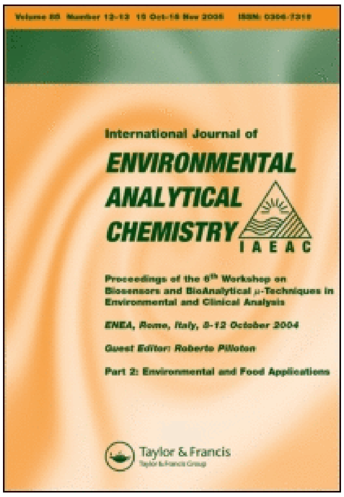

International Journal of Environmental Analytical Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

Determination of Some Organochlorine Compounds in the Atmosphere

C. Nerin[a]; T. Polo[a]; C. Domeño[a]; I. Echarri[a]
[a] Departamento de Quimica Analitica, Centro Politécnico Superior, Universidad de Zaragoza, Zaragoza, Spain

To cite this Article Nerin, C. , Polo, T. , Domeño, C. and Echarri, I.(1996) 'Determination of Some Organochlorine Compounds in the Atmosphere', International Journal of Environmental Analytical Chemistry, 65: 1, 83 — 94

To link to this Article: DOI: 10.1080/03067319608045545

URL: http://dx.doi.org/10.1080/03067319608045545

Intern. J. Environ. Anal. Chem., Vol. 65, pp. 83–94
Reprints available directly from the publisher
Photocopying permitted by license only

DETERMINATION OF SOME ORGANOCHLORINE COMPOUNDS IN THE ATMOSPHERE

C. NERÍN, T. POLO, C. DOMEÑO and I. ECHARRI

Departamento de Química Analítica, Centro Politécnico Superior, Universidad de Zaragoza, c/Maria de Luna 3, 50015 Zaragoza, Spain

(Received, 14 October 1995; in final form, 23 July 1996)

Organochlorine compounds were measured in the air of two different sites. In the air of a Spanish National Park in the Pyrenees Mountains (Ordesa and Monteperdido) and in the surroundings of an industrial waste dump (Sabiñánigo near to Huesca). The air sampling was carried out with a high volume air sampler, using polyurethane foam (PUF) and glass fiber filters (GFF) to collect both the gas phase and the particulate phase of these compounds. Recovery data of the analytical procedure as well as breakthrough values are shown. γ-HCH, α-HCH, α-endosulfan and hexachlorobenzene were found in all National Park samples in the range from 70 to 3076 pg/m^3. The chlorobenzenes had the highest concentrations (ΣCB = 1551–3512 ng/m^3) in the dumping site. α-HCH and γ-HCH were found in the range from 28 to 78 ng/m^3.

KEY WORDS: Organochlorine pesticides, chlorobenzenes, air analysis, polyurethane foam, high volume air-sampler, National Park of Ordesa and Monteperdido, industrial waste dump

INTRODUCTION

It is well-known that most of the organochlorine pesticides (OCPs) such as DDT or drin groups are banned in many developed countries. However, they are still in use in some developing countries, from which the atmospheric transport can be enough for generating a contamination problem in remote areas. This is the case of wild protected areas in which the only entrance of chemicals is via the atmosphere (see ref. 1 and references therein). Consequently, the determination of these compounds in the atmosphere is of environmental relevance. According to data obtained world-wide on these organochlorine compounds at different sites[2-4], a very low concentration level is expected, and consequently, a large volume of air should be pumped and filtered through an adsorption bed in order to be able to surpass the detection limit for each compound under study.

The present paper deals with the experimental study carried out in two natural sites. One of them is the surrounding atmosphere of an industrial waste dump in which both lindane and HCHs residues are involved. The second part shows the study of 16 organochlorine pesticides in the atmosphere of a Spanish National Park in the Pyrenees (Ordesa and Monte Perdido). The analytical features and the results obtained in both cases are discussed.

EXPERIMENTAL

Apparatus and conditions

A high volume air-sampler CAV-A/HF (MCV S.A., Barcelona, Spain) modified to work with polyurethane foam sheets of 25 × 20 cm × 18 mm thickness and 0.022 $g.cm^{-3}$ density supplied by Pikolin S. A. (Zaragoza, Spain).

Two stainless steel grids, one of them placed on the top and the other on the bottom of the solid bed system were used to keep the foam in place during the air sampling.

A Hewlett Packard 5890 Series II Gas Chromatograph equipped with a splitless injector, a Hewlett-Packard 7673 autosampler and ECD ^{63}Ni as detector were used. The data were obtained and processed with a compatible PC and the HP 3365 Chemstation System.

A Varian Star 3400 CX Gas Chromatograph equipped with both split-splitless and SPI (on-column and temperature programmable injector) injectors, a Varian 8200 CX autosampler and ECD ^{63}Ni as detector. The chromatographic data were obtained and processed in a Star Chromatography Workstation.

Two different capillary columns were used: SPB-5 (Supelco, Bellefonte, P.A., USA) 60 m × 0.25 mm i.d. × 0.25 µm film thickness and MFE-1701 (Análisis Vínicos, Tomelloso, Spain) 60 m × 0.25 mm i.d. × 0.25 µm film thickness. A 2 m × 0.32 mm i.d. pre-column (J&W, Scientific Fisons) was used in both cases.

The chromatographic conditions were as follows:

Splittless injection. Injector temperature: 210°C

SPI injection: initial temperature 50°C, rate at 150°C/min up to 250°C, held at 250°C.

Oven temperature: initial temp. 50°C, held for 2 min., rate at 20°C/min up to 185°C, held at 185°C for 10 min., rate at 3°C/min up to 250°C, held at 250°C for 10 min.

Detector temperature: 300°C

Carrier gas: Hydrogen at 1.45 ml/min.

Soxhlet extractors of 500 ml and 125 ml were used to extract the polyurethane foams and the GFFs.

Reagents and solutions

The solvents n-hexane and diethyl-ether were of residue analysis grade (Merck, Darmstadt, Germany).

The polyurethane foam sheets were cleaned before using with a hexane-diethylether (95:5) mixture in a soxhlet for 12 hours and they were dried under nitrogen atmosphere.

Gelman A/E glass microfiber filters of 26 × 21 cm were used. They were cleaned at 320°C for 6 hours before using.

Florisil (60–100 mesh) from Fluka (Buchs, Switzerland) was previously activated at 500°C for 6 hours and then it was deactivated to 10%(w/w) with distilled water.

Anhydrous sodium sulphate of analytical reagent grade (Panreac, Spain) was used to dry the organic extracts.

The following standards of pesticides were used: heptachlor, heptachlor-epoxide, α-endosulfan, endosulfan-sulphate and hexachlorobenzene (Riedel de Häen, Cromlab, Spain), α-hexachlorocyclohexane (α-HCH), β-hexachlorocyclohexane (β-HCH), γhexachlorocyclohexane (γ-HCH, lindane), dieldrin, endrin, aldrin, β-endosulfan, 4,4'-DDD, 4,4'-DDE, 4,4'-DDT and chlorpiryfos (Dr. Ehrensdorfer, Sugelabor, Spain), endrin aldehyde (Accu Standard, Teknokroma, Barcelona) and PCB-209 (Chem-Service, U.K.).

Solutions containing 500 μg.g^{-1} of each pesticide in n-hexane were prepared and they were stored at 4°C in 100 ml glass flasks. Gravimetric control of all solutions was applied. Suitable dilutions of these standard solutions were used when necessary.

Sampling procedure

For this work, the filter holder of a conventional filter-only high-volume air sampler was modified to use with polyurethane foam sheets and GFFs. A 20 × 25 cm stainless steel box with a supporting screen was welded on the bottom of the filter holder to hold up to four PUFs, each measuring 20 × 25 × 1.8 cm thickness. On top of this box, a second stainless steel supporting screen was added to hold a glass fiber filter (GFF). Figure 1 shows a scheme of the high-volume air filter sampler used.

After this modification, the air sampler could operate at 65 m^3/h for 24 hours without problems. Such a flow was necessary in order to pump through the solid bed between 1000 and 2000 m^3 of air in a maximum period of 24 hours.

To obtain the breakthrough value, up to 4 PUF sheets were placed simultaneously in the sampler. In the normal sampling, two or three different sheets were simultaneously placed in the monitor, together with the glass microfiber filter (GFF) on the top.

After the sampling, both the GFF and each PUF sheet were independently wrapped in baked aluminium foil and stored in a hermetic glass container before being extracted with the hexane-diethylether (95/5) mixture. The extraction of each PUF sheet was carried out within the next 24 hours after the sampling. Each one was soxhlet-extracted

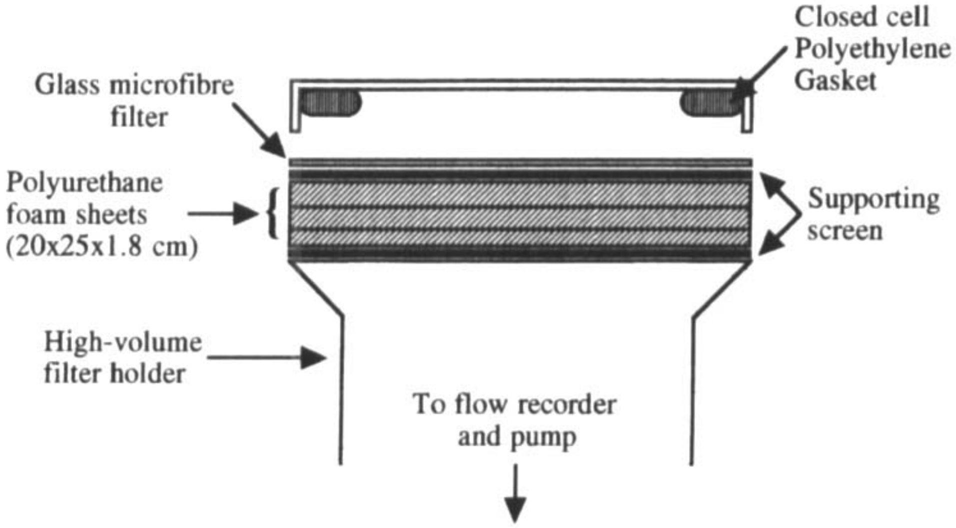

Figure 1 Scheme of the high volume air filter sampler used.

with 600 ml of the hexane-diethylether (95/5) mixture for 12 hours (aprox. 35 cycles). The extraction of the GFF was done in a soxhlet with 125 ml of the same organic mixture for 6 hours. All the organic extracts were concentrated in a rotary evaporator at 35°C up to 2 ml.

Sample clean-up

Each organic extract (about 2 ml) was cleaned in a glass column of 18 cm × 20 mm containing 7 g of 10% (w/w) deactivated Florisil and 1 g of anhydrous sodium sulphate on the top. This column was sequentially eluted with several 15 ml fractions of hexane-diethylether 95:5, 75:25, 60:40 and 30:70 mixtures. These fractions were then evaporated under nitrogen stream at 30°C up to 2 ml. All the extracts were gravimetrically controlled. 400 μl of a standard solution containing the appropriate amount of tetrachloronaphtalene (TCN) and PCB-209, used as internal standards, were added to the samples from the National Park, after checking that none of them were present in the real samples. Because of the great range of concentrations of the various pesticides (from 0.1 to 2000 pg/m^3), two injections were made, one of them from the 2 ml extract using TCN as an internal standard, and the second one after a reconcentration of the extract up to 100 μl with PCB-209 as internal standard. It is possible that the chromatogram obtained in the first extract of each PUF (elution mixture n-hexane/diethylether 95:5) for this second reconcentration were not clean enough to quantify some of the compounds. If so, it is recommended to make a first elution with 4 ml of n-hexane, that will desorb most of the PUF's degradation compounds. This improves the detection limits greatly for most of the compounds under study.

In the study of the waste dump, chlorpiriphos was used as an internal standard and the elution was made only with the first eluent. A second reconcentration was not necessary. Blank samples were used in all cases to assure the absence of interferences due to the procedure, reagents or handling (in the process).

RESULTS AND DISCUSSION

Atmospheric sampling

Studying the entrance of organochlorine pesticides in a wild environment without human activity through the atmosphere implies the sampling of more than 1000 m^3 of air to obtain a signal over the detection limits of the compound of concern. To obtain such a volume of air in a short period of time the sampling pump must work at a high flow. However, the flow depends critically on the solid bed through which the air has to cross. Solid beds used as adsorbents for organochlorine pesticides are Florisil, Tenax, Amberlite XAD-2 or active charcoal[5–9] but all of them produce an important pressure drop which increases the sampling period. The literature also describes the use of polyurethane foams (PUF) as preferred adsorbent for medium and low volatility organochlorine pesticides[7–11].

The size and shape of the PUF filters used also affects greatly the flow. Cartridges of 75 cm diameter reached a maximum flow of 40 m^3/h[11-13], whereas with wider and thinner plugs flows of 60 m^3 and over[10] can be obtained. As it was mentioned under the

Experimental Section, sheets of PUF of only 1.8 cm thickness were the ones used in this work in order to obtain a flow of 65 m^3/h.

Although the use of combined solid PUF beds and granular adsorbents are recommended for improving the sampling of the most volatile compounds such as chlorobenzene[5,7,14,15], the low flow obtained in such cases (20 m^3/h or less) prompt us to consider only PUF as an adsorbent.

On the other hand, pesticides appear in the atmosphere in two different physical states, as vapours in gas phase and as solids on the surface of particulate matter which means like an aerosol. Both phases can be separately sampled for a comprehensive study of semivolatile organic compounds in the atmosphere, because processes such as wet and dry deposition depend, fundamentally, on their physical state. Therefore, the use of a glass microfiber filter combined with the adsorbent plug is highly recommended.

As for the selection of pesticides to be analyzed in this study, the compounds were chosen taking into account the previous studies carried out in biota living in the same area[16]. Even some of these compounds were expected to be metabolites from their parent pesticides.

Sample treatment

One of the main problems with PUF cartridges is the likely degradation of polyurethane when it is in contact with light, air or organic solvents. This process usually produces very dirty extracts in which the chromatographic analysis is very difficult[9]. For this reason, it is necessary to use an efficient clean-up procedure. Several procedures such as the use of small columns of alumina or silicagel[15], 3% or 1,25% deactivated Florisil[17], or even the acid-base separation or the treatment with concentrated sulphuric acid[13] have been described elsewhere. However, the selection of the clean-up procedure depends on both the polarity and the nature of the pesticides to be analyzed. Sulphuric acid treatment, for example, destroys the pesticides containing oxygen, such as aldrin, endrin and endosulfan, whereas some of the granular adsorbents highly activated irreversibly adsorb other pesticides, such as β-endosulfan. In this case, the selected pesticides have very different polarities and this adds difficulties to the clean-up procedure. In order to obtain a quantitative recovery, different organic mixtures, in which the polarity was increased, were used as sequential eluents of a 10% deactivated Florisil column. Table 1 shows the results obtained. It can be observed that very polar compounds such as β-endosulfan, endosulfan sulphate or endrin aldehyde need a very polar eluent to reach a quantitative recovery, whereas the other pesticides appear mostly in the fraction eluted with the n-hexane/diethylether (95:5) mixture. All the pesticides under study were quantitatively recovered.

Trapping efficiency and breakthrough

Trapping efficiencies were determined by injection of small volumes of the compounds under study in n-hexane directly into the first PUF of a solid bed of 4 PUF sheets. The system was kept for 1 hour at room temperature to evaporate the solvent and three additional PUF sheets were placed over the system for prefiltration of the intake air. The system worked to pump through this solid bed a total volume of 1500 m^3 of air in 24 hours. Every sheet of PUF was then extracted according to the procedure explained above under the Experimental Section.

Table 1 Elution of these compounds in a 10% deactivated Florisil column.

Compound	*% eluted in each eluent**				*% total eluted*
	n-hexane/ether 95:5 22 ml	*n-hexane/ether 75:25 15 ml*	*n-hexane/ether 60:40 15 ml*	*n-hexane/ether 30:70 15 ml*	
α-HCH	84.1				84.1
β-HCH	83.0				83.0
γ-HCH	92.9				92.9
δ-HCH	8.4	91.4	2.4		102.2
Aldrin	96.8				96.8
Heptachlorepoxide	82.2				82.2
α-Endosulfan	80.6				80.6
pp'-DDE	99.8				99.8
Dieldrin	99.6				99.6
Endrin	85.9	1.7			87.6
β-Endosulfan		51.9	42.2		94.1
pp'-TDE	103.7				103.7
Endosulfan sulphate			68.0	16.2	84.2
Endrin aldehyde			17.5	68.3	85.8
pp'-DDT	98.7				98.7
Hexachlorobenzene	80.1				80.1
Heptachlor	97.2				97.2

*% eluted in this eluent of the total amount injected.

The results obtained after the independent analysis of each PUF are shown in Table 2. α-HCH, β-HCH, γ-HCH, δ-HCH, heptachlor, heptachloroepoxide, endrin, endosulfan-sulphate, pp'-DDE, pp'-TDE and pp'-DDT were quantitatively retained with retention efficiencies between 80.0% and 104.5%. The retention efficiency for dieldrin is nearly quantitative with 75%. Hexachlorobenzene, aldrin, α-endosulfan, β-endosulfan and endrin aldehyde were not quantitatively retained in these conditions. This means that they likely have breakthrough values lower than 1500 m^3, which could be attributed to their higher volatility compared to the others. These results agree with some data found in the literature[18].

The collection efficiencies at higher concentrations of OCPs were obtained by fortifying the glass fiber filter with one mililiter of the compounds under study in n-hexane, added dropwise to the filter. After 24 hours with a 65 m^3/h air flow, the filter and foam plugs were analyzed individually. The results obtained are shown in Table 2. As can be seen, the results are similar to those found when lower concentration values are present in the atmosphere.

Following the same procedure, the detection limits (D.L.) in the atmosphere were obtained. These values were calculated as three times the background signal at the retention time of each pesticide when an extract of a blank of PUF was injected into the capillary column. These data are also included in Table 2.

Breakthrough of chlorobenzenes during sampling

Breakthrough of an analyte on an adsorbent is a function of the ambient temperature, the sample volume, the adsorbent volume, the affinity of the analyte for the adsorbent, and the chromatographic efficiency of the sorbent system as measured by the number of

Table 2 Trapping efficiency of OCPs in PUF.

Compound	*Amount added (ng)*	*Amount found (ng)*	*Trapping efficiency (%)*				*Detection limits (pg/m³)*
			PUF 1	*PUF 2*	*PUF 3*	*Total*	
α-HCH	157[1]	163	39.7	44.7	12.4	100.9	1
	1365[2]	1365	53.1	37.9	9.0	100	–
Hexachlorobenzene	2220[2]	539	1,1	7.1	16.1	24.3	1
β-HCH	160[1]	160	99.9	0.2	–	100.1	0.5
	1457[2]	1384	94.0	1.0	–	95.0	–
γ-HCH	123[1]	114	70.5	20.9	–	93.0	0.5
	1111[2]	1031	74.5	11.7	–	92.7	–
δ-HCH	412[1]	328	76.4	0.6	–	80	0.5
	4002[2]	3547	85.6	3.1	–	88.7	–
Aldrin	194[1]	66	21.1	12.8	–	33.9	1
	1509[2]	239	15.9	–	–	15.9	–
Heptachlorepoxide	148[1]	135	87.8	3.6	–	91.4	1
	1372[1]	1216	88.6	–	–	88.6	–
α-Endosulfan	140[1]	62	27.3	16.9	–	44.2	1
	1005[2]	290	21.1	2.8	5.0	28.9	–
pp'-DDE	150[1]	144	95.2	0.9	–	96.3	0.5
	1669[2]	1433	85.8	–	–	85.8	–
Dieldrin	297[1]	223	73.7	1.3	–	75.0	1
	2648[2]	1557	58.9	–	–	58.9	–
Endrin	151[1]	158	104.4	0.1	–	104.5	1
	1378[2]	1290	93.4	–	–	93.4	1
β-Endosulfan	1210[2]	246	20.4	–	–	20.4	0.5
pp'-DDD	201[1]	183	90.8	–	–	90.8	0.5
	1676[2]	1245	74.3	–	–	74.3	–
Endosulfan sulphate	1397[2]	1182	83.9	–	–	83.9	1
Endrin aldehyde	1272[2]	257	20.2	–	–	20.2	0.5
pp'-DDT	153[1]	135	90.8	0.3	–	91.1	1
	1316[2]	1047	73.6	1.6	4.3	79.5	–
Heptachlor	1361[2]	1155	64.3	19.5	1.0	84.8	1

[1] mean temperature = 8°C, injection of the compounds into the first PUF
[2] mean temperature = 14°C, addition of the compounds to the glass fiber filter

theoretical plates N. When several adsorbent traps are used, the efficiency of the trapping process can be monitored by comparison of the amount of material found on each trap. Table 4 shows data with breakthrough values for the bed system. These breakthrough values are given as:

$$B_{2,1}(\%) = [(S/(F + S)] \times 100\%,$$
$$B_{3,2}(\%) = [T/(S + T)] \times 100\%, \text{ and}$$
$$B_{3,2+1}(\%) = [T/(S + F + T)] \times 100\%$$

where T is the concentration found on the third PUF, S the concentration on the second PUF and F the concentration on the first PUF.

As it was mentioned in the Atmospheric sampling section, the literature usually recommends the use of granular adsorbents or combinations of PUF and granular adsorbents for compounds having a P_LO (vapor pressure of the subcooled liquid) less than 0.1 Pa[19], such as chlorobenzene because of the small breakthrough volumes for these compounds[20]. However, the conditions in which the sampling was carried out allowed the quantitative trapping of all the compounds under study. This is due to several factors. First of all, the high concentrations of these compounds in the sampling area which allow the collection of only a few m^3 (about 25 m^3). This way, the sensitivity of the procedure is more than enough to surpass the detection limits. Secondly, the low environmental temperatures during the sampling improve the retention on solid adsorbents, according to the adsorption laws. Finally, the configuration of the sampling device with a wide adsorbent surface and consequently a low linear face velocity of only 23 $cm.s^{-1}$, is able to compensate the limited number of theoretical plates of about 5.5 according to the previous theoretical studies of Bidleman *et al.*[19]. This attempt can be demonstrated with the data from Table 3, in which the breakthrough values of the chlorobenzenes for the two samplings are shown. It can be seen that two PUF could be enough to achieve a nearly quantitative retention for 1,2,4-trichlorobenzene, 1,2,3-trichlorobenzene, 1,2,4,5-tetrachlorobenzene, 1,2,3,4-tetrachlorobenzene and pentachlorobenzene. In all these cases the $B_{2,1}$ values are lower than 20%, and the $B_{3,1+2}$ values lower than 10%. For the other four chlorobenzene under study, a third PUF is necessary to obtain a good retention of the compounds.

Determination of OCPs in the surrounding atmosphere of a waste dump

An industrial waste dump containing residues of lindane, chlorobenzenes and HCHs close to Sabiñánigo was restructured in order to prevent the release of such compounds to both the atmosphere and water. During the works, it was necessary to assure the health of the workers involved as well as to advise the local government about the efficiency of the works carried out to protect the health of the population. For all these reasons, an atmospheric study was done following the same procedure described above.

The dump was placed in a rural area near a small village named Sabiñánigo (Huesca, Spain) and an industrial pole. Two air samples were analyzed. One of them was taken

Table 3 Breakthrough values of the chlorobenzenes.

Compound	$B_{2,1}$			$B_{3,2}$			$B_{3,2+1}$		
	Sample 1	*Sample 2*	*Mean*	*Sample 1*	*Sample 2*	*Mean*	*Sample 1*	*Sample 2*	*Mean*
1,3-Dichlorobenzene	45.8	54.2	50.0	35.2	8.1	21.7	19.9	4.6	12.3
1,4-Dichlorobenzene	44.0	53.5	48.7	33.5	8.9	21.2	18.8	5.0	11.9
1,2-Dichlorobenzene	44.2	56.2	50.2	29.4	10.1	19.8	15.6	6.0	10.8
1,3,5-Trichlorobenzene	38.4	46.7	47.6	33.5	15.7	24.6	16.9	8.0	12.1
1,2,4-Trichlorobenzene	20.4	15.7	18.1	32.5	27.0	29.7	9.0	5.5	7.3
1,2,3-Trichlorobenzene	14.8	7.1	11.0	27.6	15.1	21.3	5.3	1.2	3.3
1,2,4,5-Tetrachlorobenzene	0	8.7	4.4	*	*	*	0	3.5	1.8
1,2,3,4-Tetrachlorobenzene	2.8	5.0	3.9	*	*	*	2.8	3.6	3.3
Pentachlorobenzene	5.0	15.1	10.1	*	*	*	0	1.2	0.6

$B_{2,1}$ (%) = [S/(F + S)] × 100%
$B_{3,2}$ (%) = [T/(S + T)] × 100%
$B_{3,2+1}$ (%) = [T/(S + F + T)] × 100%
T = concentration found on the third PUF
S = concentration found on the second PUF
F = concentration found on the first PUF
* Concentration of compound in PUF 2 and PUF 3 less than 1% of total concentration

when the surface of the dump was excavated and moved (Sample 1), at a distance of 20 m away from the excavating area. The second one was taken at a distance of 15 m of the hole when the deepest part of the waste-dump was dug up (Sample 2). The sample volume was 26 m^3 and 24 m^3, respectively. The meteorological conditions (5°C and 20 km/h of wind speed) and the sampling flow (40 m^3/h) were the same in both cases.

Table 4 shows the results obtained, together with the concentration of each compound in the solid industrial residue. The differences in percentage up to 100% weight are due to other compounds as well as moisture. There were no data about the content of pentachlorobenzene in the solid residue.

From this data it is apparent that a close relationship exists between the volatility of the compounds and their concentrations in the atmosphere. As can be seen, chlorobenzenes have higher concentration values than HCHs even though the latter are considerably more concentrated on the solid residue.

Determination of OCPs in a wild protected area

Three different samples in several seasonal periods were taken in a wild protected area that belongs to the National Park Ordesa, sited in the Pyrenees. The sampling point was at 1500 m above sea level.

Table 5 shows the results obtained in which a good correlation within the three samples can be observed. Some relationships can be found between the behaviour of α-HCH, γ-HCH, hexachlorobenzene and α-endosulfan and the seasonal and meteorological conditions in which the samples were monitored. Local seasonal agricultural activities involve the use of γ-HCH and α-endosulfan and this fact can explain the high values found for these compounds and for hexachlorobenzene, which is a degradation product from γ-HCH. Sample 2 has the highest concentration for all the compounds studied, but this sample was taken in the early Summer, when the agricultural activities take place and when the temperature is quite high. Consequently, the concentration of the most volatile compounds should be higher too. As can be seen, the concentrations of sample 2 were 5 times higher than those of sample 1 and 10 times than those of the sample 3 for both compounds, whereas in the case of α-HCH this seasonal and temperature

Table 4 Results obtained in the determination of chlorobenzenes and HCHs in the surrounding atmosphere of a waste dump.

Compound	*Sample 1 (ng/m^3)*	*Sample 2 (ng/m^3)*	*Percentage in weight*[1]
1,3-Dichlorobenzene	57.8	12.3	0.035
1,4-Dichlorobenzene	553	107	0.065
1,2-Dichlorobenzene	787	136	0.075
1,3,5-Trichlorobenzene	36.4	16.9	0.013
1,2,4-Trichlorobenzene	1474	442	0.375
1,2,3-Trichlorobenzene	202	297	0.052
1,2,4,5-Tetrachlorobenzene	138	219	0.011
1,2,3,4-Tetrachlorobenzene	243	297	0.010
Pentachlorobenzene	18.4	21.7	–
α-HCH	38.8	77.4	85.37
γ-HCH	27.9	58.6	1.90

[1] Percentage in weight for the HCHs solid waste

Table 5 Concentration of OCPs in air samples of the National Park of Ordesa and Monteperdido.

Compound	*Sample 1 (pg/m^3)*	*Sample 2 (pg/m^3)*	*Sample 3 (pg/m^3)*
α-HCH	71	185 (*18.5%*)	144 (*12.2%*)
β-HCH	< Q.L.	3	< Q.L.
γ-HCH	738	3076 (*0.2%*)	269 (*0.5%*)
δ-HCH	< Q.L.	7	< Q.L.
Aldrin	< Q.L.	12 (*1.6%*)	< Q.L.
Heptachloroepoxide	< Q.L.	< Q.L.	< Q.L.
α-Endosulfan	188 (*10.8%*)*	1091 (*0.2%*)	101 (*37.5%*)
pp’-DDE	< Q.L.	3.4	< Q.L.
Dieldrin	< Q.L.	6	3
Endrin	< Q.L.	< Q.L.	< Q.L.
β-Endosulfan	< Q.L.	1	< Q.L.
pp’-TDE	< Q.L.	< Q.L.	–
Endosulfan sulphate	< Q.L.	< Q.L.	< Q.L.
Endrin aldehyde	< Q.L.	< Q.L.	< Q.L.
pp’-DDT	< Q.L.	4 (*34.0%*)	< Q.L.
Heptachlor	< Q.L.	< Q.L.	< Q.L.
Hexachlorobenzene	161	209	240

Q.L.: Quantification Limit (values given in Table 2)

(*Italics*): % of the compound retained in the glass microfiber filter

Environmental conditions:

Sample 1: Sampling date 10 April 1995, air direction south/southwest, mean temperature 9.0°C, air collected 1572 m^3

Sample 2: Sample date 23 June 1995, air direction east, mean temperature 19.3°C, air collected 1539 m^3

Sample 3: Sampling date 23 August 1995, air direction east and northwest, mean temperature 14°C, air collected 1573 m^3

dependance is not so clear, and its concentration was only slightly higher. These results are in good agreement with those found in other studies[21,22]. These works show that γ-HCH concentrations in the atmosphere are much higher during the warmer months and that they are strongly dependant on temperature through the vapor pressure of the compound, whereas for α-HCH no temperature-concentration dependance was observed.

From the ratio between α-HCH and γ-HCH or pp’-DDE and pp’-DDT additional information about the origin of the pollution can be obtained. According to the hypothesis of Oehme[23] and Atlas[17] the ratio of α-HCH/γ-HCH is an indicator of the age of the air pollution, and high values of this ratio appear in old atmosphere, while a low ratio means a closer source of the air pollution.

Most of the experimental data shown in the literature have a ratio higher than 1, even in the case when the source was γ-HCH[12,13]. However, in our case, this ratio is very low which suggests that the source of HCHs is very near. In the same way, the ratio between pp’-DDE and pp’-DDT can give information about the age and origin of the air pollution. Since pp’-DDE is a pp’-DDT metabolite, high values of this ratio suggest a remote pollution. Both compounds were quantified only in sample 2 and the obtained ratio for them was 0.85.

The concentrations in sample 3 are not so high as expected. This could be explained by the fact that the rainfalls from this day and the day before could produce a washout of the atmosphere with a decrease in the pollutant concentration.

It can be pointed out that the real air concentration of α-endosulfan and hexachlorobenzene will be probably greater than the measured values because of their retention are not quantitative.

Figures in brackets in Table 5 represent the percentage of each compound found as solid matter trapped on the glass microfiber filter. These values are higher when the volatility of the compound is lower, as expected. In this sense, sampling temperature affects the partition of each compound in the two phases, and consequently, the independent sampling of the two fractions, solid and gaseous, is necessary.

There is a good correlation between the organochlorine pesticides found in these air samples and the compounds found in a previous work in the serum of wild goats living in the same area[16]. α-Endosulfan and γ-HCH have the highest concentration in both air and serum samples and both were present in all samples. The concentration of other compounds such as α-, β- and δ-HCH, aldrin, dieldrin, β-endosulfan, pp'-DDT and his metabolites was not so high or were only present in some of the serum samples. Endosulfan-sulphate, a metabolite of α-endosulfan, was found too in all wild goats at high concentrations.

CONCLUSIONS

Twelve organochlorine pesticides of very different polarities can be quantitatively sampled in the atmosphere at concentration levels of a few picograms per cubic meter, using two polyurethane foam sheets of only 1.8 cm thickness. The trapping efficiency ranges from 75.0% to 104.3% when 1573 m^3 are pumped through the solid bed of PUF. Another five compounds, hexachlorobenzene, aldrin, endrin aldehyde, α- and β-endosulfan, were not quantitatively retained under these conditions.

The use of polyurethane foam as solid adsorbent for trapping chlorobenzenes with a high volume air sampler can be recommended but only if the volume of air pumped is not higher than the breakthrough values for these compounds. These are quantitatively retained with three PUF sheets, of 25 × 20 × 1.8 cm thickness each, if the sample volume does not exceed 25 m^3.

A sequential elution with different organic mixtures having increasing polarity enable the quantitative elution of all the compounds, even the highly polar β-endosulfan, endrin aldehyde and endosulfan-sulphate.

The experimental study carried out in a Spanish wild protected area in the Pyrenees (National Park of Ordesa and Monteperdido) shows the presence of several OCPs in the atmosphere. The highest concentrations are for γ-HCH, α-endosulfan, hexachlorobenzene and α-HCH. All these pesticides were found in a previous study carried out in the serum of wild goats living in this area. The ratio found between α-HCH and γ-HCH suggests a near source of air pollution for these compounds, which could be the local usage of lindane in agricultural works in the surrounding area of the Park.

Acknowledgements

This Project has been financed by the Project "Incidence of air-transported organochlorine pesticides in the National Park of Ordesa and Monte Perdido" PMA/1393 CONAI-DGA 1995.

References

1. K. Ballschmiter. *Angew. Chem. Int. Ed. Engl.* **31**, 487–515, 1992.
2. R. D. Arthur, J. D. Cain and B. F. Barrentine. *Bull. Environ. Cont. Toxic.* **15**, 129–134, (1976).
3. P. Larsson. *Atmos. Environ.* **23**, 2151–2158, (1989).
4. K. Ballschmiter and R. Wittlinger, *Environ. Sci. Tech.* **25**, 1103–1111, (1991).
5. R. G. Lewis and K. E. MacLeod, *Anal. Chem.*, **54,** 310–315 (1982).
6. H. Rothweiler, P. A. Wäger and C. Schlatter, *Atmos. Environ*, **25B**, 231–235 (1991).
7. M. P. Ligocki and J. F. Pankow, *Anal. Chem.*, **57**, 1138–1144 (1985).
8. C. Nerin, M. Martinez, B. Pons and J. Cacho, *Talanta*, **40**, 1769–1774, (1993).
9. C. Nerin, M. Martinez-Galera, J. L. Martinez and A. R. Tornés, *Fresenius J. Anal. Chem.*, **352**, 609–611, (1995).
10. K. M. Hart, L. M. Isabelle and J. F. Pankow, *Environ. Sci. Technol.*, **26**, 1048–1052 (1992).
11. R. G. Lewis, A. R. Brown, and M. D. Jackson. *Anal. Chem.*, **49**, 12 (1977).
12. E. Atlas and C. S. Giam, Water, *Air and Soil Pollution*, **38**, 19–36 (1988).
13. T. F. Bidleman, U. Wideqvist, B. Jansson and R. Söderlund, *Atmos. Environ.* **21**, 641–6541 (1987).
14. G. W. Patton, L. L. McConnell, M. T. Zaranski and T. F. Bidleman, *Anal. Chem.*, **64**, 2858–2861 (1992).
15. W. N. Billings and T. F. Bidleman, *Environ. Sci. Technol.* **14**, 679–683 (1980).
16. M. C. Martinez, S. Gargallo, P. Ferrando, J. Maluenda, D. Raldua, J. Quilez, J. Gonzalo and C. Pedrocchi, *Lucas Mallada*, **5**, 101–105 (1993).
17. C. S. Giam, G. Atlas, H. S. Chan and G. S. Neff, *Atmos. Environ.*, **14**, 65–69 (1980).
18. R. G. Lewis and M. D. Jackson, *Anal. Chem.*, **54**, 592–595 (1982).
19. T. F. Bidleman, C. G. Simon, N. F. Burdick and Feng You, J. *Chromatogr.* **301**, 448–453 (1984).
20. M. T. Zaranski, G. W. Patton, L. L. McConnell and T. F. Bidleman, *Anal. Chem.*, **63**, 1228–1232 (1991).
21. R. M. Hoff, D. C. G. Muir, and N. P. Grift, *Environ. Sci. Technol.*, **26**, 276 (1992).
22. S. Fingler, B. Tkalcevic, Z. Fröbe and V. Drevenkar, *Analyst*, **119**, 1135–1141 (1994).
23. M. Oehme and Ottar, *Geophys. Res. Lett.*, **11**, 1133 (1984).