

LEVELS IN ABIOTIC COMPARTMENTS

TOXICITY ASSESSMENT OF CONTAMINANT MIXTURES IN SEDIMENTS OF THE BAIONA LAGOON, RAVENNA, ITALY

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Introduction

In November 1999, a sediment core was sampled in the Piailassa Baiona, a coastal lagoon of the Northern Adriatic Sea. The lagoon is part of the ecosystem of the Po River delta and is included in the Ramsar list. The Piailassa Baiona lagoon covers an area of 10 km² and is formed of a number of small ponds (average water depth 60 cm) and of deeper distributary channels in a herring-bone arrangement. The lagoon is connected to the sea through the harbour channel of Ravenna.

The toxicity of sediments (TEQs) for 2,3,7,8-substituted PCDD/Fs isomers and 12 dioxin-like PCBs were calculated by the sum of the products of their concentrations with the appropriate WHO-TEF, an approach widely applied for better understanding of the potential toxicity of PCDD/Fs and PCBs.

Recent works have also studied and evaluated the dioxin-like toxicity of HCB and PAHs. Inclusion of HCB in the TEF approach for assessing health hazards from mixtures of TCDD and dioxin-like compounds were proposed by van Birgelen¹ and were considerable reasonable in an investigation by the Agency for Toxic Substances and Disease Registry².

Toxicity assessment of PAHs was based on 3 different approach, which identified the role of PAHs in dioxin-like activity and established TEFs for some compounds. Willett et al.³ determined the induction potency of PAHs with respect to 2,3,7,8-TCDD in rat hepatoma H4IIE cells. Clemons et al.⁴ examined the ability of PAHs to induce AhR-mediated luciferase activity in mouse hepatoma cells. Klimm et al.⁵ determined TEFs for PAHs by comparing the induction of EROD activity by PAH standards with those of a 2,3,7,8-TCDD standard.

Total toxicity values were calculated in order to evaluate the contribution of each contaminant in the environment.

Materials and Methods

A 65-cm sediment core was collected in November 1999 from the Magni pond in the Piailassa Baiona. Sub-samples from the upper part of the cores were thinner (1-cm) than those of the bottom part (8-cm). Sample levels were recalculated considering a coefficient of compaction. At this site, Matteucci et al.⁶ estimated the sedimentation rate as 0.36 ± 0.04 cm y⁻¹ and the thickness of the sediment investigated was deposited presumably in the last 150 years.

Sediment samples were transported to the laboratory on ice and stored at 4°C before analysis. In the laboratory, they were thoroughly mixed with a stainless steel spatula, and 10.0±0.1-g sub-samples were transferred to glass beakers. They (10.0±0.1g) were first spiked with a series of 15 ¹³C₁₂-labeled 2,3,7,8 PCDD/F (EDF8999), 12 ¹³C₁₂-labeled PCB (EC4937), ¹³C₁₂-HCB (CLM351) substituted isomers, and 5 deuterated PAHs (Acenaphthene-D10, Chrysene-D12, Naphtalene-D8, Perylene-D12, Phenanthrene-

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D10) as internal standards, mixed with Spe-ed Matrix. Extraction by ASE 200 (DIONEX, Sunnyvale, CA) was performed with 50 mL of n-hexane/dichloromethane 50/05 at 150 °C, 1500 psi, 7 min. heat-up, and 2 cycles of 10 min static time. Extracts were transferred to hexane before clean-up treatment.

Sample extracts were first spiked with $^{37}\text{C}_4$ -labeled 2,3,7,8 PCDD (EDF6999) and 3 $^{13}\text{C}_{12}$ -labeled PCB (EC4978), and then cleaned using the automatic system, Dioxin Prep (Fluid Management System Inc.). Pre-packed disposable columns containing multilayer silica and sodium sulphate were used for PAH clean-up. After PAH analysis, extracts were treated with sulphuric acid (98 %) and potassium hydroxide (20 %) in a 100-mL separatory funnel, and then cleaned using the automatic three-column system with pre-packed disposable columns containing multilayer silica, alumina and carbon for PCDD/F, PCB and HCB.

HRGC/HRMS analyses were conducted using a HP 6890 plus gas chromatograph coupled to a Micromass Autospec Ultima mass spectrometer, operating in EI mode at 35 eV and with a resolution of 10.000 (5 % valley).

Quantitative determination of PCDD-Fs, PCBs, HCB and PAHs was performed by isotope dilution methods, using relative response factors previously obtained from standard solution injections⁷⁻⁸.

All solvents (n-hexane, dichloromethane, acetone, toluene, ethylacetate, benzene) were pesticide-free reagent-grade (Carlo Erba, Milan). Two preparation/reagent blank samples, two duplicate samples and two duplicate matrix spike samples were prepared for each analytical batch, consisting of approximately 30 samples.

Results and Discussion

TEQ values referring to PCDD/Fs ($\text{TEQ}_{\text{PCDD/Fs}}$) and PCBs (TEQ_{PCBs}) varied from 0.09 to 53.3 pg g^{-1} dw and from 0.01 pg g^{-1} to 17.3 pg g^{-1} dw, respectively. The total WHO-TEQ values ($\text{TEQ}_{\text{PCDD/Fs}} + \text{TEQ}_{\text{PCBs}}$) ranged between 0.1 to 59.0 pg g^{-1} of dw (Fig. 1, Table 1) and exceeded the safe sediment value of 20 pgTEQ g^{-1} dw⁹ above 13.5 cm depth (from the mid-1960s).

Total WHO-TEQs discriminated 2 peaks from the 1970s to the late 1980s (3.5-11 cm) and in the late 1990s (0-2.5 cm). In the former, $\text{TEQ}_{\text{PCDD/Fs}}$ accounted for 90 % of the total WHO-TEQ, and in the latter for 68 %, with a great increase in PCB toxicity (Fig.1). The higher peak was characterised not only by the highest TEQ_{PCB} value but also by an increase in the $\text{TEQ}_{\text{PCDD/F}}$ values, mainly due to the highest concentrations of 2,3,7,8-TCDF and 2,3,4,7,8-PCDF.

Table 1 also lists the TEQ values for HCB, which accounted for lower toxicity (<04 pgTEQ g^{-1} dw), and TEQ_{PAHs} .

Applying the TEFs proposed by Willett et al.³, the principal contributors to TEQ_{PAHs} were benzo[b]fluoranthene, benzo[k]fluoranthene indeno[1,2,3cd]pyrene, with average percentages of 25 %, 26 % and 43 % respectively. Applying the TEFs of Clemons et al.⁴, benzo[b]fluoranthene and chrysene accounted for 78 % and 16 %, respectively; and those of Klimm et al.⁵, benzo[b]fluoranthene, benzo[a]pyrene and indeno[1,2,3cd]pyrene accounted for 12 %, 31 %, 30 % and 26 %, respectively. However, in all cases, TEQ_{PAHs} were one or more orders of magnitude higher than $\text{TEQ}_{\text{PCDD/Fs}} + \text{TEQ}_{\text{PCBs}}$. The lower TEQ_{PAH} values were obtained by applying the TEFs of Klimm et al.⁵ (8-36 times higher $\text{TEQ}_{\text{PCDD/Fs}} + \text{TEQ}_{\text{PCBs}}$), followed by those of Willett et al.³ (57-342 times higher $\text{TEQ}_{\text{PCDD/Fs}} + \text{TEQ}_{\text{PCBs}}$). Lastly, the highest values were obtained by applying the TEFs of Clemons et al.⁴ (199-2595 times higher $\text{TEQ}_{\text{PCDD/Fs}} + \text{TEQ}_{\text{PBC}}$).

TEQ_{PAH} results turned out to differ considerably according to the various approaches, and to be consistent with other recent works for marine sediments in various environments, with the marked contribution of PAHs to dioxin-like activity in sediments^{10, 11, 12, 13}.

In conclusion, the Piallassa Baiona contains heavily contaminated sediments. The TEQ approach highlighted the importance of the contribution of other contaminants (especially PAHs) and also

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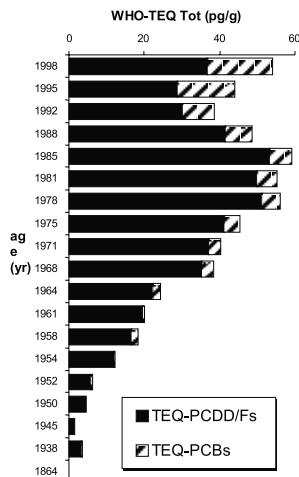


Figure 1. WHO-TEQ contribution of 17 toxic PCDD/F congeners and 12 dioxin-like PCBs.

Table 1. Contributions of WHO-TEQ, TEQ_{HCB} and TEQ_{PAHs} for various approaches.

Sample levels cm	Time interval yr	Total WHO-TEQ	HCB-TEQs (van Birgelen ¹)	PAHs-TEQs (Willet et al ³)	PAHs-TEQs (Clemons et al. ⁴)	PAHs-TEQs (Klimm et al. ⁵)
				pg/g		
0-1.2	1997-1999	54.03	0.38	3061	10742	413
1.2-2.5	1993-1997	43.75	0.30	3335	10786	445
2.5-3.5	1990-1993	38.45	0.26	3833	11376	501
3.5-5	1986-1990	48.45	0.22	5356	14683	698
5-6	1983-1986	58.98	0.14	6502	17193	849
6-7	1980-1983	55.18	0.13	6141	16933	813
7-8.5	1976-1980	55.98	0.10	6089	16815	795
8.5-10	1973-1976	45.30	0.08	4946	14293	654
10-11	1970-1973	40.11	0.07	7408	25948	897
11-12	1966-1970	38.16	0.07	4781	14061	596
12-13.5	1963-1966	24.09	0.04	2713	7926	350
13.5-14.5	1959-1963	19.96	0.03	2359	7069	304
14.5-16	1956-1959	18.18	0.04	1990	6370	274
16-17	1953-1959	12.07	0.07	1942	5793	259
17-18	1951-1953	5.99	0.00	1082	3306	138
18-19	1948-1951	4.35	0.00	667	2489	88
19-21	1942-1948	1.36	0.00	350	1466	43
21-23.5	1935-1942	3.34	0.03	417	1470	49
56-64	1825-1843	0.10	0.00	36	270	4

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discriminated three different phases of contamination, as follows:

1. maximum intensity of toxicity due to TEQ_{PAHs} in the early 1970s;
2. increased toxicity and the highest values of $TEQ_{PCDD/Fs}$, from the late 1970s to the mid-1980s;
3. Maximum values of TEQ_{PCBs} and increases in $TEQ_{PCDD/Fs}$ in the late 1990s.

However, other researches are required in order to reveal the toxicity of PAHs, which do not appear to be well calibrated when the various approaches are compared. High values in background levels, deposited before the development of the industrial area, were highlighted, especially using the approaches of Willett et al.³ and Clemons et al.⁴.

Acknowledgements

Ms Gabriel Walton revised the English text. This is IGM-CNR scientific contribution No. 1282

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