Recent Levels of PCDD/Fs in the Terrestrial Ecosystem of Seveso

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Introduction

In 1995 a new series of sampling campaigns was started in Seveso, Meda, Cesano Maderno, and Desio near Milan. These municipalities, located around and downwind the former ICMESA plant, had been contaminated during the "Seveso accident" in 1976 from a toxic cloud containing 2,3,7,8-TCDD. An initial analytical survey of the contamination in soil directly after the accident resulted in a division into three zones of decreasing contamination. Zone A with average TCDD levels > 50 μgm^{-2}, Zone B the natural extension of Zone A with > 5 μgm^{-2}, and Zone R enclosing Zones A and B with > 0.75 μgm^{-2}. Zone A was further divided in 7 sub-zones of which A6 and A7 (here referred to as ex A6 and ex A7) were included later in Zone B *(Pocchiari et al. 1986)*.
The aim of the present study was - 20 years after the accident - to reinvestigate the current risk associated with the remaining Dioxin contamination in the region.
Investigations initially focussed on the so-called Seveso Park ("Bosco delle Querce") located in the subzones A1-A5. Zone A had undergone complete reclamation by exchanging between 20 cm and 90 cm of the surface soil between 1977 and 1983. Subsequently the "Bosco delle Querce" was created. The park remained closed to the public until recently and the results of this survey were used for a final evaluation of the efficiency of the restoration.
The survey was later expanded into Zones B and R which had been subjected partially to reclamation (e.g. through ploughing or covering of the surface with fresh soil) to decrease the TCDD concentration in the superficial soil layer.

Materials and Methods

Sampling

During 1995 and 1996, soil cores were collected from the northern part (subzones A2 and A3) of the "Bosco delle Querce". Cores were taken within an orthogonal grid of 25 m and subdivided into two depths, topsoil (0-15 cm) and subsoil (15-30 cm). In the same area, samples of conifer needles, tree leaves, grass, mushrooms, moss and earthworms were taken in 1994, 1995 and 1996. Additionally, 3 liver samples from wild rabbits were analysed in 1994.
During 1997, soil cores were taken from the covering layer of two basins ("Collina di Seveso" in subzone A4 and "Collina di Meda" in subzone A1) where part of the residues from the accident was deposited. Since the soil layer there did not exceed a total depth of 20 cm, samples were subdivided into layers of 0-10 cm and 10-20 cm.
From 1997 to 1999 soil cores from 0-30 cm were collected in Zone B and the northern part of Zone R within an orthogonal grid of 150m

Analysis

All samples were freeze dried and soil samples were sieved and the fraction < 2mm analysed. The dry samples were extracted for 48h in Soxhlet extractors using hexane/acetone (220:30, v: v). The extracts were purified by adsorption chromatography using automated instrumentation (Dioxin Prep) from Fluid Management Systems. The measurements were made on a high resolution gaschromatograph (HP-5890) coupled with a double focusing high resolution sector field mass spectrometer (VG AUTOSPEC Ultima) at a resolution of 10000. The quantification was based on isotope dilution except for octachlorodibenzofurane which was quantified using the ^{13}C-labelled octachlorodibenzo-p-dioxin spike. All 2,3,7,8-substituted PCDD/Fs were determined and International Toxicity Equivalencies (I-TEQ) calculated. The analytical procedures were performed under a strict quality control procedure.

Results and Discussion

Zone A - soil

The average concentration (I-TEQ as well as TCDD) in the topsoil generally did not differ to any remarkable extent from the subsoil, thus indicating a homogeneous concentration profile in the upper 30 cm. Therefore, concentrations given in *Table 1* were calculated for a soil depth of 0-30 cm (0-20 cm for subzones A1 and A4). Average I-TEQs of A1, A2 & A3, and A4 did not exceed 10 pg/g and maximum I-TEQ was 39 pg/g. Ex A6 and ex A7 were to some extent higher, showing average I-TEQs of 25 and 36 pg/g and maximum I-TEQs of 35 pg/g and 122 pg/g. Comparing Zone A with other industrialised areas, most of the analysed soil samples are within a typical concentration range. The median of 20 pg/g I-TEQ is considered as urban background burden for soils in cities like Hamburg *(FHH 1993)*. At the I-TEQ levels measured in Zone A, Italian guidelines do not require any further reclamation for the recent type of land uses as a park in A1 to A5 and mainly commercial and residential use in ex A6 and ex A7 *(Di Domenico, 1990)*.

Zones A2 & A3 - biota

I-TEQ levels in biota (except those in rabbit livers) did not exceed the soil concentrations. Mushrooms had neglectable I-TEQs below 1 pg/g. Earthworms were contaminated at average with 18 pg/g I-TEQ, with PCDD/F patterns identical to those of the soil. Average I-TEQs of different type of vegetation did not exceed 6 pg/g. With increasing distance from the soil surface, I-TEQs and in particular the contribution of TCDD decreased. Simultaneously, the PCDD/F pattern changed from the pattern found in the soil to a typical atmospheric pattern. These findings indicate an ongoing evaporative release of TCDD from soil that is subsequently adsorbed by the plant's surfaces, especially by those species growing close to the ground.

A special situation occurred in the case of the wild rabbit liver, where just some exemplary samples were collected. Although the I-TEQ ranged from 228 to 418 pg/g, the concentration of 2,3,7,8-TCDD was low and did not contribute more than 6 % to the total toxicity. The I-TEQ was made up to more than 60 % by 2,3,4,7,8-PeCDD, followed by tetrachloro- and hexachlorofurans. Thus, it is not indicated to relate the high I-TEQs to the accidental history of the sites. The high abundance of 2,3,4,7,8-PeCDD, and other furans indicates more an impact of non-specific sources. As an example, wild hare livers from the surroundings of a hazardous waste landfill in Muenchehagen, Germany, showed a similar isomer distribution at I-TEQs being around two times lower *(Ende, 1991)*.

Table 1: averaged (x) and maximum (max) concentrations of PCDD/Fs (I-TEQ in pg/g dry mass) and 2,3,7,8-TCDD (pg/g dry mass). Number of samples (n).

Zones	**Matrix**	**n**	**I-TEQ 1995-1999**		**TCDD 1995-1999**	
			x	**max**	**x**	**max**
A1	Soil, 0-20 cm	8	3.3	7.5	2.4	7
A2 & A3	Soil, 0-30 cm	53	5.5	39	3.3	38
A4	Soil, 0-20 cm	10	7.1	14	4.7	13
A5	Soil	-	Under investigation in 1999			
ex A6	Soil, 0-30 cm	4	25	35	22	32
ex A7	Soil, 0-30 cm	10	36	122	34	120
B	Soil, 0-30 cm	84	45	253	35	250
R, north	Soil, 0-30 cm	21	15	44	6	17
A2 & A3	Fungus, diverse	2	0.60	1.0	0.30	0.50
biota	Moss, diverse	9	6.0	22	3.3	19
	Grass, diverse	2	3.2	5.4	1.7	3.1
	Deciduous trees	4	2.3	3.4	0.21	0.34
	Spruce, pinus silvestris	3	1.9	3.8	0.70	1.9
	Earthworm, diverse	7	18	38	13	29
	Wild rabbit liver	3	332	418	11	19

Zone B - soil

The average I-TEQ in Zone B was 45 pg/g and the maximum TEQ was 253 pg/g measured in an agricultural cultivation. Almost all investigated sited exceded 10 pg/g I-TEQ and many samples were higher than 50 pg/g I-TEQ. A level of 10 pg/g USEPA-TEQ[&] was proposed as "maximum tolerable limit" for "farmable soil" and 50 pg/g USEPA-TEQ is the limit for "not farmable soil" in Italy *(Di Domenico, 1990)*. This would denote that the various types of agricultural activities present in Zone B have to be carefully evaluated in terms of potential TCDD transfer into human consumption.

[&] The USEPA-TEQ system differs from the I-TEQ system concerning its TEFs given to some of the 2,3,7,8-substituted congeners. However, 2,3,7,8-TCDD receives a factor of 1 in both systems. Since the toxicity of the samples discussed in this paper is mainly deriving from 2,3,7,8-TCDD, USEPA-TEQ and the I-TEQ are quasi identical for most samples with TEQ > 5 pg/g.

Zone R - soil

I-TEQs in soil taken from Zone R did not exceed 44 pg/g and were at average 15 pg/g.

TCDD contribution to the overall toxicity (I-TEQ)

Not unexpectedly, results showed that the toxicity in soil samples with I-TEQs of higher than 5 pg/g derives mainly from TCDD. *Table 1* shows that the maximum I-TEQ concentrations found in the soil of all Zones (except the R-Zone) derive almost exclusively from TCDD. Usually, 2,3,7,8-TCDD is of minor relevance for the PCDD/F toxicity in atmospheric deposition to soil. It is known that the typical contribution of 2,3,7,8-TCDD to the total toxicity in the flue gas of waste incinerators is about 4% *(Hagenmeier 1989)*. Bulk deposition samples collected in 1992 from 7 industrialised cities in Nordrhein Westfalen (Germany) showed an average contribution of 2,3,7,8-TCDD of 6 ± 2% of the total toxicity *(Hiester et al. 1993)*.
It is obvious that the high contribution of 2,3,7,8-TCDD to the total toxicity of some soil samples in the investigated area is still a result of the accidental input in 1976.

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