PRESENCE OF ORGANOCHLORINE POLLUTANTS IN DATED AND RECENT SEDIMENTS FROM FLUVIAL-ESTUARINE SYSTEM OF HUELVA

Gómara B[1], Abad E[2], Rivera J[2], and González MJ[1]

[1] Instrumental Analysis and Environmental Chemistry Department, General Organic Chemistry Institute, CSIC. Juan de la Cierva 3, 28006 Madrid, Spain.
e-mail: bgomara@iqog.csic.es
[2] Laboratory of Mass Spectrometry, Ecothecnologies Department, IIQAB, CSIC. Jordi Girona 18-26, 08034 Barcelona, Spain.

Introduction

Organochlorine compounds such as PCDDs, PCDFs, PCBs as well as DDTs are well known as toxic and persistent contaminants that are associated with water particles in aquatic ecosystems due to their lipophilic character. This fact makes that the main removal process of persistent organochlorine pollutants (POPs) from aquatic systems was sedimentation [1]. In recent years there has been an increasing concern for these chemicals mainly due to their estrogenic properties that affect to the individuals living in aquatic ecosystems.

The estuary of Tinto-Odiel Rivers, located in the Southwest of Spain, with a high variety of inputs from industrial, mine and agricultural activities in its surroundings [2], is one of the estuarine systems at the confluence of the Atlantic Ocean and the Mediterranean Sea. This area is a very important rearing zone of marine species and some of those zones were given official protections by local institutions. There are a variety of papers studying the influence of anthropogenic activities in the chemical contamination of the sediments. But any of them have studied the influence and possible contribution of natural contamination to the total pollutant levels found in them

The present study shows the levels and profiles of 23 PCB congeners (including the most persistent, abundant and toxic), the seventeen 2,3,7,8-substituted PCDD/Fs and DDTs (including, *p,p'*-DDT and its two main metabolites, *p,p'*-DDE and *p,p'*-TDE) in surface and dated sediments along the Tinto and Odiel River basins. The influence of natural and anthropogenic contamination in the mentioned POPs in the sediments of the area has been evaluated.

Materials and Methods

Samples were collected superficially in five different points along the Tinto and Odiel River basins as it is showed in Figure 1. One more location was used as control, where two different samples were obtained one of them from the surface and the other dated approximately two hundred years ago. All samples were dehydrated at 60 ºC along five days, homogenized and stored at room temperature until analysis.

The procedure used for sample preparation briefly consists on a Soxhlet extraction of the sediment samples spiked with a mixture containing 15 $^{13}C_{12}$-labeled 2,3,7,8-substituted PCDD/Fs and $^{13}C_{12}$-labeled non-*ortho* PCBs 77, 126 and 169, followed by a clean-up of the extracts using two columns of neutral silica and silica modified with sulphuric acid and potassium hydroxide. Supelclean™ Envi-Carb® SPE cartridges were used for the fractionation of the different families of compounds, as described elsewhere [3], obtaining three different fractions. The first one contained *ortho* PCBs and DDTs, the second one corresponded to non-*ortho* PCBs and the last one to PCDD/Fs.

Final determination of PCDD/Fs was carried out using GC-HRMS on a GC 8000 series (Carlo Erba Instrument, Milan, Italy) coupled to an Autospec Ultima mass spectrometer (MS) (Micromass, Manchester, UK) [4]. PCB congeners were analyzed by GC with two different detectors, ITD (MS/MS) (GC 3800 coupled with Saturno 2000, Varian, CA, USA) for no-*ortho* PCBs (congeners 77, 81, 126 and 169) [5] and micro-ECD (Agilent 6890 Series II, PA, California, USA) for the rest of PCB congeners investigated (PCBs 28, 52 , 95, 101, 105, 114, 118, 123, 132, 138, 149, 153, 156, 157, 167, 170, 180, 183, 189 and 194), *p,p'*-DDT, *p,p'*-DDE,and *p,p'*-TDE [6].

Results and Discussion

PCB, DDT, and PCDD/Fs concentrations obtained for all the sediments analyzed are show in Table 1, expressed in ng or pg per g of dry weight sediment (d.w.). Whit regard to DDTs, calculated as the sum of *p,p'*-DDT, *p,p'*-DDE and *p,p'*-TDE, a decrease in the concentration from the upper part of the two rivers (sampling points 2, 3, and 4) to the mouth (sampling points 2, 3 and 4) were found, showing the highest concentration of DDTs in sediments located in point 2 (5.1 ng/g d.w.). Sediments sampled upstream of industrial area (sampling point 1) presented the lowest concentrations (0.94 ng/g d.w.) which it is far away from industrial activities. DDTs Concentration found in control dated sediment (1.8 ng/g d.w.) was lower than that found superficially in the same geographical localization (3.7 ng/g d.w.).

Regarding PCBs, the highest concentration was found in sampling point 2 (53 ng/g d.w.) followed by point 4 (36 ng/g d.w.) and point 3 (19 ng/g d.w.). All these sampling points are located near industrial activities. On the other hand, sampling points 1 and 5 presented the lowest PCB concentrations (1.4 and 3.3 ng/g d.w., respectively). As in the case of DDTs, those results could be related to the fact that sampling point 1 are located upstream and far away from the most important industrial activities in the area and sediments from sampling point 5 were collected in the mouth of the two rivers, where there is a water interchange with the sea. PCB concentrations found in control sediment sample collected both superficially and dated (12 and 16 ng/g d.w., respectively) were within the interval found in the other sample stations. PCB profiles (calculated as the percentage of contribution of each individual congener to the total of PCB concentrations) of control sediments (dated and surface sediments) and points 2, 3,and 4 were similar to Arochlor 1260 profile, while PCB profiles found in sampling points 1 and 5 were different with a high contribution of lower chlorinated congeners. With regard to non-*ortho* substituted PCBs (the most toxic ones) a decrease in the concentrations along both rivers from control to sampling point 5 were observed. As was happened for total PCBs, the non-*ortho* PCB levels found in dated sediments were very similar to point 1 and they were lower than the rest of the sediment samples studied. Among the three non-*ortho* PCBs, PCB 77 was the most abundant congener (≈75 %) followed by PCB 126 (≈25 %).

In all sampling points, PCDD concentrations were higher than those of PCDFs. It is important to note that dated control samples jointly with sampling points 1 and 5 showed the highest PCDD/F concentrations, just the contrary of what happened for PCB and DDT concentrations. The high PCDD/F concentrations found in dated sediment could probably indicate that dioxins could also be naturally produced in the environment, as it was suggested by other authors [7]. OCCD showed the highest contribution to 2,3,7,8-PCDD/F in all sediments investigated.

PCB and DDT concentrations found in sediment from Tinto-Odiel estuary were higher than those found in sediments from west coast of Sri Lanka (PCB concentrations ranged from 0.45 to 4.4 ng/g d.w. and DDTs from 0.09 to 1.6 ng/g d.w.) [8] and Kara Sea in Russia (PCBs: 0.41±0.34 ng/g d.w. and DDTs: 0.44±0.30 ng/g d.w.) [9] but they were far below from concentrations obtained in Tamar River estuary in Tasmania (PCB concentrations ranged from 459 to 2681 ng/g d.w. and DDTs ranged from 2.2 to 12.8 ng/g d.w.) [10]. PCDD/Fs mean concentrations found in all the sediments investigated in the present study showed higher levels than those found in Kara Sea [9].

As conclusion, significant differences among levels and profiles were found in the sediments studied. The PCDD/F concentrations found in dated sediments were higher than those found in recent ones, while the opposite happened with the rest of the POPs investigated. Concentration of the families of POPs investigated were in most of the cases higher than those found in sediments from different aquatic ecosystems studied by other authors.

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Figure 1. Localisations of the sampling points along Tinto and Odiel River basins.

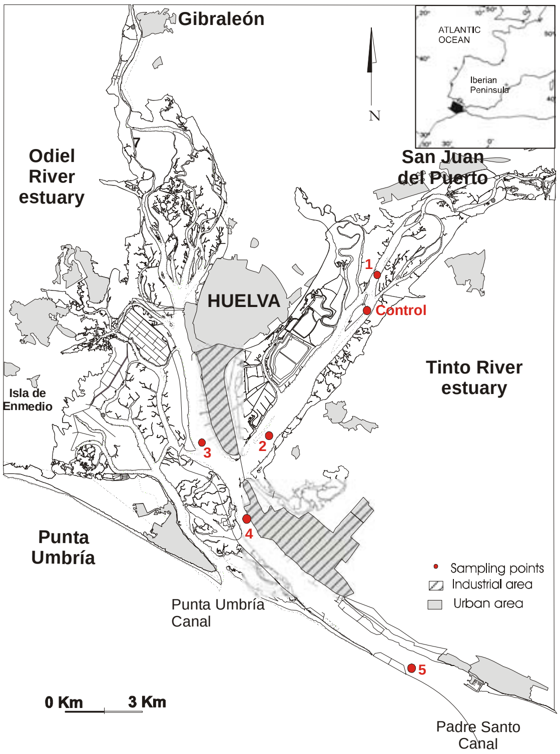

Table 1. PCB, DDT and PCDD/F concentrations (ng/g sediment) of the different sediments analyzed.

Congener	Control (DATED)	Control (RECENT)	S.P.1	S.P.2	S.P.3	S.P.4	S.P.5
			ng/g sediment				
DDE	0,68	2,2	0,33	2,5	2,8	2,4	0,34
TDE	0,46	0,50	0,14	1,1	0,96	0,49	0,13
DDT	0,69	1,0	0,47	1,5	1,1	1,0	0,48
∑DDTs	***1,8***	***3,7***	***0,94***	***5,1***	***4,8***	***3,9***	***0,96***
28	0,13	0,36	0,11	0,46	0,36	0,35	0,62
52	0,10	0,42	0,12	1,1	0,88	0,42	0,22
95	0,53	0,73	0,13	2,3	1,3	1,4	0,35
101	0,91	0,86	0,21	2,9	1,5	1,8	0,48
123+149	1,8	1,2	0,13	5,8	1,7	3,7	0,20
118	0,15	0,33	0,09	0,70	0,72	0,66	0,27
114	0,02	0,03	ND	0,17	0,04	0,06	0,01
153	2,7	1,7	0,16	8,2	2,9	6,3	0,32
132	0,62	0,38	0,01	2,2	0,62	1,3	0,06
105	ND	0,09	0,03	ND	0,27	ND	0,10
138	2,4	1,7	0,17	8,2	2,8	5,7	0,36
183	0,59	0,24	ND	1,5	0,51	1,2	ND
167	0,02	0,01	ND	0,11	0,07	0,10	ND
156	0,40	0,28	0,03	1,2	0,46	0,90	0,05
157	0,06	0,03	ND	0,26	0,11	0,19	ND
180	3,8	1,9	0,13	11	3,2	7,9	0,15
170	1,1	0,73	0,03	4,1	1,1	2,3	0,04
189	0,04	0,05	0,01	0,14	0,04	0,08	0,03
194	0,95	0,50	0,01	2,9	0,89	1,8	0,01
∑ortho *PCBs*	***16***	***12***	***1,4***	***53***	***19***	***36***	***3,3***
			pg/g sediment				
81	ND	0,57	0,04	ND	ND	ND	0,22
77	8,8	62	5,5	37	29	16	12
126	1,8	5,7	1,3	8,3	9,9	8,5	0,49
169	ND	0,68	ND	0,81	0,41	ND	ND
∑non*-ortho *PCB	***11***	***69***	***6,8***	***46***	***39***	***25***	***13***
2378 TCDF	1,2	19	5,9	1,7	1,2	5,5	0,08
12378 PeCDF	0,33	5,1	0,75	0,47	0,37	0,90	0,02
23478 PeCDF	0,43	7,1	1,5	1,1	0,86	2,2	0,04
123478 HxCDF	0,92	12	1,5	1,2	0,81	1,7	0,05
123678 HxCDF	0,40	4,6	0,54	0,46	0,32	0,56	0,02
234678 HxCDF	0,45	4,1	0,66	0,54	0,38	0,78	0,02
123789 HxCDF	0,14	0,30	0,06	0,08	0,09	0,14	N.D.
1234678 HpCDF	3,5	13	2,5	1,7	1,2	2,6	0,05
1234789 HpCDF	0,36	1,2	0,29	0,20	0,11	0,35	0,01
OCDF	14	6,6	9,2	2,3	1,5	8,9	0,12
2378 TCDD	0,08	0,42	0,13	0,06	N.D.	N.D.	N.D.
12378 PeCDD	0,18	0,65	0,18	0,12	0,11	0,15	N.D.
123478 HxCDD	0,17	0,38	0,24	0,06	0,07	0,16	N.D.
123678 HxCDD	1,3	0,74	0,87	0,52	0,35	0,72	0,02
123789 HxCDD	1,2	1,3	0,71	0,75	0,55	0,79	0,03
1234678 HpCDD	24	5,8	19	3,6	2,5	17	0,15
OCDD	228	61	192	28	19	206	1,3
∑PCDFs	***21***	***72***	***23***	***9,7***	***6,8***	***24***	***0,41***
∑PCDDs	***255***	***71***	***214***	***33***	***22***	***225***	***1,5***
∑PCDD/Fs	***276***	***143***	***237***	***43***	***29***	***249***	***1,9***