

PRELIMINARY BUDGET OF DIOXINS AND DIOXIN-LIKE PCBs IN THE LAGOON OF VENICE

A. Marcomini¹, S. Della Sala², G. Ferrari³, A. Giacometti¹, S. Guerzoni⁴, S. Raccanelli⁵, and R. Zonta⁶

1. Department of Environmental Sciences, University of Venice, Calle Larga S. Marta, 2137; 30123 Venezia (Italy)
2. Autorità Portuale di Venezia, Direzione Ambiente; Zattere, 1401, 30123 Venezia (Italy)
3. Magistrato alle Acque di Venezia, Sezione Antiinquinamento, S. Polo, 19; 30125 Venezia (Italy)
4. CNR-IGM; via Gobetti, 101, 40129 Bologna (Italy)
5. Consorzio Interuniversitario la Chimica per l'Ambiente (INCA), via della Libertà 5/12, 30175 Marghera, Venezia (Italy)
6. CNR-ISDGM; S. Polo, 1364, 30125 Venezia (Italy)

Introduction

Since the finding of high amounts of dioxins in the sediments of the industrial canals of Porto Marghera, spatial and temporal distributions of organochlorinated compounds in the sediments of the whole lagoon were investigated. Moreover, several investigations [1,2] were undertaken to identify past and present, primary and secondary, sources, to characterize transport pathways, to elucidate the effects on the lagoon organisms and to assess the impact of the lagoon contamination on human health through dietary intake. Here we report a preliminary budget of dioxins (PCDD/Fs), dioxin-like PCBs, as well as hexachlorobenzene (HCB) in the whole lagoon sediments. Moreover, the estimated actual loadings from the catchment area drained by the rivers flowing into the lagoon, the total (i.e., dry and weight) atmospheric depositions, the municipal and industrial effluents discharging directly into the lagoon, are also presented.

Table 1

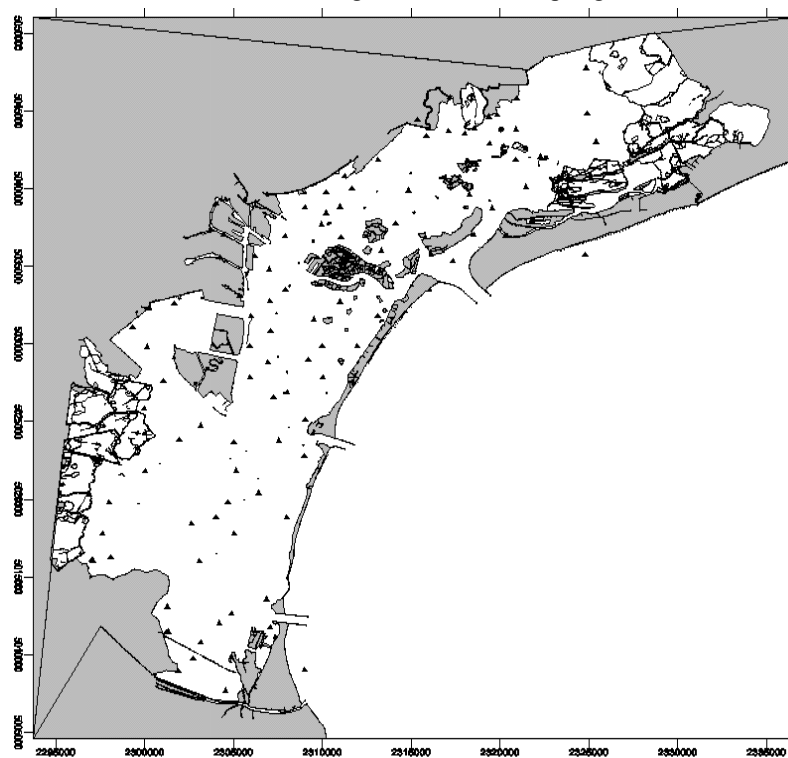
Parameters used for estimating the total dry sediment mass and number of samples analyzed for each type of sediment.

Sediment location	Area (Km ²)	Average depth (m)	Dry fraction (%)	Total dry sediment mass (ton)	Number of samples
North lagoon	110	0.5	65	3.6×10^7	21
Central lagoon	130	0.5	65	4.3×10^7	31
South lagoon	170	0.5	65	5.5×10^7	29
Industrial canals	3.43	3.0	55	5.6×10^6	48
Navigable lagoon canals	21.6	2.0	55	2.4×10^7	31
Urban canals (rii)	1.22	1.0	55	6.8×10^5	8
Total	436	-	-	1.6×10^8	168

Table 2

Quantities of PCDDs, PCDFs, and dioxin-like PCBs (g I-TE) stored in different lagoon sediments.

Sediment location	PCDD/Fs (ng I-TE/ Kg d.w.)	Total PCDD/Fs (g I-TE)	PCBs (ng I-TE/Kg d.w.)	Total PCBs (g I-TE)
North lagoon	2.1±1.8	76±65	1.1±0.9	40±32
Central lagoon	5.9±5.9	254±254	2.2±1.8	95±77
South lagoon	2.7±4.4	149±242	1.0±1.2	55±66
Industrial canals	142±286	799±1612	20±18	113±15
Navigable lagoon canals	2.9±3.0	70±73	0.74±0.94	18±2.5
Urban canals (rii)	16.6±8.1	11±5.5	-	-
Total	-	1359	-	321

Figure 1
Sediment GPS-georeferenced sampling stations.

Materials and methods

Chemicals-All solvents (n-hexane, dichloromethane, acetone, toluene, ethylacetate, benzene) were pesticide free reagent grade (Carlo Erba, Milano). Native and $^{13}\text{C}_{12}$ -labeled PCDD and PCDF standards were purchased from Cambridge Isotope Laboratories, Woburn, MA.

Sampling-The 150 mm top sediment and deeper sediment were sampled in GPS geo-referenced sites (Fig. 1) by using 100 mm i.d. Plexiglas corers. Atmospheric depositions were collected by a bulk sampler similar to that already reported [3]. Five liters, comprised of subsurface and near-bottom waters of river samples, were collected by dimethyldichlorosilanized bottles and sent immediately to the laboratory for analysis.

Procedure-All glassware was washed with basic detergent, rinsed with distilled water, treated with a solution of ammonium persulphate 350 g/L in sulphuric acid (98%) and rinsed twice with distilled water and acetone. Subsequently, the cleaned glassware was treated with dimethyldichlorosilane 5% in toluene, rinsed twice with distilled water and acetone, heated to 300 °C for 3 hrs. and covered with aluminium foil.

Extraction-Within 3 hours from sampling, the wet sediment samples were freeze-dried and then manually ground until a fine powder was obtained, then homogenized, sieved by a stainless steel sieve (2 mm) and stored at 4 °C.

The samples (10g) were firstly spiked with a series of 15 $^{13}\text{C}_{12}$ -labeled 2,3,7,8-PCDD/F substituted isomers as internal standard, and then ASE 200 (DIONEX Sunnyvale, CA) extracted with toluene. The extracts were transferred to hexane before the clean up treatment.

The river water (2-5 L) and the meteoric water (total) samples were spiked with a series of 15 $^{13}\text{C}_{12}$ -labeled 2,3,7,8 PCDD/F substituted isomers as internal standards to deliver 25 pg/ μL in a 10 μL final volume; this concentration is lower than that recommended by the US-EPA (200 ppt in a 20 μL) [4], in order to allow a more realistic estimate of the actual concentration of native analytes, and therefore a better approximation of their behavior during extraction, concentration and chromatographic analysis. The samples were extracted with dichloromethane (4x50 mL) in a 2 L separatory funnel; the extracts were transferred to hexane before the clean up treatment.

Clean up-The sample extracts were treated with sulphuric acid (98%) and potassium hydroxide (20%) in a 100 mL separatory funnel and then cleaned up using the automatic three column system, Dioxin Prep (Fluid Management System Inc.). Pre-packed disposable columns containing multilayer silica, alumina and carbon were used.

Analysis-The 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). Sample injections were performed in the splitless mode on a 60 m Rtx 5 ms column (Restek 0.25 mm ID, 0.25 μm film) and on a 30 m Rtx 200 one (Restek 0.25 mm ID, 0.25 μm film) for verification.

The quantitative determination of PCDD/Fs was performed by an isotope dilution method using relative response factors previously obtained from five standard solutions injections (EDF 9999 Cambridge Isotope Laboratories, Woburn, MA.), as recommended by the US-EPA [4].

At the beginning of each day of analysis, GC/MS system performance was verified for all PCDD/Fs and labeled compounds with the CS3 calibration verification standard and the isomer specificity test standard.

The recoveries were always in the range 50-110%. Reproducibility did not exceed 20%.

Results and discussion

The amounts of PCDD/Fs and dioxin-like PCBs stored in the whole sediment of the Venice lagoon were calculated by summing up (Table 1) the sediment of industrial canals (average depth: 3 m; surface: 3.4 Km²) (A), historical center canals (average depth: 1 m; surface: 1.22 Km²) (B), the shallow sediments of the northern, central and southern lagoon (average depth: 0.5 m; surface: 110, 130, and 170 Km², respectively) (C), and deeper sediments of the navigable canals (average depth: 2 m; surface: 21.6 Km²) (D). The average concentration attributed to the A, C, and D types of sediments was inferred from the results of recent surveys undertaken by the local Water Authority (Magistrato alle Acque di Venezia) as well as by the Port Authority (Sediment A), while the average concentration of urban sediment was taken from Marcomini et al. [5]. The dry sediment density was assumed equal to 1.0 Kg/L according to a sediment survey conducted in the central lagoon [6].

While the local contribution of PCBs to the total I-TE may exceed remarkably that of PCDD/Fs (Marcomini et al. 1999) [7], PCBs account for only ca. 30% of the total I-TE on the whole lagoon sediment. The majority of both PCDD/Fs and PCBs is still stored in the sediment of the industrial canals. The total atmospheric depositions and the river inflow contribute similarly to the actual annual loading of PCDD/Fs (see Tables 3 and 4) whereas the atmospheric deposition of PCBs is significantly higher than that from rivers.

In spite of the scarcity of data for the annual loadings of PCDD/Fs, dioxin-like PCBs, and HCB from industrial and municipal sewage discharged into the lagoon, the few available data seem to indicate that the total load of PCDDs and PCDFs from these sources is in the range of 0.05-0.10 g/year. Assuming the industrial and municipal treated effluents (48×10^9 L/year and 45.5×10^9 L/year, respectively) with a concentration of 0.5 pg I-TE/L, this would result in 0.043 g I-TE/year. Moreover, the municipal sewage of the historical center is discharged into the lagoon, through the urban canals, without any treatment. Because the concentration of dioxins in the feces is 4 pg/g d.w. [8] and because the average amount of feces produced per person is 100 g/day d.w., with a no-treatment population of 120,000 equivalent inhabitants, the outcome is 0.018 g I-TE/year. Summing up the contributions of treated and untreated effluents, it makes 0.065 g I-TE/year.

Conclusion

The actual dominating loading of PCDD/Fs to the Venice lagoon is the direct deposition over the lagoon and the transport of deposition from the drainage area. Most of PCDD/Fs and PCBs discharged in the past are still stored in the industrial canals.

Table 3
Estimated annual loading of PCDD/Fs, and dioxin-like PCBs (g I-TE/year) as well as HCB (g/year) from total atmospheric depositions.

district	PCDDs + PCDFs (g I-TE/year)	PCBs (g I-TE/year)	HCB (g/year)
North lagoon	69×10^{-3}	40×10^{-3}	97
Central lagoon	68×10^{-3}	352×10^{-3}	620
South lagoon	143×10^{-3}	55×10^{-3}	109
Total	0.28	0.45	826

Table 4

Estimated annual loading of PCDDs, PCDFs, and dioxin-like PCBs (g I-TE/year) as well as HCB (g/year) from Naviglio Brenta and Osellino Rivers from individual rivers and the whole catchment.

Source	PCDDs + PCDFs (g I-TE/year)	PCBs (g I-TE/year)	HCB (g/year)
Naviglio Brenta	18×10^{-3}	9.4×10^{-3}	102
Osellino River	17×10^{-3}	7.9×10^{-3}	81
Whole catchment (total)	0.23	0.12	1206

Table 5

Estimated loading of PCDD/Fs (g I-TE/year) from treated and untreated effluents discharged directly into the lagoon.

Source	PCDDs + PCDFs (g I-TE/year)
Industrial treated effluents	0.023
Municipal treated effluents	0.024
Municipal raw sewage	0.018
Total	0.065

Acknowledgments

The work was funded by the Italian Ministry of Public Works –Water Authority of Venice (Magistrato alle Acque) in the framework of the Venice safeguard activities carried out by the State Concessionaire “Consorzio Venezia Nuova”, and by the Port Authority of Venice.

Reference

1. Water Authority of Venice (Magistrato alle Acque), Project DRAIN, 1998.
2. Water Authority of Venice (Magistrato alle Acque), Project ORIZZONTE 2023, 1998.
3. M. Horstmann and M. McLachlan (1997) “Sampling bulk deposition of polychlorinated dibenzo-*p*-dioxins and dibenzofurans”, *Atmospheric Environment*, **31**, 2977-2982.
4. US-EPA Method 1613: Tetra-Through Octa-Chlorinated Dioxins and Furans by Isotope Dilution HRGC/HRMS.
5. A. Marcomini, M. Zanette, F. D’Andrea, and S. Della Sala (1997) “Dioxins environment and health, the lagoon of Venice as a case study” (in Italian), Arsenale Ed., Venezia.
6. A. Marcomini, A. Sfriso and M. Zanette (1994) “Macroalgal blooms, nutrient and trace metal cycles in a coastal lagoon”, J.W. Rijstenbil and S. Haritonidis Eds. CEC Bridge Report, 66-90.
7. A. Marcomini, A. Giacometti, S. Degetto and Vladimiro Bonamin (1999) “Occurrence of organohalogen pollutants in three dated sediment cores from the lagoon of Venice”, *Organohalogen Compounds*, in press.
8. C. Rappe (2 June 1997) “Technological feasibility of zero-discharge for organic micropollutants, dioxins”, *Proceedings of the Conference “Salvaguardia ambientale e sviluppo sostenibile: contributi scientifici al progresso delle conoscenze sulla laguna di Venezia”, 1st Session.*

ORGANOHALOGEN COMPOUNDS 486
Vol. 41 (1999)