

LEVELS IN ABIOTIC COMPARTMENTS

COMPARISON OF POLYCHLORINATED BIPHENYLS (PCBs) AND ORGANOCHLORINE PESTICIDES CONCENTRATION LEVELS IN SEDIMENT AND BIOTA. ANALYSIS BY HRGC/HRMS.

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Introduction

Polychlorinated biphenyls (PCBs) and organochlorine pesticides as hexachlorocyclohexane (HCH), hexachlorobenzene (HCB), hexachlorobutadiene (HCBu), aldrin, dieldrin, endrin, isodrin, and DDT and metabolites are considered persistent organic pollutants (POPs). These chemicals are characterised by its persistence and ubiquity and its tendency to bioaccumulate in biota. The characteristics mentioned above and the low levels found in environmental samples requires the use of a high sensibility and high specificity technique as high-resolution mass spectrometry (HRMS).

In this study is presented the methodology for the analysis of seven BCR indicator PCBs (IUPAC nos. 28, 52, 101, 118, 153, 138, and 180), the α , β and γ isomers of hexachlorocyclohexane, hexachlorocyclobenzene, hexachlorobutadiene and DDT and metabolites (DDE and DDD) by isotope-dilution HRGC/HRMS. Also, this study discusses results obtained from samples of sediments and fishes from different rivers of Catalonia (Spain).

Methods and Materials

The analytical methodology used is based in the method US-EPA 1668 for the analysis of PCBs by HRGC/HRMS and conveniently adapted for the analysis of pesticides. A Soxhlet extraction was made with n-hexane/dichloromethane 1:1 for 24 hours. Prior to the extraction, sample was spiked with the ¹³C-labeled internal standards (Table 1). To remove possible interferences from the sample a clean-up was made with Florisil® or Alumina 5 % deactivate, for sediments and fishes respectively. The columns were eluted with a mixture of n-hexane/dichloromethane in different proportion to get different fractions. PCBs and pesticides elute in the first fraction. This clean-up allows analysing other organics compounds such as polycyclic aromatic hydrocarbons, alquilbenzenes and nonilphenols in other fractions. Finally it was reconcentrated to a volume of 250-500 ml and ¹³C-labeled internal standards were added to calculate the recovery.

The purified extracts were analysed by HRGC/HRMS on an Autospec-Q mass spectrometer (Micromass, Manchester UK) coupled to HP gas chromatograph (Palo Alto, CA USA). The capillary column used was a DB-5 (J&W Scientific, Folsom, CA, USA) fused-silica (60 m x 0.25 mm ID, 0.28 mm film thickness). The injection mode was split-less and helium as a carrier gas at a linear velocity of 28 cm/s (T: 70°C). The operating conditions of mass spectrometer were: electron ionisation (70eV ionisation energy), acquisition mode SIM (Selected Ion Monitoring, SIR Voltage), ion source temperature 255 °C, interface temperature 275 °C. The minimum static resolution used was 8000 (10 % definition valley). Verification of the resolution was obtained by measuring perfluorokerosene (PFK) reference peaks. The ions monitored are listed in Table 1.

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Accuracy and precision of the method were evaluated by analyzing certified reference materials (SRM 1939a and IAEA 142) and in intercalibration exercises participation.

Table 1. Internal standard used in isotope dilution method for PCBs and organochlorine pesticides and m/z monitored in HRMS experiment.

COMPOUN		Labelled Internal standard (Isotope Dilution)	Fragments and m/z ratios of native analytes*		
Organochlorine Pesticides	HCHs	$^{13}\text{C}_6\text{-}\gamma\text{-HCH}$	$\text{C}_6\text{H}_5\text{Cl}_4^+$	216,9145	218,9116
	HCBu		C_4Cl_5^+	222,8446	224,8413
	HCB		C_6Cl_6^+	283,8102	285,8072
	DDT and DDD	$^{13}\text{C}_6\text{-o,p'DDE}$	$\text{C}_{13}\text{H}_9\text{Cl}_2^+$	235,0081	237,0052
	DDE		$\text{C}_{14}\text{H}_8\text{Cl}_2^+$	246,0003	247,9974
	Aldrin, Dieldrin				
	Endrin, Isodrin		$\text{C}_7\text{H}_2\text{Cl}_5^+$	260,8599	262,8570
Tri-CBs	PCB#28	$^{13}\text{C}_{12}\text{-PCB#28}$	$\text{C}_{12}\text{H}_7\text{Cl}_3^+$	255,9613	257,9584
Tetra-CBs	PCB#52	$^{13}\text{C}_{12}\text{-PCB#52}$	$\text{C}_{12}\text{H}_6\text{Cl}_4^+$	289,9224	291,9194
Penta-CBs	PCB#101	$^{13}\text{C}_{12}\text{-PCB#101}$			
	PCB#118	$^{13}\text{C}_{12}\text{-PCB#118}$	$\text{C}_{12}\text{H}_5\text{Cl}_5^+$	325,8804	327,8773
Hexa-CBs	PCB#153				
	PCB#138	$^{13}\text{C}_{12}\text{-PCB#153}$	$\text{C}_{12}\text{H}_4\text{Cl}_6^+$	361,8385	363,8357
Hepta-CBs	PCB#180	$^{13}\text{C}_{12}\text{-PCB#180}$	$\text{C}_{12}\text{H}_3\text{Cl}_7^+$	393,8025	395,7995

HCHs: isomers α , β and γ of hexachlorocyclohexane

Results and Discussion

As an example of application of analytical method described, table 2 shows the results of 8 fishes (*Leuciscus cephalus*, *Cyprinus carpio*, *Barbus ssp* and *Salmo trutta*) and 8 surface sediments from the same point of six Catalan rivers. Concentrations of PCBs are ranged between 5,1 and 36,8 ng/g in sediments and between 5,7 and 159,3 ng/g fresh weight in fishes. Concentrations for the sum of all POCs are between 9,0 and 108,8 ng/g for sediments and between 6,8 and 63,1 ng/g for fishes. In all cases, recoveries have ranged between 40-125 % and detection limits were below 0,05 ng/g. Concentrations that were found are consistent with characteristics of sample's zone. PCBs levels are higher in most industrial areas and pesticides levels in agriculture areas. In general, levels of PCBs in the fish are higher than in the same sediments (Figure 1). This tendency is followed too in the case of organochlorine pesticides. The PCBs pattern in fishes is characteristic⁽²⁾ and different that is showed in sediments. In the case of fishes, in all samples, the majority of PCBs are hexa-CBs and pattern shown is similar to Aroclor 1260. In the case of sediments, the pattern found is variable and the majority of congeners are hexa, penta and tetra-CBs (Table 3).

Aldrin, dieldrin, endrin and isodrin were not detected in all samples. DDX pattern is different for sediments and fishes. For fishes, the major compound is DDE while in sediments is DDT (Table 4).

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Table 2. Concentration of total PCBs (BCR) and organochlorine pesticides in sediment and fish.

SAMPLE REFERENCE		TOTAL PCBs (BCR) RESULTS*		TOTAL POCs RESULTS	
RIVER	Sample Point	Sediment	Fish	Sediment	Fish
Ter	Flaçà	22,8	12,5	108,8	10,6
Llobregat	Abrera	10,3	159,3	10,5	37,7
Llobregat	Pont de Vilomara	5,9	67,9	10,0	22,1
Llobregat	St. Joan Despí	36,8	82,3	82,2	63,1
Foix	Castellet i la Gornal	5,1	41,0	9,1	35,0
Fluvià	Besalú	7,9	5,7	23,9	6,8
Congost	La Garriga	5,6	17,7	9,5	11,9
Cardener	Castellgalí	11,4	89,8	9,0	48,3
UNITS		ng/g dry weight	ng/g fresh weight	ng/g dry weight	ng/g fresh weight

*Total POCs: sum of concentration of α , β and γ isomers of HCH, hexaclorociclobenzene, hexaclorobutadiene and DDT and metabolites (DDE and DDD).

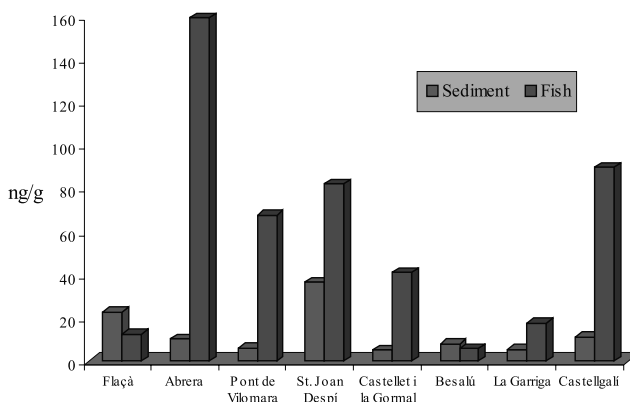


Figure 1. Different concentrations of PCBs (BCR) levels in fish and sediment.

Table 3. PCBs congeners concentrations.

Sample Point		PCB#28	PCB#52	PCB#101	PCB#118	PCB#138	PCB#153	PCB#180
Ter, Flaça	Sed.	4,5	3,9	2,5	1,8	3,7	2,7	3,8
	Fish	0,6	1,0	1,4	1,4	3,0	3,2	1,9
Llobregat, Abrera	Sed.	0,8	1,0	2,5	1,6	1,8	1,5	1,1
	Fish	1,3	7,1	24,5	24,5	43,5	37,8	20,5

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Llobregat, Pont de Vilomara	Sed.	0,9	0,8	1,4	0,9	0,8	0,7	0,4
	Fish	2,6	7,6	9,4	8,4	14,7	16,0	9,2
Llobregat, St. Joan Despí	Sed.	2,9	4,1	5,7	2,8	8,2	7,2	5,8
	Fish	3,9	7,3	14,9	11,4	24,0	21,8	10,4
Foix, Castellet i la Gornal	Sed.	0,4	0,8	0,9	0,5	1,0	0,8	0,7
	Fish	0,6	1,6	6,3	5,1	11,0	11,3	5,2
Fluvà, Besalú	Sed.	0,6	1,4	1,4	0,8	1,6	1,3	0,8
	Fish	0,1	0,4	0,5	0,5	1,3	1,8	1,1
Congost, La Garriga	Sed.	0,4	1,1	0,8	0,4	1,0	0,7	1,1
	Fish	0,4	0,4	1,4	2,9	4,8	5,1	2,6
Cardener, Castellgalí	Sed.	0,9	1,2	2,8	1,6	2,0	1,5	1,3
	Fish	3,8	6,2	13,0	10,5	21,8	20,9	13,6
UNITS		ng/g (of dry weight for sediments and fresh weight for fishes)						

Table 4. Results of individual organochlorine pesticides.

Sample Point		HCHs	HCB	HCBu							DDX
					o,p'DDD	p,p'DDD	o,p'DDT	p,p'DDT	o,p'DDE	p,p'DDE	
Ter, Flaça	Sed.	1,2	26,8	47,1	1,6	5,0	<ldd	21,1	0,2	5,9	
	Fish	1,6	0,4	0,8	n.d	1,8	n.d	n.d	n.d	6,0	
Llobregat, Abrera	Sed.	1,3	n.d	n.d	0,6	1,5	n.d	4,0	n.d	3,2	
	Fish	1,0	0,8	0,2	1,3	5,7	n.d	0,3	n.d	28,5	
Llobregat, Pont de Vilomara	Sed.	n.d	4,5	n.d	0,3	0,9	n.d	2,8	n.d	1,5	
	Fish	0,8	0,5	0,6	0,8	3,4	n.d	n.d	n.d	16,0	
Llobregat, St. Joan Despí	Sed.	2,8	6,4	3,8	2,8	5,1	n.d	4,6	8,6	48,3	
	Fish	4,0	1,5	0,3	1,6	7,2	n.d	0,6	1,8	46,1	
Foix, Castellet i la Gornal	Sed.	n.d	n.d	2,4	0,4	1,2	<ldd	2,6	n.d	2,6	
	Fish	5,6	0,3	0,6	0,5	3,3	n.d	n.d	<ldd	24,8	
Fluvà, Besalú	Sed.	n.d	2,3	3,0	n.d	1,1	n.d	15,8	n.d	1,7	
	Fish	2,0	0,2	1,0	n.d	0,4	n.d	n.d	n.d	3,0	
Congost, La Garriga	Sed.	n.d	2,3	n.d	0,4	1,6	n.d	2,9	n.d	2,4	
	Fish	0,5	0,2	n.d	0,2	1,3	n.d	n.d	n.d	9,7	
Cardener, Castellgalí	Sed.	1,7	<ldd	n.d	0,7	1,9	<ldd	3,0	<ldd	1,8	
	Fish	1,6	1,8	0,3	2,7	9,9	<ldd	1,0	0,8	30,3	
UNITS		ng/g (dry weight for sediments and fresh weight for fishes)									

References

1.US-EPA. Method 1668, Revision A: Chlorinated Biphenyl Congeners in Water, Soil, Sediment and Tissue by HRGC/HRMS.

2. L.J. Jackson, S.R. Carpenter, J. Manchester-Neesvig, C.A. Stow. (2001) Environ. Sci. Technol. 35, 856-862.