PCDD/Fs AND PCBS IN SEDIMENTS FROM THE SPANISH NORTHERN ATLANTIC COAST

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Introduction

Persistent Organic Pollutants (POPs) have become of increasing concern at a global scale due to their potential risk to cause adverse effects, to bioaccumulate through the food chain, to persist in the environment or to be transported across long distances. Different international instruments and agreements have resulted from this issue with the aim to protect human health and the environment [1,2]. Most of these POPs consist of chemical substances which are not produced and used any longer, or by-products unintentionally released during some industrial processes that, once in the environment they can enter the aquatic systems via atmospheric deposition, river input and point sources and due to their hydrophobic nature and high partition coefficients, PCBs and PCDD/Fs strongly adsorb to suspended and bottom sediments, which act both as a sink and a source of contamination to benthic organisms entering this way the food webs.[3]

There is clearly a need to identify and quantify levels of POPs in the environment by monitoring them in sediments, which act as indicators of the different anthropogenic pressures to the environment for long periods of time, in order to gain insight of the current status and a base for further evaluation of the efficiency of the control instruments. Little information is there available regarding POPs in sediments from the Spanish Northern Atlantic Coast [4,5,6] and specially, regarding polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs) there is no available reference in any environmental matrix. Bearing this in mind, the aim of this work is to carry out a preliminary survey to provide background concentrations of PCDD/Fs, dioxin-like and marker PCBs in Spanish northern coastal sediments, sampled in the Cantabria region, and to compare them with reported values for coastal sediments from other low contaminated areas and with sediment quality guidelines.

Materials and methods

Surface coastal sediments (0-10 cm) were collected from six sites located at the estuaries of Asón River (Santoña Site), Pas-Pisueña River (Mogro Site) and Nansa River (Tina Menor Site), in the Cantabrian region, on the Northern Atlantic Spanish Coast. Physico-chemical characterization of sediments was carried out in order to determine organic matter and the fines fraction (< 63 µm).
Analytical methodology was based on Soxhlet extraction with toluene after samples spike with 15 ^{13}C-PCDD/Fs and 12 ^{13}C-dl-PCBs to check the recoveries. The fractionation and clean-up was carried out in an automated solid phase extraction (SPE) Power-Prep™ System (FMS, Inc, MA, USA) through a multilayer silica column, then a basic alumina and finally a PX-21 active carbon column. Instrumental analysis was performed according to EPA method 1613 by HRGC-HRMS by means of a TRACE GC Ultra™ gas chromatograph coupled to a DFS high-resolution magnetic sector mass spectrometer (Thermo Fisher Scientific, Bremen, Germany) set at a resolution of 10 000. Quantification was done according to the isotope dilution technique. Final results were expressed in WHO_{1998}-TEQ. Average recoveries were 80% ±18 for 15 $^{13}C_{12}$-labelled 2,3,7,8-PCDD/Fs congeners and 78% ±18 for 12 $^{13}C_{12}$-labelled PCBs. Blanks covering the whole analytical methodology were included showing that congeners were either not detected or below limit of detection. Matrix spike was carried out to check the analytical performance by addition of known quantities of EPA 1613-PAR standard.

Results and discussion:

Sediment was characterised by a low total organic carbon content (TOC) (mean 1.4% ±0.5), a higher organic matter content (mean 7.1% ±2.1) and a low fine fraction (<63µm) (mean 6.5% ± 4.1).

All the studied PCBs congeners were detected in the analyzed samples, showing their ubiquity in coastal sediment samples from Northern Spain. Marker PCBs ranged from 406.8 pg/g dry-weight (d.w.) to 3752.5 pg/g d.w., as it can be seen in Table 1, with a uniform congeners distribution at all sites and a clear predominance of PCB 153, PCB 138, which are the most abundant congeners in commercial PCBs products (Aroclor 1260).

Table 1. Average PCDD/Fs and PCBs levels in sediments in a dry weight basis.

	PCBs			PCDD/Fs		
	$\sum_6$ marker PCBs (pg/g)	**$\sum_{12}$ Dl-PCBs (pg/g)**	**$\sum_{12}$ Dl-PCBs (WHO-TEQ pg/g)**	**$\sum_{17}$PCDD/Fs (pg/g)**	**$\sum_{17}$ PCDD/Fs (WHO-TEQ pg/g)**	***WHO-TEQ$_{Dl\text{-}PCBs+PCDD/Fs}$***
Santoña Site	406.8	155.35	0.12	1.77	0.07	0.19
Mogro Site	3752.55	643.25	0.15	0.83	0.05	0.2
Tina Menor Site	2130.75	388.6	0.27	2.59	0.1	0.37

In general, regarding dioxin like compounds $\sum_{17}$ PCDD/Fs concentrations were lower than those of $\sum_{12}$ dl-PCBs in all analysed samples. Mean concentrations of $\sum_{17}$ PCDD/Fs ranged from 0.83 pg/g d.w. to 2.59 pg/g d.w. and on average PCDDs contributed about 65 % to the total amount of $\sum_{17}$ PCDD/Fs. The congener pattern of PCDD/Fs in sediments is shown in Figure 1 and it was characterized by a clear predominance of OCDD, contributing on average 54 % to the total $\sum_{17}$ PCDD/Fs concentrations. OCDD is known to be present in high proportions in sewage sludge, is the main congener in most air samples and it is also an impurity in technical pentachlorophenol which in general it characterizes a typical environmental sink profile in different media [7,8]. $\sum_{12}$ dl-PCBs was in the range 155.3 pg/g d.w. to 643.3 pg/g d.w. A typical pattern in sediments was found in coastal samples from northern Spain for dl-PCBs, where PCB 118 presented the highest contribution of nearly 63 % on average, followed by PCB 105 (17%), a profile which is in agreement with other reported studies[9]. Dl-PCBs and marker PCBs concentrations are well correlated (R^2=0.90) showing possible common sources, which might be attributable based on the profiles to the use of commercial PCB mixtures in electric transformers and other applications rather than from combustion sources.

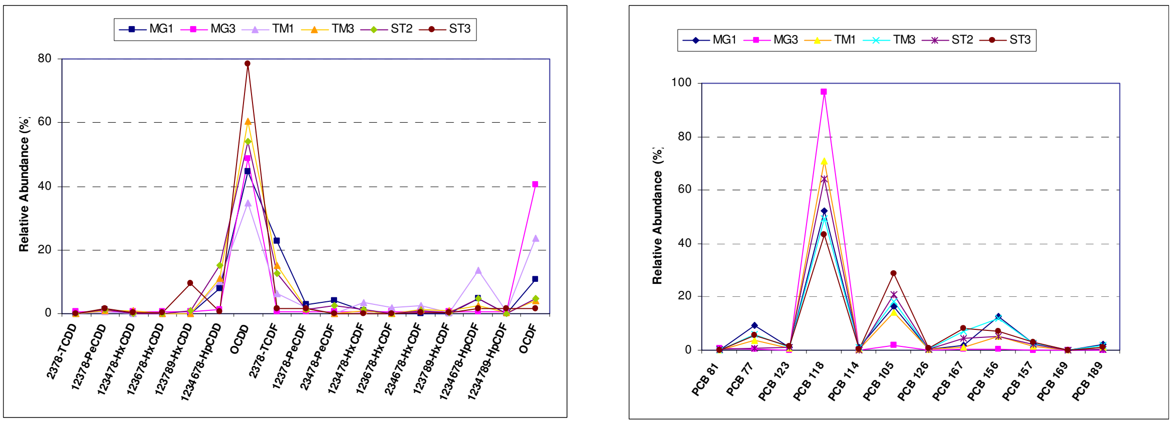

Figure 1. Percentage PCDD/Fs and dl-PCBs contribution of homologues to the $\sum_{17}$PCDD/Fs and $\sum_{12}$dl-PCBs in sediments.

PCDD/Fs and dioxin-like toxicity was in the range 0.19 – 0.37 pg WHO_{1998}-$TEQ_{dl\text{-}PCBs+PCDD/Fs}$/g d.w. However, dl-PCBs constituted by far the largest proportion of the toxic equivalent with 75% of the total WHO_{1998}-$TEQ_{dl\text{-}PCBs+PCDD/Fs}$, and indicating that a complete characterization of the TEQ values for sediments requires to consider not only dioxins and furans but also dioxin-like PCBs.

$\sum_{17}$PCDD/Fs and $\sum_{12}$dl-PCBs concentrations in sediments were compared with national guidelines and quality standards that have been developed in other countries (Table 2). Mean sediment quality guideline quotients were calculated taking into account the 3 families of contaminants, showing no exceedance of screening values for marine sediments at any stations meaning no ecotoxicological risk.

Table 2. Environmental quality criteria for PCDD/Fs, dl-PCBs and marker PCBs in marine sediments issued by different authorities and countries and comparison with the detected concentrations in Northern Spain (Cantabria region)

Pollutant	This work	Norway					Italy	Canada	
		Background	Class II	Class III	Class IV	Class V	EQS	TEL	PEL
WHO_{1998}-TEQ PCDD/Fs/dl-PCBs[a]	0.08 – 0.52	<10	10-30	30-100	100-500	>500	1.5	0.85	21.5
∑ marker-PCBs[b]	0.385 – 4.0	<5	5-17	17-190	190-1900	>1900	4*	21.5*	189*

[a] pg/g d.w.; [b] ng/g d.w.; * Total PCBs

Furthermore, an evaluation of background levels from the North-East Atlantic Coast allowed to define a baseline concentration of around 1 pg/g total WHO_{1998}-TEQ in coastal sediments. Data obtained in this study compare well with levels reported for the near Atlantic Coast in France and Belgium. However, relative higher concentrations have been reported for the Gulf of Bothnia (0.97 – 64 pg I-TEQ/g d.w.), Swedish Coasts (0.8 – 82.2 pg I-TEQ/g d.w.) or in the Baltic Sea(5.56 – 50 pg I-TEQ/g d.w.)[8,10,11,12]

To conclude, PCDD/Fs and dl-PCBs have been reported for the first time in sediments from the Spanish Northern Atlantic Coast, getting background concentrations, and marker PCB levels have been surveyed at new sites never studied before also in the Cantabria region.

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