PCDD AND PCDF CONTAMINATION LEVELS IN AIR, DEPOSITION AND SOIL IN MANTUA

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Introduction

In an area inside the city of Mantua, in Northern Italy, an excess of cases of soft tissues sarcomas was recorded[1] and the emission of PCDD and PCDF from a nearby incinerator of industrial wastes was suggested as a possible cause[2].
The incinerator is still operating but significant changes were made both in the waste composition and in the combustion and emission treatment technology.
An assessment of past emission from the plant was carried out through recognition of past analyses, whilst the search of other possible sources was made through a census of all industrial activities in the area.
A study was also set up to investigate the actual and possibly the past air levels of PCDD and PCDF in the area where the cases were recorded.
An exposure capable to produce such kind of effects may have occurred over a long period of time in the last decades, caused by a stable source; or it may have had accidental or episodic causes such as short duration events of high intensity. These, if real, may also have ceased. However, the authorities and the population of the area need to know exactly what the actual air contamination levels are.
The air contamination is measured through analyses of both the deposition and the airborne particulate matter. The latter was sampled by means of high volume samplers. It was also thought that, if some air contamination episode, accidental or continued, occurred in the past, some trace of it would still be visible through analysis of undisturbed soil.
The preliminary results obtained in the summer 2000 period are here presented.

Methods and Materials

Eight different locations were selected for monitoring deposition; they were chosen in order to represent areas exposed to supposedly different emission sources, including several sites surrounding the zone where sarcoma cases occurred. The deposition samples were collected each season; airborne particulate matter was sampled by means of high volume (HV) samplers, equipped with PM10 probe; these were placed in four out of the eight deposition sites. Selected daily HV samples were pooled to represent a seasonal sample. Each pooled sample includes the same sampling days for each of the sites, so that the samples represent the same temporal situation. Five soil samples were collected from sites where earth was presumably left undisturbed in the past 30 years and close to the locations where air and deposition are sampled. Three of the locations were in the area where the sarcoma cases occurred, whilst the fourth was in the fallout area of the industrial site; the fifth was in a remote site, far from industrial plants and civil residences. Carrots 50 cm long were taken and cut into five pieces 10 cm each.

Extraction: 9 daily filters form the HV samplers were inserted into 5 extraction stainless steel cells of a Dionex Accelerated Solvent Extractor (ASE) apparatus, spiked with a mixture of isotopically labeled standard and exctracted with dichloromethane.
The acqueous deposition samples were filtered on 47 mm filters; these were dried, spiked with a mixture of isotopically labeled standard and extracted with the ASE apparatus with a 1/1 *n*-hexane/acetone mixture. The water phase was extracted in separatory funnel with *n*-hexane, which was added to the filter extract together with the *n*-hexane washings of the collection glass vessel.
Soil samples were dried and sifted through a 1mm sieve. A 30 g portion of the roughly homogeneous soil sample was inserted on a 33 mL ASE cell with 9 g of copper powder, spiked with a mixture of isotopically labeled standard and extracted with a 1/1 n-hexane/acetone mixture.
Clean-up: The exctracts from all kind of samples were concentrated and then eluted on a column packed with concentrated sulfuric acid coated on an inert support (Extrelut, Merck) with 150 mL of n-hexane. The concentrated residue was then purified on an allumina column for the deposition samples whilst the air particulate and the soil a further passage on a carbon column was performed.
Determination: The quantification was carried out on an Autospec GC-HRMS system equipped with a BPX-5 column 50 m long, 0.32 mm i.d.

Table 1. Deposition values (pg/m^{2}d) in eight Mantua locations during the summer season.

Location	1	2	3	4	5	6	7	8
2,3,7,8-TCDD	<0,53	<0,90	<0,37	<0,23	<0,89	<0,33	<0,42	<0,22
1,2,3,7,8-PeCDD	<1,2	<1,4	<0,55	<0,35	<1,1	<0,77	<0,83	<0,71
1,2,3,4,7,8-HxCDD	<1,2	<2,3	<0,69	<0,49	<2,2	<0,69	<1,2	<0,85
1,2,3,6,7,8-HxCDD	<1,0	<2,1	<0,63	<0,44	<1,6	<0,59	<0,88	<0,77
1,2,3,7,8,9-HxCDD	<1,3	<2,7	<0,80	<0,56	<2,1	<0,66	<1,1	<0,98
1,2,3,4,6,7,8-HpCDD	3,94	5,51	2,71	2,83	4,15	4,40	4,61	2,16
OCDD	20,8*	14,7	13,2	12,5	14,7*	17,1*	21,6	10,3
2,3,7,8-TCDF	1,03	0,924	0,670	0,604	<0,63	0,716	1,47	0,401
1,2,3,7,8-PeCDF	0,935	<1,7	<0,59	0,727	<1,2	0,414	0,426	0,827
2,3,4,7,8-PeCDF	1,32	<1,8	0,694	0,959	1,28	0,876	0,984	0,899
1,2,3,4,7,8-HxCDF	1,21	<1,8	0,839	1,11	1,17	1,13	0,930	0,675
1,2,3,6,7,8-HxCDF	1,07	<1,8	0,768	0,764	0,835	0,722	0,706	0,805
1,2,3,7,8,9-HxCDF	<0,79	<2,4	<0,59	<0,54	<0,69	<0,53	<0,41	<0,45
2,3,4,6,7,8-HxCDF	1,00	<2,0	0,64	1,22	1,05	1,29	0,739	0,877
1,2,3,4,6,7,8-HpCDF	4,39	5,36	3,49	3,91	5,08	7,29	4,08	3,43
1,2,3,4,7,8,9-HpCDF	0,782	<1,6	0,343	0,415	<1,2	1,26	0,586	1,00
OCDF	3,14**	5,70	3,19	3,84	4,20**	26,6*	8,56*	6,78
TOT pgI-TE/m^{2}d	2,03	2,26	1,20	1,28	2,16	1,50	1,62	1,29

Results and Discussion

The deposition data are reported in Table1; they compare favorably to recent data from Germany [4]; the air data are reported in Table 2. They show that the actual contamination levels are low and comparable to levels found in the summer in rural areas of the U.S.[5] The summertime contamination levels are generally lower than the wintertime ones[4,6]; this is however more true for air particulate than for deposition. There are no significant differences in the deposition samples throughout all the area; the ones closest to the zone where the carcinoma cases occurred (locations 2, 3, 4) did not show higher pollution load than the others, in this period.

In Table 3 the soil data are reported. The soil contamination is again low, comparable to remote areas and generally lower than urban sites[7],except for spot 8, which is the remote location and it is located in a wood. Its value is similar to the ones reported for forest sites, which generally display higher dioxin levels than most of the other kinds of non urban soils[8]. At present the soil analysis seems to show that these samples were not affected by atmospheric deposition or fallout of heavily contaminated airborne particles. The study is still in progress and the winter samples are now being analyzed.

Table 2: Air contamination (fg/m^3)in three Mantua sites in the summer season

Location	1	3	5
2,3,7,8-TCDD	< 0,89	< 0,75	< 0,41
1,2,3,7,8-PeCDD	< 1,6	< 1,9	< 1,0
1,2,3,4,7,8-HxCDD	< 1,2	< 1,0	0,989
1,2,3,6,7,8-HxCDD	1,53	< 0,86	1,26
1,2,3,7,8,9-HxCDD	1,28	< 0,85	1,14
1,2,3,4,6,7,8-HpCDD	18,4	21,7	19,7
OCDD	75,9	55,9	65,4
2,3,7,8-TCDF	< 1,3	0,986	0,949
1,2,3,7,8-PeCDF	1,55	< 2,4	1,72
2,3,4,7,8-PeCDF	2,23	2,99	3,95
1,2,3,4,7,8-HxCDF	4,81	5,78	7,10
1,2,3,6,7,8-HxCDF	4,46	7,64	4,29
1,2,3,7,8,9-HxCDF	< 2,6	< 5,3	< 2,9
2,3,4,6,7,8-HxCDF	7,24	12,1	10,0
1,2,3,4,6,7,8-HpCDF	38,5	35,6	43,6
1,2,3,4,7,8,9-HpCDF	7,40	8,95	9,47
OCDF	63,8	54,6	70,0
TEQ fgI-TE/m^3	5,02	6,24	6,09

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Table 3. PCDD/PCDF soil (depth 0-10 cm) concentration pg/g in five locations in Mantua

Location	8	6	5	4	3
2,3,7,8-TCDD	0,375	0,149	< 0,13	< 0,18	< 0,24
1,2,3,7,8-PeCDD	0,918	0,258	< 0,37	< 0,23	< 0,52
1,2,3,4,7,8-HxCDD	1,56	0,193	< 0,18	< 0,37	< 0,20
1,2,3,6,7,8-HxCDD	1,90	0,302	< 0,18	< 0,19	< 0,20
1,2,3,7,8,9-HxCDD	1,94	0,248	< 0,18	< 0,27	< 0,20
1,2,3,4,6,7,8-HpCDD	19,6	8,50	2,21	1,82	3,48
OCDD	80,9	49,9	13,4	9,09	22,2
2,3,7,8-TCDF	3,56	1,07	0,266	0,315	0,788
1,2,3,7,8-PeCDF	0,903	0,378	< 0,15	< 0,33	0,477
2,3,4,7,8-PeCDF	3,48	0,710	0,217	< 0,27	0,635
1,2,3,4,7,8-HxCDF	5,15	0,918	0,255	0,665	0,574
1,2,3,6,7,8-HxCDF	1,71	0,514	< 0,12	0,286	0,419
1,2,3,7,8,9-HxCDF	< 0,34	< 0,35	< 0,12	< 0,21	< 0,29
2,3,4,6,7,8-HxCDF	3,41	0,441	0,143	0,317	0,312
1,2,3,4,6,7,8-HpCDF	39,5	6,34	2,95	6,65	2,54
1,2,3,4,7,8,9-HpCDF	4,44	0,527	0,330	0,633	0,390
OCDF	37,3	5,73	3,15	12,3	2,91
TEQ pg I-TE/g	5,31	1,25	0,449	0,546	0,934