

Air Dioxin Concentrations in Seveso Area

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Introduction

In July 1976, following the explosion of the production reactor of the *Icmesa* factory in Seveso, a substantial amount of the isomer 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (2,3,7,8-TCDD) spread and settled over a large area surrounding the chemical plant. The polluted area was divided in three risk zones corresponding to the decreasing levels of contamination. The Zone A (2,3,7,8-TCDD concentration $>50 \mu\text{g}/\text{m}^2$ soil), immediately close to the *Icmesa* plant, was cleaned-up by collection and disposal of the contaminated soil and reconverted as a park (*Bosco delle Querce*). The zones B and R, affected by a lower contamination (2,3,7,8-TCDD concentration $5\text{-}50 \mu\text{g}/\text{m}^2$ and $<5 \mu\text{g}/\text{m}^2$), were reclaimed by mixing the most contaminated points with uncontaminated underlying layers, in order to decrease the 2,3,7,8-TCDD concentrations down to the safety levels (1).

Since the long half-life of the 2,3,7,8-TCDD (2), low but measurable soil residues of 2,3,7,8-TCDD should still be present in the area. The purpose of this study was to quantify the atmospheric levels of polychlorinated dibenzo-*p*-dioxin and dibenzofurans (PCDD/F) in the area affected by the accident and to assess if the PCDD/F burden was enriched in residual 2,3,7,8-TCDD arising from mobilisation of soil particles and/or volatilisation.

Material and Methods

Long-term air samples collection was carried out in three locations: ex Zone A (*Bosco delle Querce*), ex Zone B (*Via del Tramonto*) and in a reference location in Milan (*Via Eritrea*) in a high traffic area. The air samplers were working for 15 minutes every two hours for a year. Four samples, corresponding to the four seasons, were analysed for each location. The air samplers were constituted of a glass fiber filter followed by a prewashed polyurethane foam

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plug that was connected to a suction pump (3). Both airborne particles and vapour-phase PCDD/F were collected. Before sampling the glass fiber filters were spiked with a mixture of ten ¹³C-labelled 2,3,7,8-substituted congeners to compensate the losses of the analytes during both the sampling and the entire analytical procedure. The glass fiber filters and the polyurethane foam plugs were Soxhlet extracted with toluene and purified by Extrelut column coated with sulfuric acid, alumina column and finally activated carbon (4,5). Instrumental analysis was carried out with a DANI 6500 VG 70-250 gas chromatograph-mass spectrometer (GC-MS). A Chrompack capillary column CP sil 88, 50 m x 0.25 mm, film thickness 0.25 µm and splitless injections were used. Temperature programme: 100°C for 2 min, 30°C/min until 190°C, then 5°C/min until 230°C, maintained for 50 min. Column head pressure 180 kPa; injector temperature: from 60°C to 260°C by programmed temperature vaporization (PTV). The GC-MS was employed in the selected ion recording (SIR) mode (6).

Results and Discussion

Average annual concentrations of total toxic equivalents (Σ TEQ) were 0.35, 0.26, and 0.22 pg/m³ in air of ex Zone B and A of Seveso and in Milan respectively, and the total levels of PCDD and PCDF resulted 16.8, 12.1 and 9.36 pg/m³ respectively. These values are somewhat higher than concentrations detected in urban air of other industrialised countries as United Kingdom, Germany and Sweden (7-9), and similar to the values recently detected in Spain by Abad *et al.* (8) in high traffic areas.

Table I. Seasonal homologue PCDD/F and Σ TEQ concentrations (pg/m³) in air samples analysed.

	Zone A				Zone B				Milan			
	Win.	Sp.	Sum.	Aut.	Win.	Sp.	Sum.	Aut.	Win.	Sp.	Sum.	Aut.
TCDD	0.36	0.21	0.10	0.60	0.47	0.10	0.50	2.01	0.56	0.08	0.10	0.31
PnCDD	0.79	0.26	0.17	1.58	0.72	0.38	0.92	1.42	0.61	0.16	0.17	1.18
HxCDD	1.34	0.37	0.25	1.70	1.88	0.74	1.27	1.38	1.36	0.30	0.34	1.40
HpCDD	1.53	0.96	0.31	2.54	1.84	0.52	0.67	3.69	1.37	0.43	0.25	1.06
OCDD	2.91	1.91	0.59	2.93	3.36	0.82	0.55	2.61	1.91	0.75	0.31	1.73
TCDF	2.17	1.02	0.63	4.08	4.45	0.91	1.86	12.13	2.98	0.79	0.92	2.45
PnCDF	1.11	0.95	0.42	4.21	3.50	1.25	1.27	4.27	2.48	0.70	0.35	2.10
HxCDF	1.28	0.80	0.59	2.53	2.17	0.94	1.12	1.55	2.10	0.90	0.34	1.66
HpCDF	0.56	1.33	1.02	2.57	1.02	0.69	1.87	1.16	0.92	0.98	0.28	1.58
OCDF	0.32	0.59	0.18	0.60	0.43	0.07	0.48	0.27	0.45	0.25	0.17	0.67
PCDDs/Fs	12.39	8.40	4.27	23.33	19.85	6.43	10.52	30.49	14.73	5.32	3.23	14.15
Σ TEQs	0.32	0.15	0.06	0.44	0.59	0.21	0.15	0.46	0.48	0.13	0.04	0.23

The results of homologues and Σ TEQ concentrations for each season are shown in Table I. For the TEQ levels, the lowest values were found in samples collected in Summer for all three the sampling locations, while the highest in samples collected in Winter for the ex Zone B and Milan, and in Autumn for the ex Zone A. The trend of the total PCDD/F concentrations showed some differences: in ex Zone B the lowest values were found in Spring and not in Summer and the highest in Autumn. The amounts of the 2,3,7,8-TCDD, expressed as a percentage of total TCDD, ranged between 0.64 and 5.96% and they were generally lightly

higher in the ex Zone B than in the other sampling sites suggesting that a small contribute could arise from residual 2,3,7,8-TCDD still present in soil. Nevertheless these percentages are within the range reported in the investigations mentioned above and typical of combustion sources.

As reported earlier (3) for an Italian site and more recently on atmospheric PCDD/F levels in Germany (10), these results showed a strong seasonality since the PCDD/F concentrations detected in Autumn/Winter were considerably higher than those in Spring/Summer in all the three sampling locations. This seasonality could be related to differences on emission sources but it also could be a consequence of a reduced atmospheric mixing during winter months and/or of photodegradative processes occurring in the Summer months. Nevertheless in this last case an enrichment of higher chlorinated compounds should be expected in the homologue profiles since their lower photodegradation potential in comparison to the less chlorinated homologues (11), and it was not clearly observed in the homologue profiles of the analysed samples in this study (Figure 1).

In almost all the samples the ratio PCDD/PCDF was <1 indicating a major contribute of PCDF to the dioxin air burden. The homologue profiles (Figure 1) show a quite high variability both within the same sampling location and within the same season suggesting that different sources with different temporal trend could contribute to the contamination.

Thus the results of this study indicate that Seveso air is affected from a PCDD/F contamination, probably arising from the several industrial activities located in the area, and the residual 2,3,7,8-TCDD due to accident, is not a dominant contributor to this PCDD/F air burden.

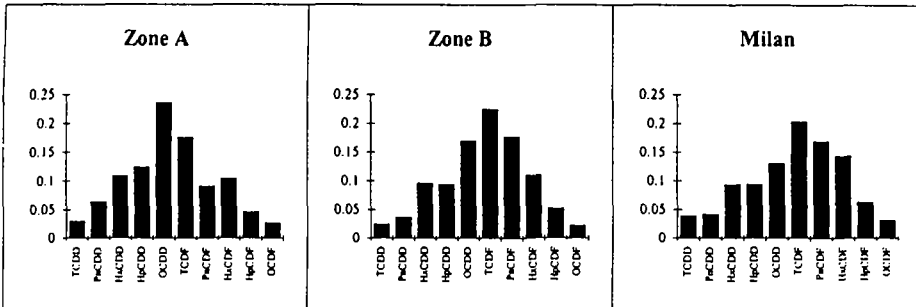
Acknowledgements

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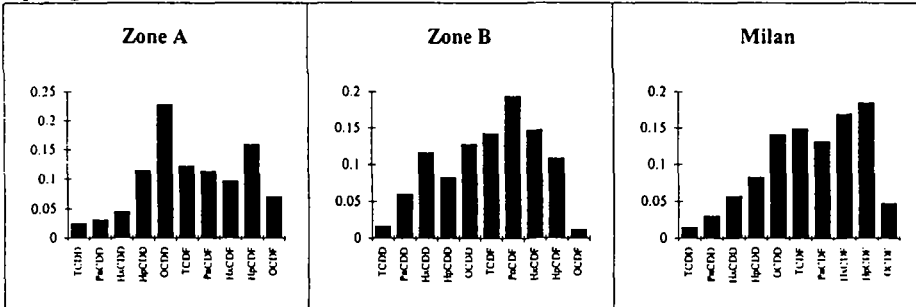
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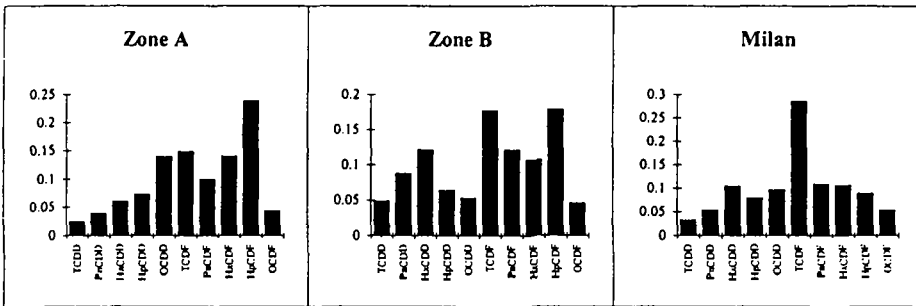
Winter



Spring



Summer



Autumn

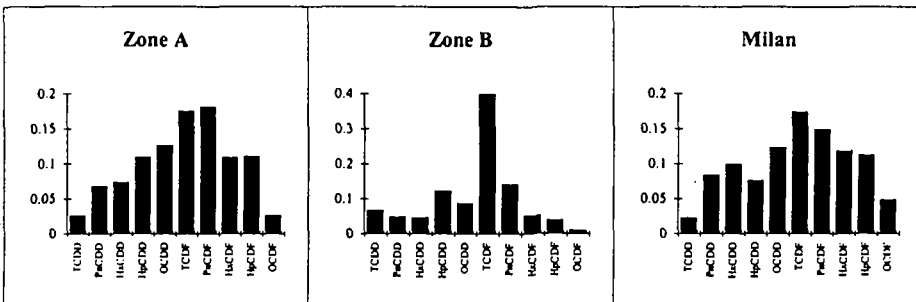


Figure 1. Normalized PCDD/F homologue profiles to the sum of total PCDD/F of air samples analysed