HEALTH RISK ASSESSMENT OF PCDD/Fs FOR A POPULATION LIVING IN THE VICINITY OF A HAZARDOUS WASTE LANDFILL

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Introduction

Landfills are currently considered as the last alternative of municipal and hazardous waste disposal in the EU. Unfortunately, valorization methods of certain waste have not been established and/or extended yet. Fly ash is a common by-product originated during gas depuration in incineration and sinter plants, and with a potential high content of polychlorinated dibenzo-*p*-dioxins and furans (PCDD/Fs)[1, 2]. Fly ashes must be therefore safely deposited in appropriate facilities, such as hazardous waste landfills (HWLs). However, waste landfills have been pointed out as potential release sources of organic pollutants such as polychlorinated biphenyls (PCBs) to soil, air and groundwater[3, 4].

The only class-III (most dangerous) HWL of Catalonia (Spain) is located in Castellolí. It is currently used as a deposit for fly ashes from municipal waste incinerators, asbestos, as well as solid residues of diverse characteristics. From the beginning, the presence of this facility meant an important concern for the local population and authorities. Due to this concern, a surveillance program was initiated in 2007 in order to evaluate the health risks of the Castellolí HWL for the people living nearby. The purpose of the present investigation was to determine the PCDD/F concentrations in air and soil in the vicinity of the HWL of Castellolí, and to assess human health risks derived from the exposure to PCDD/Fs.

Materials and methods

In July 2007, samples of soil and air were collected in 4 locations in/around the HWL of Castellolí. Samples were collected in the HWL of Castellolí, in the villages of Castellolí and Òdena (located at 2.5 and 3 km, respectively, from the HWL), and in the town of Jorba (situated at 11 km), which was used as a blank. An additional soil sample was obtained in the village of Copons, as a control not directly impacted by a motorway.

The sampling methodology has been described elsewhere[5, 6]. Briefly, samples of surface soil (0-5 cm) were taken as bulk samples representing an area of 10 m^2. Samples were kept in polyethylene bags. Once in the lab, they were dried at room temperature, sieved through a 2-mm mesh screen, and properly stored until the analysis. Air samples were obtained according to the US EPA method TO-9. A high volume active sampling device TE-1000 PUF (Tisch Environmental, Cleves, OH, USA), equipped with a polyurethane foam (PUF) and a quartz fiber filter, was used to separately obtain the gas and particulate phases of PCDD/Fs, respectively. A total amount of 600-700 m^3 of air were collected in a sampling time of approximately 48 h. Samples were kept in hermetic amber glass jars to avoid potential losses due to photodegradation.

PCDD/F levels were determined according to the German method VDI 3499. Prior to the pre-treatment, recovery internal standards were spiked to calculate recovery percentages. An Accelerated Solvent Extraction with toluene was done, while the clean-up consisted on a multicolumn adsorption chromatography. The purified extract was analyzed by high resolution gas chromatography coupled to high resolution mass spectrometry (HRGC/HRMS).

Statistical treatment was done by means of SPSS 15.0 software package. The Levene test was applied to study whether or not data followed a normal distribution. Subsequently, an analysis of variance (ANOVA) or a Kruskal-Wallis test was executed. A probability of 0.05 or lower ($p < 0.05$) was considered as significant. For calculations, values below the limit of detection (LOD) were considered as one-half of that limit. Toxic equivalents (TEQ) were calculated according to the updated WHO-TEF system[7].

Results and discussion

PCDD/F concentrations in air and soil

PCDD/F levels in air and soil samples collected around the HWL of Castellolí are summarized in Table 1. Total concentrations of PCDD/Fs in air ranged from 3.4 to 4.1 fg WHO-TEQ/m^3. Most individual PCDD/F congeners presented values below the LOD, reflecting that the state of pollution by PCDD/Fs in the zone is really low. OCDD was the most abundant congener, while 2,3,4,7,8 PeCDF presented the highest contribution to total WHO-TEQ/m^3. The levels of the PCDF homologues were higher than those of PCDDs. As previously reported[8], a decreasing pattern of PCDFs according to the chlorination degree was observed. Anyhow, the current PCDD/F concentrations in air of Castellolí are in the lowest part of the range, in comparison to other areas of Catalonia[9].

Regarding to soils, PCDD/F concentrations of 5 samples collected around the HWL ranged between 0.17 and 1.50 ng WHO-TEQ/kg dry weight (dw). A higher concentration of PCDD/Fs was noted in samples taken in or close to the HWL, than in those obtained in blank sites (1.21 vs. 0.17 ng WHO-TEQ/kg dw). This difference could be due to the past deposition of some chromate-derivates and high PCDD/F-containing fly ashes on the HWL of Castellolí. In any case, the current concentrations of PCDD/Fs in soil samples collected in populated areas near and far the HWL are lower than those previously reported in other areas of Catalonia[10]. Moreover, the PCDD/F level found in the soil sample of the HWL (1.50 ng WHO-TEQ/kg dw) is really low when compared with concentrations found in the literature concerning to hazardous and municipal solid waste landfills[11-14]. In the present investigation, the concentration of the individual PCDD/F congeners ranged from <LOD (for most congeners in the control area) to 183 ng/kg (OCDD in Castellolí sample). In fact, OCDD was, as in air, the most abundant PCDD/F congener, while 2,3,7,8-TCDD was not detected in any sample.

Human health risk assessment

The health risks derived from the exposure to PCDD/Fs were evaluated for the population living in the surroundings of the HWL of Castellolí. Environmental exposure to PCDD/Fs through three different pathways (air inhalation, dermal absorption through soil and dust, and ingestion of soil and dust) was separately calculated[15, 16]. The concentrations of PCDD/Fs in air were used to determine the inhalation, while dermal absorption and ingestion of soils and dust were calculated from the PCDD/F levels in soils. The environmental exposure to PCDD/Fs through those 3 routes, for adults and children living near (2.5-3 km) and far (11 km) from the HWL of Castellolí, is depicted in Figure 1. The residents in the surroundings of the HWL seemed to be more exposed to PCDD/Fs than the population living far. The higher concentration of PCDD/Fs found in soils of Castellolí and Òdena resulted in a higher exposure to PCDD/Fs through dermal absorption and ingestion of soils and dust. On the other hand, air inhalation of PCDD/Fs was very similar in both areas. Notwithstanding, total environmental exposure to PCDD/Fs was quite lower than those reported for other industrial and urban areas[16, 17], with values ranging between $1.29\text{-}0.65 \cdot 10^{-6}$ and $2.12\text{-}0.91 \cdot 10^{-6}$ for adults and children, respectively.

Dietary inatke has been largely demonstrated to be the main exposure route to PCDD/Fs, meaning more than 95%. Recently, we determined the dietary intake of PCDD/Fs for the Catalan population. The ingestion of PCDD/Fs through foodstuffs was calculated to be $3.7 \cdot 10^{-4}$ and $9.7 \cdot 10^{-4}$ ng WHO-TEQ/kg/day for adults and children, respectively[18]. Therefore, the environmental exposure would currently mean only <0.3% of the total exposure to these pollutants in the area under evaluation.

Non-carcinogenic risks were evaluated by comparing the total exposure and the maximum tolerable daily intake suggested by the World Health Organization (4 pg I-TEQ/kg/day)[19]. The Hazard Quotient (HQ) was estimated to range $1.61\text{-}3.23 \cdot 10^{-4}$ for adults, while HQ for children was $2.29\text{-}5.29 \cdot 10^{-4}$. In turn, the carcinogenic risks were assessed by considering $1 \cdot 10^{-3}$ pg I-TEQ/kg/day as an estimator of upper bound cancer risk[20]. A cancer risk index of 0.6-2.1 was established, meaning between 0.01 and 0.03 cancers per year in an adult population of one million people.

In conclusion, relatively higher concentrations of PCDD/Fs were found in soils of the HWL of Castellolí and the villages located in the vicinity than in those obtained in samples collected far away. This fact resulted in a slightly increase of PCDD/F exposure, mainly though dermal absorption and ingestion of soils and dust. However, because the low PCDD/F levels in air, the current environmental exposure is notably lower than that reported in other industrial and urban areas of Catalonia, as well as remarkably lower than the dietary intake of PCDD/Fs. In summary, the HWL of Castellolí does not mean an important increase of non-carcinogenic and carcinogenic risks for the health of the local population. However, the state of pollution in the environment of the HWL should still be monitored to assure that the levels of PCDD/Fs, especially in soils, do not experiment an increasing tendency.

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Table 1: PCDD/F concentrations in soils (ng/kg dw) and air (pg/m^3) collected at different locations in/around the HWL of Castellolí (Catalonia, Spain)

	Soil					Air			
	HWL	Castellolí	Òdena	Jorba	Copons	HWL	Castellolí	Òdena	Jorba
2,3,7,8-TCDD	<0.1	<0.1	<0.1	<0.1	<0.1	<0.002	<0.002	<0.002	<0.002
1,2,3,7,8 PeCDD	<0.1	0.1	<0.1	<0.1	<0.1	<0.002	<0.002	<0.002	<0.002
1,2,3,4,7,8-HxCDD	0.2	0.2	0.1	<0.1	<0.1	<0.002	<0.002	<0.002	<0.002
1,2,3,6,7,8-HxCDD	0.7	0.6	0.2	<0.1	<0.1	<0.002	<0.002	<0.002	<0.002
1,2,3,7,8,9-HxCDD	0.4	0.3	0.3	<0.1	<0.1	<0.002	<0.002	<0.002	<0.002
1,2,3,4,6,7,8-HpCDD	5.5	25.8	5.6	<0.5	0.5	<0.010	<0.010	<0.010	<0.010
OCDD	13.8	183	33.4	<1.0	3.2	0.022	<0.020	<0.020	0.022
2,3,7,8-TCDF	0.5	0.7	0.3	0.1	<0.1	0.002	<0.002	0.003	0.002
1,2,3,7,8 PeCDF	0.9	0.2	0.8	<0.1	<0.1	<0.002	0.002	<0.002	<0.002
2,3,4,7,8 PeCDF	1.2	0.5	1.4	<0.1	<0.1	0.003	0.002	<0.002	0.003
1,2,3,4,7,8-HxCDF	1.7	0.3	1.8	<0.1	<0.1	<0.002	0.003	<0.002	<0.002
1,2,3,6,7,8-HxCDF	1.6	0.2	1.8	<0.1	<0.1	<0.002	<0.002	<0.002	<0.002
1,2,3,7,8,9-HxCDF	<0.1	<0.1	0.2	<0.1	<0.1	<0.002	<0.002	<0.002	<0.002
2,3,4,6,7,8-HxCDF	2.1	0.3	1	<0.1	<0.1	<0.002	0.003	<0.002	<0.002
1,2,3,4,6,7,8-HpCDF	11.1	4.0	2.6	<0.3	<0.3	<0.006	0.009	<0.006	<0.006
1,2,3,4,7,8,9-HpCDF	0.9	<0.3	0.4	<0.3	<0.3	<0.006	<0.006	<0.006	<0.006
OCDF	32.3	9.8	1.1	<1.0	<1.0	<0.020	<0.020	<0.020	<0.020
Total WHO-TEQ	1.5	0.93	1.21	0.17	0.17	0.0039	0.0041	0.0034	0.0039

Figure 1: Environmental exposure to PCDD/Fs for adults and children living near (2.5-3 km) and far (11 km) the HWL of Castellolí (Catalonia, Spain)