ENVI (po)

Levels of PCDD/F in soil samples in the vicinity of a municipal solid waste incinerator

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1. Introduction

Because of the lack of available landfills, as well as the environmental degradation resulting from municipal waste landfills, it is expected that in most developed countries the number of municipal solid waste incinerators (MSWI) will increase in the coming years. However, MSWI pose a variety of potential environmental risks that should not be underestimated.[1-3] In public discussion, the main argument against waste incineration is the environmental release of pollutants, especially metals, semivolatile compounds, and polyclorinated dibenzodioxins (PCDD) and dibenzofurans (PCDF). Although several classes of toxic organic compounds have been identified in emissions from MSWI, most research has focused on PCDD/F due to their extraordinary toxicologic properties.[1-4]

It is well established that incineration of municipal, hazardous and hospital waste can be generally considered as the major contributor to PCDD/F emissions into air,[5] with MSWI being now considered to be the major sources of PCDD/F in aerial emissions.[6-7] Once in the atmosphere, PCDD/F become dispersed throughout the environment. Soil surveys from several countries indicate that PCDD/F are ubiquitous.[8] Soils are uniformly distributed, relatively easy to collect and handle, and they are a conservative matrix for PCDD/F.[9] The deposition of PCDD/F to soils occurs by the processes of wet and dry deposition. For each process PCDD/F can be in two phases. In the case of wet deposition, PCDD/F are dissolved in the precipitation and they are associated with atmospheric aerosols scavenged by the precipitation. In the case of dry deposition, PCDD/F are deposited to soils by vapor-phase diffusion into the soil, or are associated with particles that deposit to soils by gravitational settling. Some studies of PCDD/F behavior in soils indicate that these compounds are highly immobile once deposited, whereas other studies concluded that PCDD/F absorption to soils may approach irreversibility due to the encapsulation of the compounds in the soil organic and mineral matter.[10] Losses due to erosion or degradation of PCDD/F in soils must also be considered, although in a soil stabilized by vegetation such losses are generally much less than 1% per year.

Degradation of PCDD/F in soils is considered to be slow or nonexistent under natural conditions. PCDD/F are transported from soil to aerial parts of plants and can reach the food chain. In the estimation of the risk of human exposure, Kimbrough and associates[11] advised that a concentration level of 1 ppb TCDD (2,3,7,8-tetrachlorodibenzo-*p*-dioxin) in soil might be a level of concern. The

purpose of this study was to assess the magnitude and distribution of PCDD/F in the vicinity of a MSW incinerator from Tarragona (Catalonia, Spain) by determining their concentrations in the top layer of soil as a measure of former emissions from the incinerator stack.

2. Methods

A wide description of the incinerator plant was previously given.[12] Duplicate soil samples were collected at 250, 500, 750 and 1000 m from the stack in each of the three main directions of the wind rose (NE, SE, SW). Selection and collection of representative soil samples were carried out according to the results of a dispersal model (EFFECT). Twenty-four homogenized soil samples were dried and sieved (2 mm mesh). Samples were subsequently transferred into a soxhlet apparatus and spiked with 1 ng of each of 10 different ^{13}C-labelled PCDD/F standards, corresponding to the tetra-to octachloro homologues (Wellington Laboratories, Guelph, Canada). After extraction with toluene for 48 h, the extracts were evaporated to 2 mL. The clean-up was carried out using a three column disposable set: multilayer silica column, florisil, and basic alumina. If necessary, a fourth column with active carbon was used to eliminate background interferences.

Samples were analysed for each of the five chlorinated dibenzo-p-dioxin and dibenzofuran congener groups (with four to eight chlorines) by HRGC/HRMS with a Fiasons 8060 Gas Chromatograph equipped with a 60 m DB-5 (J&W Scientific) fused silica capillary column (0.25 mm ID, 0.25 μm film) coupled to a VG-AutoSpec Ultima Mass Spectrometer operating in the EI mode at 10.000 resolving power. Quantitative determination of PCDD/F was performed by an isotope dilution method using relative response factors previously obtained from five calibration standard solutions (CHEMSYN Science Laboratories). A blank sample was analyzed for every batch of 6 samples. Recoveries of internal standards, as determined against external standard, generally varied between 80-110%. The relative standard deviation of the method was 15%. The detection limit was between 0.013 pg/g to 0.188 pg/g from isomers tetra-to octachloro dioxins and dibenzofurans. pH and the total organic carbon content in soil samples were also determined.

3. Results and Discussion

Because retention of PCDD/F in soils is a function of both organic carbon content and the levels of PCDD/F deposited in soils, results were reported based on dry weight and organic carbon content. Figure 1 shows a representative example of most soil samples (I-TEQ = 0.537 pg/g). The I-TEQ dioxin/furan ratio was 0.647. The predominant congeners and contributors to I-TEQ were tetra- and pentafurans. PCDD/F ranged from 0.224 to 1.262 I-TEQ and the highest concentration was found at 750 m from the stack in the NE direction. In most samples, OCDD was the predominant congener and contributor to the I-TEQ. The congener group profiles of soils were similar to those reported elsewhere for urban soils.[8,13]

PCDD/F levels in soil samples at different distances from the stack are summarized in Table 1. As it can be seen, the concentrations of PCDD/F increased from 0 to 750 m and then decreased again. Tables 2 shows the concentrations of PCDD/F in soils according to the different wind directions. The highest PCCD/F levels corresponded to the SE direction. It is in agreement with the results of a previous survey of metal levels in the vicinity of the same incinerator plant, when the highest metal concentrations were also found in the samples collected in the SE direction.[12]

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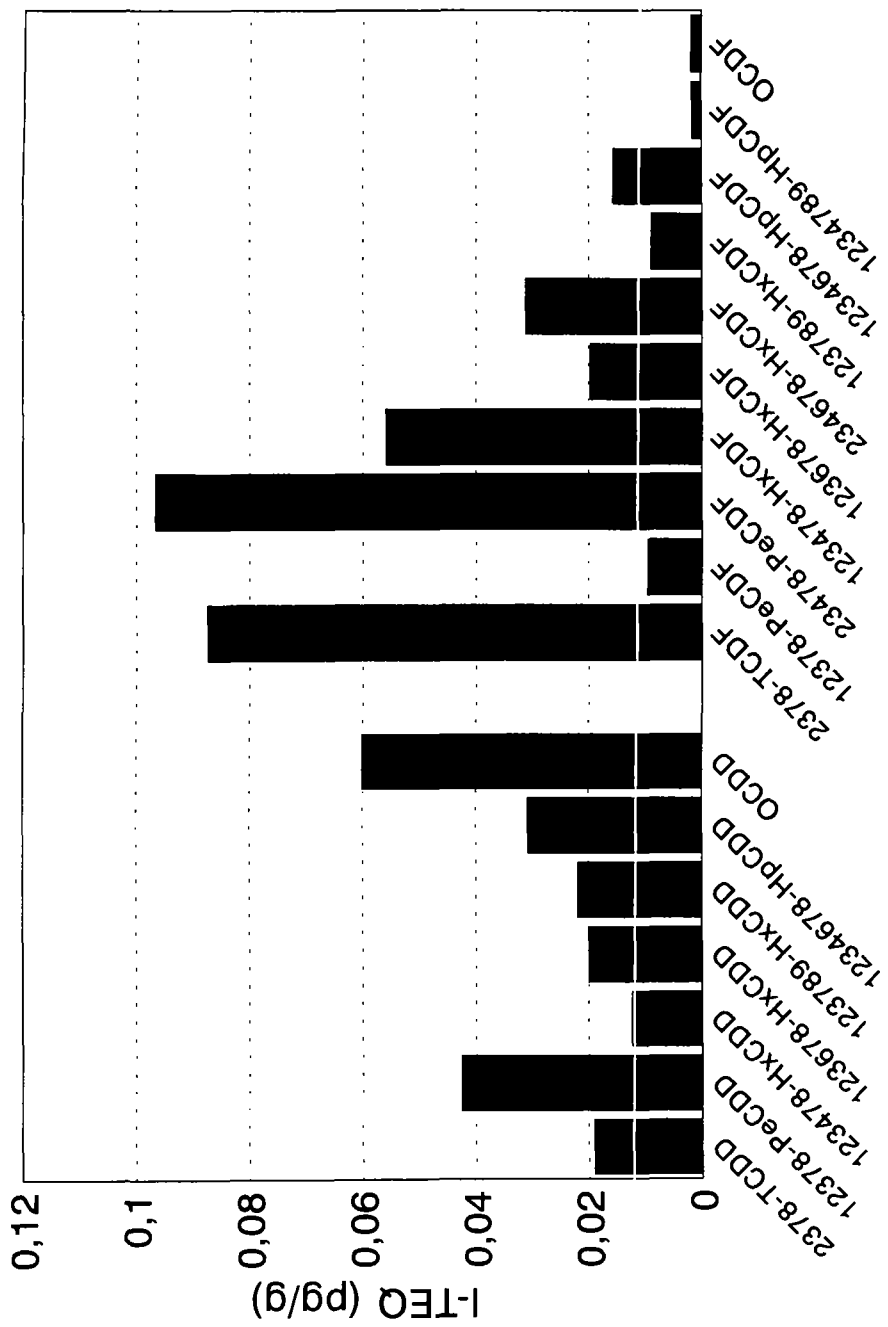

Fig 1. Mean congener group profiles

Table 1. Levels of PCDD/F (pg/g) in soil samples collected at different distances from a MSWI

	250	500	750	1000
2,3,7,8-TCDD	ND[a]	0.03	0.01	0.02
1,2,3,7,8-PeCDD	0.10	0.06	0.11	0.09
1,2,3,4,7,8-HxCDD	0.05	0.12	0.18	0.08
1,2,3,6,7,8-HxCDD	0.09	0.22	0.26	0.14
1,2,3,7,8,9-HxCDD	0.17	0.15	0.35	0.21
1,2,3,4,6,7,8-HpCDD	2.12	3.39	6.67	1.72
OCDD	234.07	23.11	54.76	7.62
2,3,7,8-TCDF	0.34	0.69	1.28	1.14
1,2,3,7,8-PeCDF	0.09	0.20	0.21	0.22
2,3,4,7,8-PeCDF	0.10	0.12	0.33	0.25
1,2,3,4,7,8-HxCDF	0.22	0.23	1.18	0.64
1,2,3,6,7,8-HxCDF	NQ*	0.09	0.43	0.23
2,3,4,6,7,8-HxCDF	0.17	0.15	0.61	0.33
1,2,3,7,8,9-HxCDF	ND[b]	0.06	0.15	0.10
1,2,3,4,6,7,8-HpCDF	0.51	0.64	3.60	1.33
1,2,3,4,7,8,9-HpCDF	NQ*	0.09	0.31	0.15
OCDF	0.84	0.85	3.88	1.38
I-TEQ PCDDs	0.336	0.162	0.262	0.133
I-TEQ PCDFs	0.133	0.199	0.579	0.396
I-TEQ TOTAL	0.48	0.36	0.84	0.53

ND: Not detected ([a]detection limit, 0.02; [b]detection limit, 0.096).
NQ*: Data not quantified (the relation S/N > 3 was not reached).

Table 2. Levels of PCDD/F (pg/g) in soil samples collected at different wind directions

	NE	SE	SW
2,3,7,8-TCDD	0.03	0.04	NQ*
1,2,3,7,8-PeCDD	0.06	0.08	0.05
1,2,3,4,7,8-HxCDD	0.07	0.23	0.07
1,2,3,6,7,8-HxCDD	0.08	0.45	0.13
1,2,3,7,8,9-HxCDD	0.11	0.23	0.12
1,2,3,4,6,7,8-HpCDD	0.69	8.11	1.37
OCDD	2.27	60.00	7.06
2,3,7,8-TCDF	0.35	1.27	0.45
1,2,3,7,8-PeCDF	0.07	0.49	0.05
2,3,4,7,8-PeCDF	0.08	0.18	0.09
1,2,3,4,7,8-HxCDF	0.16	0.33	0.19
1,2,3,6,7,8-HxCDF	0.07	0.12	0.09
2,3,4,6,7,8-HxCDF	0.14	0.14	0.18
1,2,3,7,8,9-HxCDF	0.09	0.05	0.04
1,2,3,4,6,7,8-HpCDF	0.40	0.95	0.57
1,2,3,4,7,8,9-HpCDF	0.08	0.11	0.07
OCDF	0.36	1.46	0.71
I-TEQ PCDDs	0.095	0.312	0.078
I-TEQ PCDFs	0.130	0.317	0.150
I-TEQ TOTAL	0.225	0.629	0.228

NQ*: Data not quantified (the relation S/N > 3 was not reached).

Because PCDD/F have an extremely high K_{OC} value, soils with a great content of organic matter are characterized by high PCDD/F concentrations. Brzuzy and Hites[9] reported a high correlation of PCDD/F with organic carbon indicating that soil acts as a conservative matrix. The process of sorption to organic carbon would be the dominant mechanism. By contrast, Fiedler and associates[15] did not find any correlation between the organic carbon content of the soils and the levels of PCDD/F. The levels of PCDD/F here obtained were lower than those found by de Jong and co-workers[14] near MSWI in the Netherlands. In the present study, a high correlation between hexafurans ($r = 0.9947$, $p < 0.01$) was found. The current results show that soils can be used to estimate the PCDD/F deposition from a MSWI.

The emission rates of PCDD/F from the stack ranged between 1-3 ng I-TEQ/m^3 (unpublished data). Since the plant handles an annual amount of about 144000 tons of municipal waste, and considering an emission of 5140 Nm^3/Tm, an anual PCDD/F emission between 0.7 and 4.6 g TEQ/year could be estimated. For assesment of human exposure risk, examination of the TEQ values indicates that the highest value (1.26 ppt) is 1/793 the interin multimedia soil guideline of 1 ppb I-TEQ. According to the above results, the enviromental levels of PCDD/F in the vicinity of the incinerator plant here evaluated, as well as the potential hazard for adverse health effects would be rather low.

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