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TOXICITY ASSESSMENT OF ATMOSPHERIC FALL-OUT AT VENICE

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Introduction

Data on atmospheric fall-out of dioxins and furans (PCDD-Fs), dioxin-like polychlorobyphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs) and hexachlorobenzene (HCB) were provided by collecting bulk depositions in four stations inside the Lagoon of Venice. A total of 44 monthly samples was collected in one site near an industrial area, one site in the city of Venice, and two sites in the southern and northern ends of the Lagoon.

Materials and methods

Sampling of atmospheric depositions was carried out monthly during the period July 1998–July 1999 in one site near the industrial area of Porto Marghera (Site D), one in the city of Venice (Site A), and two sites in the more remote southern (Site C) and northern (Site B) ends of the Lagoon (Figure 1). Bulk samplers were polymer structures formed of a cylindrical container and a protection ring to avoid damage by birds and animals. A pyrex bottle with a funnel treated with dimethyldichlorosilane 5% in toluene, in order to avoid retention of particles, was placed in the support[1].

After removal insects, total atmospheric samples were first spiked with a series of 15 $^{13}C_{12}$-labeled 2,3,7,8 PCDD-Fs, 12 $^{13}C_{12}$-labeled PCB, $^{13}C_{12}$-HCB substituted isomers, and of 5 deuterated PAH (Acenaphthene-D10, Chrysene-D12, Naphtalene-D8, Perylene-D12, Phenanthrene-D10) as internal standards, and then extracted in a separatory funnel with dichloromethane. The extracts were transferred to hexane before clean-up treatment.

Sample extracts were first spiked with $^{37}C_4$-labeled 2,3,7,8 PCDD and 3 $^{13}C_{12}$-labeled PCB, and then cleaned using an 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 the 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-Fs, 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 injections[2,3].
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

In order to evaluate the toxicity of atmospheric fall-out, the total 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD) toxicity equivalents (TEQs)[4] of deposition samples were calculated (Table 1). Recently, van Birgelen[5] proposed that hexachlorobenzene (HCB) is a major contributor to dioxin-like activity in chemical mixtures[5,6], and Table 1 also lists the relative contribution of this compound to total TEQ.
TEQ values range from 1.3 to 29.1 pg $m^{-2}d^{-1}$, with a mean relative contribution of PCDD-Fs in all sites of 61, 67, 68 and 48%, respectively. In sites A, B and C, HCB accounted for 1-20% of total TEQ, but reached 40-50% in site D (samples D4, D6, D7, D8).
As already reported by us in a recent paper[1], several samples exceed the guideline and limit values proposed by the Flemish Institute for Technological Research and the EU target values - 3.4, 13.6 and 7 pg TE m^{-2} d^{-1} respectively[7,8]. In fact, as may be seen from Table 1, 9% of samples exceed the limit value, 25% exceed the EU target value, and 48% exceed the guideline value. Samples near or exceeding the limit value were collected from sites A and D in July and August 1998 and October and February 1999.
Moreover, as also reported by Eljarrat *et al.*[9], recent studies have examined the role of PAHs in TCDD-like activity and have established Toxicity Equivalent Factors (TEFs) for some PAHs[10,11,12].
Figure 2 shows the results of total TEQ obtained by adding to the PCDD-F, PCB and HCB values the toxicity derived from PAHs, calculated with the various TEFs proposed. The results differ considerably but, in all cases, the TEQ_{PAH} value greatly exceeds that due to other compounds.

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Table 1. Toxicity equivalents[4,5] of samples collected during study period.

Code	Period	HCB	PCDD-Fs	PCBs	Total TEQ	PCDD-Fs	PCBs	HCB
		pgTE $m^{-2}d^{-1}$	pgTE $m^{-2}d^{-1}$	pgTE $m^{-2}d^{-1}$	pg $m^{-2}d^{-1}$	%	%	%
A1	Jul 1998	0.8	5.5	21.8	28.1	20	78	3
A2	Aug 1998	1.0	5.9	3.6	10.6	56	35	10
A3	Sep 1998	0.1	5.2	2.5	7.8	67	32	1
A4	Oct 1998	0.7	4.5	2.4	7.6	59	32	9
A5	Nov 1998	0.1	1.2	1.1	2.3	52	46	2
A6	Dec 1998	1.0	5.4	0.5	6.9	79	7	14
A7	Jan 1999	0.2	1.7	0.5	2.5	70	20	10
A8	Feb 1999	0.2	8.8	2.8	11.8	74	24	2
A9	Mar 1999	0.1	1.7	2.0	3.8	46	52	2
A10	Apr 1999	0.1	3.1	0.7	3.9	79	19	2
A11	May 1999	0.2	1.2	0.7	2.0	59	33	9
A12	Jun 1999	0.0	1.2	0.5	1.8	68	30	2
A13	Jul 1999	0.0	1.1	0.6	1.8	64	34	2
B1	Nov 1998	0.0	1.0	0.6	1.7	62	36	2
B2	Dec 1998	0.9	3.1	0.5	4.5	68	12	21
B3	Jan 1999	0.1	1.8	0.5	2.4	74	22	4
B4	Feb 1999	0.2	3.3	0.5	4.0	82	12	5
B5	Mar 1999	0.1	1.8	0.5	2.4	74	20	6
B6	Apr 1999	0.1	1.7	1.9	3.7	47	52	2
B7	May 1999	0.0	0.9	0.5	1.4	65	34	1
B8	Jun 1999	0.0	1.0	0.5	1.5	67	31	2
B9	Jul 1999	0.0	0.8	0.5	1.3	63	36	1
C1	Nov 1998	0.0	1.5	0.6	2.1	70	28	2
C2	Dec 1998	0.2	3.9	0.5	4.6	85	11	5
C3	Jan 1999	0.4	2.4	0.5	3.2	73	15	12
C4	Feb 1999	0.3	6.1	0.5	6.9	88	8	4
C5	Mar 1999	0.1	1.3	0.5	1.9	69	28	4
C6	Apr 1999	0.1	1.0	0.5	1.7	62	32	6
C7	May 1999	0.0	1.5	0.5	2.0	75	24	1
C8	Jun 1999	0.0	0.9	0.5	1.4	63	35	2
C9	Jul 1999	0.0	0.9	1.8	2.7	32	68	1
D1	Jul 1998	0.5	5.5	23.1	29.1	19	79	2
D2	Aug 1998	1.9	6.2	5.6	13.7	45	41	14
D3	Sep 1998	0.3	4.3	2.6	7.2	60	36	5
D4	Oct 1998	9.3	4.4	4.7	18.3	24	25	51
D5	Nov 1998	0.1	2.1	1.2	3.4	61	36	3
D6	Dec 1998	4.0	3.5	0.6	8.2	43	7	49
D7	Jan 1999	2.5	2.9	0.5	6.0	49	9	42
D8	Feb 1999	5.3	4.5	3.6	13.4	34	27	40
D9	Mar 1999	0.1	1.9	1.0	2.9	64	33	3
D10	Apr 1999	0.1	1.5	1.1	2.7	55	40	5
D11	May 1999	0.1	0.9	0.5	1.5	60	35	4
D12	Jun 1999	0.1	1.8	0.6	2.4	74	23	4
D13	Jul 1999	0.0	0.9	1.9	2.8	31	68	1

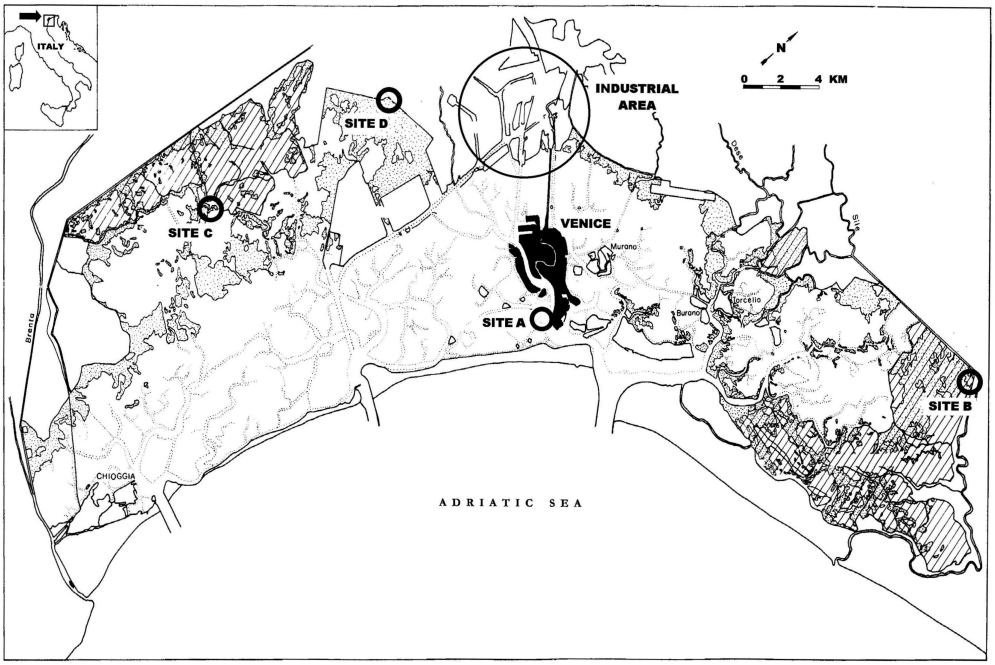

Figure 1. Location of atmospheric deposition sampling sites. A=city of Venice; B=Valle Dogà; C=Valle Figheri; D=Dogaletto.

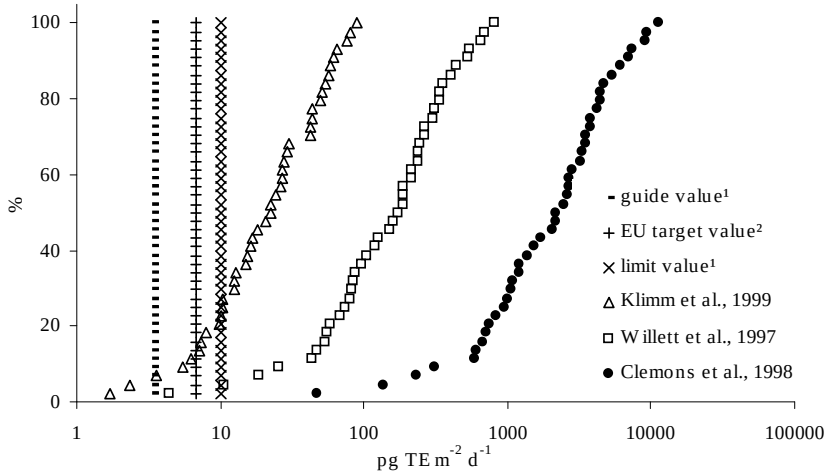

Figure 2. Cumulative frequency of samples exceeding guidelines using TEFs proposed for PAHs. [1] = reference 7, [2] = reference 8.