] and have also been detected in precipitation collected at remote ocean sites[11] suggesting the presence of diffuse biogenic sources. Compounds of known anthropogenic origin, e.g. PAH and pentachlorophenol, were also common constituents of the rainwater extracts. Three other anthropogenic compounds found, which were observed in only one sample, are *tris*-chloroethylphosphate, lindane and 2,4-dinitrophenol. Furthermore, the presence of a "hump" in the chromatogram (Figures 1a and 1b) is thought to be associated with fuel combustion and automobile exhaust and largely consists of complex mixtures of alkyl-substituted aliphatic and aromatic hydrocarbons.[12] Unresolved complex mixtures were a common feature of all rainwater extracts, although the hump was less pronounced in extracts of summer rainfall. This observation would support the designation of the Medmenham site as "semi-rural", since although the site is situated in a rural setting, the atmospheric deposition collected was indicative of cloud formations having travelled over urban areas. Wind directions during all sampling periods were from the west or south west which would have taken cloud formations over the urban areas of Bristol, Swindon, Newbury and Reading.

Some of the largest peaks on the chromatograms were contributed by ketone, ester and hydrocarbon components, many of which are of biogenic origin. However, the polycyclic aromatic ketones which have been reported in diesel emission particulates,[13] and phthalate esters which are commonly used as plasticisers were common constituents of the rainwater extracts.

The majority of the compounds are probably present at the low $\mu g\,l^{-1}$ level or less in rainwater. It was not possible to accurately quantitate all of the compounds identified, however, it was possible to quantify some of the alkylbenzenes, alkylphenols and PAH present by using the deuterium labelled compounds spiked

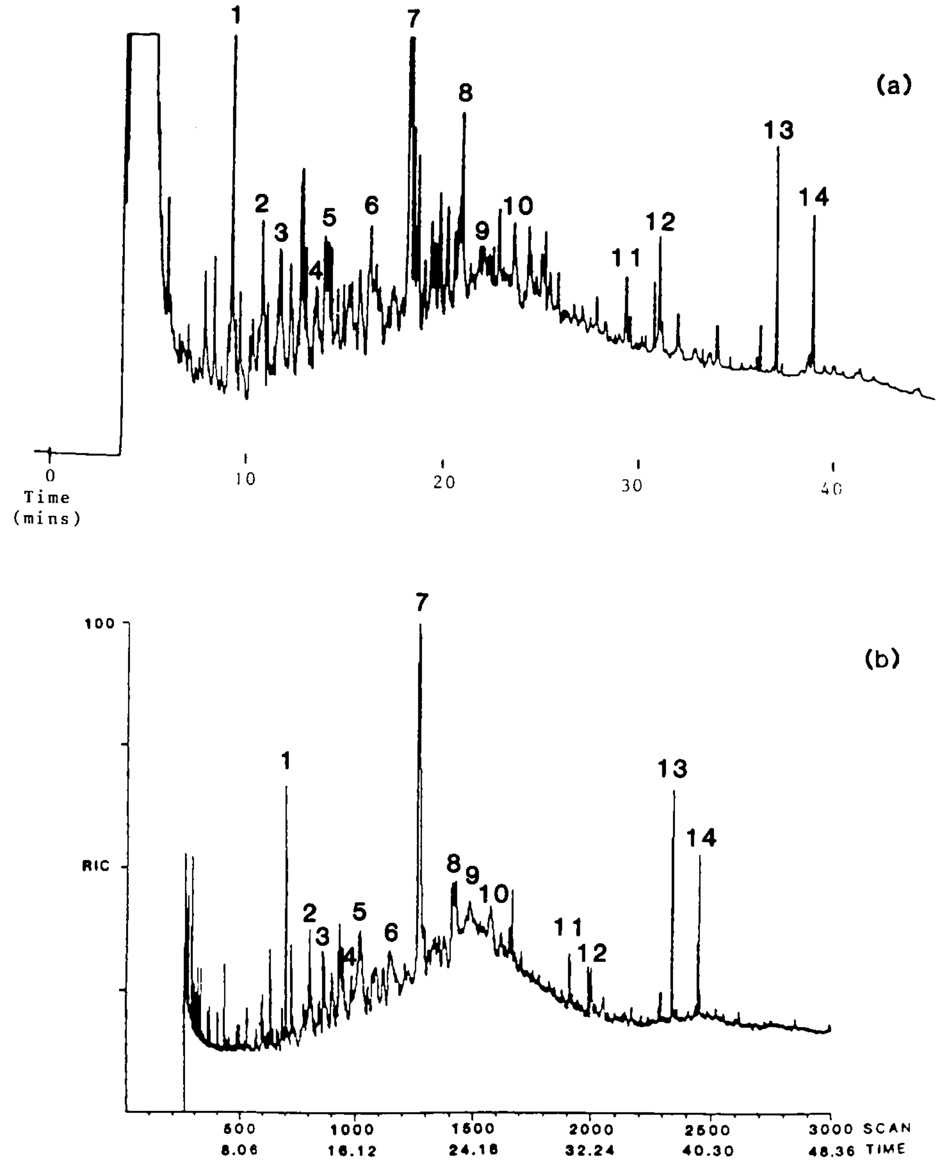

Figure 1 Capillary GC (a) and TIC chromatograms (b) of a rainwater extract (sample no 5).

Major compounds identified from Figure 1

Peak no.	*Scan*	*Compound*	*Major ions*
1	704	3,4-dimethyl-3-penten-2-one	39, 41, 43, 69, 112
2	808	Benzaldehyde	77, 106, 165
3	870	Phenol	94, 66, 39
4	987	Methylbenzaldehyde	65, 91, 119, 120
5	1020	Heptanoic acid	43, 60, 73
6	1150	Mixture of dimethylbenzaldehyde dimethylphenol, C_8 fatty acid and naphthalene	43, 73, 91, 128
7	1272	2,5-dihydro-3,4-dimethylfuran	41, 55, 69, 83, 98
8	1413	1-(methylphenyl) ethanone	43, 71, 119
	1425	2-methyl-3-hydroxy-2,4,4-trimethylpentyl propanoate	56, 71, 89, 152, 173
9	1485	N-propylbenzamide	99, 105, 133, 163
10	1575 (also at 1413, 1545, 1619 1658, 1661)	Phenylalkanone	131, 103
11	1908	Dibutylphthalate	149
12	1992	Dibutylphthalate	149
13	2339	Dioctyladipate	259
14	2449	Dioctylphthalate	149

into the rainwater samples before analysis as internal standards and assuming that compounds of similar chemical structure will be recovered with similar efficiency. Concentration levels for these compounds in the nine samples examined are given in Table 4. The 3- and 4-methylphenols and the 2,4- and 2,5-dimethylphenols were not resolved on the capillary column used for this study and the quoted concentrations represent the sum of each of these pairs of compounds.

Concentrations measured for the phenolic compounds are of the same order of magnitude as those reported previously in rainwater samples collected at the same time of the year in Los Angeles,[14,15] Southern California and Portland, USA[16] and an urban and a rural site in Switzerland.[17] Sample 6, which was collected in mid May, showed considerably lower concentrations of phenols than the other samples, probably because this sample was taken towards the end of a rain event which had started several hours earlier. Undoubtedly, the phenolic compounds would have been present at higher concentrations at the start of the rain event and were depleted by washout. Considering the low values of their Henry's law constants e.g. 1.1×10^{-7} atm.m^3/mol at 8 °C for phenol, gas scavenging is an efficient atmospheric removal process for these compounds.

In the other samples total concentrations of phenols measured ranged up to $>20\,\mu g\,l^{-1}$ in one case and were always $>10\,\mu g\,l^{-1}$. This represents a significant contribution to the total organics present and suggests that phenols may be the most abundant group of organic compounds in rainwater. The presence of small quantities of phenols and methylphenols in raw waters used for potable supplies is

Table 3 Organic compounds identified in atmospheric deposition samples

Compound class	*Type*	*Range*
Aromatic hydrocarbons	Alkylbenzenes	C_1–C_5
	PAH	2–5 rings
	Alkyl-PAH	2–4 rings
Phenols	Phenol	
	Alkylphenols	C_1–C_2
	Pentachlorophenol	
Hydrocarbons	Alkanes	C_6–$>C_{30}$
Aldehydes	Benzaldehyde	
	Alkylbenzaldehydes	C_1–C_2
	Alkanals	C_4–C_8
Ketones	Alkanones	C_4–C_8
	Alkylfuranones	C_1–C_2
	Methylbenzofuranones	
	Keto-PAH	2–4 rings
Esters	Dialkylphthalates	C_2–C_8
	Dioctyladipate	
Ethers	Methoxybenzene	
	Dimethoxybenzenes	
Acid	Fatty acids	C_2–C_{18}
Others	Tributylphosphate	
	Benzthiazole	
	Trifluralin[a]	
	Siloxanes[a]	

[a] Only detected in Hi-Vol air samples

of interest to the Water Industry, since chlorination applied during water treatment can lead to chlorinated phenols which have extraordinarily low taste and odour thresholds.[3] Previous studies[15,18] have also reported the presence of several chloro- and nitrophenols in rainwater, but at considerably lower concentrations than the alkylphenols. During the course of this work, 2,4-dinitrophenol and pentachlorophenol were observed although they were not specifically monitored.

Dimethylbenzene and PAH concentrations measured in this study were again remarkably similar to previously published figures[19] for dissolved (filtered rainwater) concentrations in rainwater collected in Portland, Oregon, USA. Levels ranged from low $\mathrm{ng\,l^{-1}}$ in sample 6 to a maximum $>1\,\mu\mathrm{g\,l^{-1}}$ for phenanthrene in samples 7 and 8. All of these compounds are anthropogenic and arise principally from fossil fuel combustion.[20]

High Volume Air Samples

Details of the nine high-volume (Hi Vol) air samples collected are given in Table 2. The sampling period was kept constant at 24 hours to give a total throughput of air of approximately $1000\,\mathrm{m^3}$. Typical GC-MS total ion current chromatograms are shown in Figures 2a and 2b for the filter and PUF extracts respectively,

Table 4 Concentration of selected organic compounds in rainwater samples

Compound	*Concentration* (μG 1 − 1)									*Mean Conc* (μg *l* − *l*)
	1	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*9*	
C_2-benzene(1,4-dimethyl)	0.02	0.24	0.008	0.03	0.02	0.003	0.74	1.28	0.11	0.27
C_2-benzene(1,3-dimethyl)	0.07	0.090	0.044	0.15	0.08	0.025	0.76	0.84	0.10	0.24
C_2-benzene(1,2-dimethyl)	0.06	0.020	0.054	0.067	0.035	0.025	0.16	0.30	0.10	0.09
Phenol	2.0	8.6	6.02	1.0	1.5	0.26	1.15	1.14	0.36	2.45
2-methyl phenol	5.0	3.35	1.8	2.9	4.57	0.053	0.71	0.32	nda	2.34
3- + 4-methyl phenol	nda	7.4	4.0	4.08	7.65	0.11	2.20	1.74	nda	3.88
C_2-phenol (ethyl)	nda	0.025	0.1	0.41	nda	nda	nda	0.30	0.24	0.22
C_2-phenol(2,6-dimethyl)	nda	0.34	0.30	0.4	nda	0.004	nda	nda	0.28	0.15
C_2-phenol(2,4- + 2,5-dimethyl)	nda	2.8	nda	2.25	4.85	0.023	0.40	nda	2.44	2.13
C_2-phenol(2,3-dimethyl)	nda	3.8	1.35	1.68	5.15	0.027	1.54	1.36	2.00	2.11
C_2-phenol(3,5-dimethyl)	nda	1.1	0.4	0.17	1.51	nda	nda	nda	0.26	0.69
C_2-phenol(3,4-dimethyl)	nda	0.94	nda	0.57	nda	nda	nda	nda	2.40	1.30
Naphthalene	0.1	0.075	0.073	0.12	0.075	0.025	1.22	1.60	0.80	0.45
Fluorene	0.03	0.025	nda	0.025	0.022	0.004	0.05	0.024	0.24	0.05
Fluoren-9-one	0.01	0.1	0.042	0.08	0.067	0.009	0.04	0.015	0.32	0.08
Phenanthrene	0.2	0.16	0.041	0.12	0.075	0.035	1.46	1.32	0.54	0.44
Fluoranthene	0.2	0.15	0.035	0.071	0.075	0.047	0.014	nda	nda	0.10
Pyrene	0.125	0.13	0.021	0.061	0.055	0.040	nda	nda	nda	0.07

nda = not determined due to interferences

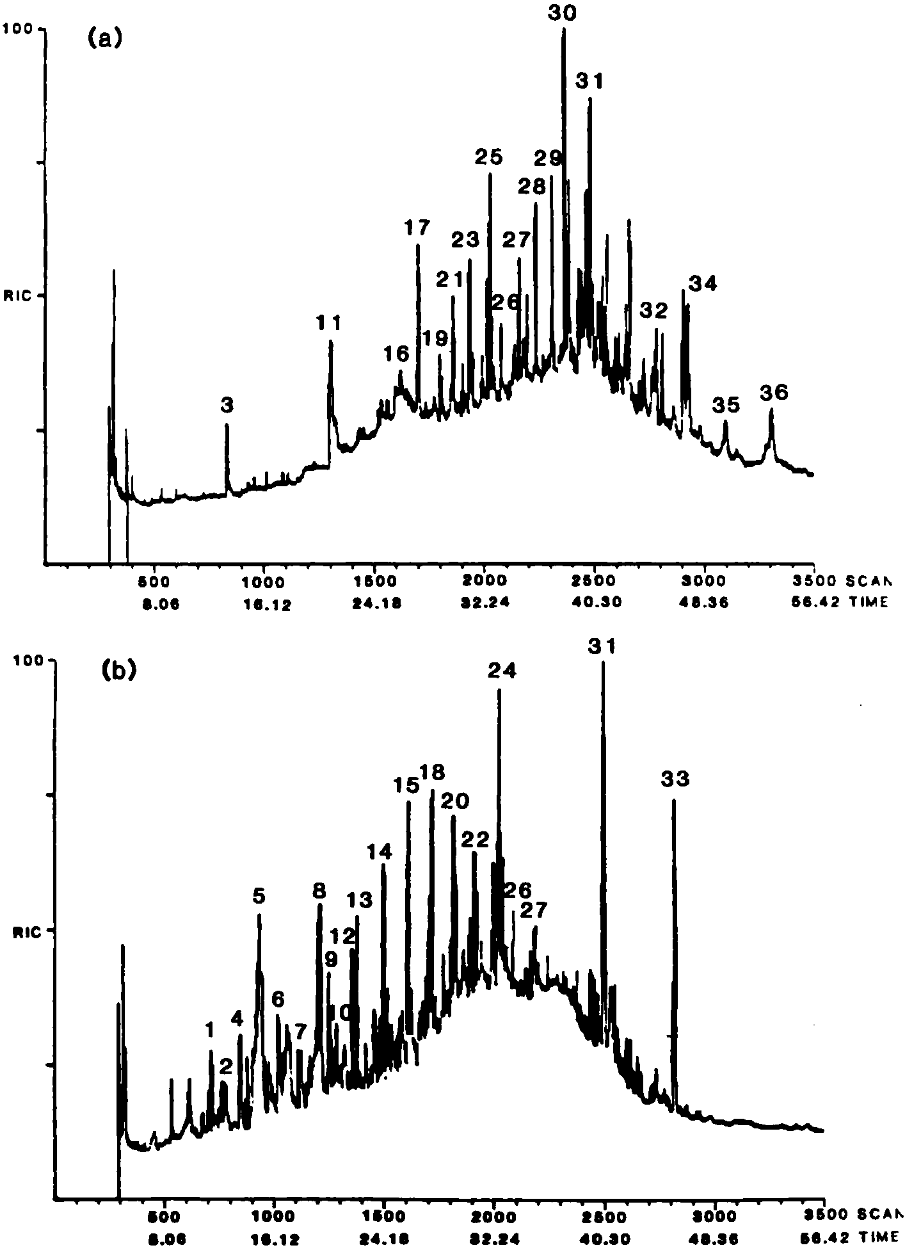

Figure 2 TIC chromatograms of a filter extract (a) and a PUF extract (b) (Air sample no 4).

Major compounds identified from Figure 2

Peak no.	*Scan*	*Compound*	*Major ions*
1	723 (also at 708, 763)	C_2-benzenes	91, 106
2	783	2-butoxyethanol	84, 57, 28
3	839	Trichloropropane	75
4	851	Benzaldehyde	77, 106, 165
5	936 (also at 870, 911, 980)	C_3-benzenes	28, 94, 105, 120
6	1068 (also at 1051, 1077)	C_4-benzenes	28, 91, 105, 120
7	1125	2-nitrophenol	39, 65, 139
8	1212	Naphthalene	128
9	1254	n-C_{12} alkane	28, 43, 57, 135
10	1287	4-methyl-2-nitrophenol	77, 153
11	1305	2,5-dihydro-3,4-dimethylfuran	41, 55, 69, 83, 98
12	1363	1-methylnaphthalene	115, 141, 142
13	1381	n-C_{13} alkane + methylnaphthalene	43, 57, 71, 142
14	1500	n-C_{14} alkane + methylnaphthalene	43, 57, 71, 142
15	1613	n-C_{15} alkane + an alkyl phenol	43, 57, 71, 205
16	1627	Siloxane	73, 147, 221
17	1705	Si_7 siloxane	73, 147, 221
18	1718	n-C_{16}-alkane	43, 57, 71
19	1805	Siloxane	73, 147, 221
20	1818	n-C_{17} alkane	43, 57, 71
21	1866	Siloxane	73, 147, 221
22	1911	n-C_{18} alkane	43, 57, 71
23	1940	Diisobutylphthalate	149
24	2026	Dibutyl phthalate	149
25	2036	n-C_{16} fatty acid	43, 60, 73
26	2080	n-C_{20} alkane	282
27	2160	n-C_{21} alkane	296
28	2240	n-C_{22} alkane	310
29	2320	n-C_{23} alkane	324
30	2373	dioctyladipate	57, 129, 259
31	2490	dioctylphthalate	149
32	2798	n-C_{29} alkane	43, 57, 71
33	2816	Squalane	81, 137
34	2958	n-C_{31} alkane	43, 57, 71
35	3118	n-C_{33} alkane	43, 57, 71
36	3278	n-C_{35} alkane	43, 57, 71

which clearly show that these extracts, like the rainwater extracts, consist of mixtures of several hundred compounds and contain humps due to unresolved complex mixtures of hydrocarbons. The major compound classes detected in the air extracts are the same as those detected in the rainwater extracts (Table 3). Comparison of the TIC chromatograms shows that as expected the PUF extract (Figure 2b) contains greater proportions of more volatile compounds than the filter extract (Figure 2a). This observation is in agreement with previous studies using high-volume collection of airborne organics which have shown that filter-retained organics contain the high molecular weight and low vapour pressure species.[21]

Examination of the mass spectral data showed that the major peaks of the chromatograms were due to a series of n-alkanes (range C_7 to C_{35} for filter and range C_6 to C_{30} for PUF) and a series of fatty acids (range C_{12} to C_{18} for filter and range C_7 to C_{16} for PUF). The range of concentration of these compounds is between 1 and 15 ngm^{-3} estimated by direct comparison of detector response with known concentration of authentic standards. These compounds probably originate from plant materials.[9] Other prominent components in air samples were a series of siloxanes, the most abundant of which in all samples was hexadecylmethyl heptasiloxane (approximately 10 to 20 ngm^{-3}). The presence of a uniform distribution of siloxanes at such relatively high concentrations would suggest that they originated from a material used in the construction of the Hi-Vol sampler e.g. sealant, although their detection in aerosols has been previously reported[22] in concentrations ranging from 0.1 to 20 ngm^{-3}. Sources of siloxane contamination will be further investigated.

Air samples collected during the spring and summer (samples 7 to 9) contained only a few PAH and alkyl-PAH in PUF extracts and none of these compounds were present in the filter extracts (with the exception of benzopyrene at $<500\,pgm^{-3}$ in sample 8F). Several studies[23,24] have shown that PAH having two to four rings are present in air primarily in the vapour phase and are not readily retained by filters because of their volatility. Conversely, sample 4P, collected in mid-winter, contained a series of alkylnaphthalenes and alkylbiphenyls in an estimated concentration range of 0.8 to 2 ngm^{-3}. The PAH's fluorene, fluoranthene, phenanthrene and pyrene were also detected at an approximate concentration of 5 ngm^{-3} per component, and fluoranthene was detected in the corresponding filter extract (4F) (approximate concentration of 5 ngm^{-3}). These results suggest that seasonal variations occur in the composition of organics detected in air samples which are likely to be the result of changes in fossil fuel combustion and ambient air temperatures. Further seasonal variations in composition were also observed in two samples, 1P and 8P collected in autumn and spring respectively, which contained phenol (approximately 10 ngm^{-3}) and a series of alkylphenols (estimated concentration range 200–400 pgm^{-3}). These compounds, however, were absent from the corresponding filter extracts, and absent also from samples 2F, 2P, 4F and 4P which were collected after rain events 8 and 9 (Table 1) indicating removal of these compounds from the atmosphere by partitioning from vapour to the aqueous phase.

CONCLUSIONS

Sampling and analysis methodology for organic compounds in atmospheric deposition has been established at a semi-rural site near the WRc Medmenham Laboratory situated in the Thames Valley. Rainwater samples were collected on an event bases, using a manually operated wet-only sampler, and aerosol and vapour samples were collected using a high-volume ($750 \mathrm{l\,min}^{-1}$) air sampler containing a glass fibre filter and a polyurethane foam plug adsorption trap.

More than two hundred compounds were detected in the sample extracts consisting of a wide range of compound classes, ranging in polarity from alkanes to fatty acids. Many of the compounds detected were of biogenic origin, but compounds of known anthropogenic origin, such as phenolic compounds and PAH were major components of the organic matter in rainwater and air samples. A series of siloxanes, at respectively high concentrations were present in all the high-volume air samplers, but may originate from materials used in the construction of the sampler.

Seasonal variations in the PAH and alkyl-PAH content of the air samples were observed. The type and concentration or organic compounds detected in atmospheric deposition during this study show similarities to those previously reported for urban and rural areas in the USA.

Acknowledgements

Authors with to thank Mr. P. Stockton for the collection of samples and technical assistance in the laboratory, Mr. T. Gibson for obtaining the GC-MS data, Dr. A. J. Dobbs for helpful and stimulating discussions.

References

1. World Health Organization, Health hazards of the human environment. (World Health Organization, Geneva, 1972). Chap. 2, Water, pp. 47–65.
2. M. Fielding and H. Horth, The formation and removal of chemical mutagens during drinking water treatment. Proc. of 5th European Symp; Organic micropollutants in the aquatic environment. Rome, Oct. 20–22 (1987) pp. 284–298.
3. F. Dietz and J. Traud, GWF: Gas-Wasserfach: *Wasser/Abwasser* **119**(6), 318 (1978).
4. W. J. Maier and W. R. Swain, *Water Res.* **12,** 403 (1978).
5. EC Directive Relating to the Quality of Water Intended for Human Consumption, EEC/80/778.
6. M. A. Mazurek, B. R. T. Simoneit, L. J. Standley, D. Friedman and C. Beeman, *Water, Air and Soil Pollution* **36,** 171 (1987).
7. M. P. Ligocki and J. F. Pankow, *Anal. Chem.* **57,** 1138 (1985).
8. B. R. T. Simoneit and M. A. Mazurek, *Atmos. Environ.* **16,** 2139 (1982).
9. G. Eglinton and R. J. Hamilton, *Science* **156,** 1322 (1967).
10. T. E. Graedel, Chemical compounds in the atmosphere (Academic Press, New York, 1978) pp. 256–265.
11. C. Leuenberger, J. Czuczwa, J. Tremp and W. Giger, Atmospheric occurrence of phytotoxic pollutants, *Chemosphere* **17**(3), 511 (1988).
12. K. W. Boyer and H. A. Laitinen, *Environ. Sci. Technol.* **9,** 457 (1975).
13. D. R. Choudhury, *Environ. Sci. Technol.* **16**(2), 102 (1982).

14. K. Kawamura and I. R. Kaplan, *Environ. Sci. Technol.* **17**, 497 (1983).
15. C. Leuenberger, M. P. Ligocki and J. F. Pankow, *Environ. Sci. Technol.* **19**, 1053 (1985).
16. K. Kawamura and I. R. Kaplan, *Atmos. Environ.* **20**(1), 115 (1986).
17. J. Czuczwa, C. Leuenberger, J. Tremp, W. Giger and M. Ahel, *J. of Chrom.* **403**, 233 (1987).
18. M. Mazurek and B. R. T. Simoneit, Characterization of biogenic and petroleum-derived organic matter in aerosols over remote, rural and urban areas. In: *Identification and Analysis of Organic Pollutants in Air* (L. H. Keith, ed.) (Ann Arbor Science/Butterworth, Boston, 1984) p. 353.
19. M. P. Ligocki, C. Leuenberger and J. F. Pankow, *Atmos. Environ.* **19**(10), 1609 (1985).
20. P. E. Strup, R. D. Giammar, T. B. Stanford and P. W. Jones, Improved measurement techniques for polycyclic aromatic hydrocarbons from combustion effluents. In: *Carcinogenesis Vol. 1: Polynuclear Aromatic Hydrocarbon Chemistry, Metabolism and Carcinogenesis* (R. E. Freudenthal and P. W. Jones, eds.) (Raven Press, New York, 1976) pp. 241–251.
21. T. J. Murphy and C. P. Rzeszutko, *J. Great Lakes Res.* **3**, 305 (1977).
22. C. J. Weschler, *Atmos. Environ.* **15**(8), 1365 (1981).
23. H. Yamasaki, K. Kuwata and H. Miyamoto, *Environ. Sci. Technol.* **16**(4), 189 (1982).
24. F. You and T. F. Bidleman, *Environ. Sci. Technol.* **18**(5), 330 (1984).