ASSESSMENT OF PERSISTENT ORGANIC POLLUTANTS IN RIVER SEDIMENTS FROM CATALONIA (SPAIN). ANALYSIS BY HRGC/LRMS AND HRGC/HRMS

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Introduction

Since 1995 the Mass Spectrometry Laboratory, in agreement with some different administrations (Catalan Water Agency, Riverine Basin Autority of Ebro river), conducted an extensive project on the characterization of different persistent organic pollutants (POPs). Several environmental and biotic matrices, such as surface and ground water, sewage sludges, biota, and marine and river sediments, were analysed. Target analytes varied depending on the kind of major impact source. Commonly investigated compounds were PCDDs/PCDFs, PCBs, PAHs, polyethoxylated nonylphenols (NPnEO), organochlorinated pesticides, such as hexachlorocyclohexane (HCH) and DDX (isomers and metabolites of DDT).

Majority of analyses were carried out by isotopic dilution-Gas Chromatography coupled to Low or High Resolution Mass Spectrometry (HRGC/LRMS or HRGC/HRMS). Isotopic dilution, based on the use of labelled internal standards (EPA methods 1625 and 1668), provides a reliable and robust method for analysing and quantifying POPs in environmental samples. High Resolution Mas Spectrometry was necessary for the determination of very low concentrations of several compounds, such as PCBs and organochlorinated pesticides in complex matrices with a high presence of interferences.

Materials and methods

Samples were collected in different sampling points from Llobregat, Besós and Ebro river basins (Catalonia, Spain) during the period 1998-2001. The analyses were carried out by isotopic dilution-HRGC/LRMS and isotopic dilution-HRGC/HRMS (EPA methods 1625 and 1668).

Prior to extraction, samples were spiked with known amounts of labelled internal standards (^{13}C-PCDDs/PCDFs, ^{13}C-PCBs, $^{13}C_{12}$-o,p'-DDE, $^{13}C_6$-Lindane, *d*-PAHs and $^{13}C_6$-NPnEOs). Samples were extracted with a Soxhlet apparatus during 18h using hexane:dichloromethane 1:1 as extraction solvent. After a clean-up with alumina, the extracts were concentrated and analysed by HRGC/MS.

PAHs and NPnEO (n=0,1) were analysed by HRGC/LRMS on an integrated quadrupole MD-800 from Fisons (Manchester, UK). The ionisation was made using Electronic Impact mode. The acquisition was performed in SCAN mode (m/z=45-450) with a scan time of 0.6 s. Data were processed using the Masslab software.

PCDDs/PDCFs, PCBs, DDXs and HCHs were analysed by HRGC/HRMS on an AutoSpec-Q mass spectrometrometer (Micromass, Manchester, UK), using a positive ionization (EI+) source and operating in the SIM mode at 10000 resolving power (10% valley definition). Data were processed using the OPUS 3.4 software.

Chromatographic separation was achieved with a DB-5 (J&W Scientific, CA, USA) fused-silica capillary column (60 m, 0.25 mm ID, 0.25 :m film thickness) with helium as carrier gas in the splitless injection mode.

Results and Discussion

As an example, the results obtained from a sample collected near the mouth of Llobregar river are shown in table 1.

Table1. Levels of organic pollutants detected in a sediment from the mouth of Llobregat river

FAMILY OF COMPOUNDS	CONCENTRATION
PAHs	202
NPnEOs (n=0,1)	1749
PCBs (total BCR)	71.2
DDX	649.4
HCHs	n.d.

n.d.: not detected **units in ng/g**

Otherwise, the range of organic pollutant concentrations found in 2 sampling points from Ebro river are shown in table 2. An atypical profile of DDX was detected in these samples, where the maximum concentracion is related to p,p'-DDT instead of p,p'-DDE. This profile is different from the commonly found distribution of DDX in sediments, and it can be explained by recent inputs of DDT from chemical industry. The analysis of PCDDs/PCDFs was carried out only in sampling point 1. The result was 17.83 pg I-TEQ/g.

The chromatograms obtained from the analysis of PCBs, HCHs, and NPnEO (n=0,1) in different samples are shown in figures 1-3. Figures 1 and 3 show the chromatograms related to analytes and internal standards for PCBs and NPnEO (n=0,1). An atypical profile of HCHs is shown in figure 2, where ∀-HCH is the dominant isomer. This profile can be explained by inputs of technical-grade HCH and it is different from the commonly found distribution of HCHs, where the highest concentracion is related to (-HCH (lindane).

Table 2. Range of organic pollutant concentrations detected in samples collected in 2 sampling points from Ebro river related to industrial areas (sampling period: 1998-2001).

COMPOUND	SAMPLING POINT 1	SAMPLING POINT 2
o,p'-DDE	0-4.0	0-0.4
p,p'-DDE	12.0-38.2	4.0-18.0
o,p'-DDD	5.0-56.0	5.0-20.0
p,p'-DDD	19.0-118.0	15.0-99.0
o,p'-DDT	0-375.3	11.4-63.0
p,p'-DDT	13.0-3896.7	82.0-1578.0
HCHs	0-149.2	0-5.5
3 PCBs (BCR)	8.4-214.1	1.0-93.3
PAHs	92-979	71-2491

units in ng/g

Figure 1. HRGC/HRMS profile related to the analysis of PCBs in a sample from Llobregat river.

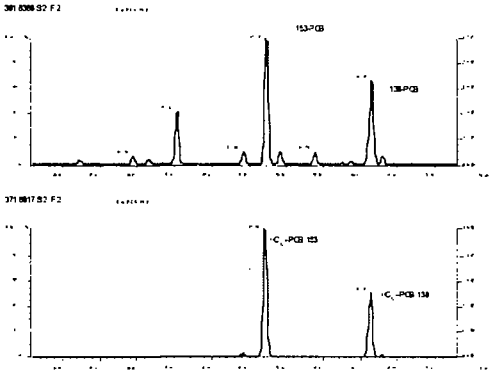


Figure 2. HRGC/HRMS profile of HCHs found in a sample from Besòs river basin.

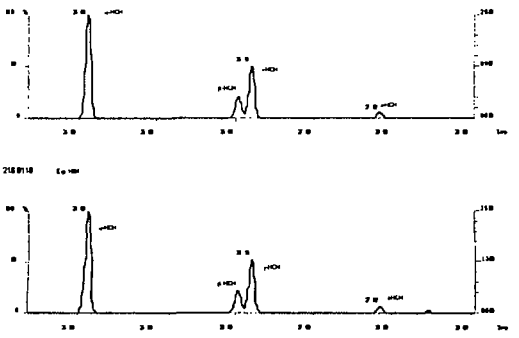
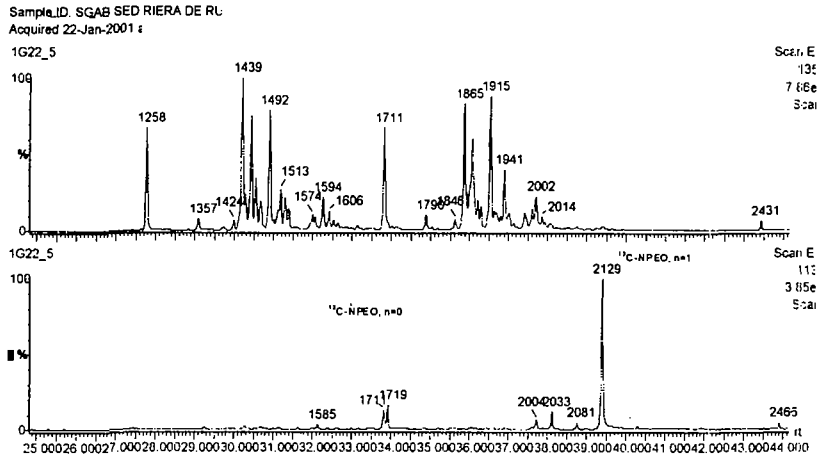


Figure 3. HRGC/MS profile related to the analysis of NPnEO (n=0,1) in a sample from Llobregat river.



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