# ASSESSMENT OF THE TOXIC POTENCY OF PCDDs, PCDFs AND PCBs IN MARINE SEDIMENTS FROM CATALONIA, SPAIN

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***Introduction***

From the late 1970s to the present, a great deal of emphasis has been placed on the analysis of PCDDs and PCDFs. Recently, special attention has been focused on a few selected PCB congeners which are stereo-chemically similar to 2378-TCDD and have toxicological properties similar to 2378-TCDD. These congeners are potent inducers of liver microsomal aryl hydrocarbon hydroxylase (AHH) and are thus referred to as dioxin-like PCBs. The WHO has identified 12 PCBs as being similar in toxicity to PCDDs and PCDFs. These dioxin-like PCB congeners are classified according to the number of chlorines in the *ortho*-position: 4 non-*ortho* (IUPAC Nos. 77,81,126 and 169) and 8 mono-*ortho* (IUPAC Nos. 105,114,118,123,156,157,167 and 189)[1]. All of these twelve congeners, as well as the 17 toxic PCDD/F congeners, have an assigned WHO-TEF.

The contribution of each contaminant to the total toxicity of environmental samples depended on the relative order of potency along with the contamination levels in the environment. Dioxins are the most potent contaminants, however their levels in sediments and sludge were lower than those presented by other POPs, such as PCBs or PCNs. For this reason, greater toxicity contributions of less potent contaminants with higher concentrations could be found.

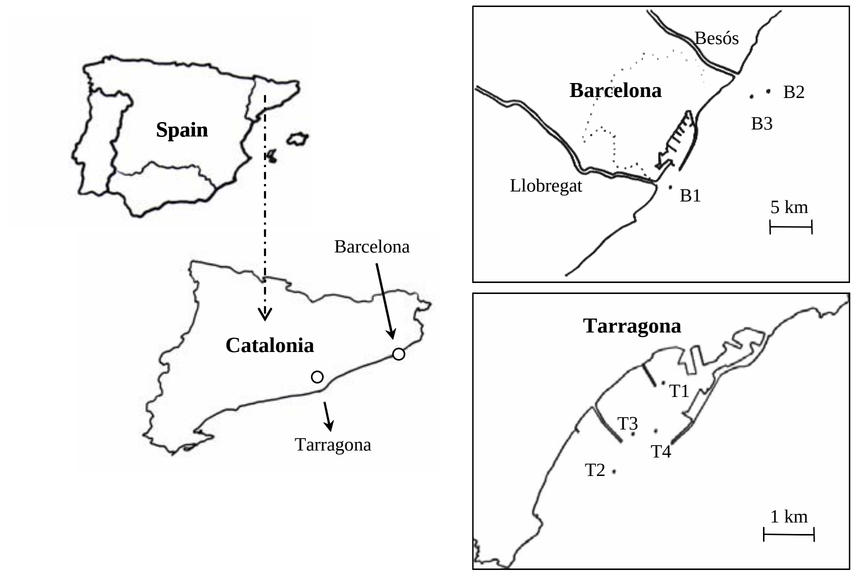
The aim of this study was to determine the dioxin-like PCB levels in sediments and sewage sludge from Spain, and to compare them with the PCDD and PCDF concentrations in order to evaluate the contribution of each contaminant in the total toxicity of the samples. Further objectives were to assess the effects of PCDDs and PCDFs in sewage sludge discharged into the sea, as well as to correlate data obtained with quality objectives.

***Methods and Materials***

A total of 10 samples of marine sediments and 3 samples of sewage sludge was analyzed. Sediment samples were collected from several hot spots on the Spanish coast, such as the harbors of Tarragona and the mouths of the Besós and Llobregat rivers. Sampling sites are shown in Figure 1.

A generic analytical procedure based on Soxhlet extraction followed by an automated cleanup system[2] and gas chromatography-ion trap-mass spectrometry[3] was employed for determining the toxic congeners of PCDDs and PCDFs, as well as dioxin-like PCBs in sediment and sewage sludge samples. Analysis were carried out on a CP-3800 gas chromatograph equipped with a CP-8200 autosampler, coupled with a Saturn 2000 ion trap spectrometer where Saturn 5.2 software version was used. Ion-trap parameters were adjusted to work in tandem MS/MS. Two instrumental methods were developed: one for PCDD/Fs and other for PCBs.

**Figure 1: Map of the studied areas showing the locations of the sampling sites**




***Results and Discussion***

Table 1 provides PCDD, PCDF and dioxin-like PCB results of the sediment and sludge samples analyzed. The recovery of the $^{13}$C-labeled compounds in all cases ranged from 72.1 to 92.3% for PCDD/Fs and from 89.9 to 107.3 for PCBs, indicating that the extraction and cleanup procedures worked properly. Total toxicity equivalent (WHO-TEQ) values were calculated using the WHO-TEF for dioxin-like PCBs, PCDDs and PCDFs. WHO-$TEQ_{PCDD/F}$ values ranged from 0.06 to 48.29 pg/g, whereas WHO-$TEQ_{PCB}$ values were between 0.24 and 71.05 pg/g. WHO-$TEQ_{PCB}$ contribution varied from 1 to 84%, suggesting that PCB contribution on the toxicity of the samples must be taken into account (Figure 2). Moreover, the analysis revealed the presence of high contamination near the points of sewage sludge discharge.

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**Table 1: Concentrations of PCDDs, PCDFs and dioxin-like PCBs (expressed in pg/g dry weight) in sediment and sewage sludge samples**

| | Llobregat Sediments | | | | Besós Sediments | | Tarragona Sediments | | Sewage Sludge | |
|---|---|---|---|---|---|---|---|---|---|---|
| | **B1a** | **B1b** | **B1c** | **B1d** | **B2** | **B3** | **T3** | **T4** | **Besós** | **Reus** |
| 2378-TCDD | N.D. | N.D. | 0.43 | N.D. | N.D. | N.D. | 0.23 | 0.32 | 0.52 | 1.28 |
| 12378-PeCDD | N.D. | N.D. | N.D. | N.D. | 5.38 | 8.30 | N.D. | 0.70 | 1.77 | 2.60 |
| 123478-HxCDD | N.D. | N.D. | 1.45 | N.D. | 2.93 | 5.32 | 0.60 | 1.51 | 0.77 | 1.33 |
| 123678-HxCDD | N.D. | 1.08 | 6.38 | 5.19 | 19.38 | 26.05 | 1.31 | 4.38 | 4.71 | 5.39 |
| 123789-HxCDD | N.D. | N.D. | 3.29 | 0.88 | 12.85 | 13.85 | 1.00 | 2.97 | 1.53 | 3.19 |
| 1234678-HpCDD | 5.15 | 23.92 | 186.96 | 64.45 | 570.56 | 2493.28 | 10.73 | 47.70 | 123.95 | 59.15 |
| OCDD | 67.17 | 164.86 | 1086.18 | 367.83 | 28769.28 | 17208.65 | 73.65 | 273.31 | 814.09 | 753.24 |
| | | | | | | | | | | |
| 2378-TCDF | N.D. | 1.42 | 6.96 | 1.83 | 8.35 | 8.25 | 0.92 | 1.89 | 6.46 | 3.57 |
| 12378-PeCDF | N.D. | 0.76 | 5.22 | 1.58 | 9.65 | 4.77 | 2.35 | 3.10 | 2.84 | 1.86 |
| 23478-PeCDF | N.D. | N.D. | 4.43 | 1.23 | 14.41 | 5.70 | 0.74 | 2.48 | 3.89 | 2.35 |
| 123478-HxCDF | N.D. | 3.46 | 15.76 | 4.18 | 27.91 | 10.24 | 9.09 | 17.85 | 4.15 | 4.36 |
| 123678-HxCDF | N.D. | 1.87 | 4.67 | 1.83 | 12.10 | 12.63 | 2.01 | 6.24 | 2.82 | 3.12 |
| 234678-HXCDF | N.D. | 2.79 | 6.73 | 2.62 | 20.21 | 13.89 | 3.34 | 3.90 | 4.63 | 3.33 |
| 123789-HxCDF | N.D. | N.D. | 1.85 | N.D. | 6.69 | 2.63 | 1.38 | 2.94 | 1.94 | 2.23 |
| 1234678-HpCDF | N.D. | 15.97 | 77.69 | 19.83 | 142.65 | 88.96 | 220.91 | 478.46 | 47.54 | 64.72 |
| 1234789-HpCDF | N.D. | 1.99 | 8.35 | 3.06 | 14.55 | 6.60 | 11.50 | 19.07 | 2.18 | 1.96 |
| OCDF | N.D. | 43.77 | 532.45 | 83.24 | 368.83 | 102.42 | 1356.16 | 2965.16 | 112.47 | 128.53 |
| | | | | | | | | | | |
| PCB # 81 | N.D. | 0.62 | 13.91 | 3.08 | 20.99 | 4.10 | 8.36 | 38.78 | 2.81 | 15.04 |
| PCB # 77 | 13.71 | 33.23 | 1533.30 | 62.18 | 6039.60 | 94.44 | 35.22 | 237.34 | 70.45 | 374.98 |
| PCB # 126 | 0.23 | 1.23 | 19.76 | 1.03 | 33.36 | 5.25 | 78.07 | 612.05 | 2.77 | 29.10 |
| PCB # 169 | N.D. | 0.31 | 9.26 | 0.41 | 2.98 | 1.60 | 0.80 | 1.24 | 2.41 | 7.94 |
| | | | | | | | | | | |
| PCB # 105 | 319.61 | 510.41 | 4065.28 | 305.69 | 3394.61 | 8.64 | 1593.06 | 2585.08 | 1273.50 | 3303.66 |
| PCB # 114 | 34.34 | 57.74 | 320.36 | 29.03 | 225.04 | 0.43 | 98.81 | 82.99 | 135.34 | 77.99 |
| PCB # 118 | 1169.20 | 1911.20 | 1989.70 | 947.79 | 15.21 | 7.88 | 815.70 | 4821.36 | 3967.90 | 3219.09 |
| PCB # 123 | 84.32 | 172.64 | 1158.95 | 87.84 | 1.85 | 1.23 | 84.81 | 405.47 | 1.64 | 203.96 |
| PCB # 156 | 63.41 | 150.51 | 1655.64 | 118.87 | 2149.31 | 0.48 | 493.22 | 679.99 | 731.84 | 635.90 |
| PCB # 157 | 13.86 | 26.86 | 154.76 | 21.52 | 0.68 | 0.24 | 117.74 | 172.73 | 98.41 | 313.84 |
| PCB # 167 | 25.89 | 59.72 | 501.57 | 50.64 | 0.68 | 0.30 | 247.79 | 211.07 | 274.87 | 197.17 |
| PCB # 189 | 6.50 | N.D. | 179.20 | 16.21 | 172.87 | 0.38 | 15.00 | 30.16 | 88.37 | N.D. |

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**Figure 2: Percentage contribution to the total WHO-TEQ from PCDDs, PCDFs, non-*ortho* and mono-*ortho* PCBs.**