

Environmental Levels in Sediment, Sewage, Sludge and Food

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OCCURRENCE OF ORGANOCHLORINE POLLUTANTS IN THREE DATED SEDIMENT CORES FROM THE LAGOON OF VENICE

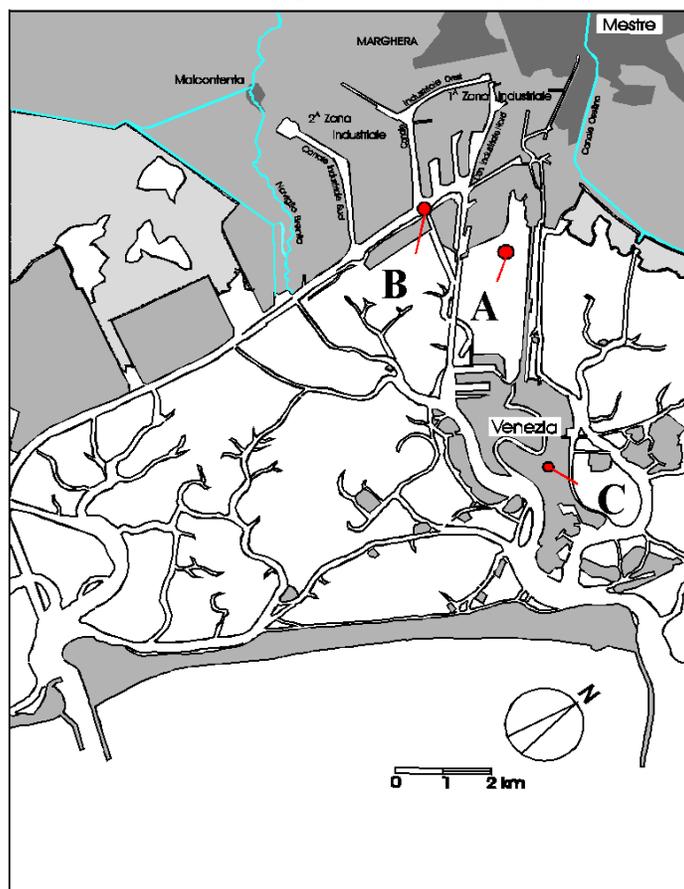
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Introduction

No information is available on the historical development of dioxin contamination in the lagoon of Venice. Apart from non-point pollution sources (i.e., atmospheric depositions and river inflows), the industrial area and the historical center of Venice appear potential significant sources of these chemicals. Organochlorine chemicals are expected to be formed by a large variety of past and present industrial activities including metal smelting facilities, oil refinery, municipal solid waste, thermal power plant incinerators, etc.. Untreated sewage discharges into the canals (rii) of the cities of Venice and Chioggia as well as in the canals of other inhabited lagoon islands (e.g., Murano) are also expected to contribute to the overall dioxin loading. The sediment of the rii exhibits a strong similarity with a raw sewage sludge where dioxins are expected to occur at levels of 10-20 I-TE ng/kg, dry weight [1,2]. Three sediment cores (**A**, **B**, **C**) were collected in lagoon areas (Fig. 1) allowing a close comparison of the first and second industrial development periods of Porto Marghera (cores **A** and **B**, respectively) and in a canal of the historical center (core **C**) where last dredging dates back to the '50s. The organochlorine compounds analyzed in the ²¹⁰Pb, ¹³⁴Cs, and ¹³⁷Cs dated sediment sections were PCDDs, PCDFs, dioxin-like PCBs and hexachlorobenzene (HCB).

Figure 1
Sediment core GPS-georeferenced sampling sites



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 and dating-The three cores were sampled on February 1997 in GPS geo-referenced sites by using a Plexiglas corer that allowed the sampling without disturbing the sediment. From the A station, 6 sediment cores of 60 mm diameter were sampled within an area of ca. 1000 m². For B and C, 2 sediment cores for each station were sampled. The cores were 100 mm in diameter and ca. 50 m far away from each other. The UTM co-ordinates of the A, B, and C stations are: core A: 33T 0287496 UTM 5037617; core B: 33T 0286101 UTM 5036346; core C: S.M. Formosa canal (eastern branch). Sediment core A refers to an unperturbed sedimentation area, which allowed the reconstruction of the recent past pollutant fluxes. Sediment cores B and C were sampled in areas with elevated sediment mixing and therefore scarcely suitable for temporal

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reconstruction. Nevertheless, they were taken because of their pollutant content distinctive of the originating areas (industrial and urban sites, respectively). Once sampled, the sediment cores were kept in vertical position and immediately transported to the laboratory, where the operations of sectioning and under-sampling followed. Sediment core processing was performed under a nitrogen atmosphere.

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.

Radiodating of the core was performed by measuring the “unsupported” ^{210}Pb activity and subtracting from this the supported ^{210}Pb activity. An independent check was done by measuring ^{137}Cs originated from nuclear fall out as well as ^{134}Cs generated during the Chernobyl accident.

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.

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 three columns containing multilayer silica, alumina and carbon were used.

Analysis-The HRGC/HRMS analyses were conducted using a HP 5970 gas-chromatograph coupled to a Micromass Autospec mass-spectrometer operating in EI mode at 35 eV and with a resolution of 10000 (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 confirmation.

The quantitative determination of PCDDs/PCDFs was performed by the 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 [3].

Results and discussion

Table 1 presents the concentrations and fluxes of 2,3,7,8-substituted PCDD and PCDF, PCBs, and HCB in each of the three sediment cores analyzed. High concentrations of PCBs and HCB were found in old sediment layers (<1935) where these compounds are not expected. Investigations are in progress to elucidate this finding. Table 2 shows the contribution of PCDD, PCDF, and PCBs to the total I-TE. The average year for each sediment section was inferred from the occurrence of ^{210}Pb , ^{134}Cs , and ^{137}Cs nuclides. Cores **A** and **B**, with the top sediment layers dating back to 1987 and 1986, respectively, were found to undergo significant erosion over the last decade. In terms of concentrations and fluxes of PCDD, PCDF, PBC, and HCB in the cores **A** and **B** near Porto Marghera, the ratio PCDF/PCDD was systematically >2, while in the core **C**, from the historical center, PCDF/PCDD < 0.5; the core **B** shows HCB by far higher than cores **A** and **C** (Table 1), while PCB maxima are in the core **C**; the major contribution to the total I-TE is from PCBs in all cores (Table 2). The congener profiles of PCDD and PCDF in cores **A** and **B** are markedly different when compared with core **C** which further suggests that core **C** is affected by different sources.

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While a decreasing trend of concentration and fluxes of the halogenated pollutants was found in the core **A**, the cores **B** and **C** showed a continued increase over the time of PCBs and HCB fluxes referred to the total concentrations (Table 1), whereas PCDD and PCDF fluxes decreased significantly in the most recent sediment layers. Vice versa, no increase (core **C**) or significant decrease (core **B**) were found for PCB in the top sediment when the I-TE fluxes are considered (Table 2). The fluxes of PCB congener profiles typical of each core are presented in Figs 2 a-c. The major congeners contributing to the total flux are PCB-126 and PCB-169. Moreover, while in the sediment core **A** the recent flux of PCB-169 exceeds significantly that of PCB-126, the opposite takes place in the cores **B** and **C**. In some more details, the comparison of Figs 2a and 2b shows that in the industrial district before mid '50s, the fluxes of PCB-126 and PCB-169 were very similar. From mid '50s on, the PCB-169 flux increased more remarkably in the area near the 1st industrial area, while PCB-126 became the dominant congener in the core **B** in front of the 2nd industrial area. The results presented here are in good agreement with those recently published on the occurrence of dioxins and PCBs in sediment cores [4,5].

Conclusion

The analyzed cores show distinctive congener distributions of PCDDs, PCDFs, and PCBs depending on the proximity of the sources differing by spatial and time discharge of organochlorinated pollutants. The obtained results suggest that dioxin-like PCBs, especially the PCB-126 and PCB-169 congeners, are the major contributors to the total I-TE in the explored areas.

Figure 2a

Average fluxes (ng I-TE/m² year) of the individual PCDD and PCDF congeners in sections of the sediment core **A** corresponding to years before (dark) and after (white) 1954. The concentrations below the detection limit were considered to be half the detection limit.

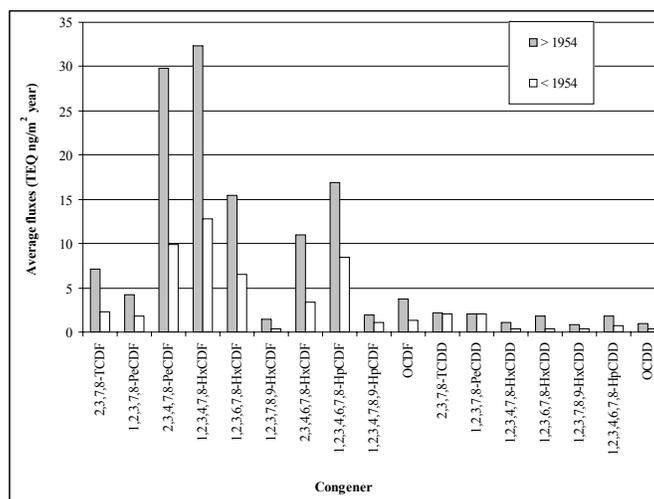


Figure 2b

Average fluxes (ng I-TE/m² year) of the individual PCDD and PCDF congeners in sections of the sediment core **B** corresponding to years before (dark) and after (white) 1949. The flux values, corresponding to the period before 1949, are multiplied by 10 for clarity of the drawing. The concentrations below the detection limit were considered to be half the detection limit.

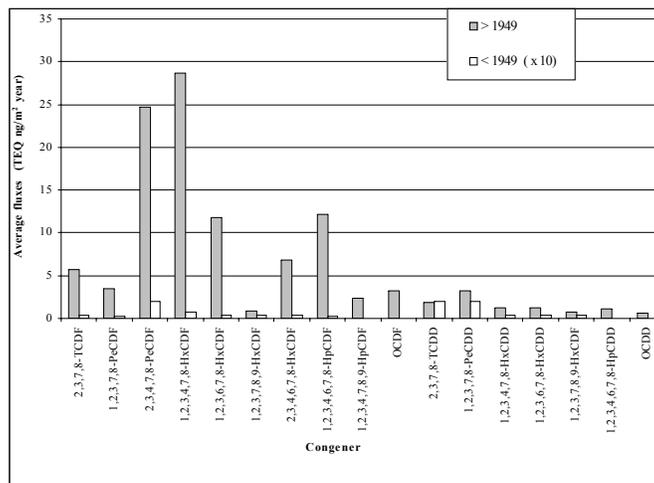


Figure 2c

Average fluxes (ng I-TE/m² year) of the individual PCDD and PCDF congeners in sections of the sediment core C corresponding to years before (dark) and after (white) 1973. The concentrations below the detection limit were considered to be half the detection limit.

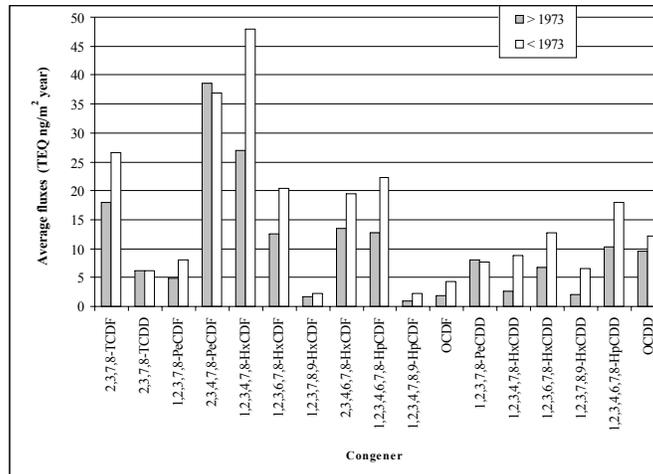


Figure 3a

Average fluxes (µg I-TE/m² year) of the individual PCB congeners in sections of the sediment core A corresponding to years before (dark) and after (white) 1954. The concentrations below the detection limit were considered to be half the detection limit.

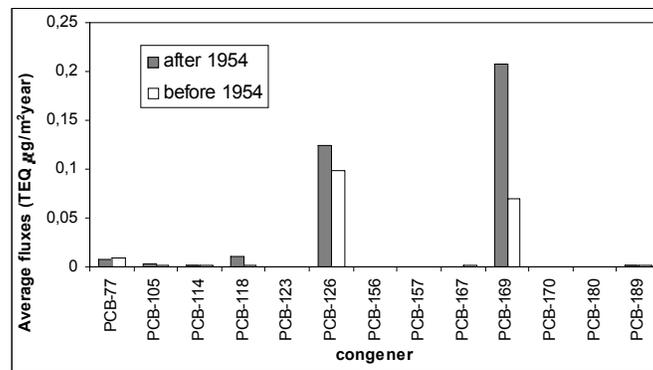


Figure 3b

Average fluxes ($\mu\text{g I-TE}/\text{m}^2 \text{ year}$) of the individual PCB congeners in sections of the sediment core **B** corresponding to years before (dark) and after (white) 1949. The flux values, corresponding to the period before 1949, are multiplied by 20 for clarity of the drawing. The concentrations below the detection limit were considered to be half the detection limit.

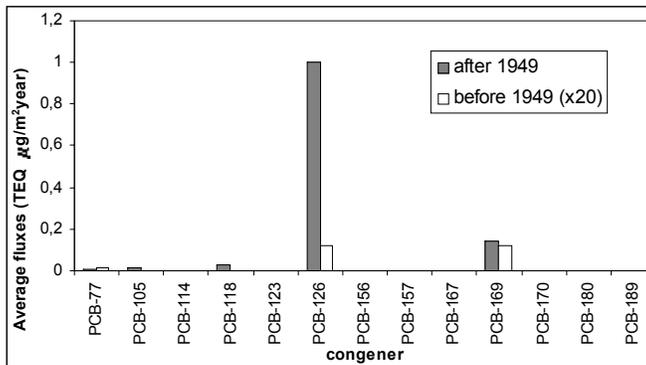
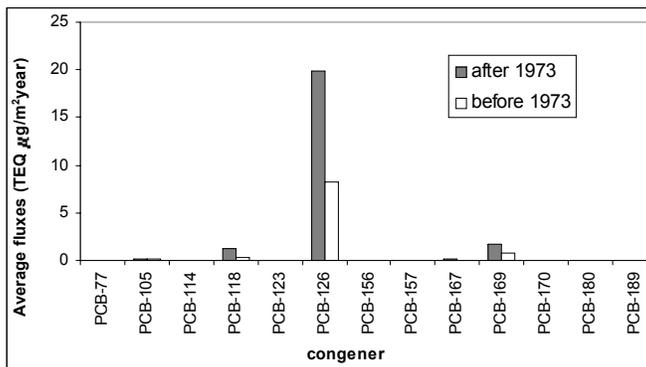


Figure 3c

Average fluxes ($\mu\text{g I-TE}/\text{m}^2 \text{ year}$) of the individual PCB congeners in sections of the sediment core **C** corresponding to years before (dark) and after (white) 1973. The concentrations below the detection limit were considered to be half the detection limit.



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Table 1

Summary of concentrations and fluxes for PCDDs, PCDFs, PCBs, and HCB in the three sediment cores analyzed: **A** (near the 1st industrial area), **B** (in front of the 2nd industrial area), **C** (in a canal of the historical center); concentrations are in ng/Kg, d.w.; fluxes are in ng/m² year

Sediment core A		1987	1980	1969	1935	1896
Concent.	PCDD	289	414	588	286	51
	PCDF	885	2255	4147	1623	193
	PCB	8700	13000	17000	8000	4300
	HCB	3100	3600	5100	1000	500
Fluxes	PCDD	760	1375	1282	572	154
	PCDF	2440	7525	9718	3328	687
	PCB	24000	44000	38000	16000	14000
	HCB	8360	11970	11410	2240	840

Sediment core B		1986	1964	1949	1912	1847
Concent.	PCDD	357	1072	181	40	23
	PCDF	2607	7895	1202	112.8	35
	PCB	265000	63000	16000	4300	4300
	HCB	119400	75800	24300	2600	500
Fluxes	PCDD	574	1302	326	5	4
	PCDF	4203	9568	2216	234	5
	PCB	427000	76000	30000	830	1200
	HCB	192000	91900	44700	500	70

Sediment core C		1996	1992	1985	1973	1958
Concent.	PCDD	612	1070	1232	1359	1229
	PCDF	277	490	311	730	732
	PCB	331000	368000	399000	342000	367000
	HCB	2300	1900	1600	3000	2500
Fluxes	PCDD	6745	9655	3617	2423	2696
	PCDF	3165	4445	933	1297	1624
	PCB	3665000	3321000	1172000	609000	807000
	HCB	25460	17160	4710	5340	5500

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Table 2

Summary of I-TEs for PCDDs, PCDFs and PCBs in three sediment cores: **A** (near the 1st industrial area), **B** (in front of the 2nd industrial area), **C** (in a canal of the historical center); concentrations are in ng I-TE/Kg, d.w.; fluxes are in ng I-TE/m² year

Sediment core A		1987	1980	1969	1935	1896
Concent.	PCDD	6.0	4.9	5.5	5.6	2.8
	PCDF	17	40	72	28	2.8
	PCB	111	163	186	166	109
	Total I-TE	134	208	263	200	115
Fluxes	PCDD	9.1	12	9.8	6.5	5.0
	PCDF	54	137	163	64	13
	PCB	222	444	407	187	183
	Total I-TE	285	593	580	257	201

Sediment core B		1986	1964	1949	1912	1847
Concent.	PCDD	5.4	14	4.3	5.0	3.5
	PCDF	49	145	23	4.4	3.0
	PCB	483	1279	730	109	109
	Total I-TE	537	1438	758	118	116
Fluxes	PCDD	7.6	18	4.8	0.50	0.54
	PCDF	81	175	45	0.50	0.45
	PCB	774	1550	1288	11	15
	Total I-TE	861	1742	1338	12	23

Sediment core C		1996	1992	1985	1973	1958
Concent.	PCDD	4.4	6.2	5.0	7.8	7.4
	PCDF	7.6	15	11	16	18
	PCB	2796	3588	2271	3955	5332
	Total I-TE	2808	3610	2287	3979	5356
Fluxes	PCDD	37	48	12	12	14
	PCDF	83	144	35	30	39
	PCB	30964	32371	6674	7046	11683
	Total I-TE	31084	32563	6720	7088	11735

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