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Analysis of trace polycyclic aromatic hydrocarbons and organochlorine compounds in atmospheric residues by solid-phase disk extraction

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Abstract

A method based on the use of solid-phase extraction disks for the analysis of polycyclic aromatic hydrocarbons and organochlorine compounds (pg l^{-1}) in deposition samples collected in remote sites is described. Diverse aspects determining extraction efficiencies such as packing composition (C_8 and C_{18}), extraction number and elution solvents have been evaluated. The lowest relative standard deviations (3–20%) and best extraction efficiencies (80–100%) have been obtained using a solvent program of methanol, cyclohexane and dichloromethane (5 ml each) and octadecylsilane disks. Detection and quantitation limits were in the order of 0.14–3.5 pg l^{-1} . These limits were achieved by gas chromatography coupled to mass spectrometry and detection in the selected ion monitoring mode. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

One of the aspects less understood in the long range transport of organic pollutants, namely organochlorine compounds (OCs) and polycyclic aromatic hydrocarbons (PAHs), is the role of wet precipitation in the incorporation of these compounds in remote ecosystems. Several aspects still need to be elucidated such as the scavenging efficiency of the diverse types of precipitation, e.g., rain, snow, fog, for the pollutants adsorbed to particles or in the gas phase, the relationship with air mass origin and temporal/seasonal dependence.

Progress in the elucidation of these questions can be obtained from the field analysis of wet precipitation samples in remote sites. However, this task

involves specific difficulties such as transport of equipment to the locations of study and limited sample sizes. Thus, large volume filtration/extraction methods [1–3] cannot be used for these type of studies and methods for the analysis of trace organic compounds in small water volumes have to be developed.

Solid-phase extraction (SPE) disks have received increasing attention in the recent years. Their use does not require sophisticated instrumentation and the system is dimensioned for water volumes in the order of 0.1–10 l. These two aspects are interesting for their application to wet precipitation studies in remote sites.

Methods for the analysis of these pollutants in drinking water have been reported in the recent years [4,5]. Furthermore, several applications encompassing the analysis of pesticides and fungicides in

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waters of diverse origin have also been described [6–8]. In the present study, this previous work is extended to applications for the analysis of trace amounts of OCs and PAHs in wet precipitation samples collected in remote sites.

2. Experimental

2.1. Chemicals

All solvents (residue analysis grade, Merck, Darmstadt, Germany) were checked by gas chromatography (GC) before used. Anhydrous sodium sulfate (analytical-reagent grade) (Merck) was cleaned by Soxhlet extraction with dichloromethane–cyclohexane (1:1, 24 h) and activated by overnight heating at 400°C before use. The PAH, *p,p'*-DDE and *p,p'*-DDT standards were purchased from Accustandard (New Haven, CT, USA) and Dr. Ehrenstorfer (Augsburg, Germany), respectively. Polychlorobiphenyls and hexachlorobenzene were from Promochem (Wesel, Germany).

Glass fiber filters (47 mm diameter, 1 µm, GF/B, Whatman, Maidstone, UK) were kiln-fired at 400°C for 12 h, weighed and wrapped into solvent rinsed aluminum foil until use.

Empore C₈ and C₁₈ extraction disks (47 mm diameter, 0.5 mm thickness) were obtained from Baker (Deventer, Netherlands).

2.2. Samples

Spiked samples were prepared by adding the corresponding volume of standard solutions in acetone to Milli-Q water (Millipore, Bedford, MA, USA). Then, they were allowed to stand at room temperature for 24 h prior to extraction.

Snow and atmospheric deposition samples were taken in a stainless steel container at two remote mountain sites in Europe. They were held at room temperature until completely melt. Prior to Empore disk extraction, samples were filtered through glass fiber filters for the removal of particulate matter.

2.3. Solid-phase extraction

Water extraction was carried out in a Millipore

filtration system. The solid-phase disks were cleaned by elution with 10 ml of dichloromethane–cyclohexane (1:1) and conditioned with 10 ml of methanol for 3 min. After this step, the vacuum was connected and filtered water samples were added paying stringent precautions to avoid drying-out during the process (extraction speed: 30 ml min⁻¹). After complete extraction the vacuum was held for a few minutes in order to remove all water.

Prior to solid-phase disk extraction, the disks were soaked with 5 ml of methanol for 3 min. Then, vacuum was connected and methanol was collected. After this step, vacuum was turned off and 5 ml of cyclohexane were added to soak the disks for 3 min. Vacuum was then connected and the extract was collected separately from methanol. Five ml of dichloromethane were added following solvent removal and were also collected under vacuum together with the cyclohexane solution.

The first methanol solution was liquid–liquid extracted with hexane (3×2 ml) and the hexane layer was combined with the cyclohexane–dichloromethane mixture. All collected extracts were dried over anhydrous sodium sulfate, concentrated to 1 ml by vacuum rotatory evaporation and brought to dryness by a gentle stream of nitrogen.

2.4. Gas chromatographic analysis

Quantitative analyses for calculation of OC recoveries were carried out by GC coupled to electron-capture detection (ECD). Samples were injected in a Hewlett-Packard Model HP-5890 chromatograph (Palo Alto, CA, USA) equipped with a 30 m×0.25 mm I.D. fused-silica capillary column (0.25 µm film thickness, DB-5, J&W Scientific, Folsom, CA, USA). The oven temperature program started at 80°C (holding time 1 min) and was heated to 140°C at 10°C min⁻¹ and to 300°C at 4°C min⁻¹ (final holding time 10 min). Injector and detector temperatures were 280 and 310°C, respectively. Helium (50 cm s⁻¹) and nitrogen (60 ml min⁻¹) were used as carrier and make up gases, respectively. Injection was performed with a Hewlett-Packard Model 7673A automatic injector operating in splitless mode (split valve closed for 35 s).

PAH recoveries were analyzed in a Carlo-Erba 5300 MEGA series gas chromatograph equipped

with a flame ionization detection (FID) system. The oven temperature was programmed from 80°C to 300°C at 6°C min⁻¹, keeping the final temperature for 10 min. Injector and detector temperatures were 300 and 330°C, respectively. Hydrogen was used as carrier gas (50 cm s⁻¹). A DB-5 fused-silica capillary column (see above) was used for the analyses.

2.5. Gas chromatography–mass spectrometry (GC–MS) analysis

Deposition and snow samples were also analyzed by GC (Carlo Erba GC8000 series) coupled to a mass spectrometer (Fisons MD800) operating in the selected ion monitoring (SIM) and electron impact (70 eV) modes. The initial oven temperature was 90°C (holding time 1 min), which was increased to 120°C at 15°C min⁻¹ and to 310°C at 4°C min⁻¹ with a final holding time of 10 min. Injector, ion source and transfer line temperatures were 280, 200 and 280°C, respectively. Helium was used as carrier gas (50 cm s⁻¹). The dwell time was 30 ms channel⁻¹. The other chromatographic conditions were similar to those described above. The SIM program was composed with the molecular ions of PAHs, hexachlorobenzene and polychlorinated biphenyls (PCBs), choosing the maximum isotopic fragment in this latter case. In addition to these mass fragments, hexachlorocyclohexanes (HCHs) and *p,p'*-DDE were quantitated with *m/z* 181 and 246, respectively.

3. Results and discussion

3.1. Solid-phase disks

Consistently with the hydrophobic character of OCs and PAHs and previous studies on drinking water [4,5], octyl- and octadecylsilane packings (C₈ and C₁₈, respectively) were considered for water extraction. Testing of these two types of disks for recoveries did not show major differences (Table 1). However, C₁₈ provided better blanks and was chosen for this reason.

GC–MS profiles corresponding to the OC and PAH mixtures of one atmospheric deposition sample collected in a remote area (Redo Lake, Eastern

Table 1

Extraction efficiencies (%) with two different solid-phase disks

Compound	C ₁₈	C ₈
Hexachlorobenzene	103±10	113±5
<i>p,p'</i> -DDE	118±8	125±11
PCB congener No. 30	82±15	92±11
PCB congener No. 28	101±6	112±6
PCB congener No. 52	113±4	113±9
PCB congener No. 101	94±5	102±10
PCB congener No. 118	105±9	107±18
PCB congener No. 153	105±8	107±14
PCB congener No. 138	106±9	110±12
PCB congener No. 180	114±15	108±9
Phenanthrene	74±16	69±6
Pyrene	89±9	91±11
Chrysene	87±9	80±11
Benzo[<i>b</i>]fluoranthene	81±8	81±6
Benzo[<i>e</i>]pyrene	83±9	85±6
Indene[1,2,3- <i>cd</i>]pyrene	76±6	77±2

Standards: 10 ng l⁻¹ organochlorine compounds, 1.5 µg l⁻¹ polycyclic aromatic hydrocarbons. Solvent elution program: 5 ml ethyl acetate and 5 ml dichloromethane (*n*=3 in all tests).

Pyrenees, 2240 m above sea level) are shown in Fig. 1. The composition of both types of compounds was recorded by SIM and the profiles shown in this figure are composited sums of all *m/z* traces included in the ion program. As shown in these chromatograms few interfering peaks are present in the PAH record. More interferences are observed in the OC profile but these do not overlap with any environmentally relevant compound. The limited number of interfering compounds obtained with these disks strongly contrast with the poor blanks reported for C₁₈-bonded porous silica cartridges [9].

As shown in Table 2, up to 8 l of water can be extracted with the selected C₁₈ packings without significant recovery losses.

3.2. Elution solvents

Two solvent programs were considered for extraction of the solid-phase disks after OC and PAH retention, methanol–ethyl acetate–dichloromethane (5 ml each) and methanol–cyclohexane–dichloromethane (5 ml each). Both elution programs provided good recoveries (Table 2) for individual OC and PAH concentrations higher than 10 ng l⁻¹ and 1.5

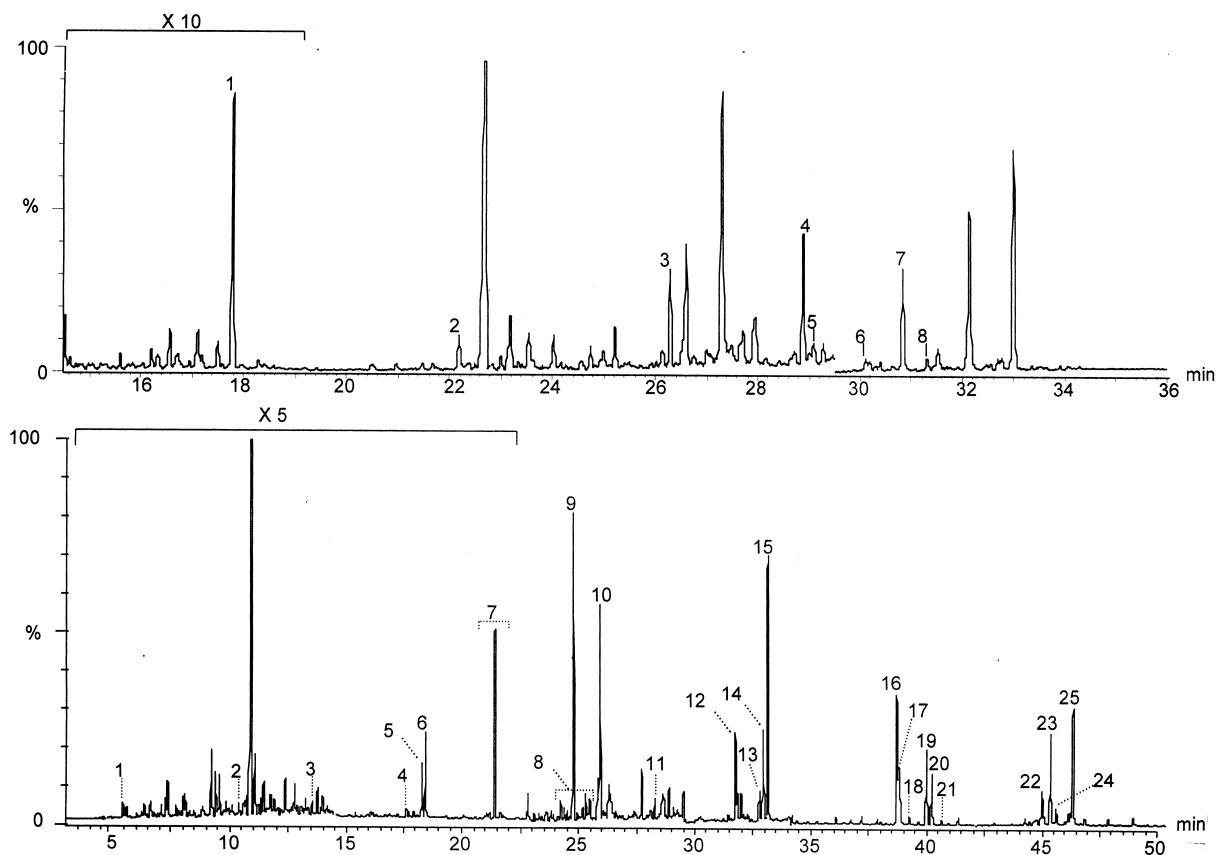


Fig. 1. GC-MS SIM profiles showing the composition of organochlorine compounds (OCs) and polycyclic aromatic hydrocarbons (PAHs) in one atmospheric deposition sample collected near Lake Redo (eastern Pyrenees, 2240 m above sea level). Top: OCs: 1= γ -hexachlorocyclohexane; 2=PCB congener No. 52; 3=endosulphan a+PCB congener No. 101; 4=endosulphan b; 5=PCB congener No. 118; 6=PCB congener No. 153; 7=endosulphan SO₄; 8=PCB congener No. 138. Bottom: PAHs: 1=naphthalene; 2=acenaphthene; 3=fluorene; 4=dibenzothiophene; 5=phenanthrene; 6=[²H₁₀]anthracene (internal standard); 7=methylphenanthrenes; 8=dimethylphenanthrenes; 9=fluoranthene; 10=pyrene+[²H₁₀]pyrene; 11=retene; 12=benzo[ghi]fluoranthene; 13=cyclopenta[cd]pyrene; 14=benz[a]anthracene; 15=chrysene+triphenylene; 16=benzo[b+j]fluoranthene; 17=benzo[k]fluoranthene; 18=benzo[a]fluoranthene; 19=benzo[e]pyrene; 20=benzo[a]pyrene; 21=perylene; 22=indene[7,1,2,3-cdef]chrysene; 23=indene[1,2,3-cd]pyrene; 24=dibenz[ah]anthracene; 25=benzo[ghi]perylene+[²H₁₂]benzo[ghi]perylene.

$\mu\text{g l}^{-1}$, respectively. The first step with methanol soaking and extraction allowed the efficient elimination of all water interferences. Other alternative methods such as on-line drying with sodium sulphate were not able to cope with the problem of extract humidity and gave rise to major recovery losses. Efforts for water elimination such as extended vacuum disk extraction times or nitrogen evaporation gave rise to major losses of volatile compounds.

The second solvent program provided significantly better recoveries at low analyte concentrations. The low recoveries of the lower-molecular-mass com-

pounds reported in Table 2 correspond to volatilization losses. The high extraction efficiency of cyclohexane followed by dichloromethane has already been observed in the analysis of PAHs from river waters [10]. Additional elution with 5 ml of cyclohexane and dichloromethane after the first extraction only provided 1–3% of additional OCs and PAHs in the second extract, showing that the first step (5 ml each solvent) was sufficient to recover the spiked compounds.

The relative standard deviations (R.S.D.s) of the replicate tests ($n=3$) in Table 2 lie between 3–20%.

Table 2
Extraction efficiencies (%) of different sample volumes and concentrated and diluted standards ($n=3$ in all tests)

Compound	Concentrated			Diluted
	2.5 l	5 l	8 l	2.5 l
Hexachlorobenzene	103±10	91±12	73±16	25±9.2
<i>p,p'</i> -DDE	118±8	129±17	106±14	25±8.6
PCB congener No. 30	82±15	64±9	72±19	44±7.4
PCB congener No. 28	101±6	100±11	87±14	45±6.0
PCB congener No. 52	113±4	97±9	— ^a	53±7.1
PCB congener No. 101	94±5	90±9	102±11	85±15
PCB congener No. 118	105±9	114±12	108±8	73±11
PCB congener No. 153	105±8	105±11	98±16	63±9.5
PCB congener No. 138	106±9	107±11	107±9	74±11
PCB congener No. 180	114±15	109±13	124±17	78±14
Phenanthrene	74±16	51±7	83±11	39±12
Pyrene	89±9	73±11	103±5	71±9.6
Chrysene	87±9	70±9	91±3	88±9.5
Benzo[<i>b</i>]fluoranthene	81±8	72±11	—	—
Benzo[<i>e</i>]pyrene	83±9	74±11	—	—
Indene[1,2,3- <i>cd</i>]pyrene	76±6	61±9	89±3	76±9

Concentrated standards: 10 ng l⁻¹ organochlorine compounds, 1.5 µg l⁻¹ polycyclic aromatic hydrocarbons. Diluted standards: 5 ng l⁻¹ organochlorine compounds, 200 ng l⁻¹ polycyclic aromatic hydrocarbons.

^a Not determined.

3.3. Detection and quantitation limits

The detection and quantitation limits of the method reported in this study are shown in Table 3. The limits were calculated from real samples by integration of noise peaks situated near the resolved compounds in the eluting chromatograms. The reported detection and quantitation limits correspond to signal-to-noise ratios of three and five, respectively. These values refer to the analysis of water volumes higher than 250 ml. Smaller volumes are reflected in higher limits since the total analyte amount is lower.

These limits correspond to the analysis of both types of compounds by GC–MS in the SIM mode. In fact, the differences between compounds reported in Table 3 are essentially related to the instrumental sensitivity [11] and not to compound-specific differences in extraction efficiency of the solid-phase disks.

3.4. Sample analysis

An example of the results obtained in the application of the method to the analysis of bulk deposition

and snow collected in a remote place is shown in Table 4 and Fig. 1. Both samples were collected near Redo Lake (Pyrenees) at 2240 m above sea level in a site free from local anthropogenic activity.

Comparison of Tables 3 and 4 shows that the detection and quantitation limits of the method are sufficient for the analysis of trace OCs and PAHs in these type of samples.

The high abundance of α - and γ -hexachlorocyclohexanes is consistent with previous observations showing the high concentration of these compounds in fish collected from the same lake [12].

A strong contrast in PAH composition is observed between the atmospheric deposition and snow samples. Whereas the PAH distributions in the deposition samples parallel the composition of the lake sediments [13] and correspond to pyrolytic sources [14], the snow exhibits a mixture of predominant petrogenic origin.

4. Conclusions

C₁₈ solid-phase disks are useful for the measure-

Table 3
Method detection and quantitation limits calculated from real samples (in pg l^{-1})

Compound	Limit of detection	Limit of quantitation
Hexachlorobenzene	0.70	1.2
α -Hexachlorocyclohexane	0.70	1.2
β -Hexachlorocyclohexane	2.1	3.5
γ -Hexachlorocyclohexane	1.3	2.2
PCB congener No. 28	1.4	2.4
PCB congener No. 52	1.0	1.7
PCB congener No. 101	0.29	0.48
<i>p,p'</i> -DDE	0.62	1.1
PCB congener No. 118	0.24	0.40
PCB congener No. 153	0.1	0.17
PCB congener No. 138	0.08	0.14
PCB congener No. 180	0.08	0.14
Naphthalene	0.67	1.1
Acenaphthylene	0.33	0.55
Acenaphthene	0.44	0.73
Fluorene	0.32	0.53
Dibenzothiophene	0.17	0.28
Phenanthrene	0.80	1.2
Anthracene	0.75	1.3
Methyldibenzothiophene	0.48	0.80
Methylphenanthrene	0.22	0.36
Dimethylphenanthrene	0.69	1.2
Fluoranthene	0.52	0.86
Acephenanthrylene	0.14	0.23
Pyrene	0.50	0.83
Retene	0.90	1.5
Benzo[<i>ghi</i>]fluoranthene	0.25	0.41
Cyclopenta[<i>cd</i>]pyrene	0.25	0.41
Benzo[<i>a</i>]anthracene	0.29	0.49
Chrysene + triphenylene	0.26	0.43
Benzo[<i>b+j</i>]fluoranthene	0.31	0.51
Benzo[<i>a</i>]fluoranthene	0.21	0.35
Benzo[<i>k</i>]fluoranthene	0.21	0.35
Benzo[<i>a</i>]pyrene	0.30	0.45
Benzo[<i>e</i>]pyrene	0.30	0.45
Indene[7,1,2,3- <i>cdef</i>]chrysene	0.14	0.23
Indene[1,2,3- <i>cd</i>]pyrene	0.14	0.23
Benzo[<i>ghi</i>]perylene	0.12	0.20
Dibenz[<i>ah</i>]anthracene	0.16	0.26
Coronene	0.15	0.25
Dibenzopyrene	0.15	0.25

ment of OCs and PAHs at pg l^{-1} levels in atmospheric precipitation samples with R.S.D.s of 3–20% and extraction efficiencies of 80–100%. Quantitation and detection limits of 0.14–3.5 pg l^{-1} can be achieved from the analysis of 0.25–10 l of water, e.g., bulk precipitation or snow. The use of C_{18} disks allows the determination of these organic pollutants in remote areas affording collection and extraction of

large numbers of samples with limited instrumentation.

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Table 4

Concentrations (in pg l^{-1}) of organochlorine compounds and polycyclic aromatic hydrocarbons in atmospheric deposition and snow samples collected in Redo Lake (Pyrenees) measured by solid-phase extraction

Compound	Atmospheric deposition	Snow
Hexachlorobenzene	— ^a	—
α -Hexachlorocyclohexane	1000	510
β -Hexachlorocyclohexane	48	—
γ -Hexachlorocyclohexane	6300	440
PCB congener No. 28	—	—
PCB congener No. 52	77	—
PCB congener No. 101	51	130
<i>p,p'</i> -DDE	98	—
PCB congener No. 118	21	400
PCB congener No. 153	20	360
PCB congener No. 138	30	350
PCB congener No. 180	—	—
Fluorene	63	39
Dibenzothiophene	28	22
Phenanthrene	500	260
Anthracene	20	3.6
Methyldibenzothiophene	82	62
Methylphenanthrene	230	110
Dimethylphenanthrene	127	800
Fluoranthene	390	120
Acephenanthrylene	20	—
Pyrene	210	130
Retene	49	22
Benzo[ghi]fluoranthene	95	—
Cyclopenta[cd]pyrene	31	—
Benz[a]anthracene	68	13
Chrysene+ triphenylene	270	6.6
Benzo[b+j]fluoranthene	520	7.0
Benzo[a]fluoranthene	23	—
Benzo[k]fluoranthene	430	—
Benzo[a]pyrene	210	14
Benzo[e]pyrene	400	—
Indene[7,1,2,3-cdef]chrysene	100	17
Indene[1,2,3-cd]pyrene	300	60
Benzo[ghi]perylene	270	36
Dibenz[ah]anthracene	62	—
Coronene	110	—
Dibenzopyrene	400	—

^a Below limit of quantitation.

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