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#### **References**

- Abrahams PW. 2002. Soils: their implications to human health. *Sci Total Environ* 291: 1-32
- Bache CA, Gutenmann WH, Rutzke M, *et al.* 1991. Concentrations of metals in grasses in the vicinity of a municipal refuse incinerator. *Arch Environ Contam Toxicol* 20: 538-542
- Belles M, Rico A, Schuhmacher M, *et al.* 1995. Reduction of lead concentrations in vegetables grown in Tarragona Province, Spain, as a consequence of reduction of lead in gasoline. *Environ Int* 21: 821-825

- Bocio A, Nadal M, Garcia F, *et al.* 2005. Monitoring metals in the population living in the vicinity of a hazardous waste incinerator: concentrations in autopsy tissues. *Biol Trace Elem Res* 106: 41-50
- BOE, 2002. RD-1073-2002 Sobre evaluación y gestión de la calidad del aire ambiente en relación con el dióxido de azufre, dióxido de nitrógeno, óxidos de nitrógeno, partículas, plomo, benceno y monóxido de carbono. . Boletín Oficial del Estado, Spain
- Bosco ML, Varrica D and Dongarra G. 2005. Case study: Inorganic pollutants associated with particulate matter from an area near a petrochemical plant. *Environ Res* 99: 18-30
- Capuano F, Cavalchi B, Martinelli G, *et al.* 2005. Environmental prospection for PCDD/PCDF, PAH, PCB and heavy metals around the incinerator power plant of Reggio Emilia town (Northern Italy) and surrounding main roads. *Chemosphere* 58: 1563-1569
- Chang LW. 1996. *Toxicology of Metals*. CRC Lewis Publishers, Boca Raton, FL
- Chen T-B, Zheng Y-M, Lei M, *et al.* 2005. Assessment of heavy metal pollution in surface soils of urban parks in Beijing, China. *Chemosphere* 60: 542-551
- Domingo JL. 1994. Metal-induced developmental toxicity in mammals: A review. *J Toxicol Environ Health* 42: 123-141
- Domingo JL, Schuhmacher M, Llobet JM, *et al.* 2001. PCDD/F concentrations in soil and vegetation in the vicinity of a municipal waste incinerator after a pronounced decrease in the emissions of PCDD/Fs from the facility. *Chemosphere* 43: 217-226
- Efroymsen RA, Sample BE and Suter li GW. 2004. Bioaccumulation of inorganic chemicals from soil by plants: Spiked soils vs. field contamination or background. *Hum Ecol Risk Assess* 10: 1117-1127
- Ferreira-Baptista L and De Miguel E. 2005. Geochemistry and risk assessment of street dust in Luanda, Angola: A tropical urban environment. *Atmos Environ* 39: 4501-4512
- Ferreira C, Ribeiro A and Ottosen L. 2003. Possible applications for municipal solid waste fly ash. *J Hazard Mat* 96: 201-216

- Garrett RG. 2000. Natural sources of metals to the environment. *Hum Ecol Risk Assess* 6: 945-963
- Generalitat de Catalunya. 1997. La Qualitat de l'Aire a Catalunya, dades del període 1997-1998. Xarxa de Vigilància i Previsió de la Contaminació Atmosfèrica de Catalunya (XVPCA). Departament de Medi Ambient i Habitatge, Barcelona, Spain
- Generalitat de Catalunya. 2000. Nivells de qualitat de l'aire mesurats durant el període 1999-2000. Xarxa de Vigilància i Previsió de la Contaminació Atmosfèrica de Catalunya (XVPCA). Departament de Medi Ambient i Habitatge, Barcelona, Spain
- Generalitat de Catalunya. 2003. La qualitat de l'aire a Catalunya. Xarxa de Vigilància i Previsió de la Contaminació Atmosfèrica de Catalunya (XVPCA). Departament de Medi Ambient i Habitatge, Barcelona, Spain
- Generalitat de Catalunya. 2005. Partícules Totals en suspensió: PST. Xarxa de Vigilància i Previsió de la Contaminació Atmosfèrica de Catalunya (XVPCA). Departament de Medi Ambient i Habitatge, Barcelona, Spain
- Glorennec P, Zmirou D and Bard D. 2005. Public health benefits of compliance with current E.U. emissions standards for municipal waste incinerators: A health risk assessment with the CalTox multimedia exposure model. *Environ Int* 31: 693-701
- Granero S and Domingo JL. 2002. Levels of metals in soils of Alcala de Henares, Spain: human health risks. *Environ Int* 28: 159-164
- Grant RL, Rodriguez RJ, Hofelt CS, *et al.* 2002. Shortcomings in USEPA's approach for predicting risk due to consumption of animal food products impacted by air emissions from hazardous waste combustion facilities: A case study involving phthalates. *Hum Ecol Risk Assess* 8: 1137-1154
- Hawley JK. 1986. Assessment of health risk from exposure to contaminated soil. *Risk Anal* 5: 289-302
- Lee CC, Chen HL, Su HJ, *et al.* 2005a. Evaluation of PCDD/Fs patterns emitted from incinerator via direct ambient sampling and indirect serum levels assessment of Taiwanese. *Chemosphere* 59: 1465-1474
- Lee JS, Chon HT and Kim KW. 2005b. Human risk assessment of As, Cd, Cu and Zn in the abandoned metal mine site. *Environ Geochem Health* 27: 185-191

- Linak WP and Wendt JOL. 1993. Toxic metal emissions from incineration: Mechanisms and control. *Prog Energ Combust* 19: 145-185
- Loska K, Wiechula D and Korus I. 2004. Metal contamination of farming soils affected by industry. *Environ Int* 30: 159-165
- Llobet JM, Granero S, Schuhmacher M, *et al.* 1999. Temporal variation in metal concentrations in soils and vegetation in the vicinity of a municipal solid waste incinerator. *Toxicol Environ Chem* 71: 63-73
- Llobet JM, Schuhmacher M and Domingo JL. 2000. Observations on metal trends in soil and vegetation samples collected in the vicinity of a hazardous waste incinerator under construction (1996-1998). *Toxicol Environ Chem* 77: 119-129
- Llobet JM, Schuhmacher M and Domingo JL. 2002. Spatial distribution and temporal variation of metals in the vicinity of a municipal solid waste incinerator after a modernization of the flue gas cleaning systems of the facility. *Sci Total Environ* 284: 205-214
- Meneses M, Llobet JM, Granero S, *et al.* 1999. Monitoring metals in the vicinity of a municipal waste incinerator: temporal variation in soils and vegetation. *Sci Total Environ* 226: 157-164
- Mesilio L, Farago ME and Thornton I. 2003. Reconnaissance soil geochemical survey of Gibraltar. *Environ Geochem Health* 25: 1-8
- Nadal M, Bocio A, Schuhmacher M, *et al.* 2005. Monitoring metals in the population living in the vicinity of a hazardous waste incinerator: levels in hair of school children. *Biol Trace Elem Res* 104: 203-213
- Nadal M, Schuhmacher M and Domingo JL. 2004. Metal pollution of soils and vegetation in an area with petrochemical industry. *Sci Total Environ* 321: 59-69
- Notten MJ, Oosthoek AJ, Rozema J, *et al.* 2005. Heavy metal concentrations in a soil-plant-snail food chain along a terrestrial soil pollution gradient. *Environ Pollut* 138: 178-190
- OJEC, 2000. Directive 2000/76/EC of the European Parliament and of the Council of 4 December 2000 on the incineration of waste. *Official Journal of the European Communities*

- Rappe C. 1991. Review of the dioxin problem. IARC Sci Publ: 1-3. Institute of Environmental Chemistry, University of Umea, Sweden
- Rimmer DL, Vizard CG, Pless-Mulloli T, *et al.* 2006. Metal contamination of urban soils in the vicinity of a municipal waste incinerator: One source among many. *Sci Total Environ* (in press)
- Ruiz-Cortés E, Reinoso R, Díaz-Barrientos E, *et al.* 2005. Concentrations of potentially toxic metals in urban soils of Seville: Relationship with different land uses. *Environ Geochem Health* 27: 465-474
- Sardans J and Peñuelas J. 2005. Trace element accumulation in the moss *Hypnum cupressiforme* Hedw. and the trees *Quercus ilex* L. and *Pinus halepensis* Mill. in Catalonia. *Chemosphere* 60: 1293-1307
- Schuhmacher M, Agramunt MC, Bocio A, *et al.* 2003. Annual variation in the levels of metals and PCDD/PCDFs in soil and herbage samples collected near a cement plant. *Environ Int* 29: 415-421
- Schuhmacher M, Belles M, Rico A, *et al.* 1996. Impact of reduction of lead in gasoline on the blood and hair lead levels in the population of Tarragona Province, Spain, 1990-1995. *Sci Total Environ* 184: 203-209
- Schuhmacher M, Bocio A, Agramunt MC, *et al.* 2002. PCDD/F and metal concentrations in soil and herbage samples collected in the vicinity of a cement plant. *Chemosphere* 48: 209-217
- Schuhmacher M, Domingo JL, Granero S, *et al.* 1999. Soil monitoring in the vicinity of a municipal solid waste incinerator: Temporal variation of PCDD/Fs. *Chemosphere* 39: 419-429
- Schuhmacher M, Granero S, Xifro A, *et al.* 1998. Levels of PCDD/Fs in soil samples in the vicinity of a municipal solid waste incinerator. *Chemosphere* 37: 2127-2137
- Schuhmacher M, Xifro A, Llobet JM, *et al.* 1997. PCDD/Fs in soil samples collected in the vicinity of a municipal solid waste incinerator: human health risks. *Arch Environ Contam Toxicol* 33: 239-246
- USEPA (U.S. Environmental Protection Agency). 1997. *Terms of Environment: Glossary, Abbreviations and Acronyms*. 175-B-97-001, Washington, DC, USA

USEPA (U.S. Environmental Protection Agency). 1999. Integrate Risk Information (IRIS). Duluth, MN, USA

USEPA (U.S. Environmental Protection Agency). 2004. Preliminary Remediation Goals. Available at <http://www.epa.gov/region09/waste/sfund/prg/index.html>

USEPA (U.S. Environmental Protection Agency). 2005. Guidelines for Carcinogen Risk Assessment. EPA/630/P-03/001F. Washington, DC, USA

Wilcke W, Krauss M and Kobza J. 2005. Concentrations and forms of heavy metals in Slovak soils. J Plant Nutr Soil Sci 168: 676-686

## **Article 2: “Monitoring PCDD/Fs in Soil and Herbage Samples Collected Near a Hazardous Waste Incinerator. Health Risks for the Population Living Nearby”**

### **Abstract**

In 1998, we started a wide environmental surveillance program focused on evaluating the environmental impact of polychlorinated dibenzo-p-dioxins and furans (PCDD/Fs) emitted by a new hazardous waste incinerator (HWI) (Tarragona County, Catalonia, Spain) and assessing the potential health risks for the population living near the facility. The HWI initiated regular operations in 1999. Since then, periodical surveys have been performed. We here report the results concerning PCDD/F levels in 40 soils and 40 herbage samples collected in 2004 and 2005, respectively, in the vicinity of the HWI. The human health risks derived from exposure to PCDD/Fs were also assessed. PCDD/F concentrations in soils ranged from 0.06 to 12.60 ng I-TEQ/kg, with median and mean values of 0.65 and 1.14 ng I-TEQ/kg, respectively. In herbage, PCDD/F concentrations ranged from 0.06 to 12.60 ng I-TEQ/kg, with median and mean values of 0.65 and 1.14 ng I-TEQ/kg, respectively. A comparison with these results with those of the baseline survey show that, after 6 years of regular operation, the HWI did not significantly increase PCDD/F levels in soils and herbage of the surrounding environment. Moreover, PCDD/F emissions from the HWI do not mean additional significant risks for the health of the individuals living in the vicinity of the facility. The results of the current study together with those of recent investigations in municipal waste incinerators indicate that, when adequately controlled for PCDD/F emissions, the modern waste incinerators should not mean any special concern for the population living in the neighborhood.

**Key Words:** Hazardous waste incinerator, dioxins and furans (PCDD/Fs), soils, herbage, health risks

## 1. Introduction

It is well known that polychlorinated dibenzo-p-dioxins and polychlorinated dibenzo-p-furans (PCDD/Fs), especially the 2,3,7,8-substituted congeners, are toxic to humans and animals, being also bioaccumulative (Kogevinas 2001; Cole et al. 2003). These chemicals are formed unintentionally in different industrial processes of combustion, such as incinerators, metal processing and chemical manufacturing plants. In addition, they may be also released to the atmosphere by accidental forest fires and vehicle traffic (Alcock and Jones 1996; Fuster et al. 2001). Among environmental PCDD/F sources, until recent years waste incinerators had a preponderant role as emitters (Fiedler 1996; Meneses et al. 2004; Kim et al. 2005; Schuhmacher and Domingo 2006). However, nowadays only PCDD/F emissions from municipal solid (MSWI) and hazardous waste incinerators (HWI) are regulated in the European Union by the 2000/76/CE Directive to maximum levels of 0.1 ng TEQ/Nm<sup>3</sup>. In Spain, as a consequence of the regulatory control, an important number of studies concerning the PCDD/F emission by combustion processes has been carried out in recent years (Abad et al. 2003, 2004, 2006; Schuhmacher and Domingo 2006). However, in spite of these strict regulations, incineration remains continues to generate great controversy and concern among the general population (Domingo 2002a, b; Meneses et al. 2004).

Due to the physico-chemical properties of PCDD/Fs, once these pollutants are emitted to the atmosphere they are dispersed through the environment and accumulated in soils and plants, reaching easily the food chain (Wuthe et al. 1993; Muller et al. 1994; Harrad and Smith 1997). Following atmospheric deposition, soils are natural sinks for PCDD/Fs (Huang and Batterman, 2003). When absorbed to the organic material of the soil, PCDD/Fs remain quite immobile. Therefore, soil is a typical long-term accumulating matrix for PCDD/Fs (Ferré-Huguet et al. 2006). In turn, vegetation receives inputs of airborne PCDD/Fs via gas phase and particulate dry matter as well as wet deposition (Meneses et al. 2002). Concentrations of PCDD/Fs in

vegetation are a more suitable indicator of the atmospheric emissions of contaminants during short periods of time (Domingo et al. 1999, 2002b).

In 1999, the first HWI in Spain initiated its regular operations in Constantí (Tarragona County, Catalonia). The plant is located in an active industrial zone, with a number of important chemical/petrochemical industries and a MSWI, which is also crossed by a highway and two motorways with heavy traffic. Because of the potential environmental and health risks, the construction of the facility generated an important concern among the local population. In 1998, we started a wide environmental surveillance program mainly focused on evaluating the impact of the HWI on the environment and assessing the potential health risks for the population living in the vicinity of the facility (Agramunt et al. 2002, 2005; Nadal et al. 2002a, 2004a; Schuhmacher et al. 2002, 2004a,b). Soils and herbage were collected in 40 different sampling points in the surrounding of the HWI. PCDD/F levels were determined in the samples. In 2003, in order to study the temporal trend of the PCDD/F levels, soil and herbage samples were again collected at the same sampling points. The health risks for the local population derived from PCDD/F exposure were also evaluated (Ferré-Huguet et al. 2006).

Although in terms of PCDD/F exposure, the HWI did not mean, in principle, a negative impact on the environment or additional risks on the population (Ferré-Huguet et al. 2006), it was decided to continue the monitoring program to get data on the environmental trend of those pollutants. In the present study, we report PCDD/F concentrations in soil and herbage samples collected around the HWI between 2003 and 2005. These results were compared with those obtained in the baseline survey. Moreover, the human health risks derived from exposure to PCDD/Fs were also assessed.

## **2. Materials and methods**

### **2.1. Sampling**

In April 2004, 40 soil samples, were collected around the HWI of Constantí (Catalonia, Spain). The sampling sites were from the same locations as the baseline and the subsequent studies (Schuhmacher et al., 1997, 1998a,b, 2000, 2002) . These sites were chosen at different distances and wind directions (E, N, NW and S) within a radius of 7 km from the stack. Thirty sampling sites were located in zones considered as rural, whereas the remaining 10 were located in areas considered as urban. At each sampling site, soil samples, 500 g approximately, were taken from the upper 5 cm of ground and stored in polyethylene bags. The bulked samples were dried at room temperature and sieved with a 2 mm mesh sieve until analysis. About 50 g (dry weight) were used for analysis.

In April 2005, samples of vegetation (*Piptatherum paradoxum* L.) were collected at the same points. Approximately 150 g were obtained by cutting at a height of approximately 4 cm from the soil. When samples were collected, the plants were about 25 cm high. All samples were immediately packed in aluminum foils. Subsequently, they were dried at room temperature, kept in a double aluminum foil and packed in labeled plastic bags until analysis. About 50 g (dry weight) were used for analysis.

### **2.2. Analytical Procedure**

The 2,3,7,8-substituted congeners of PCDDs and PCDFs in soil and herbage samples were quantified by high-resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS), following the US EPA method 1613. A mixture of <sup>13</sup>C<sup>12</sup>-marked standards were added prior to Soxhlet extraction with toluene for 24 h. The extract was subsequently subjected to an acid/base clean-up procedure followed on

micro columns of silicagel and alumina. HRGC/HRMS analysis was carried using a Fisons CE 8000 GC coupled with a VG Autospec Ultima system (EI and multiple ion detection mode, resolution 10000). Two GC columns were used: DB 5-MS for hepta- and octaCDD and CDF, and CP-Sil 88 for tetra- through hexaCDD and CDF, including the 2,3,7,8-substituted isomers. For detection, at least two masses (M+ and M2+; M2+ and M4+, respectively) were used for each native and labeled dioxin and furan homologue group. Quantitative determinations of PCDD/Fs were performed using internal standards.

### **2.3. Data Analysis**

Toxic Equivalents (I-TEQ) were calculated using the NATO/CCMS factors. In the case of PCDD/F congeners whose levels were under the respective detection limit, the concentration of that congener was assumed to be one-half of the detection limit (ND =  $\frac{1}{2}$  LOD). For statistical comparison of data between different years, the significance of the differences was computed by the non-parametric Kruskal-Wallis test and the parametric ANOVA test, depending on the sample distribution. A probability of 0.05 or less was considered as significant ( $P < 0.05$ ). All statistical analyses were carried out using the SPSS-13.0 Statistical Software Package for Windows.

## **3. Results and discussion**

### **3.1. Environmental Concentrations of PCDD/Fs**

The individual concentrations of PCDD/Fs (I-TEQ) of the 40 soil and herbage samples (urban and rural) collected during the period 2003-2005 around the HWI, as well as those obtained in the baseline survey (1998) are summarized in Tables 1 and 2. The temporal variation (%) between the 1998 study (before the HWI initiated its regular operations) (Schuhmacher et al. 2002b) and subsequent surveys (four, five and six years after starting operations) are also shown for each sample. In turn, the box plots of soil and herbage samples collected in the vicinity of the facility during the same period

(1998-2005) are depicted in Figure 1. Moreover, a summary of the concentrations of PCDD/Fs, depending on the year and the year/distance of collection are presented in Tables 3 and 4, respectively. In 1998, PCDD/F soil concentrations ranged from 0.12 to 17.2 ng I-TEQ/kg with median and mean values of 0.75 and 1.59 ng I-TEQ/kg, respectively. In 2003, PCDD/F concentrations ranged from 0.10 to 3.66 ng I-TEQ/kg, with median and mean values of 0.56 and 0.77 ng I-TEQ/kg, respectively. In 2004, PCDD/F concentrations ranged from 0.06 to 12.60 ng I-TEQ/kg, with median and mean values of 0.65 and 1.14 ng I-TEQ/kg, respectively. The highest concentrations were observed in the SV sites, located in urban areas at different directions from the facility and at a distance >4 km from the facility. The soil sample SV9 (12.60 ng I-TEQ/kg) was placed in an area presumably affected by a waste spill with an unknown scope (Schuhmacher *et al.* 2004c). The temporal changes observed in that zone could be the result of variations in SV sampling sites (moved within an area), since this zone has been subject of an important urban development expansion.

PCDD/F levels in soils increased during the period 2003-2004 in 22 of the 40 samples, whereas in the other 18 a reduction was observed. The median value increased 16%. Between 1998 and 2003, a reduction of 13% was detected. Probably, these variations are due to the standard deviations in the analytical determinations concurrently with small variations in the collection sites. However, the Mann-Whitney U-test did not show significant differences between 1998 and 2004 in none of the scenarios considered (500, 2500 and >4000 m from the HWI).

Most tetra- to octa-PCDD/Fs were detected in all soil samples. In 2003, the most toxic congener 2,3,7,8-TCDD was detected in 14 of the 40 samples (detection limit: 0.05 ng/kg), 0.13 ng/kg being the highest concentration found. In the 2004 survey, 2,3,7,8-TCDD was detected in 36 of the 40 samples with a mean value of 0.05 ng/kg (detection limit: 0.03 ng/kg). OCDD was the most abundant congener with concentrations ranging between 4.07 and 527 ng/kg, 0.38 and 460 ng/kg, and 2.50 and 415.8 ng/kg in the 1998, 2003 and 2004 surveys, respectively.

**Table 1.** PCDD/F concentrations (ng I-TEQ/kg dry matter) in soil samples collected around the HWI in 1998, 2003 and 2004.

Sample Code	Distance to the HWI	Area	1998	2003	2004	Temporal variation	
						% 1998-2004	% 2003-2004
E1	500	R	1.22	0.89	1.43	17	61
E2	1000	R	0.52	0.78	0.5	-4	-36
E3	1500	R	0.41	0.53	1.79	337	238
E4	2000	R	0.65	0.60	0.8	23	33
E5	2500	R	5.11	0.10	0.31	-94	210
E6	3000	R	0.40	0.10	1.00	150	900
E7	3500	R	0.12	0.16	1.35	1025	744
E8	4000	U	1.99	0.72	0.7	-65	-3
E9	>4000	R	0.16	0.15	0.65	306	333
N1	500	R	0.34	0.28	0.51	50	82
N2	1000	R	0.23	0.47	0.32	39	-32
N3	1500	R	0.26	0.28	2.53	873	804
N4	2000	R	0.75	0.22	0.99	32	350
N5	2500	R	0.13	2.39	0.18	38	-92
N6	3000	R	0.51	0.82	0.57	12	-30
N7	3500	R	0.60	0.59	0.38	-37	-36
NW1	500	R	0.64	0.26	0.23	-64	-12
NW2	1000	R	0.22	0.53	0.75	241	42
NW3	1500	R	0.43	0.73	1.74	305	138
NW4	2000	R	3.68	0.24	0.46	-88	92
NW5	2500	R	0.66	0.26	0.64	-3	146
NW6	3000	R	1.07	0.43	0.75	-30	74
NW7	3500	R	2.34	0.59	1.81	-23	207
S1	500	R	1.10	0.91	1.02	-7	12
S2	1000	R	1.02	0.23	0.14	-86	-39
S3	1500	R	0.75	0.53	0.38	-49	-28
S4	2000	R	0.45	1.14	0.65	44	-43
S5	2500	R	1.01	1.24	2.13	111	72
S6	3000	R	1.00	0.61	0.10	-90	-84
S7	3500	R	0.35	0.42	0.38	9	-10
S8	4000	R	1.94	1.00	3.15	62	215
SV1	>4000	U	0.15	0.36	0.51	240	42
SV2	>4000	U	2.00	0.43	0.34	-83	-21
SV4	>4000	U	3.43	0.74	1.55	-55	109
SV6	>4000	U	3.61	2.70	0.32	-91	-88
SV7	>4000	U	2.42	3.66	0.74	2	-80
SV8	>4000	U	17.2	2.30	0.06	-100	-97
SV9	>4000	U	3.06	0.35	12.6	312	3500
SV10	>4000	U	0.84	0.93	0.25	-70	-73
SV11	>4000	U	0.75	1.20	1.05	40	-13
			<b>0.75<sup>a</sup></b>	<b>0.56<sup>a</sup></b>	<b>0.65<sup>a</sup></b>	-13	16

R= Rural; U= Urban; E= East; N= North; NW= Northwest; S= South; SV= urban sites at different directions; <sup>a</sup>Median values.

**Table 2.** PCDD/F concentrations (ng I-TEQ/kg dry matter) in herbage samples collected around the HWI in 1998, 2003 and 2005.

Sample code	Distance to the HWI	Area	1998	2003	2005	Temporal variation	
						% 1998-2005	% 2003-2005
E1	500	R	0.21	0.23	0.41	95	78
E2	1000	R	0.32	0.22	0.16	-50	-27
E3	1500	R	0.19	0.16	0.19	0	19
E4	2000	R	0.22	0.21	0.17	-23	-19
E5	2500	R	0.18	0.32	0.33	83	3
E6	3000	R	0.17	0.29	0.29	71	0
E7	3500	R	0.14	0.93	0.55	293	-41
E8	4000	U	0.51	0.20	0.75	47	275
E9	>4000	R	0.43	0.23	0.59	37	157
N1	500	R	0.25	0.14	0.63	152	350
N2	1000	R	0.19	0.11	0.75	295	582
N3	1500	R	0.24	0.19	0.56	133	195
N4	2000	R	0.28	0.17	0.56	100	229
N5	2500	R	0.30	0.21	0.60	100	186
N6	3000	R	0.27	0.14	0.49	81	250
N7	3500	R	0.19	0.21	0.26	37	24
NW1	500	R	0.52	0.32	0.60	15	88
NW2	1000	R	0.20	0.24	0.29	45	21
NW3	1500	R	0.21	0.23	0.24	14	4
NW4	2000	R	0.32	0.23	0.23	-28	0
NW5	2500	R	0.32	0.21	0.31	-3	48
NW6	3000	R	0.21	0.19	0.41	95	116
NW7	3500	R	0.48	0.22	0.24	-50	9
S1	500	R	0.18	0.24	0.37	106	54
S2	1000	R	0.34	0.07	0.30	-12	329
S3	1500	R	0.23	0.05	0.21	-9	320
S4	2000	R	0.17	0.20	0.24	41	20
S5	2500	R	0.19	0.14	0.81	326	479
S6	3000	R	0.19	0.10	0.17	-11	70
S7	3500	R	0.21	0.44	0.29	38	-34
S8	4000	R	0.32	0.28	0.29	-9	4
SV1	>4000	U	0.18	0.33	0.76	322	130
SV2	>4000	U	2.01	0.44	1.57	-22	257
SV4	>4000	U	0.17	0.20	0.22	29	10
SV6	>4000	U	0.24	0.16	0.39	63	144
SV7	>4000	U	0.21	0.11	0.33	57	200
SV8	>4000	U	0.45	0.15	0.03	-93	-80
SV9	>4000	U	0.32	0.21	0.09	-72	-57
SV10	>4000	U	0.36	0.16	0.19	-47	19
SV11	>4000	U	0.25	0.13	0.13	-48	0
			<b>0.23<sup>a</sup></b>	<b>0.21<sup>a</sup></b>	<b>0.31<sup>a</sup></b>	35	48

R= Rural; U= Urban; E= East; N= North; NW= Northwest; S= South; SV= urban sites at different directions; <sup>a</sup>Median values.

**Table 3.** Summary of PCDD/F concentrations (ng I-TEQ/kg) in soil and herbage samples collected around the HWI.

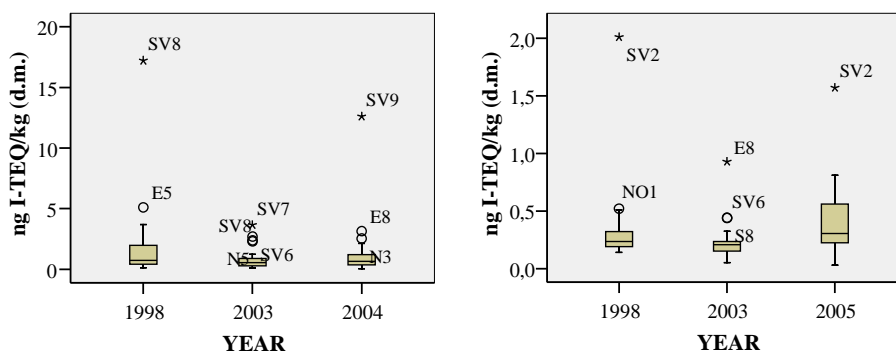
Sample	Year	Mean	SD	Minimum value	Maximum Value
Soil	1998	1.59	2.79	0.12	17.20
	2003	0.77	0.75	0.10	3.66
	2004	1.11	1.98	0.06	12.60
Herbage	1998	0.31 <sup>ab</sup>	0.29	0.14	2.01
	2003	0.22 <sup>a</sup>	0.14	0.05	0.93
	2005	0.40 <sup>b</sup>	0.28	0.03	1.57

Values showing different superscripts (a,b) are significantly different at  $P < 0.05$ . For both soil and herbage, the number of samples was 40 in each collection.

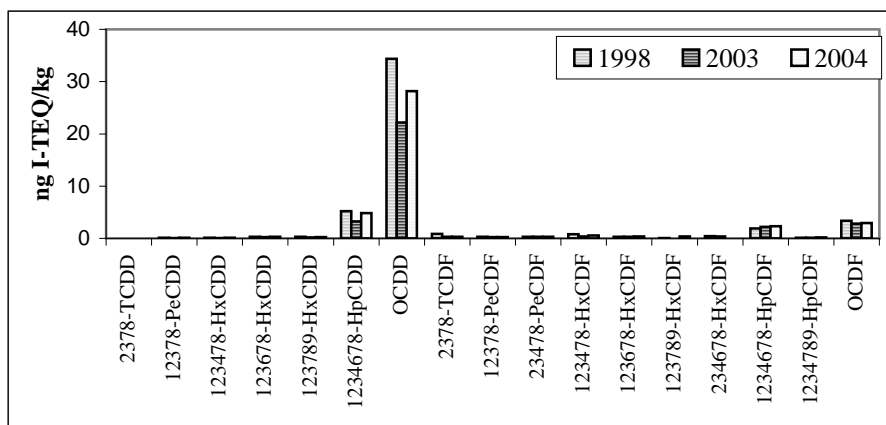
**Table 4.** Summary of PCDD/F concentrations (ng I-TEQ/kg) in soil and herbage samples taken at different distances from the HWI.

Sample	Year	Distance	500	2500	>4000
		(m)	(n=4)	(n=4)	(n=10)
Soil	1998		0.83 ± 0.41	1.73 ± 2.28	3.36 ± 5.03
	2003		0.59 ± 0.36	1.00 ± 1.06	1.28 ± 1.20
	2004		0.90 ± 0.41	0.40 ± 0.20	1.81 ± 3.81
Herbage	1998		0.29 ± 0.16	0.25 <sup>a</sup> ± 0.07	0.49 ± 0.58
	2003		0.20 <sup>a</sup> ± 0.06	0.20 <sup>a</sup> ± 0.25	0.22 ± 0.10
	2005		0.50 <sup>b</sup> ± 0.13	0.51 <sup>b</sup> ± 0.24	0.45 ± 0.48

Mean ± St. Deviation. Values showing different superscripts (a,b) are significantly different at  $P < 0.05$ .



**Figure 1.** Box plot of soil (A) and herbage (B) samples collected in the vicinity of the HWI during the period 1998-2005.



**Figure 2.** PCDD/F profile (median values) of soil samples collected around the HWI during the period 1998-2004.

Figure 2 shows the PCDD/F congener profiles in soil samples during the period 1998-2004. In most of the samples, OCDD was the most abundant congener, followed by 1,2,3,4,6,7,8-HpCDD, OCDF and 1,2,3,4,6,7,8-HpCDDF. Similar PCDD/F profiles were observed for the three years. Although in 2004, OCDD concentrations were slightly higher than those found in 2003, the differences were not statistically significant.

Most air pollutant sources emit trace element combinations that are characteristic to their specific source type. A Principal Component Analysis (PCA) was carried out to identify possible changes in congener profiles corresponding to each sampling period. The scatterplot of the component scores on both principal components showed that most soil samples were located in a main cluster with only a few samples appearing as outliers (Figure 3). The first Principal Component (PC) was correlated with the hexa-CDFs and OCDF, while the second PC was mainly correlated with OCDD, 1,2,3,4,6,7,8-HpCDD, and 1,2,3,7,8,9-HxCDD. The main cluster shows a lack of differences in emission sources of the current survey with respect to the baseline study. On the other hand, some samples of the last survey (SV9 and S8) showed elevated values of the second component (related to PeCDD). The different profile of these samples reflects that they could have been affected by punctual

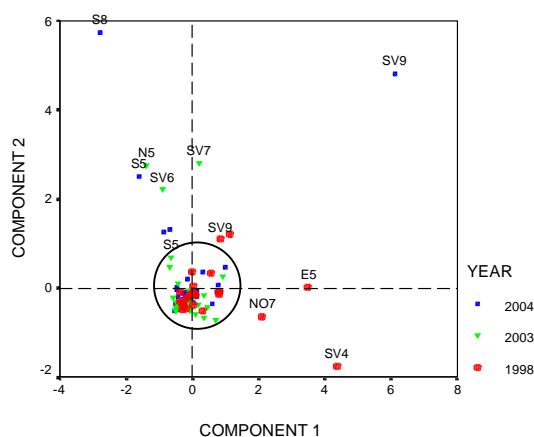
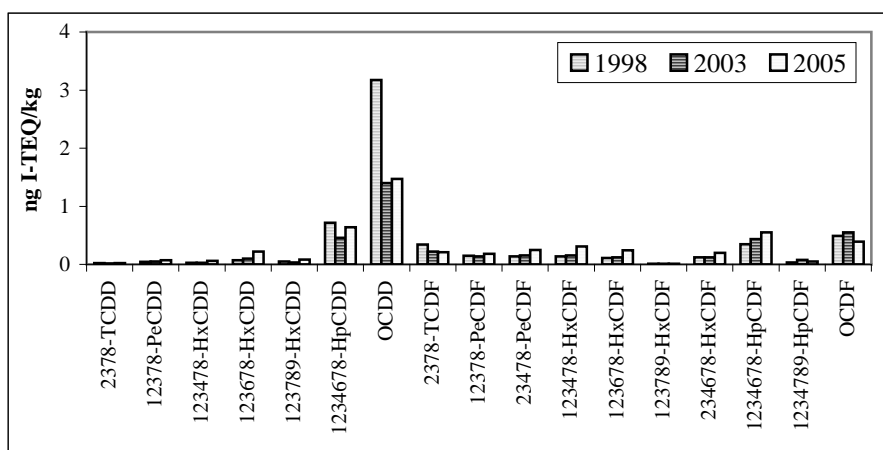


Figure 3. Principal Component Analysis for soil samples collected in the vicinity of the HWI.

pollution sources, such as traffic and agricultural burning.

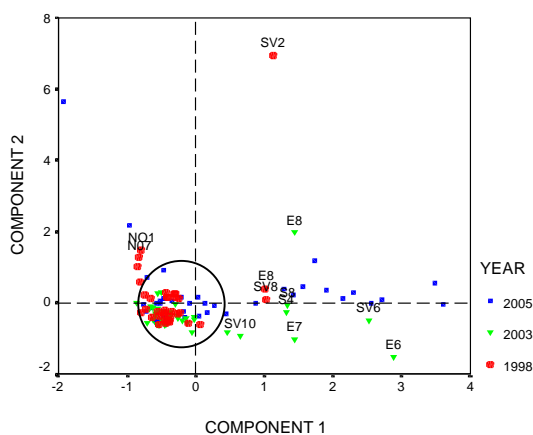
Nowadays, in Spain there is no guideline for PCDD/F levels in soils. However, the concentrations here reported are, in general terms, below 5 pg TEQ/g, the threshold limit established for the Germany soils guideline corresponding to soils used for agricultural purposes (Bassler 1994). On the other hand, all samples were notably below the 100 and 1000 pg TEQ/g established in the same guideline for children's playgrounds and residential areas, respectively. Furthermore, PCDD/F soil concentrations here reported are of the same order of magnitude as those recently found in other studies around municipal waste incinerators in Taiwan and Italy (Cheng *et al.* 2003; Caserini *et al.* 2004), as well as in background areas (Caserini *et al.* 2004; Martinez *et al.* 2006).



**Figure 4.** PCDD/F profile (median values) of herbage samples collected around the HWI during the period 1998-2005.

In 1998, PCDD/F concentrations in herbage samples ranged from 0.14 to 2.01 ng I-TEQ/kg with a median value of 0.23 ng I-TEQ/kg and a mean value of 0.31 ng I-TEQ/kg. In 2003, PCDD/F concentrations ranged from 0.05 to 0.93 ng I-TEQ/kg, with

median and mean values of 0.21 and 0.22 ng I-TEQ/kg, respectively. In the 2005 study, PCDD/F concentrations ranged from 0.06 to 12.60 ng I-TEQ/kg, with median and mean values of 0.65 and 1.14 ng I-TEQ/kg, respectively. The temporal variation between 1998 and 2005 showed that PCDD/F levels diminished in 14 of the 40 samples, whereas in the remaining 26 different increments were noted. The median value increased 35% between the baseline (1998) and the 2005 survey. Analyzing only the two last surveys (2003/2005), it can be seen that PCDD/F concentrations decreased in 6 herbage samples, increased in 27, and remained nearly unchanged in 7 samples. In general, PCDD/F herbage levels of the different surveys are similar, with the exception of samples collected in the north direction, which slightly increased. On the other hand, PCDD/F concentrations in SV samples, collected in urban areas at different directions from the facility, diminished. Significant differences ( $P < 0.05$ ) were found when the 2003 and 2005 values were compared. When samples were compared taken into account the different distances to the HWI for the same period of time, only rural samples (500 and 2500 m) showed a significant increase. On contrary, urban levels (>4000 m) remained similar. In spite of the inclusion of the PCDD/Fs in the “dirty dozen” list of the Stockholm Convention on Persistent Organic Pollutants, the importance of other non-regulated industrial, as well as diffuse sources could be increasing in recent years (Alcock *et al.* 2001; Quass *et al.* 2004).



**Figure 5.** Principal Component Analysis for herbage samples collected in the vicinity of the HWI.

Most tetra- to octa-PCDD/F were detected in herbage samples. In the 1998 survey, the 2,3,7,8-TCDD highest concentration was 0.21 ng/kg, with median and mean values of 0.02 and 0.03 ng/kg, respectively. In 2003, 2,3,7,8-TCDD was detected in 15 of the 40 samples with a mean value of 0.02 ng/kg. In the last study, 2,3,7,8-TCDD mean value was 0.03 ng/kg. OCDD mean values were 3.93 ng/kg, 1.78 ng/kg and 2.05 ng/kg for the 1998, 2003 and 2005 surveys, respectively (median values of 3.17, 1.40 and 1.47 ng/kg, respectively).

Figure 4 shows the PCDD/F profile for herbage samples collected around the HWI during the period 1998-2005. OCDD was the most abundant congener, followed by 1,2,3,4,6,7,8-HpCDD, OCDF and 1,2,3,4,6,7,8-HpCDF, respectively. That pattern fits well with that found for soil samples.

In 1998, PCDD/F significant differences between urban and rural samples were noted, levels in urban samples being higher than those found in rural samples ( $P < 0.05$ ). In the last study, PCDD/F levels in herbage diminished lightly in urban samples (-3%), with a median value of 0.28 ng/kg. In rural samples, PCDD/F concentrations increased (41%), the median value being 0.31 ng/kg of dry weight. These results reflect a reduction in the urban areas, whereas in rural areas, the levels of PCDD/F increased. The reduction was probably caused by the increasing use of unleaded fuel for motor vehicles, as well as other changes in PCDD/F emissions such as the use of new cleaning systems in incinerators. On the other hand, increased PCDD/F levels in rural areas could be caused by herbage burning. In 2005, no significant differences were found when PCDD/F levels in rural and urban herbage samples were compared ( $P > 0.05$ ).

When a PCA was carried out on herbage samples, a single two-dimensional model that accounted for 62.1 % of the variance was obtained (Figure 5). The first main PC (48.8 % of the variance) was correlated with the HpCDDFs, while the second PC (13.3 % of the variance) was correlated with TCDFs and PeCDFs. Most samples were

clustered together. However, 2003 and 2005 samples showed higher values of the first PC than that corresponding to the 1998 samples.

### 3.2. Human Health Risks

Data from the last survey of the environmental monitoring program (2004) were used to evaluate human health risks. The exposure to PCDD/Fs was divided into two pathways: environmental and dietary. Two groups of population, adults and children, were assessed according to their different sensitivity (Dourson *et al.* 2004). Three exposure routes were considered to assess the environmental exposure to PCDD/Fs: inhalation, dermal absorption through soil and dust, and ingestion of soil and dust. PCDD/F concentrations in air and ventilation rates of 20 m<sup>3</sup>/day and 7.6 m<sup>3</sup>/day for adults and children, respectively, were used to calculate inhalation through air, whereas dermal absorption and ingestion of soil and dust were determined on the basis of PCDD/F concentrations in soils (Nouwen *et al.* 2001; Nadal *et al.* 2004b). The skin coverage with soil outside, the skin coverage with dust inside, the soil fraction inside the dust and the exposed skin surface area for forehands and hands were the parameters used to evaluate the dermal exposure through soil and dust. The ingestion of soil particles, the sleeping time, the exposed time fractions and the soil fraction inside the dust were the parameters used to evaluate the dermal exposure through soil and dust. Further details on the calculations of environmental exposure such as parameters and equations, were previously reported (Domingo *et al.* 2002a; Nadal *et al.* 2004b). On the other hand, exposure to PCDD/Fs through the diet was calculated from 2003 data concerning PCDD/F concentrations and consumption of various groups of foodstuffs (Bocio and Domingo 2005). Finally, exposure was evaluated in three receptors according to the distance to the HWI: 500 m, 2500 m (rural sites) and >4000 m (urban sampling point).

**Table 5.** PCDD/F exposure for adults and children living at 500, 2500 and >4000 m from the HWI in 2004.

	500 m		2500 m		> 4000 m	
	Adults	Children	Adults	Children	Adults	Children
Environmental exposure						
PCDD/F $C_{air}$ (ng I-TEQ/m <sup>3</sup> ) <sup>a</sup>	4.47E-06		4.53E-06		2.43E-04	
PCDD/F $C_{soil}$ (ng I-TEQ/kg d.m.)	0.798		0.815		1.807	
PCDD/F <i>Inh</i> (ng I-TEQ/kg/day)	5.90E-07	7.76E-07	5.98E-07	7.87E-07	3.21E-05	4.23E-05
PCDD/F <i>Der total</i> (ng I-TEQ/kg/day)	4.89E-07	4.26E-07	5.00E-07	4.35E-07	1.11E-06	9.65E-07
PCDD/F <i>Ing total</i> (ng I-TEQ/kg/day)	1.71E-07	1.21E-06	1.73E-07	1.22E-06	2.63E-07	1.73E-06
Total environmental exposure (ng I-TEQ/kg/day)	1.25E-06	2.41E-06	1.27E-06	2.44E-06	3.35E-05	4.50E-05
Dietary exposure						
Intake of PCDD/F (ng I-TEQ/kg/day)	8.52E-04	3.24E-03	8.52E-04	3.24E-03	8.52E-04	3.24E-03
<b>Total Exposure (ng I-TEQ/kg/day)</b>	<b>8.54E-04</b>	<b>3.24E-03</b>	<b>8.54E-04</b>	<b>3.24E-03</b>	<b>8.86E-04</b>	<b>3.28E-03</b>

<sup>a</sup>PCDD/F concentrations in air particulate matter (samples collected in March 22, 2004).

The results of the human health risk assessment are summarized in Table 4. With respect to the direct exposure of PCDD/Fs, air inhalation was the main pathway in adults, especially in the urban area ( $5.90 \cdot 10^{-7}$ ,  $5.98 \cdot 10^{-7}$  and  $3.21 \cdot 10^{-5}$  ng I-TEQ/kg/day at 500, 2500 and >4000 m, respectively). It would be due to the great difference in air concentration of PCDD/Fs between rural and urban zones (4.5 and 243 fg I-TEQ/m<sup>3</sup>, respectively). In children, air inhalation was also the most important contributor to PCDD/F exposure at >4000 m, while the ingestion of soil and dust was the main pathway in those points located near to the HWI. In spite of the importance of air inhalation in the urban zones, in the current study exposure of PCDD/Fs through this route was of the same order of magnitude than that recently reported by Yu *et al.* (2005) in Guangzhou (China). These authors calculated inhalation of particulated PCDD/Fs of  $1.38 \cdot 10^{-5}$ ,  $5.68 \cdot 10^{-5}$ , and  $10.15 \cdot 10^{-5}$  ng I-TEQ/kg/day for adults in a forest park, a residential area, and a strongly industrialized zone, respectively. In our study,

the high levels of PCDD/Fs in soil and air found in the urban areas, as well as the associated environmental exposure of the population, suggest that traffic is a very important pollution source of PCDD/Fs (Lee *et al.* 2004).

The levels of the total environmental exposure for subjects living in rural zones did not show significant differences depending on the distance to the HWI. Thus, direct exposures of  $1.3 \cdot 10^{-6}$  and  $2.4 \cdot 10^{-6}$  ng I-TEQ/kg/day were estimated for adults and children, respectively, independently of the distance to the stack. These levels were lower than those reported in our previous study (2003). In that survey, the environmental exposure values were  $6.78 \cdot 10^{-6}$  and  $9.66 \cdot 10^{-6}$  ng I-TEQ/kg/day, for adults and children, respectively, living at 500 m. These values were  $5.00 \cdot 10^{-6}$  and  $7.37 \cdot 10^{-6}$  ng I-TEQ/kg/day for individuals living at 2500 m. By contrast, in the 2003 survey, a lower total direct exposure was noted for adults and children living in Tarragona city (Ferré-Huguet *et al.* 2006). In the present study, environmental exposure accounted only for 0.1% of total PCDD/F exposure for adults and children living in the rural area closer to the HWI (500 and 2500 m). It increased up to 3.8 and 1.4% of total exposure for adults and children, respectively, in the urban area (>4000 m). Consequently, it seems quite evident that dietary intake of PCDD/Fs is, by far, the main pathway of PCDD/F exposure. This is not new, as the importance of the diet as the main route of PCDD/F intake has been shown in a number of studies (Domingo *et al.* 2002a,b; Karademir, 2004; Nadal *et al.* 2004b; Schuhmacher and Domingo 2006).

The non-carcinogenic risk was assessed by comparing total PCDD/F exposure with the tolerable daily intake suggested by the World Health Organization (WHO): 1-4 pg I-TEQ/kg/day (van Leeuwen *et al.* 2000; Pohl *et al.* 2002). The risk index range at the rural sites (500 and 2500 m from the HWI) was the same as that calculated in 2003: 0.21-0.85 and 0.81-3.24 for adults and children, respectively. In the urban area, the risk was slightly higher in both groups of population (0.22-0.89 in adults, and 0.82-3.28 in children). However, the upper-threshold value of 4 pg I-TEQ/kg/day was not exceeded in any scenario. The carcinogenic risk derived from the exposure to PCDD/Fs by adults

was evaluated by considering an upper-bound risk of  $1 \cdot 10^{-3}$  (US EPA 2000). The calculation of the total PCDD/F exposure was carried out by assimilating inhalation and dermal contact to oral exposure. Cancer risks of 850 and 890 were estimated for areas close to and far away the HWI, respectively. Considering a mean lifetime of 70 years, it would mean 12 and 13 cases of cancer for a population of 1 million inhabitants in rural and urban zones of Tarragona, respectively.

The above results show that, after 6 years of regular operation, the HWI did not significantly increase PCDD/F levels in soils and herbage of the surrounding environment. Moreover, PCDD/F emissions from the HWI do not mean additional significant risks for the health of the individuals living in the vicinity of the facility. In recent years, we have performed various studies concerning the environmental impact and human health risks near several waste incinerators of Catalonia (Schuhmacher *et al.* 1998b; Domingo *et al.* 1999; Nadal *et al.* 2002b; Ferré-Huguet *et al.* 2006; Schuhmacher and Domingo 2006). We found that those incinerators whose emission levels of PCDD/Fs compared with those regulated by the European Union, did not constitute in general terms any relevant source of PCDD/Fs. Additional health risks due to PCDD/F exposure for the population living in the vicinity were not observed. Therefore, taking together the results of the current study with our investigations in MSWI indicate that when adequately controlled for PCDD/F emissions, waste incinerators should not represent any special concern for the population living in the neighborhood. To establish the role of non-regulated and diffuse sources, especially traffic and certain industrial activities, is important in order to get comparative data with PCDD/F emissions from modern incinerators.

### References

- Abad E, Caixach J and Rivera J. 2003. Improvements in dioxins abatement strategies at a municipal waste management plant in Barcelona. *Chemosphere* 50: 1175-1182

- Abad E, Caixach J, Rivera J, *et al.* 2004. Temporal trends of PCDDs/PCDFs in ambient air in Catalonia (Spain). *Sci Total Environ* 334-335: 279-285
- Abad E, Martinez K, Caixach J, *et al.* 2006. Polychlorinated dibenzo-p-dioxins, dibenzofurans and 'dioxin-like' PCBs in flue gas emissions from municipal waste management plants. *Chemosphere* 63: 570-580
- Agramunt MC, Nadal M, Schuhmacher M, *et al.* 2002. PCDD/PCDF in the vicinity of a hazardous waste incinerator in Catalonia, Spain. II. Levels in herbage. *Organohalogen Compd* 58: 309-312
- Agramunt MC, Schuhmacher M, Hernandez JM, *et al.* 2005. Levels of dioxins and furans in plasma of non-occupationally exposed subjects living near a hazardous waste incinerator. *J Expo Anal Environ Epidemiol* 15: 29-34
- Alcock R and Jones KC. 1996. Dioxins in the environment: a review of trend data. *Environ Sci Technol* 30: 3133-3143
- Alcock RE, Sweetman AJ and Jones KC. 2001. A congener-specific PCDD/F emissions inventory for the UK: do current estimates account for the measured atmospheric burden? *Chemosphere* 43: 183-194
- Bassler A. 1994. Regulatory measures in the Federal Republic of Germany to reduce the exposure of man and the environment to dioxins. *Organohalogen Compd* 20: 567-570
- Bocio A and Domingo JL. 2005. Daily intake of polychlorinated dibenzo-p-dioxins/polychlorinated dibenzofurans (PCDD/PCDFs) in foodstuffs consumed in Tarragona, Spain: a review of recent studies (2001-2003) on human PCDD/PCDF exposure through the diet. *Environ Res* 97: 1-9
- Caserini S, Cernuschi S, Giugliano M, *et al.* 2004. Air and soil dioxin levels at three sites in Italy in proximity to MSW incineration plants. *Chemosphere* 54: 1279-1287
- Cole P, Trichopoulos D, Pastides H, *et al.* 2003. Dioxin and cancer: a critical review. *Regul Toxicol Pharmacol* 38: 378-388
- Cheng PS, Hsu MS, Ma E, *et al.* 2003. Levels of PCDD/Fs in ambient air and soil in the vicinity of a municipal solid waste incinerator in Hsinchu. *Chemosphere* 52: 1389-1396

- Domingo JL. 2002a. Human health risks of dioxins for populations living near modern municipal solid waste incinerators. *Rev Environ Health* 17: 135-147
- Domingo JL. 2002b. Public fear of dioxins from modern municipal waste incinerators is not justified. *Environ Health Perspect* 110: A288-A289
- Domingo JL, Schuhmacher M, Meneses M, *et al.* 1999. Monitoring dioxins and furans near an old municipal solid waste incinerator: temporal variation in vegetation. *J Environ Sci Health A34*: 165-181.
- Domingo JL, Agramunt MC, Nadal M, *et al.* 2002a. Health risk assessment of PCDD/PCDF exposure for the population living in the vicinity of a municipal waste incinerator. *Arch Environ Contam Toxicol* 43: 461-465
- Domingo JL, Bocio A, Nadal M, *et al.* 2002b. Monitoring dioxins and furans in the vicinity of an old municipal waste incinerator after pronounced reductions of the atmospheric emissions. *J Environ Monit* 4: 395-399
- Dourson M, Charnley G, Scheuplein R, *et al.* 2004. Differential sensitivity of children and adults to chemical toxicity. *Hum Ecol Risk Assess* 10: 21-27
- Ferré-Huguet N, Nadal M, Schuhmacher M, *et al.* 2006. Environmental impact and human health risks of polychlorinated dibenzo-p-dioxins and dibenzofurans in the vicinity of a new hazardous waste incinerator: A case study. *Environ Sci Technol* 40: 61-66
- Fiedler H. 1996. Sources of PCDD/PCDF and impact on the environment. *Chemosphere* 32: 55-64
- Fuster G, Schuhmacher M and Domingo JL. 2001. Flow analysis of PCDD/Fs for Tarragona Province, Spain: Inventory as a preliminary stage. *Environ Sci Pollut Res* 8: 91-94
- Harrad SJ and Smith DJT. 1997. Evaluation of a terrestrial food chain model for estimating foodstuff concentrations of PCDD/Fs. *Chemosphere* 34: 1723-1737
- Huang YL and Batterman S. 2003. Probability and persistence of high pollutant concentrations in soils: A modeling study and implications for exposure and risk assessment. *Hum Ecol Risk Assess* 9: 1713-1728

- Karademir A. 2004. Health risk assessment of PCDD/F emissions from a hazardous and medical waste incinerator in Turkey. *Environ Int* 30: 1027-1038
- Kim B-H, Lee S-J, Mun S-J, *et al.* 2005. A case study of dioxin monitoring in and around an industrial waste incinerator in Korea. *Chemosphere* 58: 1589-1599
- Kogevinas M. 2001. Human health effects of dioxin: cancer, reproductive and endocrine system effects. *Hum Reprod Update* 7: 331-339
- Lee WS, Chang-Chien GP, Wang LC, *et al.* 2004. Source identification of PCDD/Fs for various atmospheric environments in a highly industrialized city. *Environ Sci Technol* 38: 4937-4944
- Martinez K, Abad E and Rivera J. 2006. Surveillance programme on dioxin levels in soils in the Campo de Gibraltar (Southwest Spain). *Chemosphere* 65: 382-389
- Meneses M, Schuhmacher M and Domingo JL. 2002. A design of two simple models to predict PCDD/F concentrations in vegetation and soils. *Chemosphere* 46: 1393-1402
- Meneses M, Schuhmacher M and Domingo JL. 2004. Health risk assessment of emissions of dioxins and furans from a municipal waste incinerator: comparison with other emission sources. *Atmos Environ* 30: 481-489
- Muller JF, Hulster A, Papke O, *et al.* 1994. Transfer of PCDD/PCDF from contaminated soils into carrots, lettuce and peas. *Chemosphere* 29: 2175-2181
- Nadal M, Agramunt MC, Domingo JL, *et al.* 2002a. PCDD/PCDF in the vicinity of a hazardous waste incinerator in Catalonia, Spain. I. Levels in soils. *Organohalogen Compd* 57: 309-312
- Nadal M, Agramunt MC, Schuhmacher M, *et al.* 2002b. PCDD/PCDF congener profiles in soil and herbage samples collected in the vicinity of a municipal waste incinerator before and after pronounced reductions of PCDD/PCDF emissions from the facility. *Chemosphere* 49: 153-159
- Nadal M, Bocio A, Díaz-Ferrero J, *et al.* 2004a . Monitoring PCDD/Fs in soil and herbage samples collected in the neighborhood of a hazardous waste incinerator after five years of operation. *Organohalogen Compounds* 66: 1788-1795

- Nadal M, Schuhmacher M and Domingo JL. 2004b. Probabilistic human health risk of PCDD/F exposure: a socioeconomic assessment. *J Environ Monit* 6: 926-931
- Nouwen J, Cornelis C, De Fre R, *et al.* 2001. Health risk assessment of dioxin emissions from municipal waste incinerators: the Neerlandquarter (Wilrijk, Belgium). *Chemosphere* 43: 909-923
- Pohl HR, Hicks HE, Jones DE, *et al.* 2002. Public health perspectives on dioxin risks: Two decades of evaluations. *Hum Ecol Risk Assess* 8: 233-250
- Quass U, Fermann M and Broker G. 2004. The European Dioxin Air Emission Inventory Project--Final results. *Chemosphere* 54: 1319-1327
- Schuhmacher M, Granero M, Llobet JM, *et al.* 1997. Assessment of baseline levels of PCDD/F in soils in the neighbourhood of a new hazardous waste incinerator in Catalonia, Spain. *Chemosphere* 35: 1947-1958
- Schuhmacher M, Domingo JL, Llobet JM, *et al.* 1998a. Baseline levels of PCDD/Fs in vegetation samples collected in the vicinity of a new hazardous waste incinerator in Catalonia, Spain. *Chemosphere* 36: 2581-2591
- Schuhmacher M, Domingo JL, Llobet JM, *et al.* 1998b. Temporal variation of PCDD/F concentrations in vegetation samples collected in the vicinity of a municipal waste incinerator (1996-1997). *Sci Total Environ* 218: 175-183
- Schuhmacher M, Rodriguez-Larena MC, Domingo JL, *et al.* 2000. Baseline contamination assessment for a new hazardous waste incinerator in Catalonia, Spain. *Organohalogen Compd* 46: 58-61
- Schuhmacher M, Agramunt MC, Rodriguez-Larena MC, *et al.* 2002a. Baseline levels of PCDD/Fs in soil and herbage samples collected in the vicinity of a new hazardous waste incinerator in Catalonia, Spain. *Chemosphere* 46: 1343-1350
- Schuhmacher M, Agramunt MC, Rodriguez-Larena MC, *et al.* 2002b. Baseline levels of PCDD/Fs in soil and herbage samples collected in the vicinity of a new hazardous waste incinerator in Catalonia, Spain. *Chemosphere* 46, 1343-1350.
- Schuhmacher M, Domingo JL, Hagberg J, *et al.* 2004a. PCDD/F and non-*ortho* PCB concentrations in adipose tissue of individuals living in the vicinity of a hazardous waste incinerator. *Chemosphere* 57: 357-364

- Schuhmacher M, Domingo JL, Kiviranta H, *et al.* 2004b. Monitoring dioxins and furans in a population living near a hazardous waste incinerator: levels in breast milk. *Chemosphere* 57: 43-49
- Schuhmacher M, Nadal M and Domingo JL. 2004c. Levels of PCDD/Fs, PCBs, and PCNs in soils and vegetation in an area with chemical and petrochemical industries. *Environ Sci Technol* 38: 1960-1969
- Schuhmacher M and Domingo JL. 2006. Long-term study of environmental levels of dioxins and furans in the vicinity of a municipal solid waste incinerator. *Environ Int* 32: 397-404
- USEPA (U.S. Environmental Protection Agency. 2000. Draft exposure and human health reassessment of 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD) and related compounds. EPA/600/P-00/001. US Environmental Protection Agency, Washington, DC.
- van Leeuwen FXR, Feeley M, Schrenk D, *et al.* 2000. Dioxins: WHO's tolerable daily intake (TDI) revisited. *Chemosphere* 40: 1095-1101
- Wuthe J, Link B, Walther J, *et al.* 1993. Dioxin and furan (PCDD/PCDF) levels in human blood from persons living in a contaminated area. *Chemosphere* 27: 287-293
- Yu L, Mai B, Meng X, *et al.* 2006. Particle-bound polychlorinated dibenzo-p-dioxins and dibenzofurans in the atmosphere of Guangzhou, China. *Atmos Environ* 40: 96-108

## Discussió conjunta dels articles del Capítol II

### *Nivells de metalls en herbes i sòls de les rodalies de la Incineradora de Residus Sòlids Urbans de Tarragona*

En sòls, les concentracions més elevades van correspondre al Mn i el Pb. En el període 1997-2005 es va observar una disminució de tots els metalls estudiats (excepte pel Cd i Cr), mentre que les concentracions d'As, Cr, Hg, Mn, Ni, Tl i V van mostrar una reducció significativa entre el 1999-2005. Només pel Cd i Pb es va observar un augment notable, però no significatiu. En el període 1997-2005, es va notar una disminució dels nivells de Pb en sòls. Per la majoria de metalls, les concentracions actuals (2005) van ser inferiors a les d'altres estudis fets prèviament als voltants de la incineradora de Tarragona i d'altres àrees industrials de Catalunya (Llobet i col·ls., 2002; Nadal i col·ls., 2004).

En herbes, les concentracions de Be i Tl es van trobar per sota del seu corresponent límit de detecció (0.25 i 0.03 µg/g, respectivament) en totes les mostres, mentre que les concentracions més elevades es van trobar pel Mn. Les concentracions de tots els elements analitzats van disminuir significativament ( $p < 0.001$ ) entre el 1999 i el 2004. Aquesta disminució podria indicar la tendència general a la baixa de les concentracions ambientals de molts metalls (Schuhmacher i col·ls., 2002b). Les concentracions de Pb en herbes van reflexar la reducció ambiental dels nivells de Pb causada per la prohibició de les gasolines amb plom (Bellés i col·ls., 1995; Schuhmacher i col·ls., 1996). Les diferències trobades entre les concentracions de metalls en herbes dels diferents anys estarien probablement causades per l'heterogeneïtat de les mostres, més que per les potencials diferències entre les concentracions ambientals de metalls en l'àrea estudiada. En tot cas, les concentracions de metalls en herbes trobades al 2005 als voltants de la incineradora de Tarragona van ser similars o inferiors a les detectades per altres autors en diferents

espècies vegetals (Schuhmacher i col·ls., 2003; Bosco i col·ls., 2005; Sardans i Peñuelas, 2005).

*Avaluació de riscos per exposició a metalls pesants a rodalies de la Incineradora de Residus Sòlids Urbans de Tarragona*

La relació entre les concentracions de metalls en sòls i els Preliminary Remediation Goals, va ser en tots els casos inferior a 100%, indicant que els nivells són segurs per la població. Així mateix, per tots els metalls el Hazard Quotient calculat a partir de l'exposició oral diària va estar per sota del valor d'1, considerat com a segur, tant per adults com per nens.

Només la ingestió d'As va superar el màxim risc carcinogènic acceptable de  $10^{-6}$ . Per altra banda, cal destacar que aquest límit ha estat superat per sòls de diferents països (Nadal i col·ls., 2004). De la mateixa manera, quan es va comparar la concentració d'As en sòls amb el corresponent PRG ( $0.39 \mu\text{g/g}$ ) es va superar el valor límit del 100% (amb un valor de 440), tal i com ja ho havia fet els anys anteriors 1997, 1999 i 2002 (amb valors de 1200, 1430 i 1540, respectivament). Tot i això, l'any 2005 es va observar una important disminució en els riscos carcinogènics.

*Nivells de PCDD/Fs en herbes i sòls de les rodalies de la Incineradora de Residus Industrials de Tarragona*

El 2004, després de cinc anys de funcionament de la planta incineradora de residus especials, les concentracions de PCDD/Fs en sòls van estar compreses entre 0.06 a 12.60 ng I-TEQ/kg, amb una mitjana i mediana de 0.65 i 1.14 ng I-TEQ/kg, respectivament. Les concentracions més elevades es van observar en punts urbans. En el període 2003-2004, es va observar un augment de les concentracions en 22 de les 40 mostres. El valor mitjà va augmentar un 16%. Aquestes variacions van ser causades probablement per desviacions en les determinacions analítiques junt amb

petites variacions en els punts de mostreig. Tot i això, el test U-Mann Whitney no va mostrar diferències significatives entre el 1998 i el 2004 per cap dels escenaris considerats ( 500, 2,500 i > 4,000 m de la incineradora). En general, el patró de les mostres va ser similar per tots els anys estudiats, sent l'OCDD el congènere més abundant, seguit de 1,2,3,4,6,7,8-HpCDD, OCDF i 1,2,3,4,6,7,8-HpCDF. Tot i això, l'ACP va mostrar un perfil diferent per algunes mostres que podrien haver estat afectades per fonts de contaminació puntuals com la crema de rostolls.

Pel que fa a les herbes, al 2005 les concentracions de PCDD/Fs van anar de 0.03 a 1.57 ng I-TEQ/kg, amb una mitjana i una mediana de 0.31 i 0.40 ng I-TEQ/kg, respectivament. L'evolució temporal entre el 1998 i el 2008 va mostrar que els nivells van disminuir en 14 de les 40 mostres. El valor de la mediana va augmentar en un 35%. En general es va observar un augment en les concentracions de PCDD/Fs de mostres rurals en la direcció nord, mentre que en les mostres urbanes preses en les diferents direccions es va notar un descens. La reducció podria ser causada pel nou sistema de depuració de gasos de la incineradora. Per altra banda, l'augment en les mostres rurals podria ser causat per la crema de rostolls. Els perfils de les mostres van ser semblants als trobats pels sòls, sent l'OCDD el congènere més abundant, seguit de 1,2,3,4,6,7,8-HpCDD, OCDF i 1,2,3,4,6,7,8-HpCDF. En l'ACP, com en el cas dels sòls, es va observar un cluster on s'agrupen la majoria de mostres la qual cosa indicaria que les fonts que contribueixen als nivells ambientals de PCDD/Fs de la zona han estat les mateixes els diferents anys.

*Avaluació de riscos per exposició a PCDD/Fs a rodalies de la Incineradora de Residus Industrials de Tarragona*

Es va calcular l'exposició ambiental a PCDD/Fs a partir de les dades d'aquest estudi. Per altra banda, es va calcular l'exposició a PCDD/Fs a través de la dieta a partir de dades d'un estudi anterior (Bocio i Domingo, 2005). Es va avaluar l'exposició

d'acord amb la distància a la planta incineradora: 500 m, 2,500 m (punts rurals) i >4,000 m (punts urbans) diferenciant els grups de nens i d'adults.

Respecte a l'exposició directa a PCDD/Fs, la principal via d'exposició en adults va ser la inhalació, especialment en l'àrea urbana ( $5.90 \cdot 10^{-7}$ ,  $5.98 \cdot 10^{-7}$  i  $3.21 \cdot 10^{-5}$  ng I-TEQ/kg/dia a 500, 2,500 i >4,000 m de la planta, respectivament). La raó, és la gran diferència en les concentracions de PCDD/Fs trobades en aire per la zona rural i urbana (4.5 i 243 fg I-TEQ/m<sup>3</sup>, respectivament). Pels nens a >4,000 m de la planta, la principal via d'exposició també va ser la inhalació, mentre que a la zona rural la principal via d'exposició seria la ingesta de sòls. Per les zones rurals, els nivells d'exposició total no van mostrar diferències significatives depenent de la distància a la incineradora.

Pels adults i els nens de l'àrea més propera a la planta incineradora (500 i 2,500 m), l'exposició ambiental només va representar un 0.1% de l'exposició total (ambiental més la dieta). En l'àrea urbana (>4,000 m), aquest percentatge va pujar fins a un 3.8 i 1.4% de l'exposició total per adults i nens, respectivament.

A la zona rural (500 i 2,500 m) l'exposició va ser 0.21-0.85 i 0.81-3.24 pg/kg/dia per adults i nens, respectivament. A l'àrea urbana l'índex de risc va ser 0.22-0.89 i 0.82-3.28 per adults i nens, respectivament. A l'àrea urbana, el risc va ser lleugerament superior per ambdós grups de població (0.22-0.89 per adults i 0.82-3.28 per nens). En cap cas es va sobrepassar el valor límit (4 pg I-TEQ/kg/dia). Es van estimar rics de càncer de 850 i 890 per les àrees propera i llunyana a la incineradora, respectivament. Considerant una vida mitjana de 70 anys, això suposaria un excés de risc de càncer de 12 i 13 per una població d'1 milió en les zones rural i urbana, respectivament.

Els resultats van indicar que les emissions de la incineradora no suposaven riscos addicionals per la salut de la gent que viu a les rodalies de la instal·lació.



## Capítol III

### Nivells de compostos organoclorats i metalls pesants en aire

Articles 3 i 4:

Mari M, Schuhmacher M, Feliubadaló J, Domingo JL

Air concentrations of PCDD/Fs, PCBs and PCNs using active and passive air samplers

Chemosphere 70: 1637-1643 (2008)

Mari M, Nadal M, Schuhmacher M, Domingo JL

Monitoring PCDD/Fs, PCBs and heavy metals in ambient air of an industrial area of Catalonia, Spain

Chemosphere (En premsa)



### **Article 3: “Air concentrations of PCDD/Fs, PCBs and PCNs using active and passive air samplers”**

#### **Abstract**

The concentrations of polychlorinated dibenzo-*p*-dioxins and furans (PCDD/Fs), polychlorinated biphenyls (PCBs) and polychlorinated naphthalenes (PCNs) were determined in air samples collected at four sampling sites located in two zones of Barcelona (Spain): near a municipal solid waste incinerator (MSWI) and a combined cycle power plant (3 sites), and at a background/control site. Samples were collected using high-volume active samplers. Moreover, 4 PUF passive samplers were deployed at the same sampling points during three months. For PCDD/Fs, total WHO-TEQ were 27.3 and 10.9 fg WHO-TEQ m<sup>-3</sup> at the urban/industrial and the background sites, respectively. The sum of 7 PCB congeners and the ΣPCN levels were also higher at the industrial site than at the background site. In order to compare active and passive sampling, the accumulated amounts of PCDD/Fs, PCBs and PCNs in the four passive air samplers, as well as the total toxic equivalents in each sampling site were also determined. To assess the use of PUF passive samplers as a complementary tool for PCDD/F, PCB and PCN monitoring, sampling rates were calculated in accordance with the theory of passive air samplers. PUF disks allowed establishing differences among zones for the POP levels, showing that they can be a suitable method to determine POP air concentrations in areas with various potential emission sources. Although both particle and gas phase were sorbed by the PUFs, data of gas phase congeners are more reproducible.

**Keywords:** PCDD/Fs; PCBs; PCNs; Air; High-volume samplers; PUF disks

## 1. Introduction

In recent years, a number of monitoring studies have been performed in order to investigate sources and levels in environmental compartments of the persistent organic pollutants (POP) PCDD/Fs, PCBs and PCNs, as well as to analyze behavior and fate (Harner i Bidleman, 1997; Harrad i Mao, 2004; Nadal i col·ls., 2004; Bakoglu i col·ls., 2005; Hung i col·ls., 2005; Schuhmacher i Domingo, 2006; Schuhmacher i col·ls., 2006). For air monitoring of POP, high-volume samplers are used as conventional sampling techniques. The relative high cost of the equipment, as well as the requirement of a pump and source electricity are important disadvantages of this sampling method. Moreover, only daily concentrations can be determined. Meteorological variations and punctual emissions of POP can also modify their concentrations in air during short time periods. A potential alternative is the use of passive samplers. These devices allow semi-quantitative comparisons of the atmospheric POP levels (Harner i col·ls., 2004). Semipermeable membrane devices (SPMDs), XAD resin samplers, tristearin-coated fiberglass, polymer-coated glass samplers (POG) and polyethylene based samplers have been used as different types of passive samplers. Taking into account their low cost and simple manipulation, polyurethane foam (PUF) disks are especially attractive (Jaward i col·ls., 2004a; Pozo i col·ls., 2004; Wilford i col·ls., 2004; Harner i col·ls., 2006).

In recent years, we established an environmental surveillance program in the neighborhood of a municipal solid waste incinerator (MSWI) of Sant Adrià del Besòs (Barcelona, Catalonia, Spain) (Domingo i col·ls., 2000; Schuhmacher i col·ls., 2000; Domingo i col·ls., 2002a; Domingo i col·ls., 2002b). However, due to important recent changes in town-planning, numerous soil movements have been performed in the zone under evaluation. Therefore, the characteristics of the surveillance program previously established, which involved sampling of soils and herbage, needed an important modification. The aim of the present study was to determine the atmospheric concentrations of PCDD/Fs in the same zone, an active industrial area of Barcelona

with two potentially important emissions sources of PCDD/Fs and other POP: the MSWI and a combined cycle power plant. PCBs and PCNs were also included in the current survey. A second goal of the present investigation was to assess the use of passive air samplers as a complementary tool for monitoring the levels of these POP in potentially contaminated areas.

## **2. Methods**

### *2.1. Sampling sites*

In March-April 2005, air samples were collected using high-volume active samplers at four sampling locations of Barcelona. Three sampling sites were placed in the area above indicated and were situated at different wind directions from the two main pollutant sources. A fourth sampling site was placed in a semi rural area close to a large park with no direct pollutant sources (background/control sampling site). On the other hand, four passive samplers were deployed at the same four sampling points for approximately 3 months (between March-June 2005). The average temperature and the most frequent wind directions in Barcelona during the sampling period were 14.1°C (range: 0.2°C-28.9°C) and SW, NE and NW, respectively.

### *2.2. Active and passive samplers*

Ambient air samples of PCDD/Fs, PCBs and PCNs were collected using high-volume samplers (Tisch TE-1000) complying with US EPA TO-9 (USEPA, 1999). Passive samplers consist of a PUF disk (14 cm diameter, 1.35 cm thick) purchased from PacWill Environmental (Stoney Creek, ON, Canada) contained within a stainless steel shelter made up of two dishes (30 and 25 cm diameter, respectively). The gap between the two dishes is 2.5 cm.

### 2.3. Analytical methods

Concentrations of PCDD/Fs, PCBs and PCNs in air were determined by high-resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS) according to the VDI 3499 method.  $^{13}\text{C}_{12}$ -isotopic recovery internal standards were added to the samples. Subsequently, the filter and PUF plugs were extracted by ASE (Accelerated Solvent Extraction) from Dionex 300. Toluene was used as solvent under the following conditions: heat 5 min to 100°C, and a pressure of 100 bars during 5 min. The volume of the sample extract was reduced to about 1 ml by means of a Zymark-Turbovap. The extract was subsequently subjected to an acid/base clean-up procedure followed on micro columns of silica gel and alumina. For clean-up step 1, the solution was transferred to the first column with glass wool, 20 g alkaline silica gel 33% NaOH, 20 g neutral silica gel with 44% sulfuric acid and 20 g sodium sulfate. This column was washed with 400 ml of hexane, being the solution then reduced to 1 ml. For clean-up step 2, the solution was transferred to a column with 25 g of alumina and 20 g of sodium sulfate. The column was firstly eluted with 150 ml of hexane/dichloromethane 50/50 (v/v). The solution was subsequently reduced to 1 ml. The PCDD/F fraction (or the PCB/PCN fraction) was concentrated near to dryness by a gentle stream of dry nitrogen. The final extract was spiked with the isotopic labeled internal standard and then analyzed with HRGC-HRMS (GC HP 5890 or Varian GC coupled with HR MS VG Autospec or Finnigan MAT95 ) to determine the recovery efficiencies achieved for the  $^{13}\text{C}_{12}$ -labelled internal standards. The mass spectrometer operated under electron impact (EI) positive mode (35-45 eV) and selected ion monitoring (SIM) mode, at resolving power range from 6.000 to 10.000 amu. The mass range available was 0-2.000 amu. The selected PCBs were quantified via the internal recovery standard, whereas PCNs were quantified by means of  $^{13}\text{C}_{12}$ -PCB standards (Halowax standards). For analytical quality control, clean PUF disks (blanks) were pre-extracted and similarly analyzed. Samples were spiked with isotopic labeled internal standard and then analyzed to determine the recovery efficiencies achieved for the  $^{13}\text{C}_{12}$ -labeled internal standards.

### 3. Results and Discussion

#### 3.1. PCDD/F, PCB and PCN concentrations

Table 1 shows the PCDD/F, PCB and PCN concentrations of the high-volume air samples collected in four sampling sites of Barcelona. The major contributor to total WHO-TEQ was 2,3,4,7,8-PeCDF (13-27%). According to various international studies, this congener accounts for 20-40% of total TEQ (Lohmann i Jones, 1998). Probably, the current contribution percentages were slightly lower because of the new WHO-TEF (Van den Berg i col·ls., 2006) value for this congener is smaller. The most abundant congener was OCDD (44% of the total concentration), followed by 1,2,3,4,6,7,8-HpCDD (14%) and OCDF (10%). The homologue concentrations found at the urban/industrial and background sites are depicted in Fig. 1. An ambient pattern of decreasing concentrations of PCDFs and increasing concentrations of PCDDs with increasing chlorination level could be observed in both zones (urban/industrial and background). Different ratios between 2,3,7,8-PCDDs and 2,3,7,8-PCDFs might reflect differences in local emissions, and/or different atmospheric conditions (Correa i col·ls., 2004). Taking this into account, ratios were calculated for each sampling site. Site 4 (background/control) showed the lowest ratio (1.1), whereas site 1 (urban/industrial area), showed the largest value (3.2), being the ratios at sites 2 and 3 comparatively similar (1.6 and 1.3, respectively).

Table 1

Atmospheric concentrations of PCDD/Fs ( $\text{fg m}^{-3}$ ), PCBs and PCNs ( $\text{pg m}^{-3}$ ) determined by high-volume air sampling in four sites of Barcelona (March-April 2005).

	Urban/Industrial			Background
	S1	S2	S3	S4
2,3,7,8-TCDD	<1.5	<1.5	<1.8	<1.5
1,2,3,7,8-PeCDD	3.6	2.7	3.5	1.5
1,2,3,4,7,8-HxCDD	3.7	2.8	3.5	1.5
1,2,3,6,7,8-HxCDD	12.1	11.9	11.8	4.4
1,2,3,4,7,8-HxCDD	9.1	7.5	7.6	2.1
1,2,3,4,6,7,8-HpCDD	149.6	94.3	92.9	30
OCDD	705.9	234.5	242.0	79.8
2,3,7,8-TCDF	12.9	14.8	21.5	11.0
1,2,3,7,8-PeCDF	10.6	13.3	16.8	9.1
2,3,4,7,8-PeCDF	17.2	14.9	21.8	9.8
1,2,3,4,7,8-HxCDF	17.0	14.2	19.5	7.6
1,2,3,6,7,8-HxCDF	19.7	17.4	24.4	10.6
2,3,4,6,7,8-HxCDF	1.9	1.8	1.6	1.5
1,2,3,7,8,9-HxCDF	18.8	15.3	23.4	9.7
1,2,3,4,6,7,8-HpCDF	64.2	52.4	69.5	22.7
1,2,3,4,7,8,9-HpCDF	5.7	6.6	7.9	4.5
OCDF	108.3	66.1	77.4	21.6
Ratio PCDD/PCDF	3.2	1.6	1.3	1.1
$\text{fg WHO-TEQ}^a \text{ m}^{-3}$	38.7	18.5	24.6	10.9
PCB 28	66	60	56	28
PCB 52	42	36	26	16
PCB 101	24	22	30	22
PCB 118	<10	<10	13	<10
PCB 138	13	16	24	25
PCB 153	14	18	24	26
PCB 180	<10	<10	<10	<10
$\Sigma\text{PCB}$	169	162	178	127
Sum of MonoCNs	272.8	122.7	140.1	219.1
Sum of DiCNs	218.9	122.7	99.1	208.7

Sum of TriCNs	90.9	52.0	30.8	62.6
Sum of TetraCNs	26.9	37.2	10.3	24.3
Sum of PentaCNs	2.0	3.7	1.7	2.4
Sum of HexaCNs	<1.7	<1.7	<1.7	<1.7
Sum of HeptaCNs	<1.7	<1.7	<1.7	<1.7
OctaCN	6.7	14.9	<1.7	<1.7
$\Sigma$ PCN	621.8	356.9	288.8	522.4

<sup>a</sup>To calculate total WHO-TEQ values, for those congeners below the limit of detection (LOD), concentrations were assumed to be half of the LOD.

The sum of the PCB congeners was higher at the urban/industrial zone (mean: 170 pg m<sup>-3</sup>) than at the background site (127 pg m<sup>-3</sup>). These values are in the range of a number of reported levels concerning urban areas over the world (Brunciak i col·ls., 2001; Garcia-Alonso i col·ls., 2002; Mandalakis i col·ls., 2002; Yeo i col·ls., 2004). However, it must be noted that in most studies some congeners were determined as mixtures. In the present study, PCB 180 was under its detection limit in all samples, whereas PCB 118 could be detected only at site 3 (13 pg m<sup>-3</sup>). Both PCB congeners are typical of MSWI and coal power emissions (Biterna i Voutsas, 2005). Decreasing concentrations with rising chlorination degree were observed in the urban/industrial sites. Similar results were also previously reported in both urban and rural areas (Mandalakis i col·ls., 2002; Yeo i col·ls., 2004).

Mono- and dichloronaphthalenes were the predominating PCN homologues (78% of the total contribution). However, when the most frequently analyzed homologues, tri- to octaCNs, were taken into account, the highest sum of homologues corresponded to triCNs followed by tetraCNs, which is in agreement with results of previous studies (Dorr i col·ls., 1996; Harner i col·ls., 2000). When compared with literature data (Dorr i col·ls., 1996; Harner i col·ls., 2000; Jaward i col·ls., 2004a; Manodori i col·ls., 2006), the current values seem to be enormous. Notwithstanding, it must be noted that in those studies only some PCN congeners or homologues (tri- to octaCNs) were analyzed.

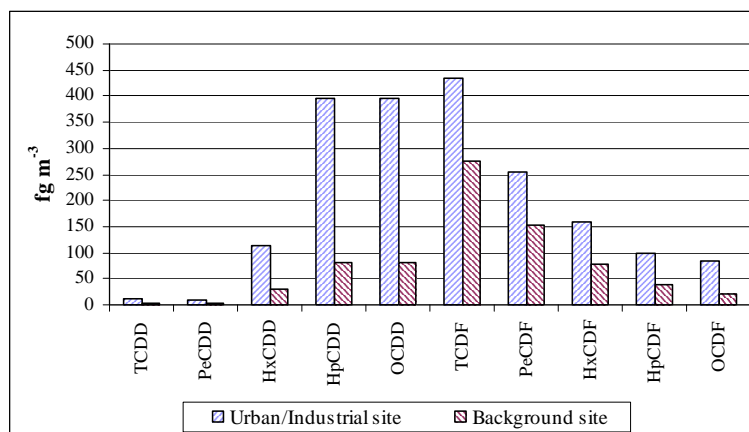


Fig. 1. Homologue concentrations of PCDD/Fs in the high-volume air samples of the urban/industrial area (mean values) and the background site.

In general terms, we found low air levels of the analyzed POP. It would reflect the global decrease of these chemicals worldwide as result of the use of new technologies in the flue gas cleaning systems of incinerators, the increasing use of unleaded fuel motor vehicles, as well as other important environmental improvements (Schuhmacher i col·ls., 2002b; Yeo i col·ls., 2004). A similar reduction was also recently observed in studies performed in the same area, when soil and herbage samples were used as environmental monitors (Domingo i col·ls., 2002a). Clean marine air could also contribute to dilute the effect of those emission sources, which are located at a few meters from the Mediterranean Sea (Gao i col·ls., 2002; Gambaro i col·ls., 2004).

### *3.2. PCDD/F, PCB and PCN concentrations in passive air samplers*

The accumulated amounts of PCDD/Fs, PCBs and PCNs in the four passive air samplers, as well as the total toxic equivalents in each sampling site are shown in Table 2. Total tetra- and penta-CDFs and tetra-CDDs were the main contributors to total PCDD/Fs. These homologues are predominant in the gas phase, tending PCDDs to be more associated with the particulate than the equivalent PCDF homologues. OCDD was the predominant congener, 62% of the total, followed by 1,2,3,4,6,7,8-HpCDD, 7%, of the total. With respect to PCDFs, OCDF accounted for 3-5% of the total 2,3,7,8-substituted congeners. These results show that most compounds associated with particles are also sequestered by the samplers. Similar findings were reported in a recent study in which PUF passive air samplers were also used (Jaward *et al.*, 2005).

With respect to PCBs, because of analytical problems no data from site 3 are reported. PCB 28 was the most abundant congener in the remaining three sites. Sites 1 and 2, situated at the urban/industrial zone, showed decreasing concentrations with the increasing number of chlorine atoms. As also observed in the active sampling, at the background site hexa- and heptaCBs (No. 138, 153 and 180) were found at higher quantities than tetraCBs (No. 52 and 101). With regard to PCNs, as for active samplers, the homologue pattern was dominated by the lower chlorinated PCNs. A very notable difference was found between the concentrations of the mono- and diCNs, which are more volatile and prone to undergo LRAT (Pribylova *et al.*, 2006), and those concerning the rest of homologues.

Table 2  
 Accumulated amounts of PCDD/Fs (pg), PCBs and PCNs (ng) by passive air samplers in four sites of  
 Barcelona during March-June 2005.

	Urban/Industrial			Background
	S1	S2	S3	S4
Sampling period (days)	97	91	97	97
2,3,7,8-TCDD	<0.5	<0.5	<0.6	<0.6
1,2,3,7,8-PeCDD	0.5	<0.5	0.9	<0.6
1,2,3,4,7,8-HxCDD	0.5	<0.5	<0.6	<0.9
1,2,3,6,7,8-HxCDD	1.5	<0.5	<0.6	<0.9
1,2,3,4,7,8-HxCDD	1.1	<0.5	<0.6	<0.9
1,2,3,4,6,7,8-HpCDD	23.3	6.8	7.2	4.2
OCDD	195.0	32.2	69.9	32.7
2,3,7,8-TCDF	4.1	2.8	2.1	<2.7*
1,2,3,7,8-PeCDF	2.7	2.6	2.7	0.9
2,3,4,7,8-PeCDF	2.4	2.9	3.3	1.8
1,2,3,4,7,8-HxCDF	3.6	2.2	2.4	2.4
1,2,3,6,7,8-HxCDF	3.4	2.6	3.6	1.8
2,3,4,6,7,8-HxCDF	<0.5	<0.5	<0.6	<0.9
1,2,3,7,8,9-HxCDF	1.8	1.3	0.9	<0.9
1,2,3,4,6,7,8-HpCDF	10.0	7.5	5.4	4.2
1,2,3,4,7,8,9-HpCDF	0.7	<1.0	<1.5	<0.9
OCDF	10.5	3.3	3.3	<6.0*
pg WHO-TEQ	3.6	2.6	3.4	2.0
PCB 28	16.4	17.2	-	12.3
PCB 52	9.6	11.0	-	7.5
PCB 101	7.3	8.6	-	6.9
PCB 118	2.0	3.0	-	<3.0
PCB 138	4.6	6.1	-	8.4
PCB 153	5.0	6.7	-	9.9
PCB 180	2.0	2.6	-	8.4
Sum of MonoCNs	105	93	85	69

Sum of DiCNs	122	114	101	82
Sum of TriCNs	4	5	5	3
Sum of TetraCNs	3	4	2	2
Sum of PentaCNs	0.4	0.4	0.3	0.3
Sum of HexaCNs	<0.1	<0.1	0.2	<0.1
Sum of HeptaCNs	<0.1	<0.1	<0.1	<0.1
OctaCN	0.2	0.1	0.2	0.2
Σ PCN	236	218	194	158

\* Increased LOD because of matrix interferences.

### 3.3. PCDD/F and PCB passive sampling rates

To evaluate the use of PUF passive air samplers as a potential complementary tool for environmental monitoring of PCDD/Fs, and PCBs and PCNs, sampling rates were calculated in accordance with the theory of passive air samplers (Harner i col·ls., 2004; Pozo i col·ls., 2004). Passive air samplers accumulate chemicals via diffusion (Shoeib i Harner, 2002). The chemical exchange between uptake and elimination processes is described using mass transfer coefficients and rate constants:

$$V_{PUF} \left( \frac{dC_{PUF}}{dt} \right) = k_A \cdot A_{PUF} \left( C_A - \frac{C_{PUF}}{K_{PUF-A}} \right) \quad (1)$$

where:

$V_{PUF}$  is the volume of the sampling medium ( $\text{cm}^3$ )

$C_{PUF}$  is the passive sampler concentration (ng)

$C_A$  is the air concentration ( $\text{ng cm}^{-3}$ )

$k_A$  is the air side mass transfer coefficient ( $\text{cm s}^{-1}$ )

$A_{PUF}$  is the planar area of the exposed portion ( $\text{cm}^2$ )

$K_{PUF-A}$  is the passive sampler medium-air partition coefficient (dimensionless)

It has been shown that  $K_{PUF-A}$  is well correlated with  $K_{OA}$ , being the time required for a chemical to reach saturation inversely proportional to  $K_{PUF-A}$  (Pozo i col-Is., 2004). It has been also demonstrated that sampling rates of chemicals with  $K_{OA} > 10^{8.5}$  remained linear (and defined by the mass transfer coefficient) over 100 days at few  $m^3 day^{-1}$  (Shoeib i Harner, 2002). Under these conditions of linearity, sampling rates for the target compounds can be calculated according to the following simple expression:

$$R_{cal} = \frac{C_{PUF}}{C_A} \cdot t \quad (2)$$

where  $R_{cal}$  is the sampling rate ( $m^3 day^{-1}$ ) measured at the calibration site,  $C_{PUF}$  is the amount of pollutant accumulated in the sampler (ng),  $C_A$  is the concentration of that contaminant in the vapor phase ( $ng m^{-3}$ ), and  $t$  is the time of exposure (days). It is important to note that this analysis considers only the gas phase transfer of contaminants, being the mass transfer coefficient strongly related to wind speed (Bartkow i col-Is., 2005). Therefore, PUFs are housed in a chamber which protects them from precipitation and sunlight, also diminishing the effect of wind. The rates can be used to estimate air concentrations using the same kind of devices.

Table 3

Sampling rates ( $\text{m}^3 \text{day}^{-1}$ ) for each PUF passive air sampler.

Congeners	PS 1	PS 2	PS 3	PS 4
2,3,7,8-TCDD	-	-	-	-
1,2,3,7,8-PeCDD	4.0 (1.4)	-	7.2 (2.7)	-
1,2,3,4,7,8-HxCDD	9.7 (1.5)	-	-	-
1,2,3,6,7,8-HxCDD	8.3 (1.3)	-	-	-
1,2,3,4,7,8-HxCDD	9.8 (1.4)	-	-	-
1,2,3,4,6,7,8-HpCDD	24.2 (2.1)	7.5 (0.6)	7.5 (0.7)	16.4 (1.4)
OCDD	224.8 (5.1)	39.6 (0.8)	80.6 (1.8)	186.2 (4.2)
2,3,7,8-TCDF	3.4 (3.3)	2.5 (2.1)	1.7 (1.0)	-
1,2,3,7,8-PeCDF	3.9 (2.6)	4.0 (2.1)	3.9 (1.7)	2.0 (0.5)
2,3,4,7,8-PeCDF	3.0 (1.4)	3.9 (2.1)	4.2 (1.6)	4.2 (1.9)
1,2,3,4,7,8-HxCDF	9.4 (2.2)	6.1 (1.4)	6.2 (1.5)	13.9 (3.3)
1,2,3,6,7,8-HxCDF	7.6 (1.7)	6.2 (1.4)	8.0 (1.8)	7.7 (1.8)
2,3,4,6,7,8-HxCDF	-	-	-	-
1,2,3,7,8,9-HxCDF	1.5 (0.9)	1.1 (0.7)	0.7 (0.5)	-
1,2,3,4,6,7,8-HpCDF	10.5 (1.7)	8.4 (1.3)	5.7 (0.9)	12.0 (1.9)
1,2,3,4,7,8,9-HpCDF	11.6 (1.1)	-	-	-
OCDF	40.6 (1.3)	13.6 (0.4)	12.8 (0.4)	-
PCB 28	2.8	3.1	-	4.5
PCB 52	2.9	3.5	-	4.9
PCB 101	3.8	4.8	-	4.2
PCB 118	1.6	2.6	-	-
PCB 138	3.4	4.8	-	4.4
PCB 153	3.4	4.9	-	4.9
PCB 180	-	-	-	-
Sum of MonoCNs	3.8	7.8	6.3	3.2
Sum of DiCNs	5.5	9.6	10.5	4.1
Sum of TriCNs	0.4	1.0	1.7	0.5
Sum of TetraCNs	1.1	1.1	2.0	0.8

Sum of PentaCNs	2.0	1.1	1.8	1.3
Sum of HexaCNs	-	-	-	-
Sum of HeptaCNs	-	-	-	-
OctaCN	-	-	-	-

In parentheses, sampling rates calculated using total air concentrations ( $c_v+c_p$ ).

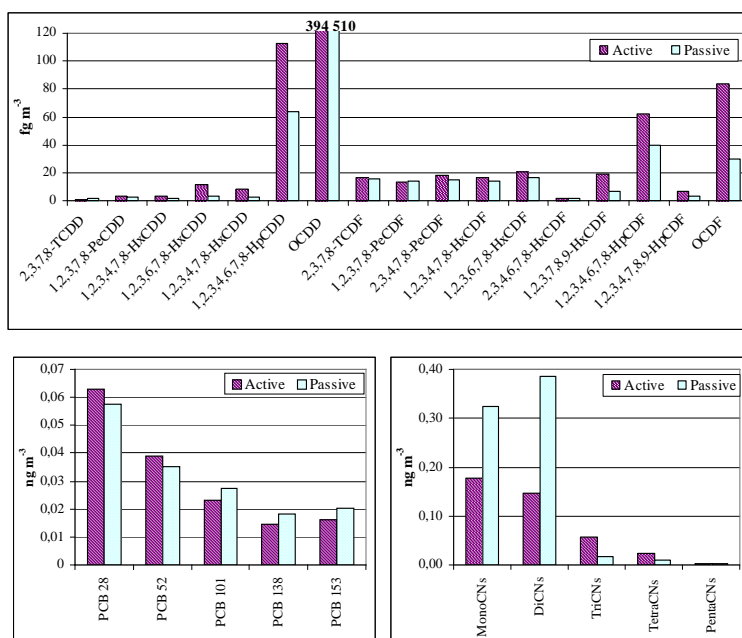


Fig. 2. Concentrations of PCDD/Fs (top) and PCBs and PCNs (bottom) in active and passive samples calculated using rates of 2 and 3  $m^3\ day^{-1}$  for PCDD/Fs, and for PCBs and PCNs, respectively.

In the current study, sampling rates ( $\text{m}^3 \text{day}^{-1}$ ) were calculated according to this theory. Passive sampler amounts of each congener were used and the corresponding vapor phase concentration determined separately in the active sampling. This approach resulted in very high rates for the heaviest PCDD/Fs, which are almost exclusively associated to the particle phase. However, as previously found in the concentrations in the PAS, they were also trapped (at least part of them) by the passive samplers (Table 2). Therefore, for rate estimation of PCDD/Fs, the total air concentration ( $C_v+C_p$ ) was also considered and a linear uptake was assumed throughout exposure time (91-97 days). The uptake/rate results for each PCDD/F and PCB congener and PCN homologues are also shown in Table 3. High substituted PCDD/F congeners resulted in very high rates when only the gas phase was considered. However, when total air concentrations were taken into account, the rates ( $0.4\text{-}5.1 \text{ m}^3 \text{day}^{-1}$ ) were lower than those obtained for most gas phase congeners (tetra- and penta- congeners) ( $1.7\text{-}7.2 \text{ m}^3 \text{day}^{-1}$ ). Data for hepta- and octa- congeners were rather heterogeneous, which could be due to the particle size in each site. The finer the particle, the more easily it is sorbed by the passive sampling device. The current results are in agreement with those of Lohmann et al. (1998), who found SPMD efficient samplers for vapor phase species with good reproducibility between samplers, but with a poorer reproducibility for particle associated species. In general terms, rates obtained for tetra- and pentaCDD/F substituted congeners were homogeneous, with a mean value of  $3.7 \text{ m}^3 \text{day}^{-1}$ . Otherwise, when total air concentrations were taken into account a mean value of  $1.7 \text{ m}^3 \text{day}^{-1}$  was obtained. Because part of the particles were sequestered by the PAS, it seemed more appropriated to use a  $2 \text{ m}^3 \text{day}^{-1}$  value for PCDD/F estimations. PCB uptake/rates ranged from  $1.6$  to  $4.9 \text{ m}^3 \text{day}^{-1}$ , with a mean value of  $3.8 \text{ m}^3 \text{day}^{-1}$ . These values are similar to those reported by Shoeib and Harner (2002),  $3\text{-}4 \text{ m}^3 \text{day}^{-1}$ , in indoor conditions. An uptake rate of  $3\text{-}4 \text{ m}^3 \text{day}^{-1}$  has been used in field-studies to assess PCB levels (Gouin i col·ls., 2004; Jaward i col·ls., 2004b). PCNs rates ranged from  $0.4$  to  $10.5 \text{ m}^3 \text{day}^{-1}$ , with the highest rates belonging to the most abundant air homologues. The mean value for PCNs was  $3.3 \text{ m}^3 \text{day}^{-1}$ . In order to validate these mean rates, PAS concentrations were calculated and compared with those of the active

samples (Fig. 2). The results indicate that the concentrations obtained with the passive samplers fit quite well with the levels obtained with the active samplers. It suggests that these devices might be used as complementary tools in environmental air monitoring.

In summary, in agreement with data of other recent studies (Gouin i col·ls., 2004; Harner i col·ls., 2006), the current results show that PUF disks may be a suitable tool to estimate POP levels in air, mainly in those areas where a number of potential emission sources are located. Both particle and gas phases are sorbed by the PUFs. However, data of most gas phase congeners are more reproducible. Consequently, estimations of low log  $K_{OA}$  species are more accurate.

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#### References

- Bakoglu, M., Karademir, A., Durmusoglu, E., 2005. Evaluation of PCDD/F levels in ambient air and soils and estimation of deposition rates in Kocaeli, Turkey. *Chemosphere* 59, 1373-1385.
- Bartkow, M.E., Booi, K., Kennedy, K.E., Muller, J.F., Hawker, D.W., 2005. Passive air sampling theory for semivolatile organic compounds. *Chemosphere* 60, 170-176.
- Biterna, M., Voutsas, D., 2005. Polychlorinated biphenyls in ambient air of NW Greece and in particulate emissions. *Environ. Int.* 31, 671-677.
- Brunciak, P.A., Dachs, J., Franz, T.P., Gigliotti, C.L., Nelson, E.D., Turpin, B.J., Eisenreich, S.J., 2001. Polychlorinated biphenyls and particulate organic/elemental carbon in the atmosphere of Chesapeake Bay, USA. *Atmos. Environ.* 35, 5663-5677.

- Correa, O., Rifai, H., Raun, L., Suarez, M., Koenig, L., 2004. Concentrations and vapor-particle partitioning of polychlorinated dibenzo-p-dioxins and dibenzofurans in ambient air of Houston, TX. *Atmos. Environ.* 38, 6687-6699.
- Domingo, J.L., Bocio, A., Nadal, M., Schuhmacher, M., Llobet, J.M., 2002a. Monitoring dioxins and furans in the vicinity of an old municipal waste incinerator after pronounced reductions of the atmospheric emissions. *J. Environ. Monit.* 4, 395-399.
- Domingo, J.L., Schuhmacher, M., Agramunt, M.C., Llobet, J.M., Rivera, J., Müller, L., 2002b. PCDD/F levels in the neighbourhood of a municipal solid waste incinerator after introduction of technical improvements in the facility. *Environ. Int.* 28, 19-27.
- Domingo, J.L., Schuhmacher, M., Müller, L., Rivera, J., Granero, S., Llobet, J.M., 2000. Evaluating the environmental impact of an old municipal waste incinerator: PCDD/F levels in soil and vegetation samples. *J. Hazard. Mat.* 76, 1-12.
- Dorr, G., Hippelein, M., Hutzinger, O., 1996. Baseline contamination assessment for a new resource recovery facility in Germany. Part V: Analysis and seasonal/regional variability of ambient air concentrations of polychlorinated naphthalenes (PCN). *Chemosphere* 33, 1563-1568.
- Gambaro, A., Manodori, L., Moret, I., Capodaglio, G., Cescon, P., 2004. Determination of polychlorobiphenyls and polycyclic aromatic hydrocarbons in the atmospheric aerosol of the Venice Lagoon. *Anal. Bioanal. Chem.* 378, 1806-1814.
- Gao, Y., Nelson, E.D., Field, M.P., Ding, Q., Li, H., Sherrell, R.M., Gigliotti, C.L., Van Ry, D.A., Glenn, T.R., Eisenreich, S.J., 2002. Characterization of atmospheric trace elements on PM 2.5 particulate matter over the New York-New Jersey harbor estuary. *Atmos. Environ.* 36, 1077-1086.
- Garcia-Alonso, S., Perez-Pastor, R.M., Quejido-Cabezas, A.J., 2002. Chemometric study of selected polychlorinated biphenyls in ambient air of Madrid (Spain). *Talanta* 57, 773-783.
- Gouin, T., Harner, T., Blanchard, P., Mackay, D., 2005. Passive and active air samplers as complementary methods for investigating persistent organic pollutants in the Great Lakes basin. *Environ. Sci. Technol.* 39, 9115-9122.

- Harner, T., Bidleman, T.F., 1997. Polychlorinated naphthalenes in urban air. *Atmos. Environ.* 31, 4009-4016.
- Harner, T., Pozo, K., Gouin, T., Macdonald, A.-M., Hung, H., Caine, J., Peters, A., 2006. Global pilot study for persistent organic pollutants (POPs) using PUF disk passive air samplers. *Environ. Pollut.* 144, 445-452.
- Harner, T., R.G.M., L., Jones, K.C., 2000. Polychlorinated naphthalenes in the atmosphere of the United Kingdom. *Environ. Sci. Technol.* 34, 3137-3142.
- Harner, T., Shoeib, M., Diamond, M., Stern, G., Rosenberg, B., 2004. Using passive air samplers to assess urban-rural trends for persistent organic pollutants. 1. Polychlorinated biphenyls and organochlorine pesticides. *Environ. Sci. Technol.* 38, 4474-4483.
- Harrad, S., Mao, H., 2004. Atmospheric PCBs and organochlorine pesticides in Birmingham, UK: concentrations, sources, temporal and seasonal trends. *Atmos. Environ.* 38, 1437-1445.
- Hung, H., Chi Lee, S., Wania, F., Blanchard, P., Brice, K., 2005. Measuring and simulating atmospheric concentration trends of polychlorinated biphenyls in the Northern Hemisphere. *Atmos. Environ.* 39, 6502-6512.
- Jaward, F.M., Barber, J.L., Booij, K., Jones, K.C., 2004a. Spatial distribution of atmospheric PAHs and PCNs along a north-south Atlantic transect. *Environ. Pollut.* 132, 173-181.
- Jaward, F.M., Farrar, N.J., Harner, T., Sweetman, A.J., Jones, J.L., 2005. Passive air sampling of polycyclic aromatic hydrocarbons and polychlorinated naphthalenes across Europe. *Environ. Toxicol. Chem.* 23, 1355-1364.
- Jaward, F.M., Meijer, S.N., Steinnes, E., Thomas, G.O., Jones, K.C., 2004b. Further studies on the latitudinal and temporal trends of persistent organic pollutants in Norwegian and U.K. background air. *Environ. Sci. Technol.* 38, 2523-2530.
- Lohmann, R., Corrigan, B.P., Howsam, M., Jones, K.C., Ockenden, W.A., 2001. Further developments in the use of semipermeable membrane devices (SPMDs) as passive air samplers for persistent organic pollutants: field application in a spatial survey of PCDD/Fs and PAHs. *Environ. Sci. Technol.* 35, 2576-2582.

- Lohmann, R., Jones, K.C., 1998. Dioxins and furans in air and deposition: A review of levels, behaviour and processes. *Sci. Total Environ.* 219, 53-81.
- Mandalakis, M., Tsapakis, M., Tsoga, A., Stephanou, E.G., 2002. Gas-particle concentrations and distribution of aliphatic hydrocarbons, PAHs, PCBs and PCDD/Fs in the atmosphere of Athens (Greece). *Atmos. Environ.* 36, 4023-4035.
- Manodori, L., Gambaro, A., Zangrando, R., Turetta, C., Cescon, P., 2006. Polychlorinated naphthalenes in the gas-phase of the Venice Lagoon atmosphere. *Atmos. Environ.* 40, 2020-2029.
- Nadal, M., Agramunt, M.C., Schuhmacher, M., Domingo, J.L., 2002. PCDD/PCDF congener profiles in soil and herbage samples collected in the vicinity of a municipal waste incinerator before and after pronounced reductions of PCDD/PCDF emissions from the facility. *Chemosphere* 49, 153-159.
- Nadal, M., Schuhmacher, M., Domingo, J.L., 2007. Levels of metals, PCBs, PCNs and PAHs in soils of a highly industrialized chemical/petrochemical area: Temporal trend. *Chemosphere* 66, 267-276.
- Pozo, K., Harner, T., Shoeib, M., Urrutia, R., Barra, R., Parra, O., Focardi, S., 2004. Passive-sampler derived air concentrations of persistent organic pollutants on a north-south transect in Chile. *Environ. Sci. Technol.* 38, 6529-6537.
- Pribylova, P., Kukucka, J., Klanova, J., Holoubek, I., 2006. Polychlorinated naphthalenes and chlorinated parafins in the air and soil samples of the Czech Republic. *Organohalogen Compds.* 68, 37-40.
- Schuhmacher, M., Bocio, A., Agramunt, M.C., Domingo, J.L., de Kok, H.A.M., 2002. PCDD/F and metal concentrations in soil and herbage samples collected in the vicinity of a cement plant. *Chemosphere* 48, 209-217.
- Schuhmacher, M., Domingo, J.L., 2006. Long-term study of environmental levels of dioxins and furans in the vicinity of a municipal solid waste incinerator. *Environ. Int.* 32, 397-404.
- Schuhmacher, M., Granero, S., Rivera, J., Muller, L., Llobet, J.M., Domingo, J.L., 2000. Atmospheric deposition of PCDD/Fs near an old municipal solid waste incinerator: levels in soil and vegetation. *Chemosphere* 40, 593-600.

- Schuhmacher, M., Jones, K.C., Domingo, J.L., 2006. Air-vegetation transfer of PCDD/PCDFs: An assessment of field data and implications for modeling. *Environ. Pollut.* 142, 143-150.
- Schuhmacher, M., Nadal, M., Domingo, J.L., 2004. Levels of PCDD/Fs, PCBs, and PCNs in Soils and Vegetation in an Area with Chemical and Petrochemical Industries. *Environ. Sci. Technol.* 38, 1960-1969.
- Shoeib, M., Harner, T., 2002. Characterization and comparison of three passive air samplers for persistent organic pollutants. *Environ. Sci. Technol.* 36, 4142-4151.
- USEPA, 1999. Compendium method TO-9A, "Determination of polychlorinated, polybrominated/chlorinated dibenzo-p-dioxins and dibenzofurans in ambient air. EPA/625/R-96/010b. Center for Environmental Research Information, Office of Research and Development, Cincinnati, OH.
- van den Berg, M., Birnbaum, L.S., Denison, M., De Vito, M., Farland, W., Feeley, M., Fiedler, H., Hakansson, H., Hanberg, A., Haws, L., Rose, M., Safe, S., Schrenk, D., Tohyama, C., Tritscher, A., Tuomisto, J., Tysklind, M., Walker, N., Peterson, R.E., 2006. The 2005 World Health Organization Re-evaluation of Human and Mammalian Toxic Equivalency Factors for Dioxins and Dioxin-like Compounds. *Toxicol. Sci.* 93, 223-241.
- Wilford, B.H., Harner, T., Zhu, J.P., Shoeib, M., Jones, K.C., 2004. Passive sampling survey of polybrominated diphenyl ether flame retardants in indoor and outdoor air in Ottawa, Canada: Implications for sources and exposure. *Environ. Sci. Technol.* 38, 5312-5318.
- Yeo, H.-G., Choi, M., Chun, M.-Y., Kim, T.-W., Cho, K.-C., Sunwoo, Y., 2004. Concentration characteristics of atmospheric PCBs for urban and rural area, Korea. *Sci. Total Environ.* 324, 261-270.

#### **Article 4: “Monitoring PCDD/Fs, PCBs and heavy metals in ambient air of an industrial area of Catalonia, Spain”**

##### **Abstract**

In 2005 and 2006, the levels of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs), polychlorinated biphenyls (PCBs) and metals (As, Be, Cd, Co, Cr, Cu, Mn, Ni, Pb, Sn, Tl and V) were measured in air samples collected in an industrial area of Sant Adrià del Besòs (Barcelona, Catalonia, Spain) where a municipal solid waste incinerator (MSWI) is placed, and in a background/control area. In general terms, concentrations of all environmental pollutants were higher at the industrial site. No significant seasonal/temporal variations were observed in any of the areas. No Pearson correlation was found between the PCDD/F concentrations and the environmental conditions of the two sampling periods considered. Principal Component Analyses (PCA) were performed to get information on the relationship among samples, pollutants, and emission sources. The results indicate that the MSWI of S. Adrià de Besòs is not a significant emission source of the above compounds for the area under its direct influence. Moreover, a notable difference in the PCDD/F congener profiles was found between ambient air and stack gas emissions, indicating that the current levels of PCDD/Fs are more related to other potential emissions sources rather than to those from the MSWI.

**Keywords:** PCDD/Fs; PCBs; Metals; Air; Municipal solid waste incinerator; Principal Component Analysis

## 1. Introduction

In recent years, a number of studies have demonstrated that emissions of toxic pollutants from modern municipal solid waste incinerators (MSWIs) have a relatively low environmental impact in comparison with other alternatives of waste disposal or different industrial activities (Schuhmacher i Domingo, 2006; Kao i col·ls., 2007; Wang i col·ls., 2008). However, waste incinerators in general, and MSWIs in particular, continue to generate a notable concern in the public opinion based mainly on the potential risks associated with the emission of hazardous substances (Domingo, 2002). Among these substances, special attention has been paid to polychlorinated dibenzo-*p*-dioxins (PCDD) and dibenzofurans (PCDF), and polychlorinated biphenyls (PCBs), taking into account the toxicity, environmental persistence, and capacity for bioaccumulation. The human exposure to these chlorinated contaminants mainly occurs via consumption of food, and more specifically, the ingestion of fatty foodstuffs (Llobet et al., 2008). However, the environmental exposure to PCDD/Fs must not be neglected. Among the different pathways of direct exposure, inhalation seems to be the most important route (Nadal et al., 2004b).

Chronic (long-term) inhalation of those substances is associated with damage to organs such as lungs, liver or kidney. In addition, some metals (i.e. chromium, cadmium, beryllium and arsenic), as well as some PCDD/F congeners are carcinogens (IARC, 1997; Ekino i col·ls., 2007).

Although environmental policies are becoming more and more stringent with respect to the emission limits of different pollutants, monitoring surveys are important in order (1) to ensure the proper working of cleaning systems, (2) to control the environmental levels, (3) to assess environmental exposure to and health risks associated with different pollutant sources, and (4) to identify the relative importance emission sources into the atmosphere to adopt the necessary measures to protect the

environment and the human health. In that context, ambient air monitoring is crucial to estimate the current emissions (Raun i col·ls., 2005).

Sant Adrià de Besòs (3.87 km<sup>2</sup> and 32,600 inhabitants) is a town situated at the NE of Barcelona (Catalonia, Spain), being part of its metropolitan area. Since 1975, a MSWI which handles 300,000 tones per year is operating there. In addition, a combined cycle power plant (783 MW) is located at only 1 km from the MSWI. Both facilities have been eventually integrated in the town landscape due to the urban expansion.

In Spring 2005, we performed a survey focused on determining the concentrations of PCDD/Fs and PCBs in air samples collected at four sampling sites in Sant Adrià de Besòs, three were located near the MSWI and one at a control site (Ekino i col·ls., 2007). The main goal of the present study was to assess the temporal trend in the ambient air levels of PCDD/Fs and PCBs near the MSWI of Sant Adrià del Besòs, as well as to obtain data on the levels of heavy metal in the area under assessment. Moreover, the influence of the MSWI and other potential emission sources was evaluated by means of the comparison with a control site using Principal Component Analysis (PCA).

## 2. Materials and methods

### 2.1. Sampling

In 2005 and 2006, air samples were collected at four sampling sites by using high-volume active samplers (TE-1000 PUF for organic compounds ( $N_{\text{PCDD/Fs}}=16$ ;  $N_{\text{PCBs}}=16$ ) and TE-6070DV Air Sampler for PM10 particulate matter ( $N_{\text{PM10}}=16$ ), Tisch Environmental, Cleves, OH, USA). Three sampling sites (SAB-1, SAB-2 and SAB-3) were located within the S. Adrià de Besòs area under the influence of a MSWI and a power plant. SAB-1 and SAB-2 were both situated at 500 from the MSWI, while SAB-3

was placed at 1 km. A fourth sampling site (BK) was located in a suburban area near a green space of Barcelona, with no direct industrial pollutant sources (Fig. 1). It was considered as background/control sampling site. Samples were collected during two different periods of the year: spring (temperature range: 6.7-23.7 °C) and autumn (temperature range: 11.9-30.1 °C). The prevailing wind directions during the sampling periods were SW, NW and W.

## *2.2. Analytical procedure*

PCDD/F and PCB concentrations were determined by high-resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS) following the German VDI 3499 method (VDI, 2003). Quartz fiber filters and polyurethane foam (PUF) plugs were used to collect separately the particle and the gas phases, respectively. Prior to the extraction,  $^{13}\text{C}_{12}$ -PCDD/F congeners were added as internal standards to compensate for any potential loss during the extraction and clean-up process. Quartz fiber filters and PUF plugs were extracted with toluene by Accelerated Solvent Extraction (ASE). The extract was subsequently subjected to an acid/base clean-up procedure followed on micro columns of silica gel and alumina. The final extract was spiked with isotopically labeled recovery standards and then analyzed by HRGC-HRMS (GC HP 5890 or Varian GC coupled with HR MS VG Autospec Finnigan MAT95, depending on the chemical). For analytical quality control, clean PUFs (blanks) were pre-extracted and similarly analyzed. Recovery percentages ranged between 60% and 130%. A quality assurance/quality control (QA/QC) process was carried out during the calibration and quantification. The sensitivity of the method was determined by checking that the HRMS signal of 1 pg of TCDD presented a signal to noise ratio higher than 10:1. Thereby, 5 ions were simultaneously monitored. The compound identification required the following criteria: a) the ratio of 2 ions obtained by the GC/MS matched the theoretical ration of the ratio obtained from the calibration standard run within  $\pm 15\%$ ; b) monitored ions to a given congener had to maximize within 2 s. Finally, the limit of

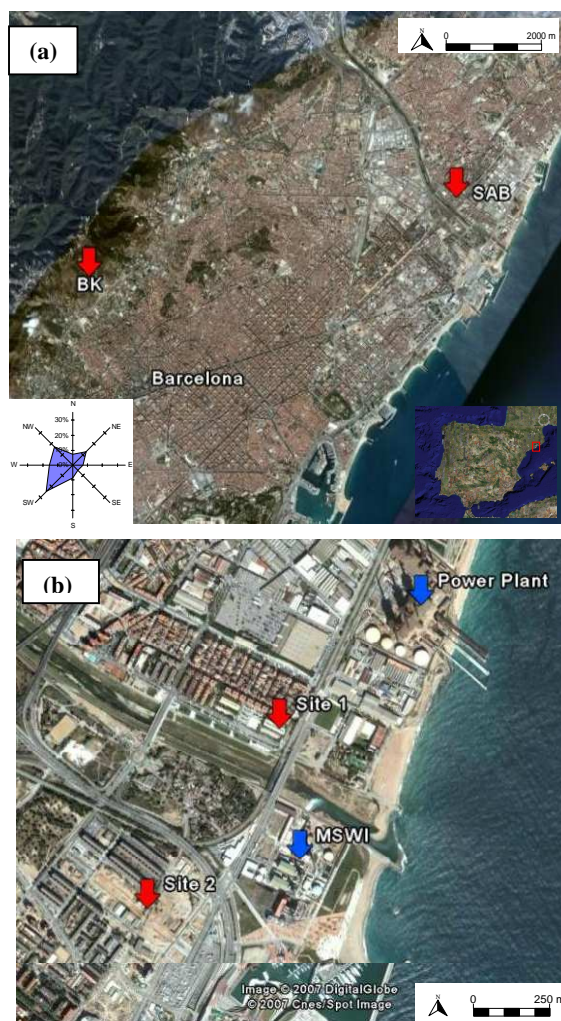


Fig. 1. Sampling locations (a) Areas of S. Adrià de Besòs (SAB) and background/control area (BK); (b) Sites of the SAB area, together with the MSWI and the power plant. Wind rose in the area of study, indicating the prevailing wind direction (coming from).

detection (LOD) for each PCDD/F congener was calculated as 3-times the signal to noise ratio.

Metal (As, Be, Cd, Co, Cr, Cu, Mn, Ni, Pb, Sn, Tl and V) concentrations were measured by inductively coupled plasma spectrometry (ICP-MS, Perkin Elmer Elan 6000) after filter digestion. One eighth part of each filter (surface: 50.3 cm<sup>2</sup>) was digested with HNO<sub>3</sub> (65% Suprapur, E. Merck, Darmstadt, Germany) and HF (37.5%, Panreac SA, Castellar del Vallès, Barcelona, Spain) in hermetic teflon bombs. Blank and control samples, as well as reference materials (Soil, Loamy clay, Resource Technology Corporation, Laramie, WY, USA, CRM 052), were used to check the accuracy of the instrumental methods. The recovery percentage of this reference material ranged from 84% to 134% for Pb and As, respectively.

### 2.3. Data analysis

For calculations, when a result was below the LOD, the value was assumed to be half of that limit (ND = 1/2 LOD). Data analysis was carried out by means of the SPSS 15.0 statistical package. The statistical significance was established by applying the Levene test to analyze whether or not the data followed a parametric distribution. Subsequently, an ANOVA test was applied. Toxic equivalents for PCDD/Fs were calculated according to the 2005 WHO-TEF system (Van den Berg i col·ls., 2006).

## 3. Results and discussion

### 3.1. PCDD/Fs

The concentrations of the 2,3,7,8-substituted PCDD/F congeners in air samples collected in S. Adrià de Besòs (SAB-samples) and the background/control site (BK-samples) in 2005 and 2006 are summarized in Table 1. The mean concentrations in the SAB industrial and BK control areas were 0.018 and 0.012 pg WHO-TEQ m<sup>-3</sup>,

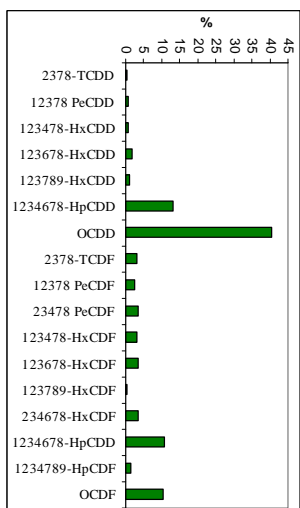
respectively. The highest concentrations corresponded to sample SAB-3.1 (0.024 pg WHO-TEQ m<sup>-3</sup>) in the industrial area, while the lowest levels were found in sample BK-4.4 (0.008 pg WHO-TEQ m<sup>-3</sup>) belonging to the background/control area.

Tetrachlorodibenzo-p-dioxin (TCDD), the most toxic congener of dioxins and furans, was found under its detection limit (<0.002 pg m<sup>-3</sup>) in all samples except SAB-3.4 (0.006 pg m<sup>-3</sup>) and BK-4.4 (0.002 pg m<sup>-3</sup>). This last sample showed a quite different profile, with very low values for all the remaining congeners. The most abundant congeners in all samples were the highest chlorinated: OCDD, whose concentration ranged between 0.027 and 0.706 pg m<sup>-3</sup>, followed by 1,2,3,4,6,7,8-HpCDD (range: 0.014-0.150 pg m<sup>-3</sup>) and OCDF (range: 0.011- 0.108 pg m<sup>-3</sup>). In terms of contribution to total WHO-TEQ, OCDF was the congener showing the lowest contribution to total WHO-TEQ in all samples (< 1%). In contrast, 2,3,4,7,8-PeCDF was the most important contributor in most samples (22-25%), with the exception of BK-4.2 (where 1,2,3,7,8-PeCDD contributed 22%) and SAB-3.4 (where TCDD contributed 31%). Notwithstanding, mean PCDD/F congener profiles of both SAB and BK areas were similar (Fig. 2). The mean profile of four emission samples recently collected in the MSWI stack gas is also shown in Fig. 2. It can be noted that ambient and source profiles were quite different, with respect to the OCDD/HpCDD ratio with OCDD and 1,2,3,4,6,7,8-HpCDD being the most abundant PCDD/F congeners in immission and emission air samples, respectively. Although the different PCDD/F congeners may undergo different reactions and/or deposition processes, by comparing source and ambient samples it seems evident that the MSWI is not primarily responsible for the environmental levels of PCDD/Fs in the area under evaluation.

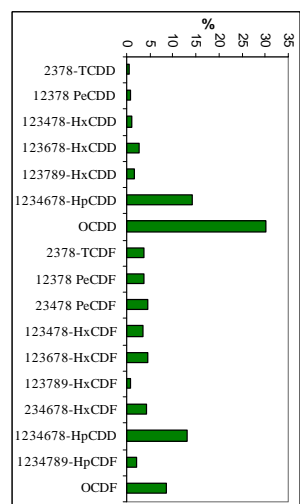
Table 1. PCDD/F concentrations ( $\text{pg m}^{-3}$ ) in active air samples collected near the MSWI of S. Adrià del Besòs in 2005 and 2006.

	SAB- 1.1	SAB- 2.1	SAB- 3.1	SAB- 1.2	SAB- 2.2	SAB- 3.2	SAB- 1.3	SAB- 2.3	SAB- 3.3	SAB- 1.4	SAB- 2.4	SAB- 3.4	BK- 4.1	BK- 4.2	BK- 4.3	BK- 4.4	
<b>2,3,7,8-TCDD</b>	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.006	<LOD	<LOD	<LOD	0.002
<b>1,2,3,7,8 PeCDD</b>	0.004	0.003	0.004	0.004	0.002	0.004	0.002	0.004	0.004	0.002	0.002	0.002	0.002	0.002	0.002	0.003	<LOD
<b>1,2,3,4,7,8-HxCDD</b>	0.004	0.003	0.004	0.003	<LOD	0.003	0.002	0.003	0.002	0.002	0.001	0.001	0.002	0.004	0.003	<LOD	
<b>1,2,3,6,7,8-HxCDD</b>	0.012	0.012	0.012	0.009	0.005	0.008	0.007	0.009	0.01	0.004	0.005	0.004	0.004	0.007	0.011	0.002	
<b>1,2,3,7,8,9-HxCDD</b>	0.009	0.008	0.008	0.006	0.003	0.007	0.005	0.004	0.006	0.002	0.003	0.003	0.002	0.006	0.005	0.001	
<b>1,2,3,4,6,7,8-HpCDD</b>	0.150	0.094	0.093	0.056	0.040	0.055	0.038	0.046	0.045	0.023	0.033	0.026	0.030	0.044	0.042	0.014	
<b>OCDD</b>	0.706	0.235	0.242	0.192	0.106	0.140	0.143	0.092	0.087	0.067	0.070	0.071	0.080	0.084	0.083	0.027	
<b>2,3,7,8-TCDF</b>	0.013	0.015	0.022	0.017	0.010	0.016	0.01	0.016	0.014	0.009	0.008	0.021	0.011	0.006	0.01	0.007	
<b>1,2,3,7,8 PeCDF</b>	0.011	0.013	0.017	0.015	0.005	0.011	0.006	0.010	0.014	0.007	0.009	0.015	0.009	0.006	0.016	0.003	
<b>2,3,4,7,8 PeCDF</b>	0.017	0.015	0.022	0.018	0.007	0.019	0.009	0.018	0.017	0.014	0.010	0.017	0.010	0.006	0.017	0.009	
<b>1,2,3,4,7,8-HxCDF</b>	0.017	0.014	0.020	0.016	0.007	0.015	0.008	0.017	0.017	0.013	0.014	0.007	0.008	0.005	0.015	0.004	
<b>1,2,3,6,7,8-HxCDF</b>	0.020	0.017	0.024	0.018	0.008	0.018	0.008	0.02	0.019	0.013	0.011	0.008	0.011	0.005	0.022	0.004	
<b>1,2,3,7,8,9-HxCDF</b>	0.002	0.002	0.002	0.003	<LOD	<LOD	<LOD	0.003	0.002	<LOD	0.001	<LOD	0.002	<LOD	0.003	<LOD	
<b>2,3,4,6,7,8-HxCDF</b>	0.019	0.015	0.023	0.016	0.007	0.015	0.008	0.018	0.019	0.019	0.013	0.007	0.010	0.007	0.018	0.003	
<b>1,2,3,4,6,7,8-HpCDF</b>	0.064	0.052	0.070	0.05	0.024	0.043	0.031	0.051	0.052	0.051	0.057	0.020	0.023	0.021	0.062	0.013	
<b>1,2,3,4,7,8,9-HpCDF</b>	0.006	0.007	0.008	0.006	<LOD	0.007	<LOD	0.01	0.007	<LOD	0.010	<LOD	0.005	<LOD	0.011	<LOD	
<b>OCDF</b>	0.108	0.066	0.077	0.052	<LOD	0.038	0.039	0.036	0.038	0.036	0.048	0.014	0.022	<LOD	0.035	0.011	
<b>Mean WHO-TEQ</b>	0.022	0.018	0.024	0.020	0.010	0.020	0.011	0.020	0.020	0.014	0.012	0.019	0.011	0.009	0.019	0.008	

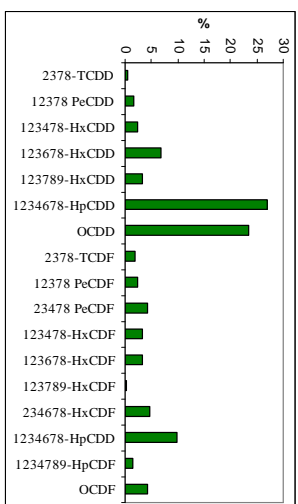
LOD: Limit of detection. SAB: S. Adrià de Besòs (Industrial area); BK: Background/Control area. The first number indicates sampling site (1, 2 and 3 in the SAB area and 4 in the BK zone). The second number refers to the sampling period (1: spring 2005; 2: autumn 2005; 3: spring 2006; 4: autumn 2006). Detection limits: TCDD and 1,2,3,7,8,9-HxCDF:  $0.002 \text{ pg m}^{-3}$ ; 1,2,3,7,8 PeCDD and 1,2,3,4,7,8-HxCDD:  $0.001 \text{ pg m}^{-3}$ ; 1,2,3,4,7,8,9-HpCDF:  $0.003 \text{ pg m}^{-3}$  and OCDF:  $0.020 \text{ pg m}^{-3}$ . WHO-TEQ calculated according to the 2005 WHO-TEF system (Van den Berg et al., 2006).



(a)



(b)



(c)

Fig. 2. PCDD/F congener profiles of air samples collected in (a) S. Adrià de Besòs (SAB), (b) background/control area (BK) and (c) emissions of the MSWI.

In our previous survey (spring 2005), mean PCDD/F concentrations of 27.3 and 10.9 fg WHO-TEQ m<sup>-3</sup> were found at the urban/industrial and the background sites, respectively (Ekino i col·ls., 2007). A detailed study of the temporal trend in each sampling point did not reveal statistically significant seasonal/temporal variations in any of the studied areas. However, the current results are in the lower range of those reported by Abad et al. (2007) in a ten year (period 1994-2004) ambient air monitoring in Catalonia. The range of values presented in that comprehensive study were: 0.013-0.357 pg I-TEQ m<sup>-3</sup> in urban/traffic sites, 0.010-0.138 pg I-TEQ m<sup>-3</sup> in suburban/traffic sites, 0.042-0.406 pg I-TEQ m<sup>-3</sup> in urban/industrial sites, 0.007-1.196 pg I-TEQ m<sup>-3</sup> in suburban/industrial sites, and 0.005-0.045 pg I-TEQ m<sup>-3</sup> in rural/industrial sites, whereas concentrations in background areas were 0.008-0.028 pg I-TEQ m<sup>-3</sup> (Abad i col·ls., 2007). The PCDD/F levels found in air of S. Adrià del Besòs fit well into the less polluted categories (urban/industrial, rural/industrial or even background areas). When compared with worldwide levels, those found in the S. Adrià de Besòs area are also relatively low. In Porto (Portugal), Coutinho et al. (2007) evaluated the effects of a MSWI through an ambient monitoring program whose median PCDD/Fs concentration was 0.130 pg I-TEQ m<sup>-3</sup>. In turn, Shih et al. (2006) reported a mean total PCDD/F concentrations in the outdoor air of 2 Taiwanese MSWIs of 0.0783 pg I-TEQ/Nm<sup>3</sup> (0.0828 pg WHO-TEQ/Nm<sup>3</sup>), ranging from 0.0216 to 0.155 pg I-TEQ/Nm<sup>3</sup>. On the other hand, the PCDD/Fs concentrations in ambient air samples collected near a MSWI in Bucheon, Korea, ranged from 0.22 to 1.16 pg I-TEQ m<sup>-3</sup>, with an average of 0.66 pg I-TEQ m<sup>-3</sup> (Van den Berg i col·ls., 2006), while Tung et al. (2005) reported an annual average (2000/2001) concentration of 0.052 pg I-TEQ m<sup>-3</sup> in Hong-Kong. Recently, ambient levels of PCDD/Fs were analyzed in different areas of Croatia by Krauthacker et al. (2006) and mean values of 0.1656 and 0.0486 pg I-TEQ m<sup>-3</sup> were found at industrial and landfill sites, respectively. In the industrial environment of Houston (TX, USA), the measurements of atmospheric PCDD/F levels over a year showed a mean concentration of 0.016 pg WHO-TEQ m<sup>-3</sup> (Raun i col·ls., 2005).

The ambient levels of PCDD/Fs are also determined by meteorological conditions. Thus, the fact that the current samples were collected in coastal sites and the most prevailing wind directions during the diverse sampling periods (W, NW and SW) blew towards the sea (away from the sampling sites) could contribute to the low levels obtained (Fig. 1.). In relation to the seasonal variation, a number of studies have reported higher concentrations in winter than in summer (Cheng i col·ls., 2003; Raun i col·ls., 2005; Tung i col·ls., 2005; Krauthacker i col·ls., 2006; Van den Berg i col·ls., 2006; Coutinho i col·ls., 2007), or in autumn (Kim i col·ls., 2007). According to Lohmann and Jones (1998), there are some seasonal factors that may affect PCDD/F ambient concentrations: (1) heating combustion sources, (2) mixing layer (temperature dependent), and (3) loss processes through deposition or chemical reactions (temperature dependent). However, as the same authors noted, the industrial and vehicular sources, which may be the most important, are not seasonally conditioned. In the present study, no Pearson correlation was found between the PCDD/F concentrations and the environmental conditions of the two sampling periods considered. The reason could be that both seasons (spring and autumn) were characterized by mild temperatures (mean: 15 °C) and/or because combustion of coal or wood are usually not used as domestic home heating methods in the area under study.

### 3.2. PCBs

The concentrations of the 7 indicator PCBs congeners in air samples collected in S. Adrià de Besòs (SAB-samples) and the background/control site (BK-samples) in 2005 and 2006 are shown in Table 2. Total PCB concentrations ranged from 0.076 to 0.297 ng m<sup>-3</sup> (mean value: 0.159 ng m<sup>-3</sup>) in the SAB area, and from 0.062 to 0.127 ng m<sup>-3</sup> (mean value: 0.095 ng m<sup>-3</sup>) in the BK area. In this study, concentrations were lower than those recently found in different urban and industrial areas of Turkey (Cetin i col·ls., 2007), but similar to those found in urban areas of Rome (Menichini i col·ls., 2007). The lowest chlorinated congener, PCB 28, was the most abundant in all

samples, with mean values of 0.055 and 0.024 ng m<sup>-3</sup> in the SAB and BK areas, respectively. Its average contribution to total PCBs was 32%. On the other hand, the levels of PCBs 118 and 180 were scarce, with concentrations under its detection limit (0.005 ng m<sup>-3</sup>) in certain cases. The highest concentration of PCB 118 was 0.013 ng m<sup>-3</sup>, while that of PCB 180 was 0.012 ng m<sup>-3</sup>. In the two areas, not only total PCB concentrations, but also PCB congener profiles were rather different. In the SAB zone, PCBs 28 and 52 were more abundant than the more chlorinated congeners, whereas in the BK area all PCB congeners showed similar concentrations. Although relatively higher levels of the lowest chlorinated PCBs than those of higher chlorinated congeners have been reported, there is not a homogeneous tendency. On the other hand, similarities of PCB congener levels have also been reported in air of background areas, such as a Mediterranean coastal lagoon (Castro-Jiménez et al., in press). As for PCDD/Fs, no correlation between PCB concentrations and the two different sampling periods considered could be noted.

Table 2. PCB concentrations (ng m<sup>-3</sup>) in active air samples collected near the MSWI of S. Adrià del Besòs in 2005 and 2006.

	SAB- 1.1	SAB- 2.1	SAB- 3.1	SAB- 1.2	SAB- 2.2	SAB- 3.2	SAB- 1.3	SAB- 2.3	SAB- 3.3	SAB- 1.4	SAB- 2.4	SAB- 3.4	BK- 4.1	BK- 4.2	BK- 4.3	BK- 4.4
PCB 28	0.066	0.060	0.056	0.117	0.043	0.036	0.033	0.048	0.023	0.046	0.055	0.076	0.028	0.016	0.014	0.039
PCB 52	0.042	0.036	0.026	0.063	0.020	0.024	0.021	0.038	0.015	0.027	0.038	0.074	0.016	0.012	0.010	0.017
PCB 101	0.024	0.022	0.030	0.028	0.013	0.022	0.015	0.025	0.010	0.017	0.024	0.055	0.022	0.016	0.011	0.019
PCB 118	<LOD	<LOD	0.013	0.012	0.004	0.008	0.005	0.010	0.004	0.004	0.005	0.012	<LOD	0.003	0.003	<LOD
PCB 138	0.013	0.016	0.024	0.014	0.010	0.016	0.010	0.018	0.009	0.006	0.012	0.028	0.025	0.011	0.009	0.015
PCB 153	0.014	0.018	0.024	0.019	0.011	0.018	0.012	0.020	0.010	0.016	0.016	0.040	0.026	0.014	0.011	0.019
PCB 180	<LOD	<LOD	<LOD	0.004	0.003	0.006	0.003	0.006	0.005	0.005	0.005	0.012	<LOD	0.003	0.003	0.006
Sum PCB	0.169	0.162	0.178	0.256	0.105	0.130	0.098	0.167	0.076	0.121	0.155	0.297	0.127	0.074	0.062	0.117

LOD: Limit of detection. SAB: S. Adrià de Besòs (Industrial area); BK: Background/Control area. The first number indicates sampling site (1, 2 and 3 in the SAB area and 4 in the BK zone). The second number refers to the sampling period (1: spring 2005; 2: autumn 2005; 3: spring 2006; 4: autumn 2006). Detection limits: PCB 118: 0.002 ng m<sup>-3</sup>; PCB 180: 0.005 ng m<sup>-3</sup>

In the previous study (spring 2005), the sum of the PCB congeners was higher at the urban/industrial zone (mean:  $170 \text{ pg m}^{-3}$ ) than at the background site ( $127 \text{ pg m}^{-3}$ ) (Ekino i col·ls., 2007). PCB levels fluctuated through the time, and a clear trend was not found. As far as it is known, there is still considerable uncertainty with respect to the relative importance of different industries as sources of PCBs (Breivik et al., 2004). However, a number of other sources, such as leakage from old equipment, building materials, stockpiles and landfill sites, are still generating even a greater concern than combustion and industrial processes (Vallack et al., 1998). Anyhow, studies on PCB profiles of potential emission sources are very scarce. For instance, Biterna and Voutsas (2005) reported that PCB 180 was predominant in particles from traffic emissions, as well as in those from residential heating and refuse burning. Other authors found this congener was also abundant in emissions from open burning (Breivik i col·ls., 2004) and MSWIs (Dyke i col·ls., 2003). However, Kim et al. (2004) found PCB 180 to be representative of Kanechlor in spite of incineration samples. In the same study, PCB 118 was found to be predominant in MSWI emissions (Yeo i col·ls., 2004). Therefore, it is rather difficult to establish relationships between PCB levels and the contribution of potential sources.

### 3.3. *Metals*

Table 3 shows the average concentrations of some trace elements (Mn, Pb, Cu, Sn, Tl, Cd, Be, Co, As, V, Cr and Ni) associated with  $\text{PM}_{10}$  particulate matter in samples from S. Adrià de Besòs (SAB-samples) and background/control sites (BK-samples) collected in 2005 and 2006. Levels are in the same range of those found in other urban areas of Barcelona (Viana i col·ls., 2005) and in other cities (Monaci i col·ls., 2000; Gao i col·ls., 2002; López i col·ls., 2005). In general terms, concentrations in the BK zone were lower than those of the SAB area. Copper showed the highest concentrations, with mean values of  $69.4$  and  $29.8 \text{ ng m}^{-3}$  in the SAB and BK areas, respectively. Copper is characteristic of emissions of automobile traffic, industrial activities and coal-fired power generation (Monaci i col·ls., 2000; Viana i col·ls., 2005;

Wang i col·ls., 2006). Thallium (mean: 0.08 and 0.20 ng m<sup>-3</sup> in the SAB and BK areas, respectively) and Be (mean: 0.04 and 0.03 ng m<sup>-3</sup> in the SAB and BK areas, respectively) showed the lowest concentrations, followed by Co (mean: 0.37 and 0.28 ng m<sup>-3</sup> in the SAB and BK areas, respectively) and Cd (mean: 0.20 and 0.31 ng m<sup>-3</sup> in the SAB and BK areas, respectively). Due to the use of unleaded gasoline, in recent years ambient Pb levels have dramatically decreased worldwide (López i col·ls., 2005). In the present study, Pb mean values were 11.50 and 8.25 ng m<sup>-3</sup> in the SAB and BK areas, respectively, notably lower than the limit established by EU Council Directive 1999/30/EC (0.5 µg m<sup>-3</sup> expressed as annual mean). Chromium levels ranged from 0.09 to 7.77 ng m<sup>-3</sup>. Although Cd, Pb and Cr are characteristic elements of waste incinerator emissions (Gao i col·ls., 2002), the levels found in the SAB area were even comparable with concentrations reported in rural and semirural areas (López i col·ls., 2005). Nickel levels ranged from 1.09 to 11.9 ng m<sup>-3</sup> in the SAB area, and from 1.34 to 2.61 ng m<sup>-3</sup> in the BK area. In turn, the levels of V ranged from 3.65 to 36.75 ng m<sup>-3</sup> in the SAB area, and from 1.95 to 6.40 ng m<sup>-3</sup> in the BK zone, respectively. These two elements are associated with combustion of fuels (Nadal i col·ls., 2004; López i col·ls., 2005). Arsenic levels ranged from 0.14 to 1.31 ng m<sup>-3</sup>. Although this element can be released to the atmosphere from natural sources such as natural erosion, in urban areas the concentrations mainly come from the burning of fuels (especially coal) and waste incineration (Wang i Mulligan, 2006).

Table 3. Concentrations of heavy metals (ng m<sup>-3</sup>) associated with PM<sub>10</sub> particulate matter.

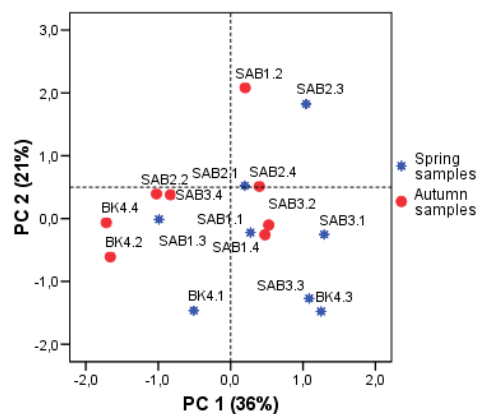
	SAB- 1.1	SAB- 2.1	SAB- 3.1	SAB- 1.2	SAB- 2.2	SAB- 3.2	SAB- 1.3	SAB- 2.3	SAB- 3.3	SAB- 1.4	SAB- 2.4	SAB- 3.4	BK- 4.1	BK- 4.2	BK- 4.3	BK- 4.4
Mn	8.60	13.8	13.8	20.6	30.0	13.1	4.75	-	3.22	5.61	18.9	4.44	18.4	8.30	4.61	2.14
Pb	10.8	12.4	12.2	22.7	12.9	12.1	10.0	6.30	8.84	0.34	12.8	17.2	6.38	10.8	12.3	3.52
Cu	44.2	114.3	62.0	123.9	75.8	57.6	60.1	94.6	23.0	44.4	75.3	57.6	22.8	13.0	15.3	68.0
Sn	1.30	3.10	2.39	7.28	5.93	4.52	5.88	4.83	3.34	1.85	4.82	5.67	1.69	5.29	1.78	1.60
Tl	< LOD	0.06	0.09	0.15	0.06	0.08	0.05	0.10	< LOD	0.02	0.09	0.11	< LOD	0.06	0.48	0.07
Cd	0.12	0.33	0.30	0.49	0.27	0.18	0.31	0.14	0.07	0.04	0.08	0.12	0.28	0.45	0.16	0.34
Be	< LOD	< LOD	< LOD	0.01	0.01	< LOD	0.12	0.02	0.09	0.04	0.04	0.02	< LOD	0.04	0.04	0.02
Co	0.20	0.35	0.27	0.45	0.47	0.36	0.55	0.30	0.41	0.10	0.53	0.49	0.50	0.13	0.29	0.19
As	0.42	0.30	0.18	0.73	0.40	0.38	1.30	0.55	1.31	0.34	0.79	0.91	0.20	0.14	0.40	0.44
V	12.0	13.6	19.4	21.0	10.0	13.8	12.7	36.8	3.65	4.79	16.0	22.4	6.40	2.85	1.95	3.92
Cr	3.20	7.7	6.8	7.22	6.62	4.96	6.41	0.09	1.69	0.16	4.06	5.43	3.60	2.59	1.77	0.89
Ni	3.40	7.40	5.8	9.37	6.50	6.22	4.95	11.9	2.34	1.09	5.49	9.24	-	2.61	1.34	1.79

LOD: Limit of detection. SAB: S. Adrià de Besòs (Industrial area); BK: Background/Control area. The first number indicates sampling site (1, 2 and 3 in the SAB area and 4 in the BK zone). The second number refers to the sampling period (1: spring 2005; 2: autumn 2005; 3: spring 2006; 4: autumn 2006). Detection limits: V: 0.147 ng m<sup>-3</sup>; Ni and Cr: 0.074 ng m<sup>-3</sup>; Mn, As, Co, Sn, Be, Cu: 0.015 ng m<sup>-3</sup>; Pb, Cd i Tl: 0.007 ng m<sup>-3</sup>.

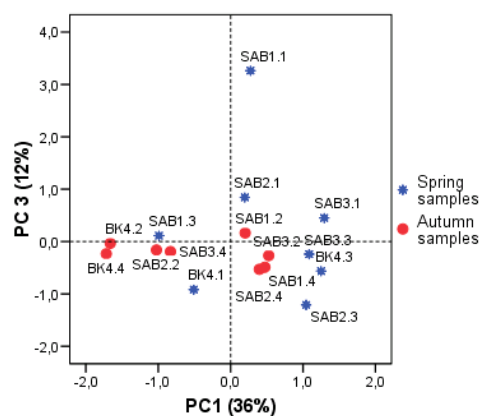
### 3.4. PCA analysis

Although in the current survey the number of samples was relatively low, two Principal Component Analyses (PCAs) were executed to get some information about the relationship among samples, pollutants and sources. The objective of a PCA is to derive a few new components (Principal Components) as a linear combination of the original variables, which provides a description of the data structure with a minimum loss of information. These analyses were here applied with a double objective: a) to compare the samples from S. Adrià de Besòs with those collected outside the direct influence of the MSWI and the power plant (background/control samples), as well as find out correlations between the different pollutants, and b) to identify the main sources affecting the ambient PCDD/F levels around the MSWI.

Firstly, a PCA was performed using the different pollutant concentrations (PCDD/Fs, PCBs and heavy metals) available for each site and sampling period. Those pollutants with concentrations below the detection limit in more than 40% of the samples were removed. The PCA provided a 3-dimensional model with 3 principal components (PC1, PC2 and PC3), explaining 36%, 21% and 12% of the variance, respectively. The scores plots of PC1 vs. PC2, and PC1 vs. PC3 are depicted in Fig. 3a and Fig. 3b, respectively. In turn, Fig. 4a and Fig. 4b show the loading plot of PC1 vs. PC2, and PC1 vs. PC3, respectively. The score plot did not show differences



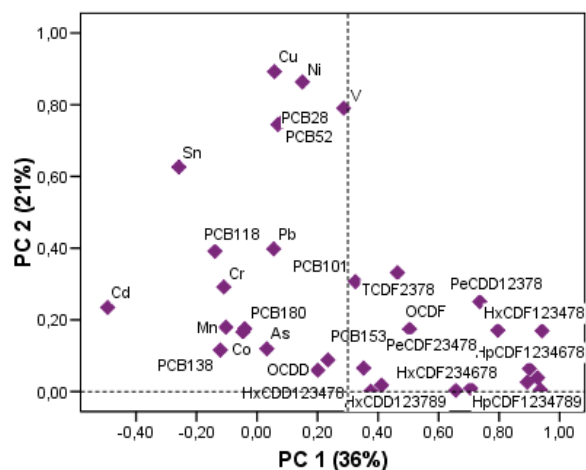
(a)



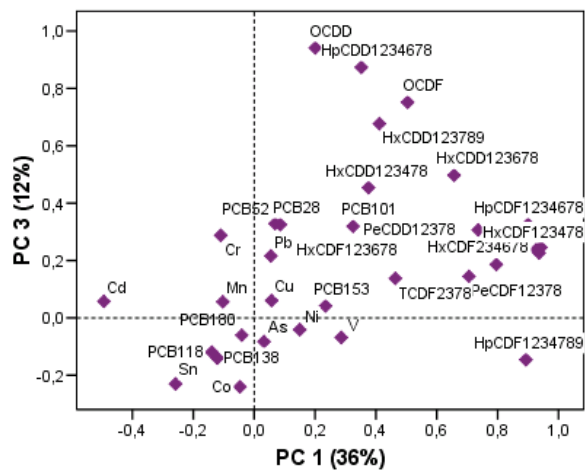
(b)

Fig. 3. Score plot of samples showing (a) PC1 vs. PC2, and (b) PC1 vs. PC3.

SAB: S. Adrià de Besòs (Industrial area); BK: Background/Control area. The first number indicates sampling site (1, 2 and 3 in the SAB area and 4 in the BK zone). The second number refers to the sampling period (1: spring 2005; 2: autumn 2005; 3: spring 2006; 4: autumn 2006).



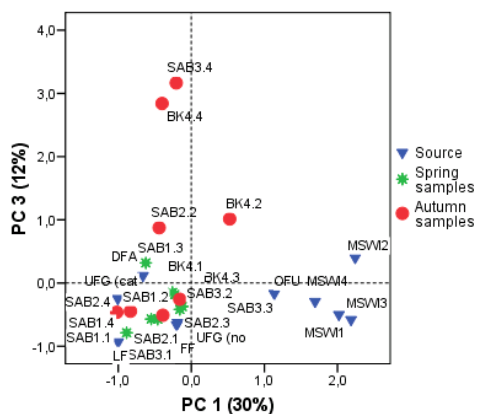
(a)



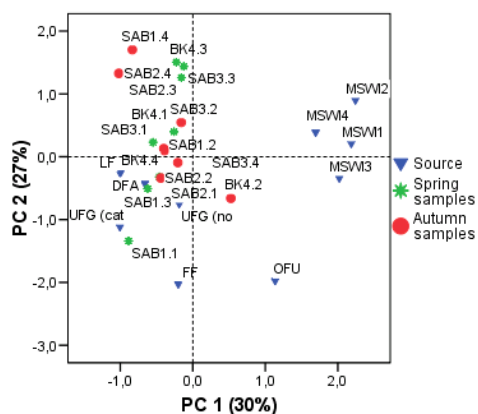
(b)

Fig. 4. Loading plot of samples showing (a) PC1 vs. PC2, and (b) PC1 vs. PC3.

SAB: S. Adrià de Besòs (Industrial area); BK: Background/Control area. The first number indicates sampling site (1,2 and 3 in the SAB area and 4 in the BK zone). The second number refers to the sampling period (1: spring 2005; 2: autumn 2005; 3: spring 2006; 4: autumn 2006).



(a)



(b)

Fig. 5. Score plot of ambient samples and source profiles showing (a) PC1 vs. PC2 and (b) PC1 vs. PC3.

DFA: Diesel fuelled Automobile; UGF (no): Unleaded Gasoline-Fuelled-without catalytic converters; UGF (cat): Unleaded Gasoline-Fuelled-with catalytic converters; MSWI: Municipal Solid Waste Incinerator; OFU: Oil Fired Utility; FF: Forest Fires; LF: Landfill Flares. SAB: S. Adrià de Besòs (Industrial area); BK: Background/Control area. The first number indicates sampling site (1, 2 and 3 in the SAB area and 4 in the BK zone). The second number refers to the sampling period (1: spring 2005; 2: autumn 2005; 3: spring 2006; 4: autumn 2006).

between areas and periods, and all samples formed a single cluster. This indicates that the industrial sources in the SAB area do not affect significantly the profiles of those pollutants. Therefore, the diffuse sources, which also affect the BK area, seem to have a great influence over total concentrations. The loading plots resulting of the PCA allow establishing the correlation between each PC and the different pollutants. Chemicals associated to the same PC, and then clustered together, are likely to have a similar environmental behavior and/or to come from the same emission source. In the loading plot, PC1 showed a positive correlation with the most-substituted PCDFs (excepting OCDF), whereas PC2 did it with Cu, Ni, V, CB-28 and CB-52, and finally, PC 3 with the highest chlorinated congeners OCDD, 1,2,3,4,6,7,8-HpCDD and OCDF. The strong correlation between PC2 and several metals (Cu, Ni and V) as well as the lowest chlorinated PCB congeners would indicate that the emission sources for those pollutants would be the same. In fact, Ni and V have been pointed out as markers of anthropogenic emission sources, such as burning of fuel oil or coal (Yatkin and Bayram, 2008).

PCDD/Fs source emission profiles have been widely studied and are available as emission factors (EF) (USEPA, 2005). Therefore, a second PCA was performed to determine the most influential PCDD/Fs sources by characterizing the air samples in a set of fingerprints. For this, the emission factors (EF) of the potential sources were included in a PCA analysis in order to find similarities with the ambient samples. For each air sample and EF, a score was assigned in each component, thus allowing a further analysis and plotting of summarized data. Each PCDD/F source is characterized by its own congener profile. According to the definition given by the US EPA (USEPA, 2007), an emission factor is a representative value that attempts to relate the quantity of a pollutant released to the atmosphere with an activity associated with the release of that pollutant. Such factors facilitate the estimation of emissions from various sources of air pollution. In most cases, these factors are simply averages of all available data of acceptable quality, and are generally assumed to be representative of long-term averages for all facilities in the source category. However, the particular profile of

certain sources may change depending on diverse operational parameters, such as the waste composition and the conditions of the combustion causing the emission. Moreover, as it has been previously mentioned, the concentrations at sampling sites are strongly dependent on the meteorological conditions. The emission factors considered for the PCA analysis were: (1) different kinds of vehicle emissions: Diesel fuelled Automobile (DFA), Unleaded Gasoline-Fuelled-without catalytic converters (UGF (no)), and Unleaded Gasoline-Fuelled-with catalytic converters (UGF (cat)); (2) Oil Fired Utility (OFU) representing the adjacent power plant; (3) Forest Fires (FF), and (4) Landfill Flares (LF). The MSWI was represented by 4 emission samples obtained in the facility stack.

In this case, PCs 1, 2, and 3 were responsible for 30%, 27%, and 12 % of the variance, respectively. Figures 5a and 5b represent the scores plot of PC1 vs. PC2, and PC1 vs. PC3. No difference was observed between BK and the SAB samples, all being grouped in a same cluster. These results indicate that the PCDD/Fs patterns of ambient samples were similar, and therefore, influenced by the same sources in both areas and periods. The four MSWI profiles appeared apart from the samples (with a high PC1), indicating a low contribution to ambient PCDD/F concentrations. On the other hand, vehicles, the unleaded fuelled gasoline with and without catalytic converters, as well as the diesel fuelled, were associated with the field samples indicating its influence on the ambient patterns. In Spain, the car density is approximately 456 per 1,000 population (ACEA, 2007), being characterized by a high diesel penetration. According to data from the Spanish DGT (Dirección General de Tráfico), in 2004 the registration of diesel vehicles surpassed those of petrol-engine vehicles (66% vs. 34%) (DGT, 2004). PCDD/Fs from light-duty diesel vehicles are approximately twice those from catalyzed cars run on unleaded gasoline (Turrio-Baldassarri i col·ls., 2005). Although there is no landfill near the area here evaluated, landfill fires, probably caused by the uncontrolled combustion of agriculture/domestic wastes, seem also influence the total ambient patterns. It must be taken into account that the power plant may actually work with either natural gas or fuel oil. However,

because no emission factors for natural gas were found in the literature, oil fired utility profiles were included in the PCA analysis. It seems that the results of PCDD/Fs in ambient samples were not affected by the oil-fired utility and forest fires. Anyhow, light fuel oil and natural gas are always fired in specially designed burners. It is rather unlikely they generate large amounts of PCDD/F, as both are very high-calorific, clean-burning fuels leaving little ash. Increased gas use for power generation (as a replacement fuel for coal and oil) results in reductions of PCDD/F from the generation sector (UNECE, 1998). In the present survey, PC1 was highly correlated with penta-, hexa-, and heptadioxins while PC2 did with penta-, hexa-, and heptafurans. PC3 was correlated with TCDD and 1,2,3,4,7,8,9-HpCDF.

In conclusion, the results of the current study suggest that the MSWI of S. Adrià de Besòs is not a strong emission source of PCDD/Fs, PCBs and heavy metals and does not contribute significantly to the air pollution in its immediate surrounding. No significant temporal, seasonal and spatial variations have been observed. Moreover, a notable difference of the PCDD/F congener profiles has been found between ambient air and emission gas, indicating that the current levels of PCDD/Fs are more related to other potential sources (e.g., traffic) rather than to emissions from the MSWI.

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### **References**

- Abad, E., Martinez, K., Gustems, L., Gomez, R., Guinart, X., Hernandez, I., Rivera, J., 2007. Ten years measuring PCDDs/PCDFs in ambient air in Catalonia (Spain). *Chemosphere* 67, 1709-1714.

- Allen, A.G., Nemitz, E., Shi, J.P., Harrison, R., Greenwood JC 2001. Size distributions of trace metals in atmospheric aerosols in the United Kingdom. *Atmos. Environ.* 35, 4581-4591.
- Biterna, M., Voutsas, D., 2005. Polychlorinated biphenyls in ambient air of NW Greece and in particulate emissions. *Environ. Int.* 31, 671-677.
- Breivik, K., Sweetman, A., Pacyna, J.M., Jones, K.C., 2002. Towards a global historical emission inventory for selected PCB congeners - a mass balance approach- 2. Emissions. *Sci. Total Environ.* 290, 199-224.
- Breivik, K., Alcock, R., Li, Y.F., Bailey, R.E., Fiedler, H., Pacyna, J.M., 2004. Primary sources of selected POPs: regional and global scale emission inventories. *Environ. Pollut.* 128, 3-16.
- Castro-Jiménez, J., Deviller, G., Ghiani, M., Loos, R., Mariani, G., Skejo, H., Umlauf, G., Wollgast, J., Laugier, T., Héas-Moisan, K., Léauté, F., Munsch, C., Tixier, C., Tronczyński, J., in press. PCDD/F and PCB multi-media ambient concentrations, congener patterns and occurrence in a Mediterranean coastal lagoon (Etang de Thau, France). *Environ. Pollut.*
- Cetin, B., Yatkin, S., Bayram, A., Odabasi, M., 2007. Ambient concentrations and source apportionment of PCBs and trace elements around an industrial area in Izmir, Turkey. *Chemosphere* 69, 1267-1277.
- Cheng, P., Hsu, M., Ma, E., Chou, U., Ling, Y., 2003. Levels of PCDD/Fs in ambient air and soil in the vicinity of a municipal solid waste incinerator in Hsinchu. *Chemosphere* 52, 1389-1396.
- Coutinho, M., Pereira, M., Borrego, C., 2007. Monitoring of ambient air PCDD/F levels in Portugal. *Chemosphere* 67, 1715-1721.
- DGT, 2004. Anuario estadístico 2004 'Evolución de la matriculación según carburante'. Ministerio del Interior, Gobierno de España [in Spanish].
- Domingo, J.L., 2002. Human health risks of dioxins for populations living near modern municipal solid waste incinerators. *Rev. Environ. Health* 17, 135-147.
- Dyke, P.H., Foan, C., Fiedler, H., 2003. PCB and PAH releases from power stations and waste incineration processes in the UK. *Chemosphere* 50, 469-480.

- Gao, Y., Nelson, E.D., Field, M.P., Ding, Q., Li, H., Sherrell, R.M., Gigliotti, C.L., Van, R., D.A., Glenn, T.R., Eisenreich, S.J., 2002. Characterization of atmospheric trace elements on PM<sub>2.5</sub> particulate matter over the New York-New Jersey harbor estuary. *Atmos. Environ.* 36, 1077-1086.
- IARC, 1997. Monographs on the Evaluation of Carcinogenic Risk to Humans. Polychlorinated Dibenzo-para-Dioxins and Polychlorinated Dibenzofurans, vol. 69. Iarc Press, Lyon, France.
- Kao, W., Ma, H., Wang, L., Chang-Chien, G., 2007. Site-specific health risk assessment of dioxins and furans in an industrial region with numerous emission sources. *J. Hazard. Mater.* 145, 471-481.
- Ke, Q., Costa, M., Kazantzis, G., Gunnar, F.N., Bruce, A.F., Monica, N., Lars, T.F., 2007. Carcinogenicity of Metal Compounds, Handbook on the Toxicology of Metals (Third Edition). Academic Press, Burlington, pp. 177-196.
- Kim, D., Min, Y., Jeong, J., Kim, G., Kim, J., Son, C., Lee, D., 2007. Ambient air monitoring of PCDD/Fs and co-PCBs in Gyeonggi-do, Korea. *Chemosphere* 67, 1722-1727.
- Kim, K.S., Hirai, Y., Kato, M., Urano, K., Masunaga, S., 2004. Detailed PCB congener patterns in incinerator flue gas and commercial PCB formulations (Kanechlor). *Chemosphere* 55, 539-553.
- Krauthacker, B., Herceg Romanic, S., Wilken, M., Milanovic, Z., 2006. PCDD/Fs in ambient air collected in Zagreb, Croatia. *Chemosphere* 62, 1829-1837.
- Llobet, J.M., Martí-Cid, R., Castell, V., Domingo, J.L. Significant decreasing trend in human dietary exposure to PCDD/PCDFs and PCBs in Catalonia, Spain. *Toxicol. Lett.* 178, 117-126.
- Lohmann, R., Jones, K.C., 1998. Dioxins and furans in air and deposition: A review of levels, behaviour and processes. *Sci. Total Environ.* 219, 53-81.
- López, J.M., Callén, M.S., Murillo, R., García, T., Navarro, M.V., de la Cruz, M.T., Mastra, A.M., 2005. Levels of selected metals in ambient air PM<sub>10</sub> in an urban site of Zaragoza (Spain). *Environ. Res.* 99, 58-67.

- Mari, M., Schuhmacher, M., Feliubadalo, J., Domingo, J.L., 2008. Air concentrations of PCDD/Fs, PCBs and PCNs using active and passive air samplers. *Chemosphere* 70, 1637-1643.
- Menichini, E., Iacovella, N., Monfredini, F., Turrio-Baldassarri, L., 2007. Atmospheric pollution by PAHs, PCDD/Fs and PCBs simultaneously collected at a regional background site in central Italy and at an urban site in Rome. *Chemosphere* 69, 422-434.
- Monaci, F., Moni, F., Lanciotti, E., Grechi, D., Bargagli, R., 2000. Biomonitoring of airborne metals in urban environments: new tracers of vehicle emission, in place of lead. *Environ. Pollut.* 107, 321-327.
- Nadal, M., Schuhmacher, M., Domingo, J.L., 2004a. Metal pollution of soils and vegetation in an area with petrochemical industry. *Sci. Total Environ.* 321, 59-69.
- Nadal, M., Schuhmacher, M., Domingo, J.L., 2004b. Probabilistic human health risk of PCDD/F exposure: a socioeconomic assessment. *J. Environ. Monit.* 6, 926-931.
- Oh, J., Choi, S., Lee, S., Chang, Y., 2006. Influence of a municipal solid waste incinerator on ambient air and soil PCDD/Fs levels. *Chemosphere* 64, 579-587.
- Raun, L.H., Correa, O., Rifai, H., Suarez, M., Koenig, L., 2005. Statistical investigation of polychlorinated dibenzo-p-dioxins and dibenzofurans in the ambient air of Houston, Texas. *Chemosphere* 60, 973-989.
- Schuhmacher, M., Domingo, J.L., 2006. Long-term study of environmental levels of dioxins and furans in the vicinity of a municipal solid waste incinerator. *Environ. Int.* 32, 397-404.
- Tung, J.W.T., Yu, J.Z., Lau, A.K.H., Louie, P.K.K., 2005. Abundance and sources of ambient dioxins in Hong Kong: A review of dioxin measurements from 1997 to 2001. *Chemosphere* 59, 1387-1398.
- Turrio-Baldassarri, L., Abate, V., Iacovella, N., Monfredini, F., Menichini, E., 2005. Occurrence of PCDD/Fs in urban air before and after the ban of leaded gasoline. *Chemosphere* 59, 1517-1524.

- UNECE, 1998. Protocol to the 1979 Convention on Long-Range Transboundary Air Pollution on Persistent Organic Pollutants. New York and Geneva. Available at: [www.unece.org/env/lrtap/full%20text/1998.POPs.e.pdf](http://www.unece.org/env/lrtap/full%20text/1998.POPs.e.pdf) .
- USEPA, 2005. The inventory of sources and environmental releases of dioxin-like compounds in the United States: the year 2000 update. Draft. EPA/600/P-03/002A. National Center for Environmental Assessment, US Environmental Protection Agency. Washington, DC. Available at: <http://www.epa.gov/ncea/pdfs/dioxin/2k-update/>.
- USEPA, 2007. Basic Emissions Factors Information. Available at: <http://www.epa.gov/ttn/chief/efpac/abefpac.html>.
- Vallack, H.W., Bakker, D.J., Brandt, I., Brostrom-Lunden, E., Brouwer, A., Bull, K.R., Gough, C., Guardans, R., Holoubek, I., Jansson, B., Koch, R., Kuylenstierna, J., Lecloux, A., Mackay, D., McCutcheon, P., Mocarelli, P., Taalman, R.D.F., 1998. Controlling persistent organic pollutants-what next? Environ. Toxicol. Pharmacol. 6, 143-175.
- Van den Berg, M., Birnbaum, L.S., Denison, M., De Vito, M., Farland, W., Feeley, M., Fiedler, H., Hakansson, H., Hanberg, A., Haws, L., Rose, M., Safe, S., Schrenk, D., Tohyama, C., Tritscher, A., Tuomisto, J., Tysklind, M., Walker, N., Peterson, R.E., 2006. The 2005 World Health Organization reevaluation of human and Mammalian toxic equivalency factors for dioxins and dioxin-like compounds. Toxicol. Sci. 93, 223-241.
- VDI, 2003. Emission measurement - Determination of polychlorinated dibenzo-p-dioxins (PCDDs) and dibenzofurans (PCDFs) - Dilution method; Example of application of DIN EN 1948 for the concentration range 0,1 ng I-TEQ/m<sup>3</sup> and supplement to DIN EN 194. Verein Deutscher Ingenieure (VDI). Düsseldorf, Germany.
- Viana, M., Pérez, C., Querol, X., Alastueya, A., Nickovic, S., Baldasano, J.M., 2005. Spatial and temporal variability of PM levels and composition in a complex summer atmospheric scenario in Barcelona (NE Spain). Atmos. Environ. 39, 5343-5361.

- Wang, J., Wang, M., Wu, E., Chang-Chien, G., Lai, Y., 2008. Approaches adopted to assess environmental impacts of PCDD/F emissions from a municipal solid waste incinerator. *J. Hazard. Mater.* 152, 968-975.
- Wang, S., Mulligan, C.N., 2006. Occurrence of arsenic contamination in Canada: Sources, behavior and distribution. *Sci. Total Environ.* 366, 701-721.
- Wang, X., Sato, T., Xing, B., 2006. Size distribution and anthropogenic sources apportionment of airborne trace metals in Kanazawa, Japan. *Chemosphere* 65, 2440-2448.
- Yatkin, S., Bayram, A., 2008. Determination of major natural and anthropogenic source profiles for particulate matter and trace elements in Izmir, Turkey. *Chemosphere* 71, 685-696.

## Discussió conjunta dels articles del Capítol III

### *Nivells de PCDD/Fs, PCBs i PCNs en aire*

Les concentracions de PCDD/Fs, PCBs i PCNs determinades en les mostres d'aire de la zona industrial del Besòs (Barcelona) (on es situen una incineradora i una central tèrmica) van ser superiors a les trobades en la zona control. Tot i això, en termes generals les concentracions trobades van ser més baixes del que en principi es podria esperar en una zona industrial. Els nivells serien un reflexe de la disminució dels nivells d'aquests compostos a nivell mundial causat per la millora en els sistemes de neteja en incineradores i d'altres millores ambientals (Schuhmacher i col·ls., 2002b; Yeo i col·ls., 2004). A més, les baixes concentracions trobades podrien ser resultat de la proximitat al mar dels punts de mostreig, ja que les masses d'aire marí net poden produir un efecte de dilució (Gao i col·ls., 2002; Gambaro i col·ls., 2004) i pel fet que les direccions predominants a la zona fossin (Oest, Nord-Oest, i swd-Oest) en direcció cap al mar.

### *Fluxe ( $m^3/dia$ ) a través dels captadors passius*

Quan pel seu càlcul només es va tenir en compte la fase gasosa de cada congènere es van obtenir un fluxes alts pels PCDD/Fs més substituïts. En canvi, quan es va considerar la concentració total (gas + particulada) es van obtenir un fluxes de 0.4-5.1  $m^3/dia$ . En general, els fluxes calculats van ser més reproduïbles pels congèneres més volàtils. Per PCDD/Fs es va concloure que el més apropiat seria utilitzar un fluxe de 2  $m^3/dia$ . Per PCBs es va obtenir un fluxe mitjà de 3.8  $m^3/dia$ , valor similar al que han determinat altres autors en condicions indoor (Shoeib i Harner, 2002). Pels PCNs el fluxe obtingut va ser 3.3  $m^3/dia$ .

### *Variació temporal dels nivells de PCDD/Fs, PCBs i metalls pesants*

Les concentracions mitjanes de PCDD/Fs el 2005 i 2006 a la zona industrial del Besòs i a la zona control van ser 0.018 i 0.012 pg OMS-TEQ/m<sup>3</sup>, respectivament. La mitjana dels perfils d'immissió de PCDD/Fs de les dues àrees van ser similars entre ells, i a la vegada diferents al perfil d'emissió de la planta incineradora del Besòs. No es van trobar diferències estadísticament significatives quan es van estudiar les variacions temporals/estacionals. Els resultats trobats estan a la part baixa del rang trobat en altres àrees de Catalunya (Abad i col·ls., 2007).

Les concentracions de PCBs van anar de 0.076 a 0.297 ng/m<sup>3</sup> (valor mitjà: 0.159 ng/m<sup>3</sup>) a la zona industrial del Besòs i de 0.062 a 0.127 ng/m<sup>3</sup> (valor mitjà: 0.095 ng/m<sup>3</sup>) a la zona control. Els tant les concentracions com els perfils dels congèneres de PCBs corresponents a les dues àrees estudiades van ser força diferents. Tampoc es va trobar correlació entre els diferents períodes estudiats.

Els nivells de metalls pesants en aire van ser similars als trobats en altres àrees de Barcelona (Viana i col·ls., 2005) i d'altres ciutats (Monaci i col·ls., 2000; Gao i col·ls., 2002; López i col·ls., 2005). En termes generals, els nivells de metalls a la zona industrial del Besòs van ser superiors als trobats a la zona control. El coure va mostrar les concentracions més elevades. Per altra banda, el tal·li, el beri-li i el cadmi van presentar els nivells més baixos. La concentració de plom va ser notablement inferior a l'establerta per la directiva europea.

## Capítol IV

### Monitorització biològica

Article 5:

Mari M, Borrajo MA, Schuhmacher M, Domingo JL

Monitoring PCDD/Fs and other organic substances in workers of a hazardous waste incinerator: A case study

Chemosphere 67: 574-581 (2007)



## **Article 5: “Monitoring PCDD/Fs and other organic substances in workers of a hazardous waste incinerator: A case study”**

### **Abstract**

The aim of this study was to measure, 6 years after regular operations, the concentrations of a number of organic substances in blood and urine of 19 workers employed at a hazardous waste incinerator (HWI) in Spain, and to establish the temporal variation with respect to baseline data and previously performed surveys. This facility was the first, and so far the only HWI in that country. The levels of hexachlorobenzene (HCB), polychlorinated biphenyls (PCB 28, 52, 101, 138, 153 and 180) and polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs) were analyzed in 6 composite plasma samples, while concentrations of di-, tri, and pentachlorophenols, as well those of 1-hydroxypyrene were measured in the urine of these workers. The current mean PCDD/F concentration, 10.4 ng I-TEQ/kg lipid, was significantly lower than that found in the baseline survey, 26.7 ng I-TEQ/kg lipid and similar to that found in the previous (2004) study (7.7 ng I-TEQ/kg lipid). PCDD/F levels in plasma were similar or even lower than those recently reported for various non-exposed populations. For the remaining analyzed substances in plasma and urine, there was not any significant increase in comparison with the levels found in the baseline survey. On the other hand, no marked differences between the concentrations of organic substances in plasma or urine were found according to the respective workplace (plant, laboratory and administration). The results of the present survey indicate that after 6 years of regular operation, the workers at the HWI are not occupationally exposed to PCDD/Fs and other organic substances in their workplaces.

**Keywords:** Hazardous waste incinerator; Biomonitoring; Workers; PCDD/Fs; Organic substances

## 1. Introduction

It is well established that among the potential methods and systems of waste management incineration is an effective way of treating municipal solid waste (MSW), hazardous waste (HW) and medical waste (MW). In comparison with other treatments for processing MSW, HW and MW, incineration has multiple advantages such as volume reduction, energy recovery, elimination of pathogen agents, and chemical-toxicity destruction, which is of particular interest for HW (Oppelt, 1990; Dempsey, 1993). However, waste management facilities in general and incinerators in particular, have been traditionally affected by the syndrome known as NIMBY (Not In My Back Yard) (Kuhn and Ballard, 1998). Thus, in many countries the potential health risks associated with stack emissions, specially those of polychlorinated dibenzo-p-dioxins (PCDDs) and dibenzofurans (PCDFs), have become a cause of great controversy and concern (Domingo, 2002a,b; Lothgren and van Bavel, 2005; Oh et al., 2006). However, although PCDD/Fs, especially the 2,3,7,8-substituted congeners, are probably the most hazardous pollutants released by incinerators, an important number of other different activities are also known sources of PCDD/F emissions (Alcok and Jones, 1996; Fiedler, 1996; Anderson and Fisher, 2002; Meneses et al., 2004; Quass et al., 2004), exceeding some of them (i.e., traffic emissions) those from incinerators (Fuster et al., 2001).

With respect to HW, incineration is often chosen as an ultimate disposal method for this kind of waste that can not be recycled, reduced, or safely deposited in secured landfill sites. Incineration of HW is a thermal oxidation process in which it is converted into gases and incombustible solid residues. In 1996, the construction of a HW incinerator (HWI) was initiated in Constantí (Tarragona County, Catalonia, Spain). Regular operations started in 1999. This facility was the first, and up until now the only HWI in Spain. Therefore, the interest and concern on its potential environmental impact and human health risks have been considerable. In response to it, a wide preoperational monitoring program was designed to assess the potential impact of

PCDD/F emissions from the new HWI on the neighborhood, as well as to establish the health risks on the population living near the facility (Schuhmacher et al., 1997,1998,1999a,b,c). This program also included the assessment of internal exposure of workers to a number of organic substances such as PCDD/Fs and polychlorinated biphenyls (PCBs). Baseline levels of these substances were determined in the future workers of the HWI during the period of construction of the facility (Domingo et al., 2001).

In occupational medicine, biological monitoring is an important tool to assess the levels of exposure to potentially harmful substances taken up from the occupational environment (Angerer et al., 1992; Hardt and Angerer, 2003; Bolt and Their, 2006). It is also useful to evaluate temporal changes in individuals environmentally or occupationally exposed to a defined contaminant. Since the baseline data were obtained (Domingo et al., 2001), we have annually measured in the workers of the HWI the concentrations of the organic substances that were also determined in the baseline survey (Schuhmacher et al., 2002; Agramunt et al., 2003,2004). The aim of the present study was to determine, after approximately 6 years of regular operations in the HWI, the concentrations in blood and urine of the organic substances and to establish which is the temporal variation of these compounds in relation to the baseline survey (Domingo et al., 2001) and the previous monitoring studies (Schuhmacher et al., 2002; Agramunt et al., 2003,2004).

## **2. Subjects and methods**

### *2.1. Subjects*

Nineteen workers (15 men and 4 women) participated voluntarily in this study. As in the previous surveys, individuals were divided into three groups according to their respective workplace and task in the facility. Group I (plant workers) included 12 subjects aged from 30 to 40 years, whose occupations were incinerator operators, boiler maintenance, furnace maintenance, control panel, and waste-gas-washing

operators; Group 2 (laboratory workers) included 5 individuals aged from 27 to 41 years with analytical jobs, and Group 3 (administration workers) included 2 subjects (28 and 31 years) with administrative tasks.

Blood samples were drawn from each individual into thoroughly cleaned glass bottles. Approximately 50 ml were centrifuged for getting plasma. Urine samples were also collected and centrifuged. To determine the concentrations of organic substances in plasma (hexachlorobenzene (HCB), PCDD/Fs, PCBs 28, 52, 101, 138, 153, and 180) and urine (2,4- and 2,5-dichloropehnol, 2,4,5- and 2,4,6-trichlorophenol, pentachlorophenol and 1-hydroxypyrene), as in the previous surveys (excepting the baseline survey) we pooled the 19 individual samples into 6 composite samples (approximately 80 ml per sample for plasma and 60 ml for urine) corresponding to plant (four samples), laboratory (one sample) and administration (one sample). Samples were mixed by equal volume per subject. The criteria used for pooling was previously reported (Schuhmacher et al., 2002). Information about each participant concerning health status and lifestyle, potential environmental exposure sources, dietary habits, as well as drinking and smoking habits were obtained using a specific questionnaire.

## 2.2 Analytical methods

The analytical determination of PCDD/Fs, PCBs and HCB in plasma was performed in accordance with the US ESPA method 1625. Samples were homogenized and subsequently extracted (liquid/liquid extraction). After evaporation of the solvent, the amount of lipid was determined and spiked with a mixture of  $^{13}\text{C}_{12}$ -PCDD/PCDF standards and a set of  $^{13}\text{C}_{12}$ -PCB and  $^{13}\text{C}_6$ -hexachlorobenzene. The clean-up procedure and fractionation of the crude extract was carried out by adsorption chromatography as a multi-step clean-up using silica and alumina columns. The final step was reduction of the PCDD/PCDF-containing fraction to the analytically needed volume. The cleaned extract was analyzed by HRGC/HRMS using an Agilent HP 6890

GC coupled to a VG Autospec Ultima HRMS (with selected ion recording at resolution 10 000). The analysis of the PCDD/F congeners took place using a non polar column of a DB5-type. The quantification was carried out using internal standards. As an indication of the uncertainty of the analysis, the relative standard deviation (RSD) of the control sample was used. The RSD of the control sample is less than 10 %. In addition to the quantification of the PCDD/F congeners, the toxic equivalents (TEQ) of the analysed PCDD/F were calculated according to the international NATO/CCMS system.

For the analysis of chlorophenols in urine, the samples were spiked with <sup>13</sup>C-marked chlorophenols. This was followed by an acid hydrolysis and an extraction with dichloromethane. The concentrated extract was analyzed by HRGC/HRMS using an Agilent HP 6890 GC coupled to a VG Autospec Ultima HRMS (with selected ion recording at resolution 10 000). The analysis of the chlorophenols took place on a non-polar column of a DB1-type. The quantification was carried out using the <sup>13</sup>C-marked internal standards. On the other hand, the analysis of 1-hydroxypyrene (1-HP) was performed after enzymatic hydrolysis to release the conjugated part of the 1-HP. To determine the conjugated and free 1-HP, the extract of the hydrolyzed urine was cleaned using a C18-SPE cartridge and the analyte was eluted with methanol. After concentration, the extract was analyzed by HPLC/Fluorescence using a Waters 600E-HPLC together with a Waters 774 fluorescence detector and a Microsphere RP18 EC reverse phase column.

### 2.3. Statistical analysis

The Leven test was used to compare the homeogeneity of the variances. Significance of the data was computed by the Kruskal-Wallis and the Mann-Whitney U-test. The statistical software SPSS version 12.0 was used for the analyses. A probability of 0.05 or less was considered as significant.

### 3. Results

Table 1 shows the current concentrations of HCB, PCBs and PCDD/Fs in plasma of the workers of the HWI. Mean and median levels, standard deviations and the minimum and maximum values are given. A comparison of the current mean concentrations of these organohalogenated compounds with those obtained since 1999 are shown in Table 2. The ratios between the results from the baseline survey (1999) and those of the present study, as well as between the previous (2004) and the present surveys, are also shown. It can be seen that although the concentrations of HCB decreased notably since the baseline survey (ratio 1999/2005: 2.1), the difference did not reach the level of statistical significance. The current HCB concentration was statistically similar to that of the previous (2004) survey (ratio: 0.9). With respect to PCBs, the current concentrations were significantly lower than the baseline levels for the congeners 28, 101, 138 and 153, while were apparently lower (but not significantly different) for the congeners 52 and 180. There were some variations between the concentrations of PCBs found in 2004 and 2005. Thus, while the current levels of PCB-28 and PCB-153 were significantly higher, those of PCB-138 were significantly lower. A detailed observation of the PCB levels obtained in the studies carried out between 1999 (baseline) and 2005 (current) show an important number of fluctuations, with increases or decreases depending on the year and the specific PCB congener. However, in comparison with the baseline concentrations a general tendency to the reduction of PCB concentrations in plasma seems to be evident.

The current mean PCDD/F concentration, 10.4 ng I-TEQ/kg lipid, was significantly lower than that found in the baseline survey, 26.7 ng I-TEQ/kg lipid. However, it was statistically similar to the concentration found in the previous study (7.7 ng I-TEQ/kg lipid), as well as to the levels detected since the 2000 survey.

Table 1. Concentrations of organohalogenated compounds in plasma of workers at a HWI. Data concerning to the 2005 survey.

	Mean	Median	Standard deviation	Minimum	Maximum
HCB	71.0	57.0	43.4	39.0	150.0
2,4,4'-Tri-PCB28	2.4	1.6	1.5	1.4	4.9
2,2',5,5'-Tetra-PCB52	0.8	0.3	0.9	0.2	2.2
2,2',4,5,5'-Penta-PCB101	1.5	0.9	1.1	0.8	3.3
2,2',3,4,4',5'-Hexa-PCB138	48.0	46.5	14.6	29	71
2,2',4,4',5,5'-Hexa-PCB153	110.8	105.0	34.4	65	170
2,2',3,4,4',5,5'-Hepta-PCB180	114.8	110.0	33.8	71	170
PCDD/Fs	10.4	8.3	6.1	6.3	22.5

Results are given in µg/kg lipid, excepting those of PCDD/Fs which are expressed in ng I-TEQ/kg de lipid.

Notwithstanding, the mean PCDD/F concentration in the 2000 survey was, in absolute value, remarkably higher than the current one (16.9 vs. 10.4 ng I-TEQ/kg lipid). The fact that the difference between these concentrations was not statistically significant ( $P > 0.05$ ) is probably due to the reduced number of composite samples (six) analyzed in both studies, in contrast to the comparatively higher number of samples analyzed in the baseline survey (28 individual samples). Thus, in the current study a very remarkable difference between the minimum and maximum PCDD/F concentrations, 6.3 and 22.5 ng I-TEQ/kg lipid, respectively, was noted (Table 1). It might explain the lack of significant differences among the annual studies performed between 2000 and 2005. With regard to the distribution of PCDD/F congeners, in the baseline survey OCDD, followed by 1,2,3,4,6,7,8-HpCDD and 1,2,3,6,7,8-HxCDD, were the PCDD congeners showing the highest contribution to TEQ, tendency that was maintained in all the remaining studies including the present one (data not shown). In contrast, PCDF congeners showed some changes. OCDF, followed by 1,2,3,4,6,7,8-HpCDF, were the main contributors to TEQ in the baseline survey, while in the remaining studies the main contributor was 1,2,3,4,6,7,8-HpCDF, being the second position variable

(1,2,3,4,7,8-HxCDF in the current study). When PCDD/Fs were determined in plasma of the non-exposed population living in the vicinity of the HWI, the same PCDD/F congeners than those found in the baseline survey were the main contributors to TEQ (Schuhmacher et al., 1999). In 2002, the last time that the general population was monitored, among the five main contributors to TEQ, only the fifth position was different, corresponding to 2,3,4,7,8-PeCDF (Agramunt et al., 2005). This congener occupied also this position in the 2001, 2002 and 2004 studies (data not shown).

On the other hand, the levels of these organohalogenated compounds in plasma of the HWI workers classified according to the specific workplace are summarized in Table 3. Data show the baseline and current results, as well those concerning to the annual monitoring studies performed between both surveys. Statistical comparison of the results according to the year could be only carried out for plant workers, as only one composite sample was annually analyzed for each group of laboratory and administration workers. Consequently, the statistical comparison among the three groups of workers was non-viable. Despite of this, a detailed observation of the data allows to note that for these organohalogenated compounds, a similar annual tendency to that found for all HWI workers (Table 2) is also seen for plant workers. Moreover, the visual (no statistical) comparison of the current data shows that the concentrations of HCB, PCB-138, PCB-153, and PCB-180 were lower in plant workers than those corresponding to the other 2 groups, while the levels of the remaining PCBs and those of PCDD/Fs were higher in that group of workers. However, it is important to remark that these differences could not be statistically evaluated, and therefore, the significance of the comparison is not scientifically relevant. Notwithstanding, a non-statistical evaluation of the data does not seem to indicate that the concentrations of these contaminants are higher in plant workers than in laboratory or administration workers, for whom a lower exposure than that corresponding to plant workers could be expected.

Table 4 shows the current urinary levels (mean, median, standard deviation, and minimum and maximum values) of chlorophenols and 1-hydroxypyrene in

composite samples belonging to the workers of the HWI. In turn, Table 5 summarizes a comparison of the current mean concentrations with those of the baseline survey and the monitoring studies performed between 2000 and 2004. The ratios corresponding to 1999/2005 and 2004/2005 are also given. There were important fluctuations in the concentrations of chlorophenols depending on the year of the survey, while 1-hydroxypyrene could be only detected in 2004.

The urinary levels of chlorophenols and 1-hydroxypyrene in the HWI workers classified according to the specific workplace are summarized in Table 6. Data show the baseline and current results, as well those concerning to the annual monitoring studies performed between both surveys. As for plasma samples, statistical comparison of the results according to the year of monitoring could be only carried out for plant workers, as only one composite sample was annually analyzed for the groups of laboratory and administration. Consequently, statistical comparison among the three groups of workers was unfeasible. For plant workers, 2,4- and 2,5-dichlorophenol levels were significantly increased with respect to the baseline survey, while those of the trichlorophenols decreased. In turn, the concentration of pentachlorophenol was the same than that found in the baseline survey. In relation to the 2004 results, no significant changes were noted for any compound. A non-statistical comparison of the current data shows that the concentrations of the dichlorophenols were higher in plant workers than those concerning the other 2 groups, while the levels of the remaining compounds, and those of 1-hydroxypyrene, were lower (or similar) in that group of workers. However, the significance of this comparison is not scientifically relevant.

Table 2. Concentrations (mean values) of organohalogenated compounds in plasma of workers at the HWI: Comparison of the current (2005) data with those from 1999 (baseline), 2000, 2001, 2002, 2003 and 2004.

	1999	2000	2001	2002	2003	2004	2005	Ratio 1999/2005	Ratio 2004/2005
HCB	152.0 <sup>abcd</sup>	115.4 <sup>abc</sup>	181.7 <sup>ad</sup>	225.5 <sup>a</sup>	49.8 <sup>bcd</sup>	61.3 <sup>cd</sup>	71.0 <sup>d</sup>	2.1	0.9
2,4,4'-Tri-PCB28	18.5 <sup>a</sup>	2.2 <sup>bde</sup>	3.4 <sup>be</sup>	2.1 <sup>be</sup>	0.3 <sup>ce</sup>	1.3 <sup>d</sup>	2.4 <sup>e</sup>	7.7	0.5
2,2',5,5'-Tetra-PCB52	10.4 <sup>ae</sup>	1.3 <sup>be</sup>	1.5 <sup>be</sup>	0.4 <sup>ce</sup>	<0.25	0.2 <sup>de</sup>	0.8 <sup>e</sup>	13.0	0.3
2,2',4,5,5'-Penta-PCB101	9.0 <sup>a</sup>	2.0 <sup>be</sup>	2.0 <sup>bce</sup>	0.9 <sup>cde</sup>	<0.25	0.6 <sup>de</sup>	1.5 <sup>e</sup>	6.0	0.4
2,2',3,4,4',5'-Hexa-PCB138	151 <sup>a</sup>	89.0 <sup>ab</sup>	74.0 <sup>bd</sup>	50.1 <sup>bd</sup>	22.1 <sup>c</sup>	76.3 <sup>b</sup>	48.0 <sup>d</sup>	3.1	1.6
2,2',4,4',5,5'-Hexa-PCB153	213 <sup>a</sup>	125.4 <sup>ab</sup>	103.8 <sup>b</sup>	103.9 <sup>b</sup>	52.6 <sup>c</sup>	40.0 <sup>c</sup>	110.8 <sup>b</sup>	1.9	0.4
2,2',3,4,4',5,5'-Hepta-PCB180	209 <sup>abd</sup>	121.7 <sup>abd</sup>	92.0 <sup>acd</sup>	198.5 <sup>bd</sup>	58.0 <sup>c</sup>	76.9 <sup>cd</sup>	114.8 <sup>d</sup>	1.8	0.7
PCDD/Fs	26.7 <sup>a</sup>	16.9 <sup>ad</sup>	10.0 <sup>bd</sup>	10.3 <sup>bd</sup>	6.0 <sup>cd</sup>	7.7 <sup>bcd</sup>	10.4 <sup>d</sup>	2.6	0.7

Results are given in µg/kg lipid, excepting those of PCDD/Fs which are expressed in ng I-TEQ /kg de lipid.

For each compound, different letters (a, b, c, d, e) indicate significant differences ( $P < 0.01$ ) according to the non-parametric test U de Mann-Whitney.

Table 3. Concentrations (mean values) of organohalogenated compounds in plasma of workers at the HWI according to their specific workplaces

	Workers			
	Year	Plant	Laboratory	Administration
HCB	1999	134 <sup>abc</sup>	182	223
	2000	84 <sup>abc</sup>	179	179
	2001	143 <sup>ac</sup>	159	359
	2002	150 <sup>a</sup>	346	408
	2003	40 <sup>bc</sup>	65	75
	2004	59.0 <sup>c</sup>	87.3	44.2
	2005	50.5 <sup>c</sup>	74	150
	P	<0.05	-	-
2,4,4'-Tri-PCB28	1999	18.5 <sup>ac</sup>	22.4	13.2
	2000	2.5 <sup>bc</sup>	1.8	1.6
	2001	3.1 <sup>bc</sup>	3.2	4.7
	2002	2.0 <sup>bc</sup>	2.4	2.6
	2003	0.3 <sup>bc</sup>	0.4	0.3
	2004	1.3 <sup>bc</sup>	1.3	1.3
	2005	2.8 <sup>c</sup>	1.5	1.7
	P	<0.001	-	-
2,2',5,5'-Tetra-PCB52	1999	10.7 <sup>a</sup>	11.9	6.4
	2000	1.5 <sup>bd</sup>	1.1	0.6
	2001	1.3 <sup>bd</sup>	1.6	1.9
	2002	0.4 <sup>cd</sup>	0.5	0.5
	2003	ND	ND	ND
	2004	0.2 <sup>cd</sup>	0.4	0.3
	2005	1.1 <sup>d</sup>	ND	ND
	P	<0.001	-	-
2,2',4,5,5'-Penta-PCB101	1999	9.1 <sup>a</sup>	9.9	6.9
	2000	2.1 <sup>bd</sup>	1.8	1.5
	2001	1.9 <sup>bcd</sup>	2.1	2.6
	2002	0.9 <sup>cd</sup>	1.1	0.9
	2003	ND	ND	ND
	2004	0.5 <sup>d</sup>	1.3	0.5
	2005	1.8 <sup>d</sup>	0.8	0.8
	P	<0.01	-	-

2,2',3,4,4',5'-Hexa-PCB138	1999	150 <sup>a</sup>	164	134
	2000	79 <sup>abe</sup>	129	91
	2001	65 <sup>bce</sup>	94	89
	2002	41 <sup>ce</sup>	77	59
	2003	20 <sup>de</sup>	68	47
	2004	68 <sup>bce</sup>	127	60
	2005	41 <sup>e</sup>	55	71
	P	<0.01	-	-
2,2',4,4',5,5'-Hexa-PCB153	1999	213 <sup>a</sup>	228	188
	2000	114 <sup>ab</sup>	179	119
	2001	93 <sup>b</sup>	130	120
	2002	87 <sup>b</sup>	151	125
	2003	50 <sup>b</sup>	20	30
	2004	38 <sup>b</sup>	61	29
	2005	94 <sup>b</sup>	120	170
	P	<0.01	-	-
2,2',3,4,4',5,5'-Hepta-PCB180	1999	228 <sup>abd</sup>	203	91
	2000	113 <sup>abd</sup>	170	110
	2001	89 <sup>acd</sup>	110	86
	2002	176 <sup>b</sup>	278	209
	2003	59 <sup>cd</sup>	41	72
	2004	71 <sup>cd</sup>	119	61
	2005	97 <sup>d</sup>	130	170
	P	<0.05	-	-
PCDD/Fs	1999	26.4 <sup>a</sup>	31.1	30.5
	2000	16.8 <sup>ad</sup>	16.4	17.8
	2001	9.4 <sup>bcd</sup>	11.7	10.4
	2002	9.2 <sup>bd</sup>	13.5	11.6
	2003	6.0 <sup>c</sup>	6.4	5.2
	2004	8.2 <sup>bcd</sup>	9.2	4.4
	2005	11.5 <sup>d</sup>	6.8	9.5
	P	<0.05	-	-

ND: not detected. Results are given in µg/kg lipid, excepting those of PCDD/Fs which are expressed in ng I-TEQ/kg de lipid. For values corresponding to plant workers, different letters (a, b, c, d, e) indicate significant differences (P < 0.05) according to the non-parametric test U de Mann-Whitney.

Table 4. Concentrations ( $\mu\text{g/g}$  creatinine) of organic compounds in urines of workers of the HWI. Data concerning to the 2005 survey.

	Mean	Median	Standard Deviation	Minimum	Maximum
2,4-DCP	6.7	5.5	5.4	ND	13.1
2,5-DCP	93.4	92.1	59.4	12.7	165.5
2,4,5-TCP	0.2	0.2	0.2	ND	0.5
2,4,6- TCP	ND	ND	-	ND	1.0
PCP	0.4	0.2	0.63	ND	1.7
1-HP	ND	ND	-	ND	0.3

ND: not detected. DCP: Dichloropheno; TCP: Trichlorophenol; PCP: Pentachlorophenol; HP: Hydroxypyrene

Table 5. Concentrations (mean values) of organic compounds in urine of workers at the HWI: Comparison of the current (2005) data with those from 1999 (baseline), 2000, 2001, 2002, 2003 and 2004.

	Mean							Ratio	Ratio
	1999	2000	2001	2002	2003	2004	2005	1999/05	2004/05
2,4-DCP	5.7 <sup>a</sup>	5.2 <sup>bcd</sup>	5.0 <sup>abd</sup>	2.4 <sup>ab</sup>	ND	7.5 <sup>cd</sup>	6.7 <sup>ad</sup>	0.9	1.1
2,5-DCP	66.1 <sup>a</sup>	121.3 <sup>bc</sup>	181.8 <sup>bc</sup>	96.8 <sup>b</sup>	ND	181.7 <sup>c</sup>	93.4 <sup>bd</sup>	0.7	1.9
2,4,5-TCP	0.4 <sup>a</sup>	0.7 <sup>a</sup>	0.4 <sup>ab</sup>	0.1 <sup>c</sup>	ND	0.2 <sup>bc</sup>	0.2 <sup>bc</sup>	2	12
2,4,6-TCP	0.9 <sup>a</sup>	2.6 <sup>bc</sup>	1.0 <sup>bd</sup>	0.5 <sup>ad</sup>	ND	2.7 <sup>bcd</sup>	ND	-	-
PCP	0.5 <sup>a</sup>	1.9 <sup>b</sup>	1.1 <sup>c</sup>	0.9 <sup>abc</sup>	0.3 <sup>a</sup>	1.4 <sup>bc</sup>	0.5 <sup>a</sup>	1	2.8
1-HP	ND	ND	ND	ND	ND	0.2	ND	-	-

ND: not detected. For each compound, different letters (a, b, c, d) indicate significant differences ( $P < 0.01$ ) according to the non-parametric test U de Mann-Whitney.

DCP: Dichloropheno; TCP: Trichlorophenol; PCP: Pentachlorophenol; HP: Hydroxypyrene

Table 6. Concentrations (mean values) of organic compounds in urine of workers at the HWI according to their specific workplaces

	Year	Workers		
		Plant	Laboratory	Administration
2,4-Dichlorophenol	1999	2.8 <sup>a</sup>	6.6	22.5
	2000	4.3 <sup>bc</sup>	3.9	9.8
	2001	3.4 <sup>abc</sup>	6.5	9.7
	2002	1.5 <sup>ab</sup>	2.6	5.7
	2003	ND	ND	ND
	2004	6.1 <sup>cd</sup>	3.7	17.0
	2005	8.4 <sup>d</sup>	3.6	3.1
2,5-Dichlorophenol	1999	19.2 <sup>a</sup>	108.7	321.5
	2000	80.7 <sup>bc</sup>	127.7	277.2
	2001	85.2 <sup>bd</sup>	177.9	571.8
	2002	48.4 <sup>be</sup>	101.6	285.8
	2003	1.92 <sup>ae</sup>	0.40	2.75
	2004	153.4 <sup>cd</sup>	115.6	360.8
	2005	104.7 <sup>cb</sup>	45.1	96.8
2,4,5-Trichlorophenol	1999	0.5 <sup>ab</sup>	0.2	0.3
	2000	0.6 <sup>a</sup>	1.2	0.4
	2001	0.3 <sup>ac</sup>	0.7	0.5
	2002	0.2 <sup>c</sup>	0.1	0.1
	2003	ND	ND	ND
	2004	0.2 <sup>bc</sup>	0.4	0.2
	2005	0.2 <sup>ac</sup>	0.3	0.3
2,4,6-Trichlorophenol	1999	1.1 <sup>a</sup>	0.15	0.3
	2000	3.5 <sup>b</sup>	1.0	0.6
	2001	0.9 <sup>ab</sup>	1.0	1.4
	2002	0.7 <sup>a</sup>	0.3	0.1
	2003	ND	ND	ND
	2004	3.4 <sup>b</sup>	0.3	0.3
	2005	ND	0.5	1.0

Pentachlorophenol	1999	0.5 <sup>a</sup>	0.1	0.5
	2000	1.9 <sup>b</sup>	1.9	1.7
	2001	1.1 <sup>b</sup>	1.0	1.4
	2002	0.6 <sup>ab</sup>	2.7	0.6
	2003	0.1 <sup>ab</sup>	0.1	0.4
	2004	1.7 <sup>b</sup>	1.1	0.6
	2005	0.5 <sup>ab</sup>	0.5	ND
1-Hydroxypyrene	1999	<0.04-1.1	<0.04-11.2	<0.04-0.2
	2000	<0.04-0.3	0.2	<0.04
	2001	<0.04-0.2	<0.04	<0.04
	2002	<0.04-0.1	<0.04	<0.04
	2003	<0.04-0.2	<0.04	<0.04
	2004	<0.04-0.3	<0.04	0.2
	2005	<0.04	<0.04	0.4

ND: not detected. For values corresponding to plant workers, different letters (a, b, c, d) indicate significant differences ( $P < 0.05$ ) according to the non-parametric test U de Mann-Whitney.

#### 4. Discussion

Since the eighties of the twentieth century, and focused mainly on emissions of PCDD/Fs, in most developed countries waste incinerators have become "a symbol" of environmental contamination and human health risks. In recent years, and due to the stringent changes in legislation (Davy, 2004), as well as a better knowledge of the risks related with these facilities (Domingo, 2002a,b), in certain ambits of the public opinion of some countries, that perception has been slightly modified. However, a strong opposition and concern regarding waste incineration is still notably present. Consequently, it is essential that information concerning these facilities are quite clear and transparent, which implies that monitoring studies are periodically performed and the results widely spread. These were the main reasons to measure baseline levels and to design a surveillance

program related with the HWI here studied. This program also includes the biological monitoring of a number of organic substances in the HWI workers. In the baseline survey, the levels of these compounds were individually measured in blood and urine samples. However, it was expected that after some years a number of workers could desist from participating in the program, while other became retired, or simply could leave the work in the HWI. Therefore, although also due to economical reasons, after the baseline survey all studies have been carried out by measuring the levels of the chemicals in composite samples.

Information concerning health risks of workers in waste incinerators are rather scarce. In addition, most health studies (respiratory function, oxidative DNA damage, hepatic function, gene expression, etc.) are more focused on workers in MSW incinerators (MSWI) (Hu et al., 2003, 2006; Charbotel et al., 2005; Yoshida et al., 2006) than in those working at HWI (Bakoglu et al., 2004). With respect to biological monitoring studies of organic substances, most of them have been also performed in subjects employed in MSWI and are mainly focused on blood PCDD/F levels. A summary of recent studies (2003-2005) is next reviewed.

Leem et al. (2003) reported that the average TEQ concentration of PCDD/Fs in workers and residents near MSW incinerators in Korea was 12.2 ng I-TEQ/kg lipid, while that in residents from an area around an industrial waste incinerator was 53.4 ng I-TEQ/kg lipid. It was found that the oxidative stress of residents near the industrial waste incinerator was higher than that in workers and residents from the area around the MSWI. No data about workers in the industrial incinerator were reported. Kumagai et al. (2004) determined the levels of PCDD/Fs in blood of subjects working in 13 Japanese MSWIs. The mean serum concentration was 28 ng TEQ/kg lipid. It was noted that the concentrations of HxCDFs and HpCDFs in serum of the workers were significantly higher than that of the

general population. Hu et al. (2004) monitored ambient air concentrations of PCDD/Fs in three MSWIs in Taiwan. Blood PCDD/F levels of 133 workers randomly selected from these facilities were also measured. The median PCDD/F concentration in blood of all workers was 15.3 ng WHO-TEQ/kg lipid (range: 5.5-59.0). Kim et al. (2005a) determined PCDD/F and co-PCB levels in blood samples of 13 workers from two MSWI from Seoul, Korea. Mean PCDD/F and co-PCB levels were 10.4 and 7.3 ng I-TEQ/kg lipid, respectively. In turn, Moon et al. (2005) reported geometric mean PCDD/F concentrations of 3.14 and 6.60 ng TEQ/kg lipid for workers and residents near MSWIs in Korea, respectively. Recently, Chen et al. (2006) determined the levels of PCDD/Fs in serum of 25 temporary MSWI maintenance workers in Taiwan before and after annual maintenance. Mean concentrations were 20.35 and 23.87 ng WHO-TEQ/kg lipid, before and after periodic maintenance respectively, being the difference statistically significant. On the other hand, Kumagai and Koda (2005) determined the levels of PCDD/Fs in serum samples of 5 workers at a infectious waste incinerator in Japan, at 1 month and 16 months after the end of occupational PCDD/F exposure. The results were compared with PCDD/F levels corresponding to controls. One month after the end of occupational exposure mean TEQ for the workers was 49 ng/kg lipid (2.7 times higher than that of controls), while at 16 months the mean decreased to 29.4 ng TEQ/kg lipid (1.6 times higher than that of controls).

With respect to biological monitoring of PCDD/Fs and related compounds in workers at industrial waste incinerators, Kim et al. (2005b) measured PCDD/F concentrations in 2 office workers and 3 plant workers of a Korean industrial incinerator. Mean values were 9.6 and 70.1 ng I-TEQ/kg lipid for office and plant workers, respectively. In addition, there were differences between PCDD/F levels in the blood of short-term and long-term workers. It was concluded that exposure to PCDD/Fs occurred as a result of the operation of the incinerator. In the current study, the mean PCDD/F concentration for all workers was 10.4 ng I-TEQ/kg lipid, while that corresponding to plant workers only was

11.5 ng I-TEQ/kg lipid, which is notably lower than that found by Kim et al. (2005b): 70.1 ng I-TEQ/kg lipid. The current mean PCDD/F concentration is also lower than those found in most of the above studies concerning blood of workers in MSW/infection incinerators (Kumagai and Koda, 2005; Hu et al., 2004; Kim et al., 2005b; Chen et al. 2006), while are similar to those reported by Leem et al. (2003).

On the other hand, it is interesting to note that the current plasma PCDD/F concentrations in workers of the HWI are also lower than those found in recent studies in which PCDD/F levels were determined in blood samples of non-exposed populations. Thus, Chen et al. (2005) reported mean PCDD/F levels of 15.2 and 17.0 ng WHO-TEQ/kg lipid in serum samples of general men and women from Taiwan, while Masuda et al. (2005) found a mean PCDD/F concentration of 15.8 ng WHO-TEQ/kg lipid in blood samples of general Japanese individuals. Moreover, the mean PCDD/F levels found in the present survey are also lower or similar to those reported for subjects living in the vicinity of MSWIs or industrial incinerators. In relation to it, Park et al. (2004) found mean PCDD/F concentrations of 12.2 and 11.0 ng I-TEQ/kg lipid in blood samples of individuals living within 5 km and 12 km, respectively, from an industrial waste incinerator of Korea. A slightly high mean value (14.1 ng I-TEQ/kg lipid) was recently reported by Lee et al. (2005) in serum samples of 95 volunteers living near a Taiwanese MSWI, while mean PCDD/F levels of 12.3 and 11.8 ng I-TEQ/kg lipid were found in blood samples of subjects living in the vicinity of MSWIs from Korea. In contrast, a comparatively high median value, 45.7 ng WHO-TEQ/kg lipid, was reported by Pirard et al. (2005) in blood samples of 10 non-occupationally exposed volunteers who had lived within a 2 km radius of an old MSWI of France for at least 25 years.

With respect to the remaining organic compounds here analyzed, the most remarkable finding is the lack of important differences in the plant workers among the

current values and those obtained in the previous annual surveys (2000-2004), while their levels are generally lower than those of the baseline survey. Moreover, although a statistical comparison could not be performed, it seems, at least apparently, that there were not important differences between the three groups of workers, differences that would be based on the levels of exposure. A comparison of the current data concerning these compounds with results from other studies is difficult taking into account the scarce data on the levels of these compounds that have been reported in blood/urine of incinerators workers.

In summary, the results of the 2005 (current) survey together with those obtained in the 2000-2004 studies, show that after 6 years of regular operation in the HWI, the workers are not significantly exposed to PCDD/Fs in their workplaces. PCDD/F levels in blood were similar or even lower than those corresponding to various non-exposed populations. A similar conclusion can be also obtained for the remaining organic substances internally biomonitoring.

#### **Acknowledgement**

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#### **References**

- Agramunt, M.C., Domingo, A., Domingo, J.L., Corbella, J., 2003. Monitoring internal exposure to metals and organic substances in workers at a hazardous waste incinerator after 3 years of operation. *Toxicol. Lett.* 146, 83-91.
- Agramunt, M.C., Domingo, J.L., Bocio, A., Nadal, M., Müller, L., 2004. Biological monitoring of organic substances in workers of a hazardous waste incinerator. *Organohalogen Compd.* 66, 2445-2450.

- Agramunt, M.C., Schuhmacher, M., Hernandez, J.M., Domingo, J.L., 2005. Levels of dioxins and furans in plasma of nonoccupationally exposed subjects living near a hazardous waste incinerator. *J. Expo. Anal. Environ. Epidemiol.* 15, 29-34.
- Alcock, R.E, Jones, K.C., 1996. Dioxins in the environment: a review of trend data. *Environ. Sci. Technol.* 30, 3133-3143.
- Anderson, D.R., Fisher, R., 2002. Sources of dioxins in the United Kingdom: the steel industry and other sources. *Chemosphere* 46, 371-381.
- Angerer, J., Heinzow, B., Reimann, D.O., Knorz, W., Lehnert, G., 1992. Internal exposure to organic substances in a municipal waste incinerator. *Int. Arch. Occup. Environ. Health* 64, 265-273.
- Bakoglu, M., Karademir, A., Ayberk, S., 2004. An evaluation of the occupational health risks to workers in a hazardous waste incinerator. *J. Occup Health* 46, 156-164.
- Bolt, H.M., Wrbikzky, R., 2006. Biological monitoring and biological limit values (BLV): the estategy of the European Union. *Toxicol. Lett.* 162, 119-124.
- Charbotel, B., Hours, M., Perdrix, A., Anzivino-Viricel, L., Bergeret, A., 2005. Respiratory function among waste incinerator workers. *Int. Arch. Occup. Environ. Health.*78, 65-70.
- Chen, H.L., Liao, P.C., Su, H.J., Guo, Y.L., Chen, C.H., Lee, C.C., 2005. Profile of PCDD/F levels in serum of general Taiwanese between different gender, age and smoking status. *Sci. Total Environ.* 337, 31-43.
- Chen, H.L., Shih, T.S., Wu, Y.L., Lin, Y.C., Lee CC., 2006. Exposure assessment of polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs) in temporary municipal-waste-incinerator maintenance workers before and after annual maintenance. *Chemosphere* (in press).
- Davy, C.W., 2004. Legislation with respect to dioxins in the workplace. *Environ. Int.* 30, 219-233.

- Dempsey, C.R., 1993. A comparison of organic emissions from hazardous waste incinerators versus the 1990 toxics release inventory air releases. *J. Air Waste Manage. Assoc.* 43, 1374-1379.
- Domingo, J.L., 2002a. Human health risks of dioxins for populations living near modern municipal solid waste incinerators. *Rev. Environ. Health* 17, 135-147.
- Domingo, J.L., 2002b. Public fear of dioxins from modern municipal waste incinerators is not justified. *Environ. Health Perspect.* 110, A288-A289.
- Domingo, J.L., Schuhmacher, M., Agramunt, M.C., Müller, L., Neugebauer, F., 2001. Levels of metals and organic substances in blood and urine of workers at a new hazardous waste incinerator. *Int. Arch. Occup. Environ. Health* 74, 263-269.
- Fiedler, H., 1996. Sources of PCDD/PCDF and impact on the environment. *Chemosphere* 32, 55-64.
- Fuster, G., Schuhmacher, M., Domingo, J.L., 2001. Flow analysis of PCDD/Fs for Tarragona Province, Spain. A preliminary inventory. *Environ. Sci. Pollut. Res. Int.* 8, 91-94.
- Hardt, J., Angerer, J. 2003. Biological monitoring of workers after the application of insecticidal pyrethroids. *Int. Arch. Occup. Environ. Health* 76, 492-498
- Hu, S.W., Cheng, T.J., ChangChien, G.P., Chan, C.C., 2003. Association between dioxins/furans exposures and incinerator workers' hepatic function and blood lipids. *J. Occup. Environ. Med.* 45, 601-608.
- Hu, S.W., ChangChien, G.P., Chan, C.C., 2004. PCDD/Fs levels in indoor environments and blood of workers of three municipal waste incinerators in Taiwan. *Chemosphere* 55, 611-620.
- Hu, S.W., Chen, C.C., Kuo, C.Y., Lin, W.H., Lin, P., 2006. Increased cytochrome P4501B1 gene expression in peripheral leukocytes of municipal waste incinerator workers. *Toxicol. Lett.* 160, 112-120.

- Kim, B.H., Ikonomidou, M.G., Lee, S.J., Kim, H.S., Chang, Y.S., 2005a. Concentrations of polybrominated diphenyl ethers, polychlorinated dibenzo-p-dioxins and dibenzofurans, and polychlorinated biphenyls in human blood samples from Korea. *Sci. Total Environ.* 336, 45-56.
- Kim, B.H., Lee, S.J., Mun, S.J., Chang Y.S., 2005b. A case study of dioxin monitoring in and around an industrial waste incinerator in Korea. *Chemosphere* 58, 1589-1599.
- Kuhn, R.G., Ballard, K.R., 1998. Canadian innovations in siting hazardous waste management facilities *Environ. Manage.* 22, 533-545.
- Kumagai, S., Koda, S., 2005. Polychlorinated dibenzo-p-dioxin and dibenzofuran concentrations in serum samples of workers at an infectious waste incineration plant in Japan. *J. Occup. Environ. Hyg.* 2, 120-125.
- Kumagai, S., Oda, H., Tabuchi, T., Akasaka, S., Kosaka, H., Yoshida, J., Koda, S., Mouri, I., 2004. Relationships between dioxin concentrations in deposited dust and those in serum of workers at municipal waste incineration plants. *Sangyo Eiseigaku Zasshi* 46, 1-9 (in Japanese).
- Lee, C.C., Chen, H.L., Su, H.J., Guo, Y.L., Liao, P.C., 2005. Evaluation of PCDD/Fs patterns emitted from incinerator via direct ambient sampling and indirect serum levels assessment of Taiwanese. *Chemosphere* 59, 1465-1474.
- Leem, J.H., Hong, Y.C., Lee, K.H., Kwon, H.J., Chang, Y.S., Jang, J.Y., 2003. Health survey on workers and residents near the municipal waste and industrial waste incinerators in Korea. *Ind. Health* 41, 181-188.
- Lothgren, C.J., van Bavel, B., 2005. Dioxin emissions after installation of a polishing wet scrubber in a hazardous waste incineration facility. *Chemosphere* 61, 405-412.
- Masuda, Y., Haraguchi, K., Kono, S., Tsuji, H., Pöpke, O., 2005. Concentrations of dioxins and related compounds in the blood of Fukuoka residents. *Chemosphere* 58, 329-344.

- Meneses, M., Schuhmacher, M., Domingo, J.L., 2004. Health risk assessment of emissions of dioxins and furans from a municipal waste incinerator: comparison with other emission sources. *Environ. Int.* 30, 481-489.
- Moon, C.S., Chang, Y.S., Kim, B.H., Shin, D., Ikeda, M., 2005. Evaluation of serum dioxin congeners among residents near continuously burning municipal solid waste incinerators in Korea. *Int. Arch. Occup. Environ. Health* 78, 205-210.
- Oh, J.E., Choi, S.D., Lee, S.J., Chang, Y.S., 2006. Influence of a municipal solid waste incinerator on ambient air and soil PCDD/Fs levels. *Chemosphere* (in press).
- Oppelt, E.T., 1990. Air emissions from the incineration of hazardous waste. *Toxicol. Ind. Health* 6, 23-51.
- Park, S., Kim, S.J., Kim, K.S., Lee, D.S., Kim, J.G., 2004. Influence of an industrial waste incinerator as assessed by the levels and congener patterns of polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans. *Environ. Sci. Technol.* 38, 3820-3826.
- Pirard, C., Eppe, G., Massart, A.C., Fierens, S., De Pauw, E., Focant, J.F., 2005. Environmental and human impact of an old-timer incinerator in terms of dioxin and PCB level: a case study. *Environ. Sci. Technol.* 39, 4721-4728.
- Quass, U., Fermann, M., Broker, G., 2004. The European dioxin air emission inventory project-final results. *Chemosphere* 54, 1319-1327.
- Schuhmacher, M., Granero, S., Llobet, J.M., de Kok, H.A., Domingo, J.L., 1997. Assessment of baseline levels of PCDD/F in soils in the neighbourhood of a new hazardous waste incinerator in Catalonia, Spain. *Chemosphere* 35, 1947-1958.
- Schuhmacher, M., Domingo, J.L., Llobet, J.M., Sunderhauf, W., Müller, L., 1998. Temporal variation of PCDD/F concentrations in vegetation samples collected in the vicinity of a municipal waste incinerator (1996-1997). *Sci. Total Environ.* 218, 175-183.

- Schuhmacher, M., Domingo, J.L., Llobet, J.M., Lindström, G., Wingfors, H., 1999a. Dioxin and dibenzofuran concentrations in blood of a general population from Tarragona, Spain. *Chemosphere* 38, 1123-1133.
- Schuhmacher, M., Domingo, J.L., Llobet, J.M., Lindström, G., Wingfors, H., 1999b. Dioxin and dibenzofuran concentrations in adipose tissue of a general population from Tarragona, Spain. *Chemosphere* 38, 2475-2487.
- Schuhmacher, M., Domingo, J.L., Llobet, J.M., Kiviranta, H., Vartiainen, T., 1999c. PCDD/F concentrations in milk of nonoccupationally exposed women living in southern Catalonia, Spain. *Chemosphere* 38, 995-1004.
- Schuhmacher, M., Domingo, J.L., Agramunt, M.C., Bocio, A., Müller, L., 2002. Biological monitoring of metals and organic substances in hazardous-waste incineration workers. *Int. Arch. Occup. Environ. Health* 75, 500-506.
- Yoshida, J., Kumagai, S., Tabuchi, T., Kosaka, H., Akasaka, S., Kasai, H., Oda, H., 2006. Negative association between serum dioxin level and oxidative DNA damage markers in municipal waste incinerator workers. *Int. Arch. Occup. Environ. Health* 79, 115-122.

## **Discussió de l'article del Capítol IV**

### *Nivells de compostos organoclorats en plasma i orina*

Es va observar un descens en les concentracions d'HCB en plasma respecte a l'estudi control (ratio 1999/2005: 2.1). En quant als PCBs, les concentracions dels congèneres 28, 101, 138 i 153 també van ser significativament inferiors a les de l'estudi control, mentre que pels congèneres 52 i 180 només aparentment inferiors (no significatiu). La tendència a la baixa en els nivells de PCBs en plasma sembla evident.

La concentració de PCDD/Fs en plasma, de 10.4 ng I-TEQ/kg lípid, va ser estadísticament inferior a la trobada a l'estudi control, 26.7 ng I-TEQ/kg lípid.

Encara que no es van poder realitzar tests estadístics degut al reduït nombre de mostres en els grups d'administració i laboratori, els resultats obtinguts no van semblar indicar que les concentracions del grup de planta (on es podria esperar que els treballadors estiguessin més exposats) fossin superiors als dels dos primers grups.

Els nivells de 2,4- i 2,5- diclorofenol en orina van ser significativament superiors als trobats a l'estudi control, mentre que els dels triclorofenols van ser inferiors. Respecte a la concentració del pentaclorofenol, va ser la mateixa a la determinada en l'estudi control.

La comparació no estadística mostra que les concentracions actuals de diclorofenols van ser superiors pels treballadors de planta respecte als altres dos grups, mentre que pels altres clorofenols i l'hidroxipirè van ser similars (o inferiors) per aquell grup.

Els resultats van indicar que els treballadors no estaven significativament exposats en els seus llocs de treball a PCDD/Fs o a les altres substàncies organoclorades monitoritzades.

## Capítol V

### Anàlisi de la incertesa en l'avaluació de riscos

Article 6 :

Kumar V, Mari M, Schuhmacher M, Domingo JL

Partitioning total variance in risk assessment: Application to a municipal solid waste incinerator

Environmental Modelling & Software (En premsa)



## **Article 6: “Partitioning total variance in risk assessment: Application to a municipal solid waste incinerator”**

### **Abstract**

Comprehensive health risk assessment based on aggregate exposure and cumulative risk calculations requires a better understanding of exposure variables and uncertainty associated with them. Although there are many sources of uncertainty in system models, two basic kinds of parametric uncertainty are fundamentally different from each other: natural/stochastic and epistemic uncertainty. However, conventional methods such as standard Monte Carlo sampling (MCS), which assumes vagueness as random property, may not be suitable for this type of uncertainty analysis. An improved systematic uncertainty and variability analysis can provide insight into the level of confidence in model estimates, and it can aid in assessing how various possible model estimates should be weighed. The main goal of the present study was to introduce, Fuzzy Latin Hypercube Sampling (FLHS), a hybrid approach for incorporating epistemic and stochastic uncertainties separately. An important property of this technique is its ability to merge inexact generated data of the LHS approach to increase the quality of information. The FLHS technique ensures that the entire range of each variable is sampled with proper incorporation of uncertainty and variability. A fuzzified statistical summary of the model results produces a detailed sensitivity analysis, which relates the effects of variability and uncertainty of input variables to model predictions. The feasibility of the method has been tested with a case study, analyzing total variance in the calculation of incremental lifetime risks due to polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) for the residents living in the surroundings of a municipal solid waste incinerator (MSWI) in the Basque Country, Spain.

**Keywords:** Uncertainty; Variability; Fuzzy set; Latin Hypercube sampling; Municipal solid waste incinerator; Health risks

## 1. Introduction

Recent health risk assessment studies often consider aggregate exposure and cumulative risk calculation. Accumulated uncertainty in the final result can produce a misleading assessment if it is not incorporated adequately. Studies in risk analysis have shown that consideration of different sources of uncertainty may be crucial for reliable results. Uncertainty and ignorance associated with assessments and predictions on which to base policies make the communication even more difficult (van der Sluijs, 2007). The characterization and quantification of uncertainty and variability in health risk assessment are important to prevent erroneous inferences in multimedia modeling and exposure assessment, which may lead to major environmental policy implications (Frey i Zhao, 2004).

Several different classifications of uncertainty have been suggested (Alefeld, 1983; Haimes, 1998; van Asselt i Rotmans, 2002; Van den Berg i col·ls., 2006). However, for the objectives of the current study, only parametric uncertainty has been considered. The parametric uncertainty has been classified on the basis of its source and nature. Sources of parameter uncertainty are measurement errors, sampling errors, variability, and the use of surrogate data (Moschandreas i Karuchit, 2005). Measurement errors refer to random (imprecision) or systematic errors (bias), while sampling errors are errors from small sample size and/or misrepresentative samples. Heterogeneity in environmental and exposure-related data includes seasonal variation, spatial variation, and variation of human activity patterns by age, gender, and geographic location, leading to variability errors. Surrogate data refer to errors from the use of substitute data. Van Asselt and Rotmans, (2002) and (Van den Berg i col·ls., 2006) classified uncertainty based on its nature. They

called it *Epistemic uncertainty/imprecision*, and *Stochastic uncertainty/natural variability*. Epistemic uncertainty which results from incomplete knowledge about the system under study, is reducible by additional studies (e.g. further research and data collection). Stochastic uncertainty which stems from variability of the underlying stochastic process is non-reducible for a given system and under specific management scenario. Natural variability has also been termed (basic) variability, randomly uncertainty, objective uncertainty, inherent variability, (basic) randomness, and type-I uncertainty. Terms for epistemic uncertainty are systematic uncertainty, subjective uncertainty, lack-of-knowledge or limited-knowledge uncertainty, ignorance, specification error, prediction error, and type-II uncertainty (Haimes, 1998; Rotmans i van Asselt, 2001; van Asselt i Rotmans, 2002; Merz i Thieken, 2005; Moschandreas i Karuchit, 2005; Refsgaard i col·ls., 2007). In this paper, the term uncertainty is used to denote epistemic, variability to denote stochastic uncertainty, and total variance or simply variance to denote total uncertainty and variability in the outcome.

In spite of this obvious distinction, uncertainty and variability have been used as synonym. Some of the reasons are the blurred knowledge about uncertainty and variability and the lack of commonly agreed guidelines on uncertainty characterization and appropriate methodology. Consequently, in uncertainty estimation both type of uncertainty are clubbed together and treated as random variables, though epistemic uncertainty is not random in nature. The purpose of uncertainty analysis is to provide decision makers with a complete spectrum of information concerning the assessment and its quality. It also gives some scope to improve predictive results (Rotmans i Asselt, 2005). When the uncertainty in the risk estimate is unacceptable for decision-making, additional data are acquired for the major uncertainty contributing model components. This process is repeated until the level of residual uncertainty is acceptable. For this we need to identify uncertainty components

which are reducible. Further, separate measurements can provide us relevant information to the risk management decision (Spencer i col·ls., 2001).

From a practical viewpoint, it is rare to encounter only one type of uncertainty. Pure variability would mean that all relations and their parameters which describe the random process are exactly known. Pure epistemic uncertainty would mean that a deterministic process is considered, but the relevant information cannot be obtained (e.g. due to the inability to measure the relevant parameters) (Merz i Thieken, 2005). For example, given a parameter  $X$  with total variance  $V_x$ , it can sometimes be straightforward to partition the variance into uncertainty and variability components, where  $\alpha$  is the uncertainty component and  $(1 - \alpha)$  attributable to variability (Fig. 1). Notwithstanding, there also can be an intermediate vague region in which uncertainty and variability commingle. So sometime it is difficult to separate and in that case it needs special handling to measure both uncertainty and variability together.

Several approaches to uncertainty analysis in environmental risk analysis have been developed (Isukapalli, 1999; Schulz i Huwe, 1999). Among them, probabilistic approaches (e.g. Monte Carlo Simulation) are quite common and have been commonly used in the treatment and processing of uncertainty for solution of system modeling (Schuhmacher i col·ls., 2001). Another prominent approach based on fuzzy set theory (e.g. fuzzy alpha-cut analysis) has been recently applied in various fields including environmental modeling for uncertainty quantification (Isukapalli, 1999; Mauris i col·ls., 2001; Cho i col·ls., 2002; Hanss, 2002; Kentel i Aral, 2004; Josephs i col·ls., 2005). However this model has been branded as too conservative and basically applied in pure epistemic condition (Mauris i col·ls., 2001). However, all these methods have been developed to handle either variability or uncertainty of the process parameters or they club

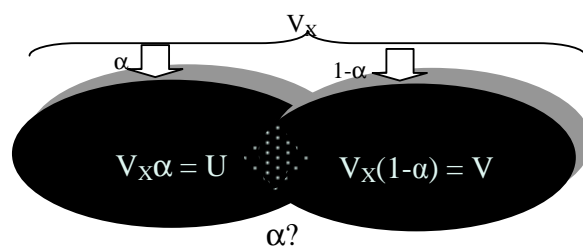


Fig. 1. Separating uncertainty and variability.

them together without valid distinction in analysis. Few recent efforts have been made to treat them separately. One common approach used in this field is 2D Monte Carlo Analysis, which classifies epistemic uncertainty as second order uncertainty (Simon, 1999). This technique requires knowledge of parameter values and their statistical distribution from which a formal mathematical description of uncertainty must be developed. However, site investigation is generally not detailed enough to determine values for some of the parameters and their distribution pattern, and sufficient data may not be collected for calibrating a model (Kentel and Aral, 2005). These approaches suffer from an obvious lack of precision and specific site-characterization, making difficult to determine how much error is introduced into the result due to assumptions and prediction. Recently, a number of authors have suggested adopting other approaches in the data limited situation. (Refsgaard i col·ls., 2007) reported: 'The test theory of classical statistics permits the testing of a sample for randomness. If the sample does not exhibit the property of randomness, other uncertainty models such as, e.g. fuzzy randomness must be adopted'. Previously, (Möller i col·ls., 2002) presented the idea of Fuzzy Randomness and formalized the concept of random variable and uncertain variable. (Kentel i Aral, 2005) introduced 2D Fuzzy Monte

Carlo and applied it in the area of health risk assessment. 2D Fuzzy Monte Carlo and Fuzzy Randomness have been classified as hybrid approach mixing the concept of probability and fuzzy set theory. The present study aims to continue this area of research and introduces a new hybrid approach, Fuzzy Latin Hypercube Sampling (FLHS), for uncertainty and variability analysis. It needs lesser computational effort and allows incorporating parameters correlation. Further we present a way to apply sensitivity analysis in fuzzy-stochastic modeling paradigm. The feasibility of the method has been validated analyzing total variance in the calculation of incremental lifetime risks due to polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) for the residents living in the surroundings of a municipal solid waste incinerator (MSWI) in the Basque Country, Spain.

## 2. Background

### 2.1. Fuzzy sets and numbers

Fuzzy set theory replaces the two-valued set-membership function with a real-valued function; that is to say, membership is treated as a possibility or as a degree of truthfulness. Likewise, one assigns a real value to assertions as an indication of their degree of truthfulness. Membership functions define the degree of participation of an observable element in the set. Fuzzy numbers are the fuzzy set defined on the set of real numbers and have special significance. They represent the intuitive concept of *approximate numbers*, such as “*around, close to, approximately etc*”. The fuzzy set that contains all fuzzy numbers with a membership of  $\alpha \in [0,1]$  and above is called the  *$\alpha$ -cut* of the membership function (Abebe i col·ls., 2000) (fig. 2). So the  *$\alpha$ -cut* represents the degree of sensitivity of the system to the behavior under observation. Fuzzy  $\alpha$ -cut technique is based on the extension principle (Zadeh, 1965), which implies that functional relationships can be

extended to involve fuzzy arguments. It can be used to map the dependent variable as a fuzzy set. In simple arithmetic operations, this principle can be analytically used. However, in most practical modeling applications involving complex structural relationships (e.g. partial differential equations), analytical applications of the extension principle are difficult. Therefore, interval arithmetic can be used to carry out the analysis (Abebe i col·ls., 2000). Arithmetic on fuzzy numbers can be defined in terms of arithmetic operations on their  $\alpha$ -cuts (on closed intervals).

This principle is generalized as: a membership level  $\mu_A(x) \in [0, 1]$  is assigned to all elements  $x$  (i.e. the elements belong to the set to a certain degree) (Klir i Yuan, 1995; Hanss, 2002). The core of the set is defined as the subset for which  $\mu_A = 1$ . The support is the subset for which  $\mu_A > 0$  (also known as the input vertex). The  $\alpha$ -cut is a generalized support: the subset for which  $\mu_A \geq \alpha$ , with  $0 < \alpha \leq 1$ . The  $\alpha$ -sublevel technique (Hanss, 2002) consists of subdividing the membership range of a fuzzy number into  $\alpha$ -sublevels at membership levels  $\mu_j = j/m$ , for  $j = 0, 1, \dots, m$  (Fig. 2). This allows numerically representing the fuzzy number by a set of  $m + 1$  interval  $[a_j, b_j]$ . A triangular fuzzy number, subdivided into intervals using  $m = 5$ , is depicted in Fig. 2.

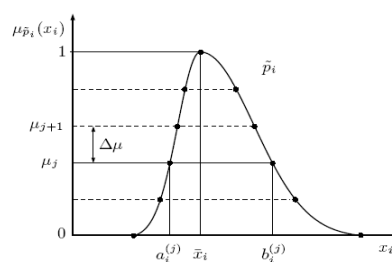


Fig. 2. Implementation of the  $i^{\text{th}}$  uncertain parameter as a fuzzy number  $\tilde{p}_i$  decomposed into intervals ( $\alpha$ -cuts).

In fuzzy simulation, for each  $\alpha$ -level of the parameter, the model is run to determine the minimum and maximum possible values of the output. This information is then directly used to construct the corresponding membership function of the output which is used as a measure of uncertainty.

## 2.2. *Latin Hypercube Sampling (LHS)*

The LHS technique proposed by (McKay i col·ls., 1979) is a type of stratified Monte Carlo sampling, where the range of each of the  $K$  variables included in the uncertainty analysis  $X_1, X_2, \dots, X_k$  is divided into  $N$  intervals in such a way that the probability of the variable falling in any of the intervals is  $1/N$ . One value is selected at random from each interval. The  $N$  values obtained for the first variable  $X_1$  are randomly paired with the  $N$  values of the second variable  $X_2$ . These pairs are furthermore randomly combined with the sampled values of the third variable, and so on. It finally results in  $N$  combinations of  $k$  variables. This set of  $k$ -tuples is the Latin hypercube sample that is used for successive execution of model runs. When using LHS, the variable space is sampled with relatively few samples and the number of samples recommended in the literature span from  $4 \cdot K/3$  ((Iman i Helton, 1985), to  $2 \cdot K$  ((McKay, 1992), to much larger ((Pebesma i Heuvelink, 1999).

## 3. Method

### 3.1. *Concept: Fuzzy Latin Hypercube Sampling technique*

In this study, the Fuzzy Latin Hypercube Sampling (FLHS) technique is proposed. This technique uses a combination of probability and possibility theory to include imprecise probabilistic information in risk analysis model. It allows the characterization of both

uncertainty and variability in one or more input variables. Parameters can be uncertain, variable, or uncertain-variable. The variability in the random variables of the model is treated using probability density functions (PDFs), while the uncertainty associated with them is treated using fuzzy membership functions for the parameters of these random variables. Thus, means and standard deviations of these PDFs are modeled as fuzzy numbers. This modeling structure gives a generalized framework for uncertainty analysis. All three uncertainty cases can be represented by a single definition. In the case of only uncertain parameters, standard deviation can be zero, whereas in the case of only variable parameters membership function (MF) can represent the highest degree of certainty (i.e.  $\mu(x) = 1$ ). Generally, membership functions used are triangular and trapezoidal. One important difference between triangular membership function and triangular PDF is that the area below the PDF is equal to the unity. The support of the membership function provides all possible values for the variable, and any number outside the support is not possible according to fuzzy set definition. The base of the probability density function covers all the values, which have positive probabilities. Our purpose was not to provide an alternative approach to 2D MCA, which treated imprecise probability or second order uncertainty, but to use FLHS for the same purpose although with a different concept. FLHS is treating uncertainty and variability in the parameters separately using hybrid fuzzy probability set theory. For a detailed discussion on Fuzzy probability, the readers can refer to the seminal paper of (Zadeh, 1984). This framework of uncertainty analysis encourages the modelers for detailed uncertainty characterization, and at the same time gives enough space to carry out modeling task in case of insufficient information on parameters distribution. If the available information is sufficient for detailed characterization of uncertainty and variability, the method can provide a detailed analysis of uncertainty and variability contribution in the final result. However, in all cases the method can give insight into uncertainty and variability contribution of different parameters in the final result, which would help modeler/decision maker to collect more data or to improve observation of major parameters in order to

improve results. The readers may also refer to (Guyonnet i col·ls., 2003) for a brief discussion of the same topic.

Since our main goal was neither to convert probability density functions into membership functions, nor to utilize one in place of another, no direct numerical comparisons for the calculated risk estimates are provided. Some researchers have attempted to compare fuzzy and stochastic simulation results but they have adopted different measures for their comparison. Guyonnet et al. (2003) have proposed possibility and necessity measures at different  $\alpha$ -cut levels to be compared with percentile value at corresponding probability level. However (Abebe i col·ls., 2000) have used the ratio of the 0.1-level support to the value  $\alpha$  for which the membership function is equal to 1 from fuzzy  $\alpha$ -cut simulation, as a basis for comparison with the ratio of the standard deviation to the mean value from Monte Carlo simulation. Kentel and Aral, (2004) have used overlapped membership function and the bar chart of the normalized frequency distribution to compare the results. Clearly these differences are due to inherent differences in the definition, meaning and treatment of the uncertainty as utilized in each method. Further research is needed to properly define adequate criteria for the comparison of FLHS methodology with other approaches. Our primary aim in this paper is however to propose a computational framework for FLHS and providing an interpretation of the results generated by FLHS.

### 3.2. *Modeling procedure*

There is no clearly agreed upon definition of Fuzzy probabilistic modeling. However, three components are nearly always at the heart of all risk modeling: 1) variability/uncertainty characterization (use of probability distributions or fuzzy distribution/membership functions to describe and represent uncertainty), 2) propagation of uncertainty through sampling (statistical, fuzzy etc) of the input parameter distributions and

multiple model runs, and 3) presentation of model outputs (again as probability distributions or fuzzy distributions) (Crowe, 2002). The FLHS implementation has been also restricted to this basic framework of risk modeling providing as additional feature the two tiered propagation of variability and uncertainty in the model simulation. Nevertheless, a comparison should not be drawn with other classical methods.

### 3.2.1. Characterization of uncertain variables

Given an arithmetic function  $f$  that depends on  $n$  uncertain parameters  $X_1, X_2, \dots, X_n$ , represented as fuzzy numbers, the function output  $q = f(X_1, X_2, \dots, X_n)$  is also a fuzzy number. Using the  $\alpha$ -level technique, each input parameter is decomposed into a set  $P_i$  of  $k + 1$  intervals  $X_i^{(j)}$ ,  $j = 0, 1, \dots, k$  where

$$P_i = \{ X_i^{(0)}, X_i^{(1)}, \dots, X_i^{(k)} \} \quad (1)$$

$$\text{with } X_i^{(j)} = [ a_i^{(j)}, b_i^{(j)} ] \text{ , } a_i^{(j)} \leq b_i^{(j)} \text{ , } i = 1, 2, \dots, n, \quad j = 1, 2, \dots, k. \quad (2)$$

where  $a_i^{(j)}$  and  $b_i^{(j)}$  denote the lower and upper bound of the interval at the membership level  $\mu_j$  for the  $i^{\text{th}}$  uncertain parameter. Instead of applying interval arithmetic like fuzzy  $\alpha$ -cut (FAC) method (Abebe i col·ls., 2000), now all parameters are transformed into an array using combinatorial combination taking each end of the interval one at a time for each parameters and at each membership level separately. A similar transformation has been used by Hanss, (2002). Purpose of this transformation is to evaluate the target function for each possible combinations arising from discretisation of uncertain parameters. These transformed arrays  $\hat{X}_i^{(j)}$  takes the following form:

$$\hat{X}_i^{(j)} = \left( \begin{array}{cccc} 6 & 4 & 4 & 44 \\ 4 & 4 & 4 & 48 \\ \left( a_{i4}^{(j)} \right) & \left( a_{i3}^{(j)} \right) & \left( b_{i4}^{(j)} \right) & \left( b_{i3}^{(j)} \right) \\ \left( a_{i4}^{(j)} \right) & \left( a_{i3}^{(j)} \right) & \left( b_{i4}^{(j)} \right) & \left( b_{i3}^{(j)} \right) \end{array} \right) \quad (3)$$

$\underbrace{\hspace{10em}}_{2^{i-1} \text{ pairs}}$   
 $\underbrace{\hspace{10em}}_{2^{n-1} \text{ elements}}$

The evaluation of function  $f$  is now carried out by evaluating the expression separately at each of the positions of the arrays using the conventional arithmetic. The obtained result is a deterministic multi-valued decomposed interval, which can be retransformed to get a fuzzy valued result using recursive approximation (Zimmermann 1991).

### 3.2.2 Characterization of random variables

Characterization of random variables has been done using Latin hypercube sampling (LHS). LHS selects  $N$  different values from each of  $n$  variables  $X_1, X_2, \dots, X_n$  in the following manner. The range of each variable is divided into  $N$  non-overlapping intervals on the basis of equal probability. One value from each interval is randomly selected with respect to the probability density in the interval. The  $N$  values thus obtained for  $X_1$  are paired in a random manner (equally likely combinations) with the  $N$  values of  $X_2$ . These  $N$  pairs are combined in a random manner with the  $N$  values of  $X_3$  to form  $N$  triplets, and so on until  $N$   $n$ -tuplets are formed. These  $N$   $n$ -tuplets are the same as the  $N$   $n$ -dimensional input vectors described in the previous paragraph. It is convenient to think on this sample (or any random sample of size  $N$ ) as forming an  $(N \times n)$  matrix of input where the  $i^{\text{th}}$  row contains specific values of each of the  $n$  input variables to be used on the  $i^{\text{th}}$  run of the computer model.

### 3.2.3 Fuzzy-stochastic measures

Taking the clue from fuzzy probability function proposed by Kato et al. (1999) when the mean and standard deviation are fuzzy numbers, we here propose a fuzzy version of stochastic measures. Using the heuristic of this method together with Fuzzy Transformation method, the fuzzy cumulative distribution function (FCDF) and fuzzy linear correlation coefficient (FLCC) for fuzzy random variables can be calculated. This procedure, for a fuzzy-stochastic variable  $\tilde{X}$  that has a normal distribution with fuzzy mean  $\tilde{m}$ , and fuzzy standard deviation  $\tilde{\sigma}$ , is next illustrated:

#### 3.2.3.1 Fuzzy CDF

For standardized normal variables, the Cumulative Distribution Function (CDF)  $F(x; m, \sigma^2)$  can be defined as:

$$F(x; m, \sigma^2) = \Phi\left(\frac{x-m}{\sigma}\right) \quad (4)$$

Here  $F$  is an arithmetic function with three uncertain parameters. Suppose  $\tilde{x}$  is a realization of fuzzy-stochastic variable  $\tilde{X}$  (which in this case are derived from output of FLHS simulation run of target model) and  $\tilde{m}$ ,  $\tilde{\sigma}$  are the fuzzy mean and fuzzy standard deviation of the fuzzy stochastic variable  $\tilde{X}$ . So all three parameters are fuzzy-random variables which can be decomposed (as in equation 2) using the  $\alpha$ -level technique, into a set of  $k+1$  intervals  $\tilde{m}^{(j)}$ ,  $\tilde{\sigma}^{(j)}$ ,  $\tilde{x}^{(j)}$   $j=0,1,\dots,k$

$$\tilde{m} = \{ \tilde{m}^{(0)}, \tilde{m}^{(1)}, \dots, \tilde{m}^{(k)} \} \quad (5)$$

$$\tilde{\sigma} = \{ \tilde{\sigma}^{(0)}, \tilde{\sigma}^{(1)}, \dots, \tilde{\sigma}^{(k)} \} \quad (6)$$

$$\tilde{x} = \{ \tilde{x}^{(0)}, \tilde{x}^{(1)}, \dots, \tilde{x}^{(k)} \}$$

where

$$\tilde{m}^{(j)} = [\tilde{m}_l^{(j)}, \tilde{m}_u^{(j)}], \tilde{\sigma}^{(j)} = [\tilde{\sigma}_l^{(j)}, \tilde{\sigma}_u^{(j)}] \text{ and } \tilde{x}^{(j)} = [\tilde{x}_l^{(j)}, \tilde{x}_u^{(j)}] \quad (7)$$

where  $l$  and  $u$  denote the lower and upper bound of the interval at the membership level  $\mu_j$ .

Now all three parameters are transformed into an array using similar combinatorial combination as used in equation 3. The resultant array will have 8 combinations at each membership level. So for  $\alpha$ -cut level  $j$ , the vertex of  $\Phi(x)$  can be calculated as:

$$\begin{aligned} F_1 &= \Phi\left(\frac{\tilde{x}_l - \tilde{m}_l^{(j)}}{\tilde{s}_l^{(j)}}\right), F_2 = \Phi\left(\frac{\tilde{x}_l - \tilde{m}_u^{(j)}}{\tilde{s}_u^{(j)}}\right), F_3 = \Phi\left(\frac{\tilde{x}_l - \tilde{m}_l^{(j)}}{\tilde{s}_l^{(j)}}\right), F_4 = \Phi\left(\frac{\tilde{x}_l - \tilde{m}_u^{(j)}}{\tilde{s}_u^{(j)}}\right), \\ F_5 &= \Phi\left(\frac{\tilde{x}_u - \tilde{m}_l^{(j)}}{\tilde{s}_l^{(j)}}\right), F_6 = \Phi\left(\frac{\tilde{x}_u - \tilde{m}_l^{(j)}}{\tilde{s}_u^{(j)}}\right), F_7 = \Phi\left(\frac{\tilde{x}_u - \tilde{m}_u^{(j)}}{\tilde{s}_l^{(j)}}\right), F_8 = \Phi\left(\frac{\tilde{x}_u - \tilde{m}_u^{(j)}}{\tilde{s}_u^{(j)}}\right) \\ j &= 0, 1, \dots, k \end{aligned} \quad (8)$$

The fuzzy-valued result  $\tilde{F}(\tilde{x})$  of the CDF can be achieved in its decomposed form:

$$\tilde{F}(\tilde{x}) = [\tilde{F}(\tilde{x})_l^{(j)}, \tilde{F}(\tilde{x})_u^{(j)}], \quad j = 0, 1, \dots, k \quad (9)$$

by retransforming the arrays  $\tilde{F}(\tilde{x})$  using recursive formulae (Zimmermann 1991)

$$\tilde{F}(\tilde{x})_l^{(j)} = \min(F_1, F_2, F_3, F_4, F_5, F_6, F_7, F_8), \quad j=0,1,\dots,k \quad (10)$$

$$\tilde{F}(\tilde{x})_u^{(j)} = \max(F_1, F_2, F_3, F_4, F_5, F_6, F_7, F_8), \quad j=0,1,\dots,k \quad (11)$$

### 3.2.3.2 Sensitivity analysis measures

The sensitivity contribution of the model parameters to the model output can be quantified by various measures (Janssen i col·ls., 1992). Many of these measures are based on regression and correlation analyses and commonly used for stochastic model analysis. They are applied to the original parameter and output values or to their rank-transformed values in case of a monotonic nonlinear relation. Given that some of these measures lead to similar results in identifying the sensitive parameters (Manache, 2001), only the linear correlation coefficient (LCC) is considered in this study. However other similar measures like the standardized regression coefficient (SRC), the semipartial correlation coefficient (SPC) can be derived in similar fashion.

#### *Fuzzy Linear Correlation Coefficient (FLCC)*

Given a sample of  $n$ -independent pairs of observations  $(x_1, y_1); (x_2, y_2); \dots; (x_n, y_n)$ , the sample correlation coefficient  $r_{xy}$  between  $x$  and  $y$  is calculated as

$$r_{xy} = \frac{\text{cov}(x, y)}{\sigma_x \times \sigma_y} \quad (12)$$

Clearly  $r_{xy}$  is an arithmetic function with three parameters. Here all three parameters may not be fuzzy-random variables. Let us assume that  $X_i$  represents input

parameters which may be fuzzy, fuzzy-stochastic or stochastic variable and  $y$  denotes the output of the target model, so in this case it will be output of FLHS simulation which will be fuzzy-stochastic variable provided any of input parameter is fuzzily combined with other stochastic variables or fuzzy-stochastic variables. Similar to Fuzzy CDF derivation, parameters are decomposed using the  $\alpha$ -level technique, into a set of  $k + l$  intervals and then transformed as in equation 3. Depending on type of  $X_i$ , it can have 4 to 8 functional combination of  $r_{xy}$  from which  $\tilde{r}_{xy}$  can be derived using recursive formulae.

Similarly the fuzzy standardized regression coefficient (FSRC), the fuzzy semipartial correlation coefficient (FSPC), and other sensitivity measure for fuzzy-stochastic variables can also be calculated. Selection of estimators depends on the problem and objective of the study. For example regression based estimators can yield results that may be statistically insignificant or counter intuitive (Neter *et al.*, 1996).

#### **4 Case Study**

Recently, a new MSWI which treats around 250,000 tones per year of domestic wastes started its regular operations in the Basque Country (North of Spain). The facility is placed at 3 km from a metropolitan area with population around a million of inhabitants. In order to estimate the impact of the new MSWI on the environment and the population living in the neighborhood, fate and transport models were applied to estimate PCDD/F concentrations in different compartments. In turn, these concentrations were used to estimate the exposure of the local population and to assess human health risks. The methodology is summarized in four main steps:

- 1) Definition of the area of study. Receptor sites were the nearest villages, in some of which agricultural activities are important.
- 2) Fate and transport model. PCDD/F concentrations were estimated in different compartments (soil, plants, meat and milk) using a multi-compartmental model.
- 3) Human exposure model. Inhalation of air and resuspended dust, dermal absorption, and ingestion of soil and local foods (vegetables, meat and milk) were the exposure pathways considered.
- 4) Risk characterization. Together with exposure results, safety PCDD/F benchmarks were used to evaluate the carcinogenic and non-carcinogenic risks (Katsumata and Kastenber, 1997; Van Leeuwen et al., 2000).

As mentioned before, the present study is focused on parametric uncertainties; however model for this case study may have other form of uncertainties like numerical uncertainties (discretisation or programming errors), topographies, climatic variability, etc. Information about the equations used in the multi-compartmental model, the exposure model, and the characterization of the health risk model for this case study can be found in the Annex I.

#### *4.1. Estimation of parameters uncertainty*

The first step of uncertainty and variability analysis is the uncertainty characterization. Once all available information has been collected and evaluated, appropriate probability density functions and membership functions can be specified for variable and uncertain parameters, respectively. Estimations are based on site specific data, previously reported values, as well as some basic assumptions (Schuhmacher i col·ls., 2001). Parameters are characterized as crisp, random/variable, uncertain/fuzzy, and uncertain-variable/fuzzy-random. Crisp variables do not contain any uncertainty. Thus, they

are represented by a single value. Variability associated with random variables is represented by probability density functions. Uncertainty associated with fuzzy variables is represented by membership functions, whereas uncertainty-variability of fuzzy-random variables is represented by fuzzy-probability density functions. As example, a sample data set is provided in Table 1. A detailed list of characterized input parameters used in the multi-compartmental model is given in Annex II.

Table 1  
 A Sample of parameters with their uncertainty characterization

Parameters	Definition	Units	Uncertainty Type	Distribution /Value	Note
TD	Total time period of deposition	year	Uncertain	Tri(30, 40, 60)	1
May	Average annual moisture (rainfall, snowfall)	cm/yr	variable	Min: 100.04; Mean: 111.74; Max: 128.93 Std: 11.06	2
Vd	Dry deposition velocity <sup>a</sup>	cm/sec	Uncertain & Variable	UniTri([4.98E-03 2.73E-02 7.41E-02], [6.22E-03 7.18E-02 1.235E-01])	3
BD	Bulk density	g/cm <sup>3</sup>	Variable	Uni(0.93-1.84)	4

<sup>1</sup>Expected life time of MSWI could be 30-60 years. <sup>2</sup>Extracted from 10 years data of the area (1994-2004).

<sup>3</sup>Depends on the size of the air particles. <sup>4</sup>From Hoffman and Baes (1979)

<sup>\*</sup> Tri = Triangular, Uni = Uniform, UniTri = Uniform Triangular (represent variability and uncertainty respectively).

<sup>a</sup> Detailed calculation is provided in Annex II (Table 2).

#### 4.2. *Simulation and propagation of uncertainty*

After characterizing the uncertainty and/or variability associated with each input parameters, the FLHS technique is used to propagate these uncertainty. The total variance in the result can then be estimated. This propagation results in a fuzzy probability distribution functions for the estimated risk. Even though the Latin Hypercube Sampling needs lesser sample size compared to normal Monte-Carlo, a higher sample size (1000) has been used to validate the results from previous work of (Schuhmacher i col·ls., 2001). Further 11 levels (0-0.1-1  $\alpha$ -cuts) of fuzzy discretisation have been used which have further been discretised into lower and upper bounds. Under consideration of the fuzzy randomness of the uncertain input values, the obtained result values were also fuzzy random variables.

FLHS simulation produces two PDFs/CDFs (i.e., one for upper and one for lower bound) for each  $\alpha$ -cut level. For the triangular membership function used in this case study, the lower and the upper bound at  $\alpha$ -cut 1.0 are the same. Thus, a total of 21 risk PDFs/CDFs were generated with 11 levels of fuzzy discretisation. These discrete distributions were used to generate fuzzy risks values corresponding to each percentile. To represent the results, box plots were used. The simplicity of the box plot makes it ideal as a means of comparing many samples simultaneously. It was used to compare distributions at different possibilities level. Box plots of the individual  $\alpha$ -cut levels were lined up side by side on a common scale, and the various attributes of the results compared at a glance. Obvious differences were immediately apparent. Data which will not lend itself to standard analysis can be identified. In the current case study, the box plots have been used to show the 5th, 25th, 50th, 75th, and 95th, percentiles of model outcome, in this case PCDD/F concentrations or risk due to exposure to PCDD/Fs. It has been drawn separately for lower and upper membership functions.

The box length gives an indication of the sample variability, while the line across the box shows where the sample is centered. The length of the notch (along the box, not its depth into the box) is a "robust estimate of uncertainty about the median". The notches should be interpreted as a rough indication of the magnitude of a significant difference. The position of the box in its whiskers and the position of the line in the box also indicate whether the sample is symmetric or skewed, either to the right or left. For a symmetric distribution, long whiskers, relative to the box length, can betray a heavy tailed population and short whiskers, a short tailed population. The commonly accepted method among statisticians for drawing the whiskers is 1.5 times the interquartile range (IQR). Any data value larger than that should be marked as an outlier.

The membership function of mean and standard deviation of different results has also been plotted to represent uncertainty associated with the result. Further sensitivity analysis to calculate relative contribution of different uncertain parameters to the total uncertainty has been also done. This is useful to handle reducible source of uncertainty in parameters.

## **5. Results and discussion**

The output of FLHS simulation is fuzzy probabilistic distributions, which can be represented in various forms (multi-plot of PDF/CDFs over different  $\alpha$ -cuts). Several forms of information can be extracted from the results. In the present case study, results have been shown according to the conventional way used by risk modeler community. The frequency distribution has been plotted at three levels of uncertainty, lower  $\alpha$ -0,  $\alpha$ -1 and upper  $\alpha$ -0, which basically represent min-mode-max pattern in triangular membership function (MF). The box plots have been plotted for all 11  $\alpha$ -cut levels at lower and upper

uncertainty levels. Further minimum, mode and maximum values for respective triangular MFs have been shown for mean and standard deviation to represent possibilistic uncertainty distribution of fuzzy variability. Sensitivity analysis is presented in Tables and pie-charts. Analysis has been broken down at each step of modeling exercise involving compartmental sub-models from air deposition models and exposure models.

### 5.1. Results from multi-compartmental model

A fuzzified statistical summary of PCDD/F concentrations in different media obtained from the multi-compartmental model is shown in Table 2. Large uncertainty in the output has been observed on the current characterization of input parameters. The distribution of PCDD/F concentrations in soil due to air deposition of the MSWI emission is depicted in Fig. 3. The distributions at different  $\alpha$ -cut levels show a different

Table 2

Mean and standard deviation of PCDD/Fs concentration in different media obtained from air deposition model with three levels of uncertainty (lower  $\alpha$ -cut 0,  $\alpha$ -cut 1, and upper  $\alpha$ -cut 0).

Media	Mean concentration			Uncertainty (Triangular Std)		
	[min	mode	max]	[min	mode	max]
Soil	[1.01,	1.98,	54.7]* E-12	[0.28,	0.48,	23.6] * E-12
Meat	[0.2,	0.9,	109.2] * E-8	[0.12,	0.53,	33.72] * E-8
Milk	[0.3,	1.2,	90.85] * E-8	[0.2,	0.6,	25.9] * E-8
Fruits	[0.3,	0.9,	20.1] * E-10	[0.12,	0.23,	37.18] * E-10
Vegetables	[0.2,	0.4,	10.0] * E-10	[0.01,	0.12,	1.86] * E-10

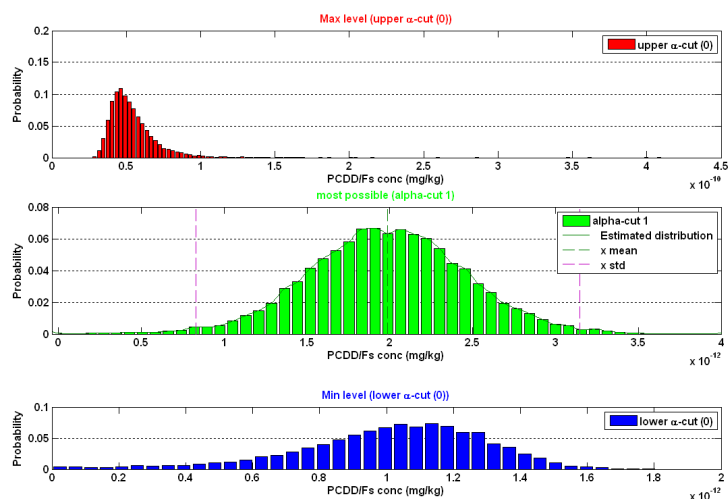


Fig. 3. Distribution of PCDD/F concentrations in soil at three uncertainty levels (upper  $\alpha$ -cut 0,  $\alpha$ -cut 1, and lower  $\alpha$ -cut 0).

behavior. The most possible value ( $\alpha$ -cut 1) shows a normal distribution, whereas the minimum value (lower  $\alpha$ -cut 0) is displaying a negative skewness, and the maximum value (upper  $\alpha$ -cut 0) is displaying a positive skewness. In turn, the box plots at 11  $\alpha$ -cut levels (Fig. 4) show a high variability across different possibility levels ( $\alpha$ -cut levels). Since the notches in the box plot do not overlap, it can be concluded with 95% confidence that the true medians differ. Sensitivity analysis shows how much each uncertain parameter contributes to the overall uncertainty of the prediction. Major contributors to uncertainty in soil deposition are soil loss constant ( $k_s$ ) (55%), dry deposition velocity ( $V_d$ ) (30%), and volumetric washout ratio for particulates ( $W_p$ ) (14%) (Fig. 5). Surprisingly, the concentration of PCDD/Fs in air ( $C_{air}$ ) is not a major source of uncertainty, which emphasizes the need to collect

more site specific data. The approximated membership function of the fuzzy expected value of PCDD/F in soil concentrations is also depicted in Fig. 5.

Similar analysis of PCDD/F concentrating in milk exhibits distributions at different  $\alpha$ -levels (Fig. 6). In this case, all three uncertainty levels exhibited a positive skewness. However, the most possible value ( $\alpha$ -cut 1) has shown a similar distribution pattern to lower

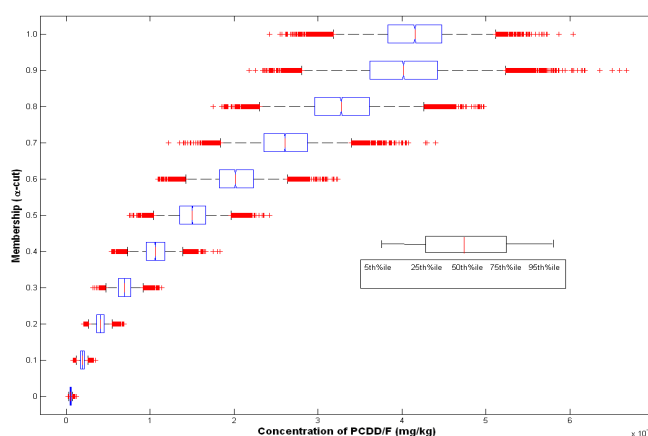


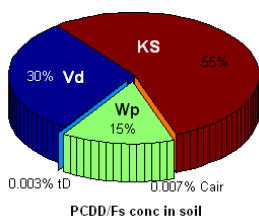
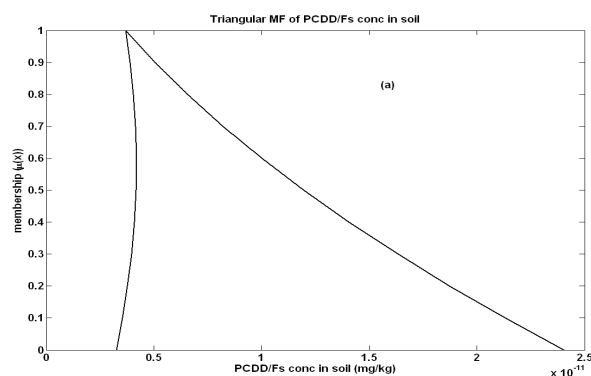
Fig. 4. Box plot of PCDD/F concentrations in soil at lower level of membership (lower  $\alpha$ -cut levels).

$\alpha$ -cut 0 (minimum value), which can further be confirmed from box plots (Fig. 7). It can be interpreted as the PCDD/F concentrations in milk would likely be at a lower side of estimation than to the max-value. There are a large number of outliers across all the possibility levels. However, those are mostly mild outliers as they hardly go beyond three times the Interquartile ranges (3IQRs). At the upper lowest possibility level (upper  $\alpha$ -cut 0) of the PCDD/F concentrations in milk, there are some extreme outliers which explain the high uncertainty toward max-value side of the  $\alpha$  result. Sensitivity analysis shows fraction of wet deposition (Fw) (33%), plant surface loss coefficient (kp) (23%), particle deposition velocity

(Vd) (22%), and volumetric washout ratio for particulates (Wp) (11%) as major contributors towards uncertainty (Table 3). However PCDD/F concentrations in air (Cair), the total time period of deposition (TD) are not a major source of uncertainty (Table 3). The approximated membership function of the fuzzy expected value of PCDD/F concentrations in milk is shown in Fig. 8. The most expected value of PCDD/F concentrations in milk denotes closeness to minimum possibility level, which can be interpreted as 'expected value of PCDD/F concentrations in milk would be low to moderate, or it has low possibility of getting maximum value'.

Table 3  
Sensitivity analysis for diet intake

Parameters	Fraction contribution of total uncertainty
Vd	0.224
Cair	1.6E-11
Wp,	0.1078
TD	2.8E-13
ks	0.0627
Fw	0.3311
kp	0.2364
SIR	0.0379



Parameters	Fraction contribution of total uncertainty
ks	0.55
Vd	0.3035
Wp	0.1464
Cair	0.00007
TD	0.00003

Fig. 5. (a) Membership Function of PCDD/F concentrations in soil and (b) sensitivity chart of uncertain parameters used in calculating PCDD/Fs concentration in soils.

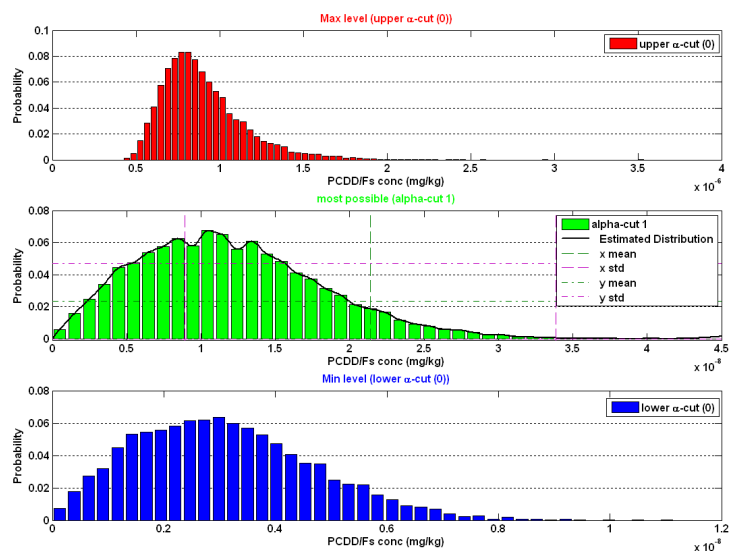


Fig. 6. Distribution of PCDD/F concentrations in milk with at three uncertainty levels (Upper  $\alpha$ -cut 0,  $\alpha$ -cut 1, and Lower  $\alpha$ -cut 0).

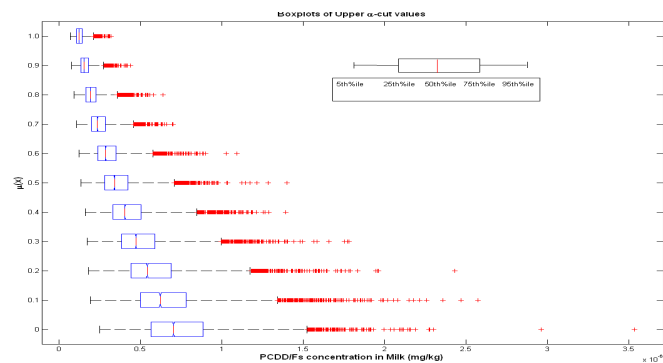


Fig. 7. Box plot of PCDD/F concentrations in milk at upper level of membership (upper  $\alpha$ -cut level).

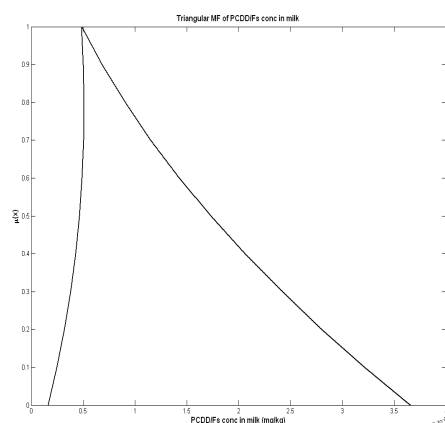


Fig. 8. Membership Function of PCDD/F concentrations in milk.

## 5.2. Results from exposure models

A fuzzified statistical summary of exposure to PCDD/Fs by the population living in the vicinity of the MSWI is presented in Table 4. The distribution of exposure due to air inhalation with three level of uncertainty band is depicted in Fig. 9. It is a positively skewed distribution with higher variability toward max-value. The distribution of total exposure to PCDD/Fs to the population through different media is shown in Fig. 10, which are positively skewed at all three levels of uncertainty. Estimated mean and standard deviation has been also shown for most possible distribution (i.e. for  $\alpha$ -cut 1). Detailed possibilistic-probabilistic analysis can be done from box plots of lower and upper  $\alpha$ -cut levels. Since most of the notches in the boxes do not overlap, we can conclude with 95% confidence that the true medians differ across different possibility levels. Further analysis of whiskers show how

distribution has been skewed at different possibility levels. It also shows the mild and extreme outliers present across the possibility levels. For example, outliers present at lower  $\alpha$ -cut 0.8 or upper  $\alpha$ -cut 0 are quite notable. From these data, it can be interpreted that there is less likelihood of getting these maximum risk value and result decision should not be based on these values. Outliers can be the result of conceptualization or modeling error so at least a detail validity analysis should be performed before considering it for risk decision. This information is particularly important comparing with classical worst case risk analysis method which doesn't give information on likelihood of decision variable.

Table 4

Mean and standard deviation of PCDD/Fs intake through different exposure media with three levels of uncertainty (lower  $\alpha$ -cut 0,  $\alpha$ -cut 1, and upper  $\alpha$ -cut 0).

Exposure Media	Mean exposure			Uncertainty (Triangular Std)		
	[min,	mode,	max]	[min	mode	max]
Food ingestion	[0.3,	0.8,	130.5]	[0.3,	0.9,	129.2]
Air inhalation	[0.22,	0.29,	0.34]	[0.07,	0.09,	0.1]
Dermal absorption	[0.0,	0.2,	10.77]	[0.0,	0.07,	4.79]
Soil ingestion	[2.0,	3.6,	205.2]	[0.9,	1.6,	111.7]
Resuspended particles inhalation	[0.4,	0.66,	24.17]	[0.17,	0.25,	12.46]

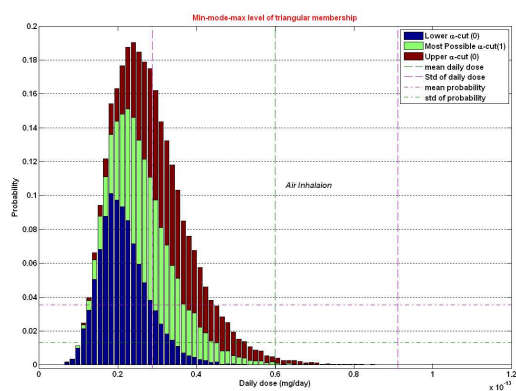


Fig. 9. Distribution of air inhalation with uncertainty band.

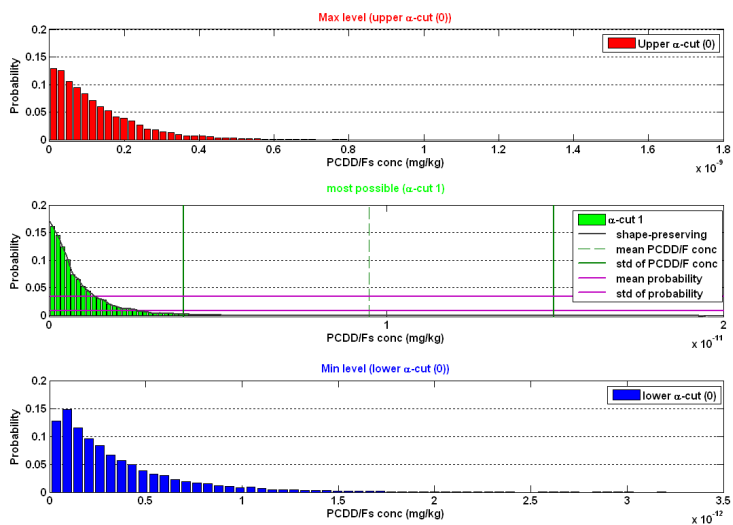


Fig. 10. Distribution of total doses at three uncertainty levels (upper  $\alpha$ -cut 0,  $\alpha$ -cut 1; and lower  $\alpha$ -cut 0).

Sensitivity analysis (Fig. 11 b) shows that 99% risk is from exposure to PCDD/F contaminated diets source. Less than 1% of the total PCDD/F exposure is due to the direct MSWI emissions, which can also be validated from previous results in this area (Schuhmacher i col·ls., 2001). The tolerable average intake levels of PCDD/Fs established by the WHO are between 1 and 4 pg WHO-TEQ/kg/day for lifetime exposure (Schuhmacher i col·ls., 2001). Closer examination of box plots (Fig. 12) reveals that excluding the extreme outliers, most values lie within 1 pg WHO-TEQ/kg/day limit. Also, the total exposure value at 50th percentile (below 0.1 pg WHO-TEQ/kg/day) and 90th percentile (below 0.2 pg WHO-TEQ/kg/day) are far below to the tolerable limit. Consequently, it can be concluded that in the current case study the MSWI would not mean a substantial risk to the population living in the area under potential influence of the emissions of the facility.

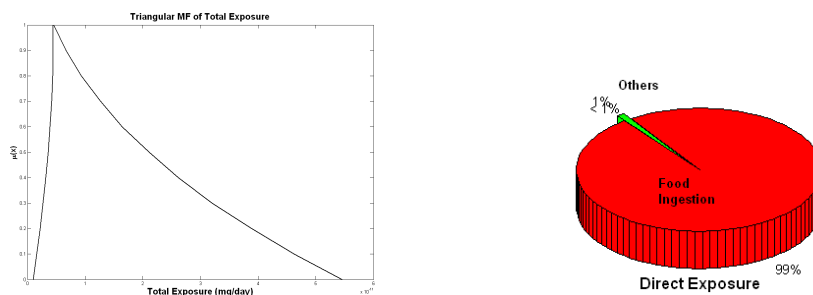


Fig. 11. (a) Membership Function of total exposure to PCDD/Fs and (b) sensitivity analysis for total exposure.

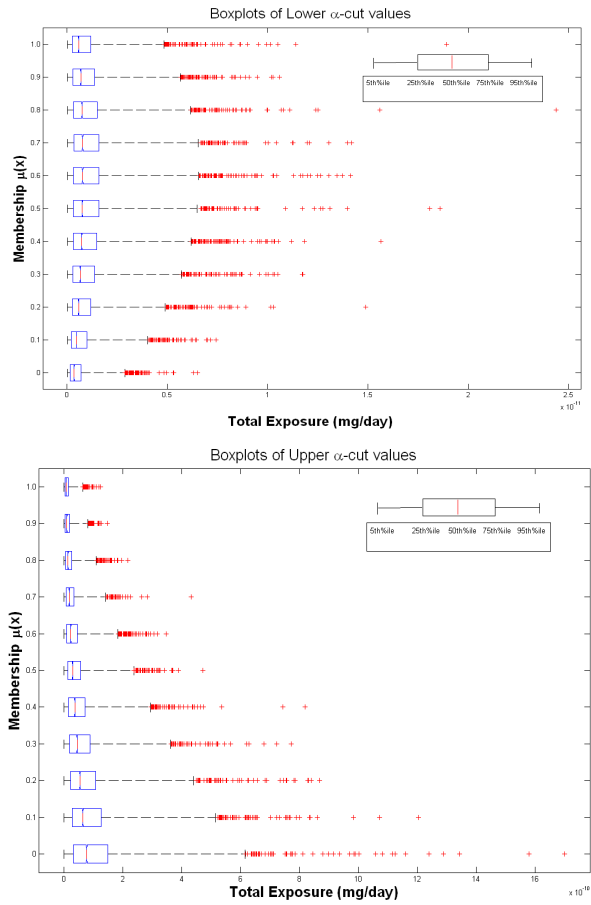


Fig. 12. Box plot of total exposure for lower (a) and upper (b) level of membership (lower and upper  $\alpha$ -cut levels)

### 5.3 Risk evaluation

The non-carcinogenic and carcinogenic risks from direct, indirect (food source), and total exposure are shown in Tables 5 and 6, respectively. The results show the mean, standard deviation, 10<sup>th</sup> percentile, the central tendency of risk (50<sup>th</sup> percentile), and the reasonable maximum exposure (RME) (90<sup>th</sup> percentiles). All this statistical measures have been calculated at three levels of uncertainty: minimum value (lower  $\alpha$ -cut 0), most possible value ( $\alpha$ -cut 1), and maximum value (upper  $\alpha$ -cut 0). It can be seen that the median (50<sup>th</sup> percentile) of non-carcinogenic risk due to PCDD/Fs for the population living in the surroundings of the MSWI is in the range of 0.0001 – 0.004 and most likely risk would be 0.002 (Table 5). The results also reveal that the uncertainty of the risk estimated, as defined by the ratio of the 90<sup>th</sup> to 10<sup>th</sup> percentile (Schuhmacher i col·ls., 2001) is in the range of 0.06 – 1383, and the most likely value would be 18.4 (Table 5).

Table 5

Non-carcinogenic risk: Mean, standard deviation, and 10<sup>th</sup>, 50<sup>th</sup>, 90<sup>th</sup> percentiles with three levels of uncertainty (lower  $\alpha$ -cut 0,  $\alpha$ -cut 1, and upper  $\alpha$ -cut 0)

		Direct Risk	Diet Risk	Total Risk
		[min, mode , max]	[min, mode , max]	[min, mode , max]
<b>Mean</b>		[1.1 1.5 1.8]*E-5	[0.2 3.4 69]*E-3	[0.21 3.41 69.02]*E-3
<b>SD<sup>a</sup></b>		[4.1 5.5 6.4]*E-6	[1.2 1.7 31]*E-4	[1.2 1.72 31.2]*E-4
<b>Percenti les</b>	<b>10<sup>th</sup></b>	[0.5 0.6 0.8]*E-5	[0.0 0.3 6.5]*E-3	[0.01 0.36 6.58]*E-3
	<b>50<sup>th</sup></b>	[0.8 1.1 1.3]*E-5	[0.1 1.9 3.9]*E-3	[0.11 1.91 3.91]*E-3
	<b>90<sup>th</sup></b>	[1.7 2.2 2.6]*E-5	[0.4 6.6 13.8]*E-3	[0.42 6.62 13.83]*E-3

<sup>a</sup> SD = standard deviation

Table 6

Carcinogenic risk: Mean, standard deviation, and 10<sup>th</sup>, 50<sup>th</sup>, 90<sup>th</sup> percentiles with three levels of uncertainty (lower  $\alpha$ -cut 0,  $\alpha$ -cut 1, and upper  $\alpha$ -cut 0)

	Direct Risk	Diet Risk	Total Risk
	[min, mode, max]	[min, mode, max]	[min, mode, max]
<b>Mean</b>	[1.9 2.5 3.0]*E-10	[0.3 5.5 114.8]*E-8	[0.32 5.53 114.81]*E-8
<b>SD<sup>a</sup></b>	[1.5 2.1 2.4]*E-10	[0.4 7.8 16.9]*E-9	[0.50 7.82 17.01]*E-9
<b>Percenti</b>	<b>10<sup>th</sup></b>	[0.3 0.4 0.4]*E-10	[0.03 0.3 5.1]*E-8
	<b>50<sup>th</sup></b>	[1.5 2.1 2.4]*E-10	[0.12 2.82 56.52]*E-8
	<b>90<sup>th</sup></b>	[4.0 5.3 6.2]*E-10	[0.7 13.8 289.1]*E-8

<sup>a</sup> SD = standard deviation

With respect to the total carcinogenic risk, the median increment in individual lifetime is in the range of  $(3.2 - 1148) \times 10^{-7}$ , and the most likely value would be  $5.53 \times 10^{-7}$  (Table 6). Similarly, the uncertainty of the risk estimated is in the range of 0.16 – 9642, being the most probable value 44.84 (Table 6). From the obtained results, it can be concluded that according to the WHO recommendations neither the emissions from the MSWI (direct exposure), nor the indirect exposure (diet) to PCDD/Fs would mean any additional risk for the health of the general population living in the vicinity of the MSWI during its life time.

## 5. Conclusions

In the current case study, only parametric uncertainty consisting of natural variability and epistemic uncertainty has been analyzed. However, the proposed methodology (FLHS) can be used to evaluate other uncertainty components (e.g. model uncertainty and scenario uncertainty). FLHS technique can encompass uncertainty in the

inventory, in fate and transport processes, and in exposure pathways to potential receptors. The outputs of these models are also fuzzy probability distributions that, if correctly constructed, represent an expected or "all possible estimates" of the risk and the uncertainty associated with that estimate, conditioned on the model assumptions. As other probabilistic models which generally include probabilistically based sensitivity and uncertainty analyses, FLHS can also give sensitivity measures that can be used in uncertainty reduction and measurement of the value of uncertainty reduction. However, in contrast to classical probabilistic sensitivity measures which failed to separate uncertainty and variability, FLHS can do it effectively. In summary, FLHS clearly separates controllable and uncontrollable uncertainty associated with models, which helps the models /and decision makers to identify the priority area in order to improve the results.

Further validation is needed to test the degree of satisfaction of compliance guideline. For example different risk compliance guidelines have been developed to compare results from stochastic simulation; similar guidelines should be developed to give general uncertainty estimates in accordance with U-V (Uncertainty-Variability) classification. Guyonnet et al. (2003) has proposed possibility and necessity measures to test the degree of satisfaction of the compliance guideline. However it still needs to be tested and adopted by different regulatory bodies before it is used more broadly in the modeller's community.

It also offers new research direction to modeler community to further improve the uncertainty analysis approach. In environmental risk analysis, an immediate need is to develop more uniform guidelines to characterize uncertainty and variability associated with different environmental models. In this study, no attempt has been made to compare FLHS with other evolving techniques in this area considering fundamental differences in assumption of defining uncertainty and variability. Comparison of the FLHS results is not straight forward. Some researchers have attempted to compare first order fuzzy and

stochastic simulation results but they have adopted different measures for their comparison ((Guyonnet i col·ls., 2003). However, FLHS is a hybrid second order uncertainty analysis method and comparison with other similar modeling paradigm like 2D Monte-Carlo, or even second order fuzzy simulation need different set of comparison criteria. Notwithstanding, as all these are emerging modeling techniques, it needs further research, and then an adequate comparison can be performed. Also further research to develop decision analysis models, which directly use U-V outcomes in risk assessment and decision making process, will enhance the framework.

#### **Software Availability**

A toolbox for Matlab has been developed for use in health risk assessment. It is still in beta version and very specialized for health risk assessment. However, in due time a generalized version will be released. It can be made available upon specific request.

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#### **References**

- Abebe, A.J., Guinot, V., Solomatine, D.P., 2000. Fuzzy alpha-cut vs. Monte Carlo techniques in assessing uncertainty in model parameters, 4th Int. Conf. Hydroinformatics, Iowa, USA.
- Alefeld, G., Herzberger, J., 1983. Introduction to Interval Computations. Academic Press, New York.
- Crowe, B., 2002. Probabilistic Modeling: Applications to Performance Assessment Maintenance Plan Studies for Low-Level Waste Disposal Facilities. DOE LFRG.

- Cho, H.N., Choi, H.-H., Kim, Y.B., 2002. A risk assessment methodology for incorporating uncertainties using fuzzy concepts. *Reliability Engineering and System Safety* 78, 173-183.
- Frey, H.C., Zhao, Y., 2004. Quantification of Variability and Uncertainty for Air Toxic Emission Inventories with Censored Emission Factor Data. *Environmental Science Technology* 38, 6094-6100.
- Guyonnet, D., Dubois, D., Bourgine, B., Fargier, H., Côme, B., Chilès, J.P., 2003. Hybrid method for addressing uncertainty in risk assessments. *Journal of Environmental Engineering* 129, 68-78.
- Haines, Y.Y., 1998. Risk modeling, assessment, and management. Wiley, New York.
- Hanss, A.M., 2002. The transformation method for the simulation and analysis of systems with uncertain parameters. *Fuzzy Sets and Systems* 130, 277-289.
- Iman, R.L., Helton, J.C., 1985. A Comparison of Uncertainty and Sensitivity Analysis Techniques for Computer Models, Technical Report SAND84-1461. Sandia National Laboratories, Albuquerque, NM.
- Isukapalli, S.S., 1999. Uncertainty Analysis of Transport-Transformation Models, Chemical and Biochemical Engineering. The State University of New Jersey, New Brunswick, NJ.
- Janssen, P.H.M., Heuberger, P.S.C., Sanders, R., 1992. UNCSAM 1.1: A software package for sensitivity and uncertainty analysis. National Institute of Public Health and Environmental Protection, Bilthoven, The Netherlands.
- Katsumata, P.T., Kastenbergh, W.E., 1997. On the impact of future land use assumptions on risk analysis for superfund sites. *Air Waste Management Association* 47, 881-889.
- Kentel, E., Aral, M.M., 2004. Probabilistic-fuzzy health risk modeling. *Stochastic Environmental Research and Risk Assessment (SERRA)* 18, 324-338.
- Kentel, E., Aral, M.M., 2005. 2D Monte Carlo versus 2D Fuzzy Monte Carlo health risk assessment. *Stochastic Environmental Research and Risk Assessment (SERRA)* 19, 86-96.

- Klir, G.J., Yuan, B., 1995. Fuzzy Sets and Fuzzy Logic, Theory and Applications. Prentice Hall, Upper Saddle River, NJ.
- Kumar, V., Schuhmacher, M., 2005. Fuzzy uncertainty analysis of system modeling. ESCAPE 2005, Barcelona, Spain.
- Manache, G., 2001. Sensitivity of a continuous water-quality simulation model to uncertain model-input parameters, Chair of Hydrology and Hydraulics. Vrije Universiteit Brussel, Brussels, Belgium.
- Mauris, G., Lasserre, V., Foulloy, L., 2001. A fuzzy approach for the expression of uncertainty in measurement. *Measurement* 29, 165-177.
- McKay, M.D., 1992. Latin hypercube sampling as a tool in uncertainty analysis of computer models, Proceedings of the 24th conference on Winter simulation. ACM Press, Arlington, VA.
- McKay, M.D., Beckman, R.J., Conover, W.J., 1979. A comparison of three methods for selecting values of input variables in the analysis of output from a computer code. *Technometrics* 21, 239-245.
- Merz, B., Thielen, A.H., 2005. Separating natural and epistemic uncertainty in flood frequency analysis. *Journal of Hydrology* 309, 114-132.
- Möller, B., Graf, W., Beer, M., Sickert, J., 2002. Fuzzy Randomness - Towards a new Modeling of Uncertainty, in: Mang, A.H., Rammerstorfer, F.G., Eberhardsteiner, J. (Eds.), Fifth World Congress on Computational Mechanics. iacm, Vienna, Austria.
- Moschandreas, D., Karuchit, S., 2005. Risk uncertainty matters: an engineer's view. *Int. J. of Risk Assessment and Management* 5, 167-192.
- Neter, J., Kutner, M.H., Nachtsheim, C.J., Wasserman, W., 1996. Applied Linear Statistical Models. Fourth Edition. McGraw-Hill: Chicago, IL.
- Pebesma, E.J., Heuvelink, G.B.M., 1999. Latin hypercube sampling of Gaussian random fields. *Technometrics* 41, 303-312.

- Refsgaard, J.C., van der Sluijs, J.P., Hojberg, A.L., Vanrolleghem, P.A., 2007. Uncertainty in the environmental modelling process - A framework and guidance. *Environmental Modelling & Software* 22, 1543-1556.
- Rotmans, J., van Asselt, M.B.A., 2001. Uncertainty management in integrated assessment modeling: Towards a pluralistic approach. *Environmental Monitoring and Assessment* 69, 101-130
- Schuhmacher, M., Meneses, M., Xifro, A., Domingo, J.L., 2001. The use of Monte-Carlo simulation techniques for risk assessment: study of a municipal waste incinerator. *Chemosphere* 43, 787-799.
- Schulz, K., Huwe, B., 1999. Uncertainty and sensitivity analysis of water transport modelling in a layered soil profile using fuzzy set theory. *Journal of Hydroinformatics* 1, 127-138.
- Simon, T.W., 1999. Two-Dimensional Monte Carlo Simulation and Beyond: A Comparison of Several Probabilistic Risk Assessment Methods Applied to a Superfund Site. *Human and Ecological Risk Assessment* 5, 823 - 843.
- Spencer, M., Fisher, N.S., Wang, W.-X., Ferson, S., 2001. Temporal Variability and Ignorance in Monte Carlo Contaminant Bioaccumulation Models: A Case Study with Selenium in *Mytilus edulis*. *Risk Analysis* 21, 383-394.
- van Asselt, M.B.A., Rotmans, J., 2002. Uncertainty in Integrated Assessment Modelling. From positivism to pluralism. *Climatic Change* 54, 75-105.
- van der Sluijs, J.P., 2007. Uncertainty and precaution in environmental management: Insights from the UPEM conference. *Environmental Modelling & Software* 22, 590-598.
- van Leeuwen, F.X.R., Feeley, M., Schrenk, D., Larsen, J.C., Farland, W., Younes, M., 2000. Dioxins: WHO's tolerable daily intake revisited. *Chemosphere* 40, 1095-1101.
- Walker, W.E., Harremoës, P., Rotmans, J., Van der Sluijs, J.P., Van Asselt, M.B.A., Janssen, P., Kreyer von Krauss, M.P., 2003. Defining uncertainty a conceptual basis

- for uncertainty management in model-based decision support. *Integrated Assessment* 4, 5-17.
- Zadeh, L.A., 1965. Fuzzy Sets. *Information and Control* 8, 338-353.
- Zadeh, L.A., 1984. Fuzzy probabilities. *Information Processing and Management* 20, 363–372.
- Zimmermann, H. J., 1991. *Fuzzy Set Theory and Its Applications*, 2nd ed., Kluwer Academic Publishers, Boston, MA.

**Annex I**

**Risk Characterization model.**

Table 7

Compartmental concentrations.

<b>COMPARTMENTAL CONCENTRATIONS</b>	
<p style="text-align: center;"><b>Environmental concentrations</b></p> <p style="text-align: center;">Soil</p> $C_s = \frac{100(Dp + Dv + L_{DIF})}{ks \cdot BD \cdot Z_s} (1 - \exp(-ks \cdot TD))$ <p>where:</p> $Dp = 0.31536 \cdot Vd \cdot Cpa$ $Dv = C_{air} \cdot May \cdot Wp \cdot 10^{-8}$ $L_{DIF} = 0.31536 \cdot Kt \cdot Cva$ $Kt = \left( \frac{Da}{Z_s} \right) \cdot \left( 1 - \left( \frac{BD}{\rho_s} \right) - \theta_{sw} \right)$	<p>Cs: concentration of contaminant in soil (<math>\mu\text{g/g}</math>);                  Dp: yearly dry deposition rate (<math>\text{g/m}^2 \text{ year}</math>); Dv:                  yearly wet deposition rate (<math>\text{g/m}^2 \text{ year}</math>); <math>L_{DIF}</math>:                  atmospheric diffusion flux (<math>\text{g/m}^2 \text{ year}</math>); ks: soil                  loss constant (<math>\text{yr}^{-1}</math>); TD: time period over which                  deposition occurs (yr); <math>Z_s</math>: soil mixing depth                  (cm); BD: bulk density (<math>\text{g/cm}^3</math>); Vd: dry                  deposition velocity (cm/sec); Cpa: particle                  bound concentration of contaminant (<math>\mu\text{g/m}^3</math>);                  Cair: concentration of contaminant in air (<math>\mu\text{g}</math>  <math>/\text{m}^3</math>); May: average annual moisture (cm/yr); Kt:                  gas phase mass transfer coefficient (cm/s);                  Cva: vapor phase air concentration of                  contaminant (<math>\mu\text{g/m}^3</math>); Da: diffusion coefficient of                  contaminant in air (<math>\text{cm}^2/\text{s}</math>); <math>\rho_s</math>: solids particle                  density (<math>\text{g/cm}^3</math>); <math>\theta_{sw}</math>: volumetric soil water                  content (<math>\text{ml/cm}^3</math>); Cpd: concentration in plant                  due to particle deposition (<math>\mu\text{g/g}</math>); Fw: fraction of                  wet deposition that adheres to plant surfaces                  (unitless); Kp: plant surface loss coefficient (<math>\text{yr}</math>  <math>^{-1}</math>); Tp: time of plant's exposure to deposition                  (yr); Yp: yield or standing crop biomass (<math>\text{kg/m}^2</math>);                  Cpr: concentration plant due to root uptake                  (<math>\mu\text{g/g}</math>); Br: soil to plant bioconcentration factor                  (g soil/g plant); <math>C_{beef}</math>: concentration in beef                  (mg/kg); Fi: fraction of plant grown on                  contaminated soil and eaten by the animal                  (unitless); Qp: quantity of plant eaten by the                  animal (kg plant/d); Cp= Cpd + Cpr (<math>\mu\text{g/g}</math>); Qs:                  quantity of soil eaten by the animal (kg soil/d);  <math>Ba_{beef}</math>: biotransfer factor for beef (d/kg); <math>C_{milk}</math>:                  concentration in milk (mg/kg); <math>Ba_{milk}</math>: biotransfer                  factor for milk (d/kg). s: quantity of soil eaten by                  the animal (kg soil/d); <math>Ba_{beef}</math>: biotransfer factor                  for beef (d/kg); <math>C_{milk}</math>: concentration in milk                  (mg/kg); <math>Ba_{milk}</math>: concentration in milk (mg/kg);  <math>Ba_{milk}</math>: biotransfer factor for milk (d/kg)</p>
<p>Plants                  Deposition</p> $Cpd = \frac{1000 \cdot (Dp + Fw \cdot Dv)}{kp \cdot Yp} \cdot (1 - \exp(-kp \cdot Tp))$ <p>Root uptake</p> $Cpr = Cs \cdot Br$	
<p style="text-align: center;"><b>Food chain concentrations</b></p> <p>Beef</p> $C_{beef} = (\sum Fi Qp \cdot Cp + Qs \cdot Cs) \cdot Ba_{beef}$ <p>Milk</p> $C_{milk} = (\sum Fi Qp \cdot Cp + Qs \cdot Cs) \cdot Ba_{milk}$	

Table 8  
 Exposure model.

EXPOSURE MODEL	
<p>Air inhalation</p> $ADD_{inh} = \frac{C_{air} \cdot IR \cdot AFI_i \cdot EF}{1000 \cdot BW \cdot 365}$ <p>Inhalation of resuspended dust</p> $ADD_{res} = \frac{C_{res} \cdot IR \cdot RET \cdot AFI_i \cdot EF}{1000 \cdot BW \cdot 365}$ <p>where:</p> $C_{res} = 10^{-6} \cdot C_s \cdot C_{pa} \cdot F_{res}$	<p>ADD<sub>inh</sub>: inhalation of air average daily dose (mg/kg day); C<sub>air</sub>: PCDD/F air concentrations g I-TEQ/m<sup>3</sup>; IR: inhalation rate (m<sup>3</sup>/day); AFI<sub>i</sub>: adsorption factor for inhalation; EF: exposure frequency (day/year); BW: body weight (kg); ADD<sub>res</sub>: inhalation of resuspended dust average daily dose (mg/kg day); C<sub>res</sub>: concentration in resuspended dust (µg/m<sup>3</sup>); RET: fraction retained in the lung (unitless); C<sub>pa</sub>: particle concentration in air (µg/m<sup>3</sup>); F<sub>res</sub>: fraction of resuspended soil in particle concentration (unitless); C<sub>s</sub>: soil concentration (µg/g); ADD<sub>d</sub>: dermal absorption daily dose (mg/kg day); AF: adherence factor (mg/cm<sup>2</sup>); SA: exposed skin surface (m<sup>2</sup>/day); ABS<sub>d</sub>: dermal absorption factor (unitless); ADD<sub>s</sub>: ingestion average daily dose (mg/kg day); CR<sub>s</sub>: soil consumption rate (mg/day); AFI<sub>g</sub>: gastrointestinal absorption factor (unitless); ADD<sub>f</sub>: food ingestion average daily dose (mg/kg day); CF<sub>i</sub>: concentration in "i" food (µg/g); CR<sub>f</sub>: consumption rate of each "i" food type (g/day); F<sub>i</sub>: fraction of food each "i" food type produced in the contaminated area (unitless).</p>
<p>Dermal absorption</p> $ADD_d = \frac{C_s \cdot AF \cdot SA \cdot ABS_d \cdot EF}{10^2 \cdot BW \cdot 365}$	
<p>Ingestion of soil</p> $ADD_s = \frac{C_s \cdot CR_s \cdot AFI_g \cdot EF_s}{10^6 \cdot BW \cdot 365}$	
<p>Ingestion of contaminated food</p> $ADD_f = \frac{CF_i \cdot CR_f \cdot F_i \cdot AFI_g \cdot EF_f}{1000 \cdot BW \cdot 365}$	

Table 9  
 Health risk characterization model.

<b>HEALTH RISK CHARACTERIZATION</b>	
No carcinogenic risk	ADD: average daily dose (mg/kg day); HQ: Hazard quotient (unitless); RfD: reference dose (mg/kg day); ER: excess cancer risk (unitless); ED: exposure duration (yr); SF: slope factor (mg/kg day) <sup>-1</sup> ; AT: average lifetime (yr).
$HQ = ADD / RfD$	
Carcinogenic risk	
$ER = ADD \cdot ED \cdot SF / AT$	

**Annex II**

Table 10

General parameters of multi-compartmental model.

Parameter	Symbol	Units	Uncertainty Type	Distribution /Value	Comments/References
Total time of deposition	TD	yr	Uncertain	Tri(30, 40, 60)	Expected life time of MSWI was assumed to be 30-60 years
Soil mixing depth	Zs	cm	Variable	Uni(10-20)	(US EPA, 1998)
Average annual moisture (rainfall, snowfall)	May	cm/yr	Variable	Min: 100.04; Mean: 111.74; Max: 128.93 Std: 11.06	Extracted from 10 years data of the area (1994-2004) (Ministerio de Medio Ambiente)
Bulk density	BD	g/cm <sup>3</sup>	Variable	Uni(0.93-1.84)	(Hoffman and Baes, 1979)
Volumetric soil water content	θsw	ml/cm <sup>3</sup>	Variable	Uni(0.03-0.40)	(Hoffman and Baes, 1979)
Solids particle density	ρs	g/cm <sup>3</sup>	Variable	Uniform(2.6-2.7)	(Hillel, 1980; Blake and Hartge, 1996)
Yield crop biomass of plant group (vegetables/fruits)	Yp	kg/m <sup>2</sup>	Variable	Uni(0.24-0.31)	(Belcher and Travis, 1989; Shor et al., 1982)
Quantity of plant eaten by the animal	Qpi	kg/day	Variable	Dairy Cattle: Uni(2.6-11); Beef cattle: Uni(0.47-8.8)	Derived from data of seven types of grains, two types of forage and two types of silage for beef and dairy cattle (US EPA, 1997)
Soil consumption rate (animal)	Qs	kg/day	Variable	Dairy Cattle: Uni(0.1367-2.64); Beef cattle: Uni(0.13-1.17)	(US EPA, 1997) (1-18% of dry matter intake)
Time of plant's exposure to deposition per harvest	Tp	yr	Variable	Uni(0.0822- 0.1644)	(Belcher and Travis, 1989)
Dry deposition velocity*	Vd	cm/sec	Uncertain & Variable	UniTri([4.98E-03 2.73E-02 7.41E-02], [6.22E-03 7.18E-02 1.235E-01])	Depends on the size of the air particles. Estimation is shown in Table 2

\* Separate calculation has been provided in table 2

### Calculation of deposition velocity

The emissions were modeled in three size classes of particles. Velocity of particle is a function of dry deposition mass flux in particle size interval and airborne particle concentration in particle size interval. Estimated velocity in particle size interval has considered percentage composition.

Table 11

Particle size distribution and velocity estimation

Particles Size	Absolute Velocity (cm/sec)	Particle Percentage (%)	Estimated Velocity (cm/sec)
< 2 µm	7.11E-03	70.0- 87.5	4.98E-03-6.22E-03
< 2-1000 µm	2.87E-01	9.5- 25.0	2.73E-02-7.18E-02
>1000 µm	2.47	3.0-5.0	7.41E-02-1.235E-01
[2 500 1000]	[7.11E-03 2.87E-01 2.47]		UniTri([4.98E-03 2.73E-02 7.41E-02], [6.22E-03 7.18E-02 1.235E-01])

Table 12  
 Contaminant Specific parameters (in this case PCDD/Fs)

Parameters	Symbol	Units	Uncertainty Type	Value/Distribution	Comments
Contaminant air concentration	$C_{air}$	mg/m <sup>3</sup>	Uncertain & Variable	Tri([2.10E-10, 9.27E-11, 3.50E-10], [1.05e-13, 1.05e-12, 1.05e-10])	Derived from routine sampling in the area (10 samples)
Water partition coefficient	$K_{ow}$		Variable	(4.62E+06, 0.73)	Caltex database
Fraction of food produced in the contaminated area	$F_i$	unitless	Variable	Uni(0.01 0.1)	The consumption of food produced in contaminated area was assumed to be 1-10%.
Diffusion coefficient of contaminant in air	$D_a$	cm <sup>2</sup> /s	Variable	Normal(4.2E-1, 0.08)	Caltex database
Fraction of wet deposition that adheres to plant surfaces	$F_w$	unitless	Uncertain	[0.5 0.6 0.7]	(US (EPA, 1998))
Soil loss constant	$K_s$	yr <sup>-1</sup>	Uncertain & Variable	Uni([0.76 0.81 0.90], [0.03 0.07 0.11])	Calculated using formula in (EPA, 1998)
Volumetric washout ratio for particulates	$W_p$	unitless	Uncertain	[1.00E+2 1.05E+2 1.1E+2]	(US (EPA, 1998))
Plant surface loss coefficient	$K_p$	unitless	Uncertain	[14.0 18.0 21.0]	(US (EPA, 1998))

Table 13  
 Input Parameters for exposure model

Parameters	Symbol	Units	Uncertainty Type	Value/Distribution	Observation
Body weight	BW	Kg	Uncertain & Variable	Lognormal(67.52 ± 12.22)	(Arija et al., 1996)
				Lognormal(77.1 ± 13.5)	(Smith, 1994)
Inhalation Rate	IR	m <sup>3</sup> /day	Uncertain & Variable	Lognormal(20 ± 2)	(Shin et al., 1998)
				Uniform(5.05-17.76)	(Finley, 1994a)
Fraction retained in the lung	RET	unitless	Uncertain	Tri( 45 60 70)	(Nessel et al., 1991)
Absorption factor for inhalation	AF <sub>li</sub>	unitless	Uncertain	100	(Nessel et al., 1991)
Soil ingestion rate (human)	CR <sub>s</sub>	mg/day	Uncertain & Variable	Lognormal(3.44 ± 0.8)	(LaGrega et al., 1994)
				Tri 25 (0.1- 50)	(Lagoy, 1987)
Consumption rate of vegetables	CRF <sub>veg</sub>	g/day	Variable	Lognormal (99 ± 80)	(Arija et al., 1996)
Consumption rate of fruit	CRF <sub>fruit</sub>	g/day	Variable	Lognormal (236 ± 174)	(Arija et al., 1996)
Consumption rate of milk	CRF <sub>milk</sub>	g/day	Variable	Lognormal (226 ± 177)	(Arija et al., 1996)
Consumption rate of beef	CRF <sub>beef</sub>	g/day	Variable	Lognormal (180 ± 84)	(Arija et al., 1996)
Gastrointestinal absorption factor	AF <sub>g</sub>	unitless	Uncertain	Tri(40 60 100)	(Nessel et al., 1991)
Exposed skin surface area (Adult: head, hands, forearms, lower legs)	SA	m <sup>2</sup> /day	Uncertain	Tri(0.20 0.53 0.58)	( US EPA, 1992)
Adherence Factor	AF	mg/cm <sup>2</sup>	Uncertain	Tri (0.52 71 0.9)	(Finley, 1994b)
Dermal absorption factor	ABS <sub>d</sub>	unitless	Uncertain	Tri (0.001 0.003 0.03)	(Katsumata and Kastenber, 1997)
Exposure Frequency	EF	day/yr	Variable	Tri 345 (180-365)	(Smith, 1994)

Table 14  
 Specific chemical parameters (PCDD/Fs) for risk evaluation

Parameters	Symbol	Units	Uncertainty Type	Value/Distribution	Observation
Average Lifetime	AT	yr	Variable	Lognormal (75 ± 5)	(Frey, 1993)
Exposure duration (adult resident)	ED	yr	Variable	Lognormal (11.4 ± 13.7)	(Israeli, 1992)
Tolerable Daily Intake	TDI	mg/kg day	Variable	Uniform (1E-9 - 4E-9)	(van Leeuwen et al., 2000)
Slope Factor	SF	(mg/kg day) <sup>-1</sup>	Variable	Uniform (34000-56000)	(Katsumata and Kastenberg, 1997)

### **References:**

- Arija, V., Salas, J., Fernández Ballart, J. Cucó G., Marti-Henneberg, C., 1996. Consumo, hábitos alimentarios y estado nutricional de la población de Reus (IX). Evolución del consumo de alimentos, de su participación en la ingestión de energía y nutrientes en relación con el nivel socioeconómico y cultural entre 1983 y 1993. Medicina Clínica 106, 174-179.
- Belcher, G.D., Travis, C.C., 1989. Modeling support for the RURA and municipal waste combustion projects: final report on sensitivity and uncertainty analysis for the terrestrial food chain model. U.S. Environmental Protection Agency, Environmental Criteria and Assessment Office, Cincinnati, OH.
- Blake, G.R., Hartge, K.H., 1996. Particle Density. Methods of Soil Analysis, Part 1: Physical and Mineralogical Methods, 2nd ed., Arnold Klute, Ed. American Society of Agronomy, Inc., Madison, WI.
- Finley, B., Paustenbach, D., 1994a. The Benefits of Probabilistic Exposure Assessment: Three Case Studies Involving Contaminated Air, Water, and Soil. Risk Analysis, 14, 53-73.
- Finley, B., Proctor, D., Scott P., Mayhall, D., 1994b. Development of a Standard Soil-to-Skin Adherence Probability Density Function for use in the Monte Carlo Analysis of Dermal Exposure. Risk Analysis, 14, 555-569.
- Frey, H.C., 1993. Separating Variability and Uncertainty in Exposure Assessment: Motivation and Method. Proceedings of the 86<sup>th</sup> Annual Meeting Air and Waste Management Association, Pittsburgh, PE.
- Hillel, D., 1980. Fundamentals of Soil Physics. Academic Press, Inc., New York.
- Hoffman, F.O., Baes, C.F., 1979. A statistical analysis of selected parameters for predicting food chain transport and internal dose of radionuclides. Oak Ridge National Laboratory, Oak Ridge, TN.
- Israeli M., Nelson C.B., 1992. Distribution and Expected Time of Residence for U.S. Households. Risk Analysis 12, 65-72.

- Katsumata, P.T., KastenberG, W.E., 1997. On the impact of future land use assumptions on risk analysis for superfund sites. *Air Waste Management Association* 47, 881-889.
- Lagoy, P., 1987. Estimated Soil Ingestion Rates for Use in Risk Assessment. *Risk Analysis* 14, 355-359.
- LaGrega, D.M., Buckingham, P.L., Evans, J.C., 1994. *Hazardous Waste Management*. McGraw Hill, New York.
- Ministerio de Medio Ambiente. Instituto Nacional de Meteorogogía-España. Available at: <http://www.inm.es/web/infmet/tobsr/emas.html>
- Nessel, S.C., Butler, J.P., Post G.B., Held J.L., Gochfeld, M., Gallo, M.A., 1991. Evaluation of the relative contribution of exposure routes in heath risk assessment of dioxin emissions from municipal waste incinerator. *Journal of Exposure Analysis and Environmental Epidemiology* 1, 283-307.
- Shin, D., Lee, J., Yang, J. and Yu, Y., 1998. Estimation of air emission for dioxin using a mathematical model in two large cities of Korea. *Organohalogen Compounds* 36, 449-453.
- Shor, R.W., Baes, C. Sharp, R., 1982. *Agricultural production in United States by country: A compilation from the 1974 census of agriculture for use in terrestrial food-chain transport and assessment models*. Oak Ridge National Laboratory, Oak Ridge, TN.
- Smith, R., 1994. Use of Monte Carlo Simulation for Human Exposure Assessment at Superfund Site, *Risk Analysis* 14, 433-439.
- US EPA, 1991. *Risk Assessment Guidance Superfund: Volume I- Human Health Evaluation Manual (Part B, Development of Risk Based Preliminary Remediation Goals)*. U.S. Environmental Protection Agency, Office of Emergency and Remedial Response, Washington, D.C.
- US EPA, 1992. *Dermal Exposure Assessment: Principles and Application*. Interim Report. EPA/600/8-91/011B. U.S. Environmental Protection Agency, Office of Research and Development, Washington, D.C.

- US EPA, 1997. Parameter Guidance Document. U.S. Environmental Protection Agency, National Center for Environmental Assessment, NCEA-0238.
- US EPA, 1998. Methodology for Assessing Health Risks Associated with Multiple Pathways of Exposure to Combustor Emissions, EPA-600/R-98-137. U.S. Environmental Protection Agency, National Center for Environmental Assessment, Cincinnati, OH.
- van Leeuwen, F.X.R., Feeley, M., Schrenk, D., Larsen, J.C., Farland, W., Younes, M., 2000. Dioxins: WHO's tolerable daily intake revisited. *Chemosphere* 40, 1095–1101.

## **Discussió de l'article del Capítol V**

Respecte al model multicompartimental, l'anàlisi de sensibilitat va mostrar que en la deposició en sòls, la constant de perdua del sòl ( $k_s$ ) (55%), la velocitat de deposició seca ( $v_d$ ) 30%), i la proporció volumètrica de neteja de partícules ( $W_p$ ) (14%) eren les variables que contribuïen majoritàriament a la incertesa.

Per altra banda, el valor més esperat de concentració de PCDD/Fs en llet va denotar la seva proximitat al nivell mínim de possibilitat, el que es podria interpretar com a que el valor esperat de PCDD/Fs en llet seria baix o moderat, amb poca possibilitat de tenir un valor alt.

Pel que fa al model d'exposició l'anàlisi de sensibilitat, va mostrar que el 99% del risc era derivat de la dieta, mentre que menys de l'1% provindria de les emissions directes de la incineradora.

Els resultats d'aquest estudi van indicar que la incineradora no suposa un risc considerable per la població que viu en l'àrea sota la seva influència.



## **Capítol VI**

### **Conclusions generals**



1. En el present estudi s'ha avaluat l'impacte ambiental i els riscos per la salut derivats de diferents incineradores de residus. Amb aquesta finalitat s'han monitoritzat els nivells de diversos compostos orgànics persistents i metalls pesants en diferents matrius ambientals i biològiques.
2. Les herbes i els sòls han demostrat ser bons monitors de contaminació ambiental a curt i llarg termini, respectivament. Per altra banda, l'aire s'ha utilitzat com a monitor d'emissions actuals. A través dels nivells en aquests monitors s'han estudiat les variacions temporals/espacials a les rodalies d'incineradores. En cap cas s'han observat variacions importants atribuïbles a les incineradores. Els nivells trobats han estat generalment en el rang més baix en comparació amb d'altres zones industrials d'arreu del món. Els resultats obtinguts impliquen que les incineradores estudiades no són una font significativa de PCDD/Fs i metalls pesants.
3. S'han avaluat els riscos per exposició a metalls pesants a les rodalies de la Incineradora de Residus Sòlids Urbans de Tarragona. La relació entre les concentracions de metalls en sòls i els PRG ha estat menor a 100% en tots els casos. Així mateix, per tots els metalls el HQ ha estat inferior a 1, indicant que els nivells són segurs per la població. Només la ingestió d'As ha superat el màxim risc carcinogènic acceptable de  $10^{-6}$ . Per altra banda, cal destacar que aquest límit ha estat superat per sòls de diferents països.
4. S'han avaluat els riscos per exposició a PCDD/Fs a les rodalies de la Incineradora de Residus Industrials de Tarragona. Per adults i nens de l'àrea més propera a la planta incineradora, l'exposició ambiental només ha representat un 0.1% de l'exposició total (ambiental més dieta). En l'àrea urbana, aquest percentatge augmenta fins a un 3.8 i 1.4% per adults i nens, respectivament.

5. Els discs PUF són una bona alternativa barata i simple de monitoritzar els nivells en aire de COPs durant períodes llargs de temps. S'han calculat els fluxes d'aire a través dels discs PUF per diferents COPs. Els resultats han estat 2, 3.8 i 3.3 m<sup>3</sup>/dia per PCDD/Fs, PCBs i PCNs, respectivament.
6. La tècnica estadística d'Anàlisi de Components Principals ha mostrat ser efectiva per:
  - a. establir diferències/similituds entre les emissions anteriors i les actuals
  - b. establir diferències/similituds entre mostres properes i llunyanes a la font de contaminació
  - c. trobar correlacions entre diferents contaminants
  - d. identificar les principals fonts que afecten a les concentracions ambientals de cada contaminant
7. S'han determinat les concentracions de diferents compostos organoclorats en sangs i orines de treballadors d'una incineradora de residus industrials amb l'objectiu de determinar si aquests estan exposats a aquestes substàncies. La monitorització biològica no ha indicat impregnació dels treballadors de la incineradora. Per altra banda, els resultats de PCDD/Fs en plasma han mostrat un descens que estaria correlacionat amb la disminució de la concentració de PCDD/Fs observada en els últims anys en totes les matrius ambientals i en aliments.
8. La tècnica del Latin Hypercube Sampling ha permès conèixer quins eren els paràmetres que introdueixen més incertesa dintre del model multicompartimental i d'avaluació de riscos i conèixer com aquesta es propaga en dels models.

9. Els resultats obtinguts no han indicat en cap cas que les incineradores estudiades fossin una font rellevant de compostos organoclorats i de metalls pesants i, per tant, un risc addicional per la gent que viu a les rodalies. A més, l'anàlisi dels resultats ha indicat que els nivells actuals de PCDD/Fs estan més relacionats amb altres tipus de fonts (pex., el trànsit) que en les pròpies emissions de les incineradores.



## **BIBLIOGRAFIA**



- Abad E, Caixach J, Rivera J (1999) *Dioxin like compounds from municipal waste incinerator emissions: Assessment of the presence of polychlorinated naphthalenes*. Chemosphere 38: 109-120.
- Abad E, Martinez K, Gustems L, Gomez R, Guinart X, Hernandez I, Rivera J (2007) *Ten years measuring PCDDs/PCDFs in ambient air in Catalonia (Spain)*. Chemosphere 67: 1709-1714.
- Abebe AJ, Guinot V, Solomatine DP, 2000. Fuzzy alpha-cut vs. Monte Carlo techniques in assessing uncertainty in model parameters, 4th Int. Conf. Hydroinformatics, Iowa, USA.
- Abrahams PW (2002) *Soils: their implications to human health*. Sci. Total Environ. 291: 1-32.
- Alefeld G, Herzberger, J., 1983. *Introduction to Interval Computations*. Academic Press, New York.
- Aoki Y (2001) *Polychlorinated biphenyls, polychlorinated dibenzo-p-dioxins, and polychlorinated dibenzofurans as endocrine disrupters- What we have learned from Yusho disease*. Enviro. Res. 86: 2-11.
- ATSDR (1992a) *Toxicological Profile for Vanadium*. Department of Health and Human Services, Atlanta, GA, USA.
- ATSDR (1992b) *Toxicological Profile for Thallium*. Department of Health and Human Services, Atlanta, GA, USA.
- ATSDR (1994) *Toxicological Profile for Pentachlorophenol*. Department of Health and Human Services, Atlanta, GA, USA.
- ATSDR (1999) *Toxicological Profile for Mercury*. US Department of Health and Human Services, Public Health Service, Agency for Toxic Substances and Disease Registry. Atlanta, GA, USA.
- ATSDR (2000a) *Toxicological Profile for Arsenic*. US Department of Health and Human Services, Public Health Service, Agency for Toxic Substances and Disease Registry. Atlanta, GA, USA.
- ATSDR (2000b) *Toxicological Profile for Chromium*. US Department of Health and Human Services, Public Health Service, Agency for Toxic Substances and Disease Registry. Atlanta, GA, USA.
- ATSDR (2000c) *Polychlorinated biphenyls*. Agency for Toxic Substances and Disease Registry, Atlanta, GA. <http://www.atsdr.cdc.gov/tfacts17.html>.
- ATSDR (2000d) *Toxicological Profile for Manganese*. US Department of Health and Human Services, Public Health Service, Agency for Toxic Substances and Disease Registry. Atlanta, GA, USA.
- ATSDR (2002a) *Toxicological Profile for Hexachlorobenzene*, U.S. Public Health Services, U.S. Department of Health and Human Services, Atlanta, GA (2002).
- ATSDR (2002b) *Toxicological Profile for Beryllium*. Department of Health and Human Services, Atlanta, GA, USA.
- ATSDR (2004a) *Toxicological Profile for Copper*. Department of Health and Human Services, Atlanta, GA, USA.
- ATSDR (2004b) *Toxicological Profile for Cobalt*. Department of Health and Human Services, Atlanta, GA, USA.

- ATSDR (2005a) *Toxicological Profile for Tin*. Department of Health and Human Services, Atlanta, GA, USA.
- ATSDR (2005b) *Toxicological Profile for Nickel*, U.S. Public Health Services, U.S. Department of Health and Human Services, Atlanta, GA, USA.
- Bache CA, Gutenmann WH, Rutzke M, Chu G, Elfving DC, Lisk DJ (1991) *Concentrations of metals in grasses in the vicinity of a municipal refuse incinerator*. Arch. Environ. Contam. Toxicol. 20: 538-542.
- Bakoglu M, Karademir A, Durmusoglu E (2005) *Evaluation of PCDD/F levels in ambient air and soils and estimation of deposition rates in Kocaeli, Turkey*. Chemosphere 59: 1373-1385.
- Baldwin D, Marshall W (1999) *Heavy metal poisoning and its laboratory investigation*. Ann. Clin. Biochem. 36: 267-300.
- Bartkow ME, Booij K, Kennedy KE, Muller JF, Hawker DW (2005) *Passive air sampling theory for semivolatile organic compounds*. Chemosphere 60: 170-176.
- Basu A, Mahata J, Gupta S, Giri A (2001) *Genetic toxicology of a paradoxical human carcinogen, arsenic: a review*. Mutation Research/Reviews in Mutation Research 488: 171-194.
- Bellés M, Rico A, Schuhmacher M, Domingo J, Corbella J (1995) *Reduction of lead concentrations in vegetables grown in Tarragona Province, Spain, as a consequence of reduction of lead in gasoline*. Environ. Int. 21: 821-825.
- Biterna M, Voutsas D (2005) *Polychlorinated biphenyls in ambient air of NW Greece and in particulate emissions*. Environment International 31: 671-677.
- Blankenship A, Kannan K, Villalobos S, Villeneuve D, Falandysz J, Imagawa T, Jakobsson E, Giesy J (2000) *Relative potencies of individual polychlorinated naphthalenes and halowax mixtures to induce Ah receptor-mediated responses*. Environ. Sci. Technol. 34: 3153-3158.
- Bocio A, Domingo JL (2005) *Daily intake of polychlorinated dibenzo-p-dioxins/polychlorinated dibenzofurans (PCDD/PCDFs) in foodstuffs consumed in Tarragona, Spain: a review of recent studies (2001-2003) on human PCDD/PCDF exposure through the diet*. Environ. Res. 97: 1-9.
- BOE, 2002. RD-1073-2002 Sobre evaluación y gestión de la calidad del aire ambiente en relación con el dióxido de azufre, dióxido de nitrógeno, óxidos de nitrógeno, partículas, plomo, benceno y monóxido de carbono. . Boletín Oficial del Estado
- Bosco ML, Varrica D, Dongarra G (2005) *Case study: Inorganic pollutants associated with particulate matter from an area near a petrochemical plant*. Environ. Res. 99: 18-30.
- Breivik K, Alcock R, Li Y, Bailey R, Fierens S, Pacyna J (2004) *Primary sources of selected POPs: regional and global scale emission inventories*. Environ. Pollut. 128: 3-16.
- Brown J (1994) *Determination of PCB metabolic, excretion, and accumulation rates for use as indicators of biological response and relative risk*. Environ. Sci. Technol. 28: 2295-2305.
- Brunciak PA, Dachs J, Franz TP, Gigliotti CL, Nelson ED, Turpin BJ, Eisenreich SJ (2001) *Polychlorinated biphenyls and particulate organic/elemental carbon in the atmosphere of Chesapeake Bay, USA*. Atmos. Environ. 35: 5663-5677.

- Capuano F, Cavalchi B, Martinelli G, Pecchini G, Renna E, Scaroni I, Bertacchi M, Bigliardi G (2005) *Environmental prospection for PCDD/PCDF, PAH, PCB and heavy metals around the incinerator power plant of Reggio Emilia town (Northern Italy) and surrounding main roads*. Chemosphere 58: 1563-1569.
- Carrera G, Fernández P, Vilanova RM, Grimalt JO (2001) *Persistent organic pollutants in snow from European high mountain areas*. Atmos. Environ. 35: 245-254.
- Cetin B, Yatkin S, Bayram A, Odabasi M (2007) *Ambient concentrations and source apportionment of PCBs and trace elements around an industrial area in Izmir, Turkey*. Chemosphere 69: 1267-1277.
- Corbella J (2000) *Esquemes de toxicologia industrial (I). Introducció-Metalls. Publicacions del Seminari Pere Mata de la Universitat de Barcelona, núm. 24*.
- Correa O, Rifai H, Raun L, Suarez M, Koenig L (2004) *Concentrations and vapor-particle partitioning of polychlorinated dibenzo-p-dioxins and dibenzofurans in ambient air of Houston, TX*. Atmos. Environ. 38: 6687-6699.
- Corsolini S, Romeo T, Ademollo N, Greco S, Focardi S (2002) *POPs in key species of marine Antarctic ecosystem*. Microchem. J. 73: 187-193.
- Coutinho M, Pereira M, Borrego C (2007) *Monitoring of ambient air PCDD/F levels in Portugal*. Chemosphere 67: 1715-1721.
- Crookes M, Howe P (1993) *Crookes MJ, Howe PD (1993) Environmental Hazard Assessment: Halogenated Naphthalenes. Department of the Environment, Directorate for Air, Climate and Toxic Substances, Toxic Substances Division*.
- Crowe B, 2002. Probabilistic Modeling: Applications to Performance Assessment Maintenance Plan Studies for Low-Level Waste Disposal Facilities. DOE LFRG.
- Chang M, Wu H, Huang C (2000) *Evaluation on speciation and removal efficiencies of mercury from municipal solid waste incinerators in Taiwan*. Sci. Total Environ. 246: : 165-173.
- Cheng P, Hsu M, Ma E, Chou U, Ling Y (2003) *Levels of PCDD/Fs in ambient air and soil in the vicinity of a municipal solid waste incinerator in Hsinchu*. Chemosphere 52: 1389-1396.
- Cho HN, Choi H-H, Kim YB (2002) *A risk assessment methodology for incorporating uncertainties using fuzzy concepts*. Reliab. Eng. Sys. Saf. 78: 173-183.
- Denier van der Gon H, van het Bolscher M, Visschedijk A, Zandveld P (2007) *Emissions of persistent organic pollutants and eight candidate POPs from UNECE-Europe in 2000, 2010 and 2020 and the emission reduction resulting from the implementation of the UNECE POP protocol*. Atmos. Environ. 41: 9245-9261.
- DGT (2004) *Anuario estadístico 2004 'Evolución de la matriculación según carburante'*.
- DOCE (2000) *DIRECTIVA 2000/76/CE DEL PARLAMENTO EUROPEO Y DEL CONSEJO relativa a la incineración de residuos*.
- DOGC (1986) *Ordre de 9 de setembre de 1986, de limitació de l'ús dels policlorobifenils i els policloroterfenils. Departament d'Indústria, Comerç i Turisme*.
- Domingo J (2004) *Polychlorinated naphthalenes in animal aquatic species and human exposure through the diet: A review*. J. Chromatogr. A 1054: 327-334.
- Domingo JL (1994) *Metal-induced developmental toxicity in mammals: A review*. J. Toxicol. Environ. Health 42: 123-141.

- Domingo JL, Schuhmacher M, Müller L, Rivera J, Granero S, Llobet JM (2000) *Evaluating the environmental impact of an old municipal waste incinerator: PCDD/F levels in soil and vegetation samples*. J Hazard. Mater. 76: 1-12.
- Domingo JL, Schuhmacher M, Llobet JM, Muller L, Rivera J (2001) *PCDD/F concentrations in soil and vegetation in the vicinity of a municipal waste incinerator after a pronounced decrease in the emissions of PCDD/Fs from the facility*. Chemosphere 43: 217-226.
- Domingo JL (2002) *Human health risks of dioxins for populations living near modern municipal solid waste incinerators*. Rev. Environ. Health. 17: 135-147.
- Domingo JL, Bocio A, Nadal M, Schuhmacher M, Llobet JM (2002a) *Monitoring dioxins and furans in the vicinity of an old municipal waste incinerator after pronounced reductions of the atmospheric emissions*. J. Environ. Monit. 4: 395-399.
- Domingo JL, Schuhmacher M, Agramunt MC, Llobet JM, Rivera J, Müller L (2002b) *PCDD/F levels in the neighbourhood of a municipal solid waste incinerator after introduction of technical improvements in the facility*. Environ. Int. 28: 19-27.
- Dorr G, Hippelein M, Hutzinger O (1996) *Baseline contamination assessment for a new resource recovery facility in Germany. Part V: Analysis and seasonal/ regional variability of ambient air concentrations of polychlorinated naphthalenes (PCN)*. Chemosphere 33: 1563-1568.
- dos Santos A, Colacciopo S, Dal Bó C, dos Santos N (1994) *Occupational exposure to lead, kidney function tests, and blood pressure*. Am. J. Ind. Med. 26: 635-645.
- Dyke PH, Foan C, Fiedler H (2003) *PCB and PAH releases from power stations and waste incineration processes in the UK*. Chemosphere 50: 469-480.
- Egebäck A, Wideqvist U, Järnberg U, Asplund L (2004) *Polychlorinated naphthalenes in Swedish background air*. Environ. Sci. Technol. 38: 4913-4920.
- Ekino S, Susa M, Ninomiya T, Imamura K, Kitamura T (2007) *Minamata disease revisited: An update on the acute and chronic manifestations of methyl mercury poisoning*. J. Neurol. Sci. 262: 131-144.
- Eljarrat E, Barcelo D (2003) *Priority lists for persistent organic pollutants and emerging contaminants based on their relative toxic potency in environmental samples*. Trends Anal. Chem. 22: 655-665.
- EPA US, 1998. *Methodology for Assessing Health Risks Associated with Multiple Pathways of Exposure to Combustor Emissions*. U.S. EPA, National Center for Environmental Assessment, Cincinnati.
- Evenset A, Christensen G, Skotvold T, Fjeld E, Schlabach M, Wartena E, Gregor D (2004) *A comparison of organic contaminants in two high Arctic lake ecosystems, Bjornoya (Bear Island), Norway*. Sci. Total Environ. 318: 125-141.
- Falandysz J (1998) *Polychlorinated naphthalenes: an environmental update*. Environ. Pollut. 101: 77-90.
- Fattorini D, Alonso-Hernandez C, Diaz-Asencio M, Munoz-Caravaca A, Pannacciulli F, Tangherlini M, Regoli F (2004) *Chemical speciation of arsenic in different marine organisms: Importance in monitoring studies*. Marine Environ. Res. 58: 845-850.
- Ferreira-Baptista L, De Miguel E (2005) *Geochemistry and risk assessment of street dust in Luanda, Angola: A tropical urban environment*. Atmos. Environ. 39: 4501-4512.

- Ferreira C, Ribeiro A, Ottosen L (2003) *Possible applications for municipal solid waste fly ash*. J. Hazard. Mat. 96: 201-216.
- Fiedler H, Hutzinger O (1990) *Dioxins: sources of environmental load and human exposure*. Toxicol. Environ. Chem. 29: 157-234.
- Finkelstein Y, Markowitz ME, Rosen JF (1998) *Low-level lead-induced neurotoxicity in children: an update on central nervous system effects*. Brain Res. Rev. 27: 168-176.
- Frey HC, Zhao Y (2004) *Quantification of Variability and Uncertainty for Air Toxic Emission Inventories with Censored Emission Factor Data*. Environ. Sci. Technol. 38: 6094-6100.
- Friess S (1987) *Risk Assessment historical perspectives*. In *Pharmacokinetics in Risk Assessment: Drinking Water and Health, Vol. 8*. National Academy of Science, Washington, DC, pp. 3-7.
- Gambaro A, Manodori L, Moret I, Capodaglio G, Cescon P (2004) *Determination of polychlorobiphenyls and polycyclic aromatic hydrocarbons in the atmospheric aerosol of the Venice Lagoon*. Anal. Bioanal. Chem. 378: 1806-1814.
- Gao Y, Nelson ED, Field MP, Ding Q, Li H, Sherrell RM, Gigliotti CL, Van Ry DA, Glenn TR, Eisenreich SJ (2002) *Characterization of atmospheric trace elements on PM<sub>2.5</sub> particulate matter over the New York-New Jersey harbor estuary*. Atmos. Environ. 36: 1077-1086.
- Garcia-Alonso S, Perez-Pastor RM, Quejido-Cabezas AJ (2002) *Chemometric study of selected polychlorinated biphenyls in ambient air of Madrid (Spain)*. Talanta 57: 773-783.
- Generalitat de Catalunya, 1997. *La Qualitat de l'Aire a Catalunya, dades del període 1997-1998. Xarxa de Vigilància i Previsió de la Contaminació Atmosfèrica de Catalunya (XVPCA)*. Departament de Medi Ambient i Habitatge, Barcelona, Spain.
- Generalitat de Catalunya, 2000. *Nivells de qualitat de l'aire mesurats durant el període 1999-2000. Xarxa de Vigilància i Previsió de la Contaminació Atmosfèrica de Catalunya (XVPCA)*. Departament de Medi Ambient i Habitatge, Barcelona, Spain.
- Generalitat de Catalunya, 2003. *La qualitat de l'aire a Catalunya. Xarxa de Vigilància i Previsió de la Contaminació Atmosfèrica de Catalunya (XVPCA)*. Departament de Medi Ambient i Habitatge, Barcelona, Spain.
- Generalitat de Catalunya, 2005. *Partícules Totals en suspensió: PST. Xarxa de Vigilància i Previsió de la Contaminació Atmosfèrica de Catalunya (XVPCA)*. Departament de Medi Ambient i Habitatge, Barcelona, Spain.
- Gilbert M (2003) *Perinatal exposure to Polychlorinated Biphenyls alters excitatory synaptic transmission and short-term plasticity in the hippocampus of the adult rat*. Neurotoxicol. 24: 851-860.
- Glorennec P, Zmirou D, Bard D (2005) *Public health benefits of compliance with current E.U. emissions standards for municipal waste incinerators: A health risk assessment with the CalTox multimedia exposure model*. Environ. Int. 31: 693-701.
- Göen T, Gündel J, Schaller K, Angerer J (1995) *The elimination of 1-hydroxypyrene in the urine of the general population and workers with different occupational exposures to PAH*. Sci. Total Environ. 163: 195-201.

- Gouin T, Cousins I, Mackay D (2004) *Comparison of two methods for obtaining degradation half-lives*. . Chemosphere 56: 531-535.
- Graham J, Hartwell J (1997) *The Greening of Industry: A Risk Management Approach*. Harvard University Press, Cambridge, MA.
- Granero S, Domingo JL (2002) *Levels of metals in soils of Alcala de Henares, Spain: human health risks*. Environ. Int. 28: 159-164.
- Grimalt JO, van Drooge BL (2006) *Polychlorinated biphenyls in mountain pine (Pinus uncinata) needles from Central Pyrenean high mountains (Catalonia, Spain)*. Ecotoxicol. Environ. Saf. 63: 61-67.
- Guyonnet D, Dubois D, Bourguin B, Fargier H, Côme B, Chilès JP (2003) *Hybrid method for addressing uncertainty in risk assessments*. J. Environ. Eng. 129: 68-78.
- Haines YY, 1998. *Risk modeling, assessment, and management*. Wiley, New York
- Hanari N, Horii Y, Taniyasu S, Falandysz J, Bochentin I, Orlikowska A, Puzyn T, Yamashita N (2004) *Isomer specific analysis of polychlorinated naphthalenes in pine trees (Pinus thunbergi Parl.) and (Pinus densiflora Sieb. et Zucc) needles around Tokyo Bay, Japan*. Polish J. Environ. Studies 13: 139-151.
- Hanss AM (2002) *The transformation method for the simulation and analysis of systems with uncertain parameters*. Fuzzy Sets Syst 130: 277-289.
- Harner T, Bidleman TF (1997) *Polychlorinated naphthalenes in urban air*. Atmos. Environ. 31: 4009-4016.
- Harner T, Bidleman T (1998) *Measurement of octanol-air partition coefficients for polycyclic aromatic hydrocarbons and polychlorinated naphthalenes*. J. Chem. Eng. Data 43: 40-46.
- Harner T, Kylin H, Bidleman T, Halsall C, Strachan W, Barrie L, Fellin P (1998) *Polychlorinated naphthalenes and coplanar polychlorinated biphenyls in arctic air*. Environ. Sci. Technol. 32: 3257-3265.
- Harner T, R.G.M. L, Jones KC (2000) *Polychlorinated naphthalenes in the atmosphere of the United Kingdom*. Environ. Sci. Technol. 34: 3137-3142.
- Harner T, Shoeib M, Diamond M, Stern G, Rosenberg B (2004) *Using passive air samplers to assess urban-rural trends for persistent organic pollutants. 1. Polychlorinated biphenyls and organochlorine pesticides*. Environ. Sci. Technol. 38: 4474-4483.
- Harner T, Pozo K, Gouin T, Macdonald A-M, Hung H, Caine J, Peters A (2006) *Global pilot study for persistent organic pollutants (POPs) using PUF disk passive air samplers*. Environ. Pollut. 144: 445-452.
- Harrad S, Mao H (2004) *Atmospheric PCBs and organochlorine pesticides in Birmingham, UK: concentrations, sources, temporal and seasonal trends*. Atmos. Environ. 38: 1437-1445.
- Hawley JK (1986) *Assessment of health risk from exposure to contaminated soil*. Risk Anal. 5: 289-302.
- Hayward D (1998) *Identification of bioaccumulating polychlorinated naphthalenes and their toxicological significance*. Environ. Res. 76: 1-18.

- Helm P, Bidleman T (2003) *Current Combustion-Related Sources Contribute to Polychlorinated Naphthalene and Dioxin-Like Polychlorinated Biphenyl Levels and Profiles in Air in Toronto, Canada*. Environ. Sci. Technol. 37: 1075-1082.
- Hong C, Tsai J, Lin S (1999) *Determination of urinary arsenic, mercury, and selenium in steel production workers*. Biol. Trace Elem. Res. 70: 29-40.
- Hotelling H (1933) *Analysis of a complex of statistical variables into principal components*. J. Educ. Psychol. 24.
- Huff J, Chan P, Nyska A (2000) *Is the human carcinogen arsenic carcinogenic to laboratory animals?* Toxicol. Sci. 55: 17-23.
- Hung H, Chi Lee S, Wania F, Blanchard P, Brice K (2005) *Measuring and simulating atmospheric concentration trends of polychlorinated biphenyls in the Northern Hemisphere*. Atmos. Environ. 39: 6502-6512.
- IARC (1983) *Polycyclic aromatic compounds: Part 1. Chemical, environmental data*. In: *IARC monographs on the evaluation of carcinogenic risks of chemicals to humans*. Vol. 32.
- IARC (1987) *Overall Evaluations of Carcinogenicity: an Updating of IARC Monographs Volumes 1 to 42*. In: *IARC Monographs on the Evaluation of Carcinogenic Risks to Humans, supplement 7*. International Agency for Research on Cancer. Lyon, France.
- IARC (1990) *Monographs on evaluation of carcinogenic risks to humans: chromium, nickel and welding*. The International Agency for Cancer Research. Lyon, France. Vol. 49.
- IARC (1995) *Monograph Volumes 1972-1994*, WHO, Geneva, Switzerland, pp 1-60, <http://www.holgr/medical/nuclear/carcinogen.htm>.
- IARC (1997) *Monographs on the Evaluation of Carcinogenic Risk to Humans. Polychlorinated Dibenzo-para-Dioxins and Polychlorinated Dibenzofurans*, Vol. 69. IarcPress, Lyon.
- Iman RL, Helton JC, 1985. A Comparison of Uncertainty and Sensitivity Analysis Techniques for Computer Models, Technical Report SAND84-1461. Sandia National Laboratories, Albuquerque, NM.
- Isukapalli SS, 1999. Uncertainty Analysis of Transport-Transformation Models, Chemical and Biochemical Engineering. The State University of New Jersey, New Brunswick.
- Janssen PHM, Heuberger PSC, Sanders R, 1992. UNCSAM 1.1: A software package for sensitivity and uncertainty analysis. National Institute of Public Health and Environmental Protection, Bilthoven, The Netherlands.
- Jarnberg U, Asplund L, De Wit C, Grafstrom A, Haglund P, Jansson B, Lexen K, Strandell M, Olsson M, Jonsson B (1993) *Polychlorinated biphenyls and polychlorinated naphthalenes in Swedish sediment and biota: Levels, patterns, and time trends*. Environ. Sci. Technol. 27: 1364-1374.
- Jaward FM, Barber JL, Booij K, Jones KC (2004a) *Spatial distribution of atmospheric PAHs and PCNs along a north-south Atlantic transect*. Environ. Pollut. 132: 173-181.

- Jaward FM, Meijer SN, Steinnes E, Thomas GO, Jones KC (2004b) *Further studies on the latitudinal and temporal trends of persistent organic pollutants in Norwegian and U.K. background air*. Environ. Sci. Technol. 38: 2523-2530.
- Jaward FM, Farrar NJ, Harner T, Sweetman AJ, Jones JL (2005) *Passive air sampling of polycyclic aromatic hydrocarbons and polychlorinated naphthalenes across Europe*. Environ. Toxicol. Chem. 23: 1355-1364.
- Jongeneelen F (2001) *Benchmark guideline for urinary 1-hydroxypyrene as biomarker of occupational exposure to polycyclic aromatic hydrocarbons* Ann. Occup. Hyg. 45: 3-13.
- Josephs K, Ahlskog J, Klos K, Kumar N, Fealey R, Trenerry M, Cowl C (2005) *Neurologic manifestations in welders with pallidal MRI T1 hyperintensity*. Neurology 64: 2033-2039.
- Kannan K, Imagawa T, Blankenship A, Giesy J (1998) *Isomer-specific analysis and toxic evaluation of polychlorinated naphthalenes in soil, sediment, and biota collected near the site of a former chlor-alkali plant*. Environ. Sci. Technol. 32: 2507-2514.
- Kannan K, Hilscherova K, Imagawa T, Yamashita N, Williams L, Giesy J (2001) *Polychlorinated naphthalenes, -biphenyls, -dibenzo-p-dioxins, and -dihenzofurans in double-crested cormorants and herring gulls from Michigan waters of the Great Lakes*. Environ. Sci. Technol. 35: 441-447.
- Kao W, Ma H, Wang L, Chang-Chien G (2007) *Site-specific health risk assessment of dioxins and furans in an industrial region with numerous emission sources*. J. Hazard. Mater. 145: 471-481.
- Karimi A, Moniri F, Nasihatkon A, Zarepoor M, Alborzi A (2002) *Mercury exposure among residents of a building block in Shirz, Iran*. Environ. Res. Section A 88: 41-43.
- Kasuya M (2000) *Recent epidemiological studies on itai-itai disease as a chronic cadmium poisoning in Japan*. Water Sci. Technol. 42: 147-154.
- Kentel E, Aral MM (2004) *Probabilistic-fuzzy health risk modeling*. Stoch. Environ. Res. Risk Assess. (SERRA) 18: 324-338.
- Kentel E, Aral MM (2005) *2D Monte Carlo versus 2D Fuzzy Monte Carlo health risk assessment*. Stoch. Environ. Res. Risk Assess. (SERRA) 19: 86.
- Kim D, Min Y, Jeong J, Kim G, Kim J, Son C, Lee D (2007) *Ambient air monitoring of PCDD/Fs and co-PCBs in Gyeonggi-do, Korea*. Chemosphere 67: 1722-1727.
- Kimbrough R (1995) *Polychlorinated biphenyls (PCBs) and human health: An update*. Crit. Rev. Toxicol. 25: 133-163.
- King R (1988) *King R (1988) Mercury poisoning and its control. (ed) United Trade Press Limited, Londres*.
- Klir GJ, Yuan B, 1995. *Fuzzy Sets and Fuzzy Logic, Theory and Applications*. Prentice Hall, Upper Saddle River, NJ, USA.
- Krauthacker B, Herceg Romanic S, Wilken M, Milanovic Z (2006) *PCDD/Fs in ambient air collected in Zagreb, Croatia*. Chemosphere 62: 1829-1837.
- Kutz F, Barnes D, Bottimore D (1990) *The international toxicity equivalency factor (I-TEF) method of risk assessment for complex mixtures of dioxins and related compounds*. Chemosphere 20: 751-757.

- Lee R, Thomas G, Jones K (2005) *Detailed study of factors controlling atmospheric concentrations of PCNs*. Environ. Sci. Technol. 39: 4729-4738.
- Lemesh R (1992) *Polychlorinated biphenyls: An overview of metabolic, toxicologic and health consequences*. Vet. Hum. Toxicol. 34: 256-260.
- Li H, Krieger R, Li Q (2000) *Improved HPLC method for analysis of 1 hydroxypyrene in human urine specimens of cigarette smokers*. Sci. Total Environ. 257: 147-153.
- Lin Y, Gupta G, Baker J (1995) *Photodegradation of polychlorinated biphenyl congeners using simulated sunlight and diethylamine*. Chemosphere 31: 3323-3344.
- Linak WP, Wendt JOL (1993) *Toxic metal emissions from incineration: Mechanisms and control*. Progr. Energy Combust. Sci 19: 145-185.
- Linna A, Oksa P, Palmroos P, Roto P, Laippala P, Uitti J (2003) *Respiratory health of cobalt production workers*. Am. J. Ind. Med. 44: 124-132.
- Lohmann R, Jones KC (1998) *Dioxins and furans in air and deposition: A review of levels, behaviour and processes*. Sci. Total Environ. 219: 53-81.
- Lönnermark A, Blomqvist P, Marklund S (2008) *Emissions from simulated deep-seated fires in domestic waste*. Chemosphere 70: 626-639.
- López JM, Callén MS, Murillo R, García T, Navarro MV, de la Cruz MT, Mastra AM (2005) *Levels of selected metals in ambient air PM10 in an urban site of Zaragoza (Spain)*. Environ. Res. 99: 58-67.
- Loska K, Wiechula D, Korus I (2004) *Metal contamination of farming soils affected by industry*. Environ. Int. 30: 159-165.
- Llobet JM, Schuhmacher M, Domingo JL (2002) *Spatial distribution and temporal variation of metals in the vicinity of a municipal solid waste incinerator after a modernization of the flue gas cleaning systems of the facility*. Sci. Total Environ. 284: 205-214.
- Mackay D, Shiu W, Ma K (1992) *Illustrated handbook of physical-chemical properties and environmental fate for organic chemicals: polynuclear aromatic hydrocarbons, polychlorinated dioxins and dibenzofurans*. Lewis Publishers. Chelsea, MI, USA.
- Manache G, 2001. Sensitivity of a continuous water-quality simulation model to uncertain model-input parameters, Chair of Hydrology and Hydraulics. Vrije Universiteit Brussel, Brussels, Belgium.
- Mandalakis M, Tsapakis M, Tsoga A, Stephanou EG (2002) *Gas-particle concentrations and distribution of aliphatic hydrocarbons, PAHs, PCBs and PCDD/Fs in the atmosphere of Athens (Greece)*. Atmos. Environ. 36: 4023-4035.
- Manodori L, Gambaro A, Zangrando R, Turetta C, Cescon P (2006) *Polychlorinated naphthalenes in the gas-phase of the Venice Lagoon atmosphere*. Atmos. Environ. 40: 2020-2029.
- Mauris G, Lasserre V, Foulloy L (2001) *A fuzzy approach for the expression of uncertainty in measurement*. Measurement 29: 165-177.
- McElroy J, Shafer M, Trentham-Dietz A, Hampton J, Newcomb P (2006) *Cadmium Exposure and Breast Cancer Risk*. J. Natl. Cancer Inst. 98: 869-873.
- McKay MD, Beckman RJ, Conover WJ (1979) *A comparison of three methods for selecting values of input variables in the analysis of output from a computer code*. Technometrics 21: 239-245.

- McKay MD, 1992. Latin hypercube sampling as a tool in uncertainty analysis of computer models, Proceedings of the 24th conference on Winter simulation. ACM Press, Arlington, Virginia, United States.
- Meijer S, Harner T, Helm P, Halsall C, Johnston A, Jones K (2001) *Polychlorinated naphthalenes in U.K. soils: Time trends, markers of source, and equilibrium status*. Environ. Sci. Technol. 35: 4205-4213.
- Meijer S, Ockenden W, Steinnes E, Corrigan B, Jones K (2003) *Spatial and temporal trends of POPs in Norwegian and UK background air: Implications for global cycling Environmental Science and Technology 37: 454-461*. Environ. Sci. Technol. 37: 454-461.
- Meneses M, Llobet JM, Granero S, Schuhmacher M, Domingo JL (1999) *Monitoring metals in the vicinity of a municipal waste incinerator: temporal variation in soils and vegetation*. Sci. Total Environ. 226: 157-164.
- Menichini E, Iacovella N, Monfredini F, Turrio-Baldassarri L (2007) *Atmospheric pollution by PAHs, PCDD/Fs and PCBs simultaneously collected at a regional background site in central Italy and at an urban site in Rome*. Chemosphere 69: 422-434.
- Merz B, Thieken AH (2005) *Separating natural and epistemic uncertainty in flood frequency analysis*. J. Hydrol. 309: 114.
- Mesilio L, Farago ME, Thornton I (2003) *Reconnaissance soil geochemical survey of Gibraltar*. Environ. Geochem. Health 25: 1-8.
- Messerer P, Zober A, Becher H (1998) *Blood lipid concentrations of dioxins and furans in a sample of BASF employees included in the IARC registry of workers exposed to phenoxy acid herbicides and/or chlorophenols* Environ. Health Persp. 106: 733-735.
- Möller B, Graf W, Beer M, Sickert J, 2002. Fuzzy Randomness - Towards a new Modeling of Uncertainty, in: Mang, A.H., Rammerstorfer, F.G., Eberhardsteiner, J. (Eds.), Fifth World Congress on Computational Mechanics. iacm, Viena.
- Monaci F, Moni F, Lanciotti E, Grechi D, Bargagli R (2000) *Biomonitoring of airborne metals in urban environments: new tracers of vehicle emission, in place of lead*. Environ. Pollut. 107: 321-327.
- Moschandreas D, Karuchit S (2005) *Risk uncertainty matters: an engineer's view*. Int. J. Risk Assess. Manage. 5: 167-192.
- Nadal M, Schuhmacher M, Domingo J (2004) *Metal pollution of soils and vegetation in an area with petrochemical industry*. Sci. Total Environ. 321: 59-69.
- Navas-Acien A, Schwartz B, Rothenberg S, Hu H, Silbergeld E, Guallar E (2008) *Bone Lead Levels and Blood Pressure Endpoints: A Meta-Analysis*. Epidemiol. 19: 496-504.
- Negri E, Bosetti C, Fattore E, La Vecchia C (2003) *Environmental exposure to polychlorinated biphenyls (PCBs) and breast cancer: a systematic review of the epidemiological evidence*. Eur. J. Cancer Prev. 12: 509-516.
- Nizzetto L, Cassani C, Di Guardo A (2006) *Deposition of PCBs in mountains: The forest filter effect of different forest ecosystem types*. Ecotoxicol. Environ. Saf. 63: 75-83.

- Notten MJ, Oosthoek AJ, Rozema J, Aerts R (2005) *Heavy metal concentrations in a soil-plant-snail food chain along a terrestrial soil pollution gradient*. Environ. Pollut. 138: 178-190.
- Nouwen J, Cornelis C, De Fré R, Wevers M, Viaene P, Mensink C, Patyn J, Verschaeve L, Hooghe R, Maes A, Collier M, Schoeters G, Van Cleuvenbergen R, Geuzens P (2001) *Health risk assessment of dioxin emissions from municipal waste incinerators: the Neerlandquarter (Wilrijk, Belgium)*. Chemosphere 43: 909-923.
- NRC (1983) *Risk Assessment in the Federal Government: Managing the Process*. NAS, Washington, DC.
- OJEC, 2000. Directive 2000/76/EC of the European Parliament and of the Council of 4 December 2000 on the incineration of waste. Official Journal of the of European Communities.
- OMS (1977) *IARC Monographs on the evaluation of the cancerogenic risk of chemicals to man. Some fumigants. The Herbicides 2,4-d and 2,4,5-t. Chlorinated Dibenzodioxins and miscellaneous industrial chemicals*. IARC núm. 15. Lyon.
- Opperhuizen A, van der Velde E, Gobas F, Liem A, van der Steen J (1985) *Relationship between bioconcentration in fish and steric factors of hydrophobic chemicals*. Chemosphere 14: 1871-1896.
- OTAN (1998) *International Toxicity Equivalence Factors (I-TEF) Method of Risk Assessment for Complex Mixtures of Dioxins and Related Compounds. Report Number 176, August 1998, Comitee on Challenges of Modern Society, Brussels, Belgium*.
- Paustenbach D, 2002. *Human and Ecological Risk Assessment Theory and Practice*, New York.
- Pearson K (1901) *On lines and planes of closest fit to systems of points in space*. Philos. Magazine 2.
- Pebesma EJ, Heuvelink GBM (1999) *Latin hypercube sampling of Gaussian random fields*. Technometrics 41: 303-312.
- Pongratz R (1998) *Arsenic speciation in environmental samples of contaminated soil*. Sci.Total Environ. 224: 133-141.
- Pozo K, Harner T, Shoeib M, Urrutia R, Barra R, Parra O, Focardi S (2004) *Passive-sampler derived air concentrations of persistent organic pollutants on a north-south transect in Chile*. Environ. Sci. Technol. 38: 6529-6537.
- Pribylova P, Kukucka J, Klanova J, Holoubek I (2006) *Polychlorinated naphthalenes and chlorinated parafins in the air and soil samples of the Czech Republic*. Organohalogen Compds. 68: 37-40.
- Rappe C (1992) *Sources of PCDDs and PCDFs. Introduction, reactions, levels, patterns, profiles and trends*. Chemosphere 25: 41-44.
- Raun LH, Correa O, Rifai H, Suarez M, Koenig L (2005) *Statistical investigation of polychlorinated dibenzo-p-dioxins and dibenzofurans in the ambient air of Houston, Texas*. Chemosphere 60: 973-989.
- Refsgaard JC, van der Sluijs JP, Hojberg AL, Vanrolleghem PA (2007) *Uncertainty in the environmental modelling process - A framework and guidance*. Environ. Model. Software 22: 1543.

- Rimmer DL, Vizard CG, Pless-Mulloli T, Singleton I, Air VS, Keatinge ZAF (in press) *Metal contamination of urban soils in the vicinity of a municipal waste incinerator: One source among many*. *Sci. Total Environ.*
- Robards K, Worsford P (1991) *Cadmium: toxicology and analysis. A review*. *Analyst* 116: 549-568.
- Rossmann T, Uddin A, Burns F (2004) *Evidence that arsenite acts as a cocarcinogen in skin cancer*. *Toxicol. Appl. Pharmacol.* 198: 394-404.
- Rotmans J, van Asselt MBA (2001) *Uncertainty in Integrated Assessment Modelling: A Labyrinthic Path*. *Integr. Assess.* 2: 43.
- Ruiz-Cortés E, Reinoso R, Díaz-Barrientos E, Madrid L (2005) *Concentrations of potentially toxic metals in urban soils of Seville: Relationship with different land uses*. *Environ. Geochem. Health* 27: 465-474.
- Rylander L, Strömberg U, Hagmar L (1996) *Dietary intake of fish contaminated with persistent organochlorine compounds in relation to low birthweight*. *Scand. J. Work Environ. Health.* 22: 260-266.
- Rylander L, Strömberg U, Dyremark E, Östman C, Nilsson-Ehle P, Hagmar L (1998) *Polychlorinated biphenyls in blood plasma among Swedish female fish consumers in relation to low birth weight*. *Am. J. Epidemiol.* 147: 493-502.
- Safe S (1990) *Polychlorinated Biphenyls (PCBs), Dibenzo-p-Dioxins (PCDDs), Dibenzofurans (PCDFs), and related compounds: Environmental and mechanistic considerations which support the development of toxic equivalency factors (TEFs)*. *Crit. Rev. Toxicol.* 21: 51-88.
- Saha A (2005) *Thallium toxicity: A growing concern*. *Indian J. Occup. Environ. Med.* 9: 53-56.
- Sardans J, Peñuelas J (2005) *Trace element accumulation in the moss *Hypnum cupressiforme* Hedw. and the trees *Quercus ilex* L. and *Pinus halepensis* Mill. in Catalonia*. *Chemosphere* 60: 1293-1307.
- Satarug S, Moore M (2004) *Adverse Health Effects of Chronic Exposure to Low-Level Cadmium in Foodstuffs and Cigarette Smoke*. *Environ. Health Perspect.* 112: 1099-1103.
- Schneider M, Stieglitz L, Will R, Zwick G (1998) *Formation of polychlorinated naphthalenes on fly ash*. *Chemosphere* 37: 2055-2070.
- Schuhmacher M, Bellés M, Rico A, Domingo JL, Corbella J (1996) *Impact of reduction of lead in gasoline on the blood and hair lead levels in the population of Tarragona Province, Spain, 1990-1995*. *Sci. Total Environ.* 184: 203-209.
- Schuhmacher M, Xifro A, Llobet JM, de Kok HA, Domingo JL (1997) *PCDD/Fs in soil samples collected in the vicinity of a municipal solid waste incinerator: human health risks*. *Arch. Environ. Contam. Toxicol.* 33: 239-246.
- Schuhmacher M, Granero S, Xifro A, Domingo JL, Rivera J, Eljarrat E (1998) *Levels of PCDD/Fs in soil samples in the vicinity of a municipal solid waste incinerator*. *Chemosphere* 37: 2127-2137.
- Schuhmacher M, Domingo JL, Granero S, Llobet JM, Eljarrat E, Rivera J (1999) *Soil monitoring in the vicinity of a municipal solid waste incinerator: Temporal variation of PCDD/Fs*. *Chemosphere* 39: 419-429.

- Schuhmacher M, Granero S, Rivera J, Muller L, Llobet JM, Domingo JL (2000) *Atmospheric deposition of PCDD/Fs near an old municipal solid waste incinerator: levels in soil and vegetation*. Chemosphere 40: 593-600.
- Schuhmacher M, Meneses M, Xifro A, Domingo JL (2001) *The use of Monte-Carlo simulation techniques for risk assessment: study of a municipal waste incinerator*. Chemosphere 43: 787-799.
- Schuhmacher M, Bocio A, Agramunt MC, Domingo JL, de Kok HA (2002a) *PCDD/F and metal concentrations in soil and herbage samples collected in the vicinity of a cement plant*. Chemosphere 48: 209-217.
- Schuhmacher M, Bocio A, Agramunt MC, Domingo JL, de Kok HAM (2002b) *PCDD/F and metal concentrations in soil and herbage samples collected in the vicinity of a cement plant*. Chemosphere 48: 209-217.
- Schuhmacher M, Agramunt MC, Bocio A, Domingo JL, de Kok HAM (2003) *Annual variation in the levels of metals and PCDD/PCDFs in soil and herbage samples collected near a cement plant*. Environ. Int. 29: 415-421.
- Schuhmacher M, Domingo JL (2006) *Long-term study of environmental levels of dioxins and furans in the vicinity of a municipal solid waste incinerator*. Environ. Int. 32: 397-404.
- Schuhmacher M, Jones KC, Domingo JL (2006) *Air-vegetation transfer of PCDD/PCDFs: An assessment of field data and implications for modeling*. Environ. Pollut. 142: 143-150.
- Schulz K, Huwe B (1999) *Uncertainty and sensitivity analysis of water transport modelling in a layered soil profile using fuzzy set theory*. J. Hydroinformatics 1: 127-138.
- Shirai J, Kissel J (1996) *Uncertainty in estimated half-lives of PCBS in humans: impact on exposure assessment*. Sci. Total Environ. 187: 199-210.
- Shoeib M, Harner T (2002) *Characterization and comparison of three passive air samplers for persistent organic pollutants*. Environ. Sci. Technol. 36: 4142-4151.
- Simon TW (1999) *Two-Dimensional Monte Carlo Simulation and Beyond: A Comparison of Several Probabilistic Risk Assessment Methods Applied to a Superfund Site*. Human Ecol. Risk Assess. 5: 823 - 843.
- Singh J, Carlisle D, Pritchard D, Patierno S (1998) *Chromium-induced genotoxicity and apoptosis: relationship to chromium carcinogenesis (review)*. Oncol. Rep. 5: 1307-1318.
- Sinkkonen S, Paasivirta J (2000) *Degradation half-life times of PCDDs, PCDFs and PCBs for environmental fate modeling* Chemosphere 40: 943-949.
- Spencer M, Fisher NS, Wang W-X, Ferson S (2001) *Temporal Variability and Ignorance in Monte Carlo Contaminant Bioaccumulation Models: A Case Study with Selenium in Mytilus edulis*. Risk Anal. 21: 383-394.
- Starr C (1969) *Social benefit versus technological risk*. Science 1365: 1232-1238.
- Sweetman A, Jones K (2000) *Declining PCB concentrations in the U.K. atmosphere: Evidence and possible causes*. Environ. Sci. Technol. 34: 863-869.
- Takasuga T, Inoue T, Ohi E, Kumar K (2004) *Formation of Polychlorinated Naphthalenes, Dibenzo-p-Dioxins, Dibenzofurans, Biphenyls, and Organochlorine*

- Pesticides in Thermal Processes and Their Occurrence in Ambient Air*. Arch. Environ. Contam. Toxicol. 46: 419-431.
- Torrente M, Colomina M, Domingo J (2005) *Metal concentrations in hair and cognitive assessment in an adolescent population*. Biol. Trace Elem. Res. 104: 215-221.
- Tosine HM, Clement RE, Ozvacic V, Wong G (1985) *Levels of PCDD/PCDF and other chlorinated organics in municipal refuse*. Chemosphere 14: 821-827.
- Tung JWT, Yu JZ, Lau AKH, Louie PKK (2005) *Abundance and sources of ambient dioxins in Hong Kong: A review of dioxin measurements from 1997 to 2001*. Chemosphere 59: 1387-1398.
- Turrio-Baldassarri L, Abate V, Iacovella N, Monfredini F, Menichini E (2005) *Occurrence of PCDD/Fs in urban air before and after the ban of leaded gasoline*. Chemosphere 59: 1517-1524.
- Uchida T, Itoh I, Harada K (1996) *Immobilization of heavy metals contained in incinerator fly ash by application of soluble phosphate-Treatment and disposal cost reduction by combined use of "High Specific Surface Area Lime"*. Waste Manag. 16: 475-481.
- UNECE (1998) *Protocol to the 1979 Convention on Long-Range Transboundary Air Pollution on Persistent Organic Pollutants*. New York and Geneva. Available at: [www.unece.org/env/lrtap/full%20text/1998.POPs.e.pdf](http://www.unece.org/env/lrtap/full%20text/1998.POPs.e.pdf).
- U.S. EPA, (1997). Terms of Environment: Glossary, Abbreviations and Acronyms
- U.S. EPA, (2005). Guidelines for Carcinogen Risk Assessment, in: EPA/630/P-03/001F (Ed.), Washington, DC.
- US EPA (1999) *Integrated Risk Information System (IRIS)*. National Center for Environmental Assessment, US Environmental Protection Agency. Washington, DC. Available at: [www.epa.gov/iris/](http://www.epa.gov/iris/).
- US EPA, (2004). Preliminary Remediation Goals.  
Available at: <http://www.epa.gov/region09/waste/sfund/prg/index.html>.
- USEPA, (2007). Preliminary Remediation Goals.  
Available at: [www.epa.gov/earth1r6/6pd/tcra\\_c/pd-n/screenexpanded.xls](http://www.epa.gov/earth1r6/6pd/tcra_c/pd-n/screenexpanded.xls).
- USEPA, (1999) *Compendium method TO-9A, "Determination of polychlorinated, polybrominated/chlorinated dibenzo-p-dioxins and dibenzofurans in ambient air*. EPA/625/R-96/010b. Center for Environmental Research Information, Office of Research and Development, Cincinnati, OH.
- USEPA, (2005) *The inventory of sources and environmental releases of dioxin-like compounds in the United States: the year 2000 update. Draft*. EPA/600/P-03/002A. National Center for Environmental Assessment, US Environmental Protection Agency. Washington, DC. Available at: <http://www.epa.gov/ncea/pdfs/dioxin2k-update/>.
- USEPA, (2007) *Basic Emissions Factors Information*. Available at: <http://www.epa.gov/ttn/chief/efpac/abefpac.html>.
- Vaglenov A, Nosko M, Georgieva R, Carbonell E, Creus A, Marcos R (1999) *Genotoxicity and radioresistance in electroplating workers exposed to chromium*. Mutation Research/Genetic Toxicol. Environ. Mutagen. 446: 23-34.
- van Asselt MBA, Rotmans J (2002) *Uncertainty in Integrated Assessment Modelling*. Clim. Change 54: 75.

- Van de Plassche E, Schwegler A, Iestra W (2002) *Polychlorinated naphthalenes and the UN-ECE POP Protocol*. *Organohalogen Compds.* 58: 89-91.
- Van den Berg M, Peterson R, Schrenk D (2000) *Human risk assessment and TEFs*. *Food Addit. Contam.* 17: 347-358.
- Van den Berg M, Birnbaum LS, Denison M, De Vito M, Farland W, Feeley M, Fiedler H, Hakansson H, Hanberg A, Haws L, Rose M, Safe S, Schrenk D, Tohyama C, Tritscher A, Tuomisto J, Tysklind M, Walker N, Peterson RE (2006) *The 2005 World Health Organization reevaluation of human and Mammalian toxic equivalency factors for dioxins and dioxin-like compounds*. *Toxicol. Sci.* 93: 223-241.
- van der Sluijs JP (2007) *Uncertainty and precaution in environmental management: Insights from the UPEM conference*. *Environ. Model. Software* 22: 590.
- Van Leeuwen F, Feeley M, Schrenk D, Larsen J, Farland W, Younes M (2000) *Dioxins: WHO's tolerable daily intake (TDI) revisited*. *Chemosphere* 40: 1095-1101.
- Viana M, Pérez C, Querol X, Alastueya A, Nickovic S, Baldasano JM (2005) *Spatial and temporal variability of PM levels and composition in a complex summer atmospheric scenario in Barcelona (NE Spain)*. *Atmos. Environ.* 39 39: 5343-5361.
- Walkowiak J, Wiener J, Fastabend A, Heinzow B, Kramer U, Schmidt E, Steingruber H, Wundram S, Winneke G (2001) *Environmental exposure to polychlorinated biphenyls and quality of the home environment: effects on psychodevelopment in early childhood*. *Lancet* 358: 1602-1607.
- Wang D, Atkinson S, Hoover-Miller A, Li QX (2007) *Polychlorinated naphthalenes and coplanar polychlorinated biphenyls in tissues of harbor seals (Phoca vitulina) from the northern Gulf of Alaska*. *Chemosphere* 67: 2044-2057.
- Wang J, Wang M, Wu E, Chang-Chien G, Lai Y (2008) *Approaches adopted to assess environmental impacts of PCDD/F emissions from a municipal solid waste incinerator*. *J. Hazard. Mater.* 152: 968-975.
- Wang S, Mulligan CN (2006) *Occurrence of arsenic contamination in Canada: Sources, behavior and distribution*. *Sci. Total Environ.* 366: 701-721.
- Wang X, Sato T, Xing B (2006) *Size distribution and anthropogenic sources apportionment of airborne trace metals in Kanazawa, Japan*. *Chemosphere* 65: 2440-2448.
- Wilcke W, Krauss M, Kobza J (2005) *Concentrations and forms of heavy metals in Slovak soils*. *J. Plant Nutr. Soil Sci.* 168: 676-686.
- Wilford BH, Harner T, Zhu JP, Shoeib M, Jones KC (2004) *Passive sampling survey of polybrominated diphenyl ether flame retardants in indoor and outdoor air in Ottawa, Canada: Implications for sources and exposure*. *Environ. Sci. Technol.* 38: 5312-5318.
- Yamashita N, Imagawa T, Miyazaki A (2000) *Concentrations and profiles of polychlorinated naphthalene congeners in eighteen technical polychlorinated biphenyl preparations*. *Environ. Sci. Technol.* 34: 4242-4254.
- Yeo H-G, Choi M, Chun M-Y, Kim T-W, Cho K-C, Sunwoo Y (2004) *Concentration characteristics of atmospheric PCBs for urban and rural area, Korea*. *Sci. Total Environ.* 324: 261-270.

- Yokota K, Johyama Y, Kunitani Y, Michitsuji H, Yamada S (2007) *Urinary elimination of nickel and cobalt in relation to airborne nickel and cobalt exposures in a battery plant*. Int. Arch. Occup. Environ. Health 80: 527–531.
- Zadeh LA (1965) *Fuzzy Sets*. Inform. Control 8: 338-353.
- Zadeh LA (1984) *Fuzzy probabilities*. Inform. Process. Manage. 20: 363–372.