

7. CONCLUSIONS

1. Els nivells plasmàtics de dioxines i furans a les poblacions de Mataró i Arenys de Mar observats el 2008 són equiparables als observats en altres països industrialitzats i els nivells de dioxines i furans en llet materna el 2008 a la població de Mataró són els més baixos dels publicats fins el moment.

2. L'evolució dels nivells sanguinis de dioxines i furans a les cohorts d'estudi va mostrar una lleugera tendència a l'augment durant el període 1995-1999 i una lleugera tendència al descens durant el període 1999-2005 i un comportament pràcticament pla durant el període 2005-08. Durant tot aquest període els nivells mitjans d'aquestes substàncies han oscil·lat entre 13 i 20 pg I-TEQ/g grassa, variacions en un marge força estret, pel que es podria considerar que s'han mantingut relativament estables al llarg de tot el període d'estudi.

3. La comparació de les mostres independents del 1995 i el 2008 mostra que durant els darrers 13 anys els nivells de dioxines i furans s'han mantingut més o menys estables a la població de Mataró (descens poc rellevant d'un 5%) i han experimentat un descens lleugerament més important a Arenys de Mar (d'aproximadament el 38%).

4. Com en les fases anteriors d'aquest estudi, el 2008 els nivells de dioxines i furans en sang al grup d'exposats a la planta incineradora no mostra diferències rellevants respecte dels grups controls, indicant que l'exposició a la planta incineradora no és un factor de risc per tenir uns nivells més elevats d'aquestes substàncies.

5. Des del 1997, els nivells sanguinis de PCBs han experimentat un descens constant en tots els grups d'estudi fins a situar-se en uns nivells molt propers a 1,0 µg/L a Mataró i a 1,4 µg/L a Arenys de Mar el 2008, uns valors que es poden considerar

baixos. El 2008 només el grup d'Arenys de Mar va trencar aquesta tendència al descens. La comparació de les mostres independents del 1995 i el 2008 mostra que durant els darrers 13 anys els nivells de PCBs han disminuït en aproximadament un 50% tant a la població de Mataró com en la d'Arenys de Mar.

6. El comportament dels nivells de PCBs al llarg dels últims 13 anys ha estat totalment independent de l'exposició a la planta incineradora.

7. En tots els grups d'estudi els nivells de plom en sang han experimentat una clara tendència a disminuir en els últims 13 anys. El 2008 no s'observa cap diferència en els nivells de plom en sang entre els diversos grups d'estudi, situant-se molt propers a 1 µg/dl en tots els casos, uns valors que es poden considerar baixos.

8. Els nivells de cadmi en sang s'han reduït a la meitat en els últims 13 anys, al llarg dels quals s'ha observat una homogeneïtzació en els valors dels diversos grups d'estudi que el 2008 eren molt propers al 0,1 µg/dl en tots els casos. Aquest descens es va produir entre el 1995 i el 2002 i, des d'aleshores, els valors de cadmi en sang a les poblacions de Mataró i Arenys de Mar s'han mantingut més o menys estables a uns valors clarament inferiors als de referència per a la població no exposada laboralment.

9. L'any 1999 es va observar un pic en la concentració urinària de crom. Des d'aleshores aquests nivells s'han mantingut estables en tots els grups a uns nivells urinaris per sota dels 0,5 µg/g creatinina, que es poden considerar baixos. Es considera que les petites diferències entre exposats i no exposats no tenen cap rellevança clínica.

10. Els nivells de mercuri en orina, que no havien mostrat cap tendència clara al llarg del període 1995-2005, han mostrat un descens en tots els grups d'estudi el 2008. No s'observen diferències en els nivells de mercuri en orina entre exposats i

no exposats a la planta incineradora, situant-se aquest nivells per sota de 1 µg/g creatinina en tots els casos, uns nivells que es consideren baixos.

11. Després d'un lleuger descens dels nivells de níquel en orina entre el 2002 i el 2005, aquests nivells s'han mantingut estables durant el període 2005-2008. Les petites diferències observades entre exposats i no exposats a la planta incineradora no es consideren clínicament rellevants i aquests valors en tots dos grups es consideren baixos.

12. Els nivells d'arsènic en orina van experimentar un ascens entre el 2002 i el 2005 i un lleuger descens entre el 2005 i el 2008. No s'observen diferències rellevants entre els diversos grups d'estudi.

13. En cap cas els nivells dels metalls pesants considerats han superat els valors de referència per la població no exposada laboralment.

14. Durant els 13 anys de seguiment de l'estudi, en els treballadors de la planta incineradora no s'han observat canvis importants en els nivells de dioxines i furans (que se situen al voltant dels 15 pg I-TEQ/g grassa), els nivells de PCBs indicadors van mostrar un pic el 1999, un important descens el 2002 i des d'aleshores una estabilització (situant-se el 2008 en uns valors inferiors a 1,2 µg/L) i, pel que fa als metalls pesants, el seu comportament no ha estat diferent a l'observat en els altres grups d'estudi.



Environmental monitoring of metals, PCDD/Fs and PCBs as a complementary tool of biological surveillance to assess human health risks

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ABSTRACT

The results of an environmental program around the municipal solid waste incinerator (MSWI) of Mataró (Catalonia, Spain), which was designed to assess the potential impact of the facility on the close environment and the health of the population living in the vicinity, are here reported. Metals, polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs) and polychlorinated biphenyls (PCBs) were analyzed in soil and air samples collected in/around the facility. In soils, Mn and Zn showed the highest metal concentrations (ranges: 136–648 mg kg⁻¹ and 29.6–97.8 mg kg⁻¹, respectively), while total concentrations of PCDD/Fs and PCBs were 0.14–0.46 ng WHO-TEQ kg⁻¹ and 167–3340 ng kg⁻¹, respectively. In air, the highest metal levels corresponded to Cu (range: 26.9–52.9 ng m⁻³) and Mn (range: 6.92–19.3 ng m⁻³), while those of PCDD/Fs and PCBs ranged 0.008–0.015 pg WHO-TEQ m⁻³ and 9.20–42.1 pg m⁻³, respectively. Carcinogenic and non-carcinogenic risks derived of exposure to metals, PCDD/Fs and PCBs did not exceed the threshold values. Complementarily analyzed with the results obtained in the concurrent biomonitoring study and the stack emissions, data indicate that the MSWI of Mataró does not mean significant human health risks derived of emissions of metals, PCDD/Fs and PCBs.

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1. Introduction

Human biomonitoring provides a measure of exposure to chemical pollutants through all relevant pathways making possible to identify trends and changes in exposure. This is the main reason to considerate it as an ideal instrument for risk assessment and management (Angerer et al., 2007). On the other hand, to elucidate the sources of the exposure, it is critical to know the environmental concentration(s) of the chemical(s) under study to correct any risk situation.

Municipal solid waste incinerators (MSWIs) are potential sources of hazardous pollutants since they entail the combustion of a wide range of residues containing chlorine atoms and heavy metals (Van Caneghem et al., 2010). If not properly cleaned, emission gases may contain dangerous substances such as polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs), polychlorinated biphenyls (PCBs) and heavy metals, among others. All those chemicals are typically associated with adverse health effects (Alcock et al., 2003; Järup, 2003). In addition to their toxicological effects, some of them (e.g., organochlorinated compounds) are also characterized by their capacity for bioaccumulation and persistence (Nadal et al., 2009).

Although MSWIs have been considered traditional sources of the above mentioned pollutants (especially PCDD/Fs) their contribution to total emission has dramatically declined in recent years (Wang et al., 2008). This is basically a consequence of the recent technologies developed to comply with the strict emission regulations. In the European Union, until now the only industrial activities whose PCDD/F emissions have been legislated are waste incinerators. However, other activities such as traffic, cement plants, agricultural burning, home heating, etc. may also emit not only PCDD/Fs but also PCBs and heavy metals (Mari et al., 2008). In spite of the strict regulations, incineration continues generating a great controversy and concern in the general population, especially those living near the facilities.

In 1994, a MSWI started its regular operations in Mataró (Barcelona, Catalonia, Spain). To assess the potential exposure of the population living near the facility, a biological monitoring study was initiated. Since then, PCDD/F concentrations have been measured in blood samples of the population in consecutive surveys (Gonzalez et al., 1998, 2000), being the last one performed in 2009 (unpublished data). The results have shown a similar trend for the inhabitants living near and far from the MSWI, making evident that PCDD/F exposure is mainly determined by dietary intake. The purpose of the present study was to develop an environmental surveillance program by analyzing metals, PCDD/Fs and PCBs in soil and air samples in order to complement the results of the biomonitoring program, which is also being carried out.

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2. Materials and methods

2.1. Sampling

In November of 2008, soil and air samples were collected at different sampling points in the neighborhood of the MSWI of Mataró. Three sampling points were located in Mataró (one inside the MSWI, and two in Mataró city at >1 km and <1 km from the facility, respectively). An additional sample was taken in a control/background site located in the village of Arenys de Mar (Barcelona, Spain, 12 km from the facility). The facility capacity is 164 000 tons/year, providing service to 28 municipalities in the region.

Sampling of air and soil, as well as the analytical methodology have been recently described (Mari et al., 2007, 2008). Briefly, air samples were collected by means of high-volume active samplers (Tisch Environmental, Clevs, OH, USA) specific for organic compounds (TE-1000 PUF) or particulate matter (TE-6070DV). In turn, particle-bound and gas-phase PCDD/Fs were separately taken by using polyurethane foam (PUF) and quartz fibre filters. Volumes ranged from 2046 to 2272 m³, 300 to 346 m³, and 577 to 759 m³, for particulate matter, PCB and PCDD/F samples, respectively. Collection times were 24 h for both particulate matter and PCBs, whereas PCDD/F air sampling lasted for 48 h. Soil samples (500 g approximately), which consisted on four subsamples within an area of 25 m², were taken from the upper 5 cm of ground, dried at room temperature, and sieved through a 2 mm mesh screen.

2.2. Analytical procedure

2.2.1. Organochlorinated compounds

The determination of PCDD/Fs and PCBs in soil samples was done via High Resolution Gas Chromatography coupled to High Resolution Mass Spectrometry (HRGC/HRMS), in combination with the isotope dilution technique. It was based on the US EPA method 1613 for PCDD/Fs, and a combination of the US EPA Method 1668 and JIS K 0311 for PCBs. The concentrations of PCDD/Fs and PCBs in air were determined by HRGC/HRMS, following the German VDI 3499 method.

Appropriate labeled extraction standards (¹³C₁₂-PCDD/Fs substituted congeners, ¹³C₁₂-PCB congeners) were added in order to control the whole sample preparation process and to evaluate potential losses. An Accelerated Solvent Extraction (ASE) was carried out by using toluene. The extract was concentrated and divided into separate parts for the determination of the target compounds. The clean-up procedure was carried out by using adsorption chromatography on a mixed silica column and adsorption/fractionation on alumina. The final obtained PCDD/F- and PCB-extracts were injected and analyzed separately on an Agilent 6890 Capillary Gas Chromatograph equipped with a DB5-MS capillary column and coupled to a Waters Autospec Ultima High Resolution Mass Spectrometer, with selected ion recording at resolution of 10 000. Recovery percentages ranged 49–139% and 75–101%, for soil and air samples, respectively.

2.2.2. Metals

The pre-treatment of soil and air samples followed that previously described (Nadal et al., 2007). Briefly, 0.5 g of sample were digested with 5 mL of HNO₃ (65% Suprapur, E. Merck, Darmstadt, Germany) in Teflon bombs for 8 h at room temperature, and eight additional hours at 80 °C. On the other hand, quartz fibre filters were treated with a mixture of 2 mL of HNO₃ (65% Suprapur, E. Merck) and 3 mL of HF (37.5%, Panreac SA, Castellar del Vallès, Barcelona, Spain) in hermetic Teflon bombs for 8 h at room temperature and 8 h at 80 °C. Subsequently, the extract was evaporated in a sand bath, and reconstituted with HNO₃. The contents of arsenic

(As), cadmium (Cd), cobalt (Co), chromium (Cr), copper (Cu), mercury (Hg), manganese (Mn), nickel (Ni), lead (Pb), antimony (Sb), tin (Sn), thallium (Tl), vanadium (V) and zinc (Zn) in both monitors were determined by means of inductively coupled plasma spectrometry (ICP-MS, Perkin Elmer Elan 6000). Blank and control samples, as well as reference materials (Soil, Loamy clay, Resource Technology Corporation US, CRM 052), were used to check the accuracy of the instrumental methods. The recovery percentages of the reference material ranged 99–138% and 88–115% in soil and air, respectively.

2.3. Human health risks

The concentrations of metals, PCDD/Fs and PCBs in air and soil samples collected in the vicinity of the MSWI were used for the evaluation of exposure and risk characterization around the facility. The exposure of the local population was estimated by considering three different routes: oral (ingestion), dermal, and inhalation. The numerical expressions for the calculations of the ingestion dermal and inhalation exposure and ingestion and dermal risks were taken from the "Spanish Royal Decree 9/2005" (RD 9/2005) on the establishment of the list of the activities potentially contaminant of soils (MMA, 2005), and the criteria and standards for the declaration of contaminated soils, which in turn are based on the US EPA RAGS methodology (EPA, 1989). The expressions (Eqs. (1)–(3)) used to evaluate the exposure through ingestion (Exp_{ing}), dermal contact (Exp_{derm}), and inhalation (Exp_{inh}) were the following:

$$\text{Exp}_{\text{ing}} = \frac{C_{\text{soil}} \times \text{EF} \times \text{IFP}}{\text{BW} \times 365} \quad (1)$$

$$\text{Exp}_{\text{derm}} = \frac{C_{\text{soil}} \times 0.000001 \times \text{AF} \times \text{ABS} \times \text{EF} \times \text{SA}}{\text{BW} \times 365} \quad (2)$$

$$\text{Exp}_{\text{inh}} = \frac{C_{\text{air}} \times \text{IR} \times \text{EF}}{\text{BW} \times 365} \quad (3)$$

The values and description of the different parameters are presented in Table 1S (supplementary information). Once exposure was calculated, the characterization of non-carcinogenic risks consisted on calculating the Hazard Quotient (HQ), which is defined as the relation between the predicted exposure and the oral reference dose (RfD_o). Since no dermal reference dose has been established yet for the pollutants here studied, this value was assumed to be equal to the RfD_o. Cancer risks (CR) through ingestion and dermal exposure were assessed by multiplying the predicted oral and dermal exposure by the oral slope factor. On the other hand, inhalation risks were calculated based on the most updated US EPA RAGS methodology for this pathway (EPA, 2009b). The new methodology (Inhalation Dosimetry Methodology) is based on exposure concentration (EC). This is different from the old intake methodology that included consideration of inhalation rate and body weight. The new methodology suggests that the amount of chemical that reaches the target site through inhalation is directly related to the exposure concentration (EC), being not a simple function of inhalation rate and body weight at all (EPA, 2009b). The expressions (Eqs. (4)–(8)) used for risk characterization were the following:

$$\text{HQ}_{\text{ing+derm}} = \frac{\text{Exp}_{\text{ing+derm}} \times \text{ED}}{\text{RfD}_o \times \text{AT}} \quad (4)$$

$$\text{HQ}_{\text{inh}} = \frac{\text{EC}_{\text{inh}}}{\text{RfC}} \quad (5)$$

$$\text{EC}_{\text{inh}} = \frac{C_{\text{air}} \times \text{ET} \times \text{EF} \times \text{ED}}{\text{AT}} \quad (6)$$

$$\text{CR}_{\text{ing+derm}} = \frac{\text{Exp}_{\text{ing+derm}} \times \text{ED} \times \text{SF}_o}{\text{AT}} \quad (7)$$

$$\text{CR}_{\text{inh}} = \text{EC} \times \text{IUR} \quad (8)$$

3. Results and discussion

3.1. Environmental concentrations in soils

Table 1 summarizes the individual concentrations of heavy metals, congeners and sum of PCDD/Fs and PCBs in soil samples collected within/around the MSWI of Mataró. Manganese and Zn showed the most elevated concentrations (ranges: 136–648 mg kg⁻¹ and 29.6–97.8 mg kg⁻¹, respectively). Antimony levels were below the detection limit in all samples, while Hg was only detected at the MSWI sample (0.11 mg kg⁻¹). Arsenic, Cu, Ni, Pb, Sn and Zn showed the highest levels in the MSWI site. However, none of the analyzed metals showed a clear and progressive reduction in concentration in relation to the distance to the facility. Metal concentrations in soils were in the same range as those recently reported near other MSWIs (Vilavert et al., 2009; Wu et al., 2009).

With respect to the individual PCDD/F congeners, the most substituted dioxins (OCDD and 1,2,3,4,6,7,8-HpCDD) and furans (OCDF and 1,2,3,4,6,7,8-HpCDF) were the most abundant, while

the lowest contribution corresponded to 1,2,3,7,8,9-HxCDF and 2,3,7,8-TCDF, with undetected values for all the samples. The 2,3,7,8-TCDD congener was only detected in two samples, with values of 0.050 ng kg⁻¹ (MSWI) and 0.052 ng kg⁻¹ (Arenys de Mar). Total PCDD/F concentrations ranged from 0.14 to 0.46 ng WHO-TEQ kg⁻¹ (within and <1 km from the MSWI, respectively). When compared to the total PCDD/F concentrations found in other sites of Catalonia under the potential influence of MSWIs (Ferré-Huguet et al., 2006; Schuhmacher and Domingo, 2006), the current levels would be in the lowest part of the range.

Nowadays, in Spain there is not a legal framework for the use of soils according to the PCDD/F concentration. However, some European countries have legislations that set the requirements relative to the use of soils depending on their PCDD/F concentrations. Hence, for preventive purposes, in Germany PCDD/F levels in soils should be below 5 ng TEQ kg⁻¹, while the threshold values are 1000 and 10 000 ng TEQ kg⁻¹ in industrial and residential areas, respectively (EPA, 2009c). In Switzerland, guide values of 5 ng I-TEQ kg⁻¹ are proposed as appropriate for any use, while 20 ng I-TEQ kg⁻¹ is the control level in case of vegetables for human/animal consumption are grown, or the use implies potential soil ingestion. Finally, the range 100–10 000 ng I-TEQ kg⁻¹ is the action level that would imply decontamination (Schmid et al., 2005).

Regarding PCB concentrations in soils around the MSWI of Mataró, the levels of the sum of seven congeners ranged from 167 ng kg⁻¹ (MSWI) to 3340 ng kg⁻¹ (>1 km from the MSWI). The site with the lowest concentration was the MSWI. In fact, in this site only three congeners, the heaviest ones, were found above the corresponding detection limit. The PCB profile observed in all samples was similar, being the most chlorinated congeners the most abundant, especially PCB#180, while the most volatile compounds showed the lowest concentrations. This is indicative of the physical-chemical characteristics of the congeners (Schuhmacher et al., 2004). High-chlorinated PCBs are more associated to the particle phase, having a tendency to deposit and accumulate in soils. On the other hand, light PCB congeners, which tend to be in the gas phase, are more frequently found in air.

3.2. Environmental concentrations in air

Table 2 summarizes the specific concentrations of heavy metals, PCDD/Fs and PCBs in air samples collected within/around the MSWI of Mataró. The highest levels in air were noted for Cu (range: 26.9–52.9 ng m⁻³) and Mn (range: 6.92–19.3 ng m⁻³). In contrast, Cr and Hg levels were below their corresponding detection limits in all samples (<0.47 and <0.19 ng m⁻³, respectively). Thallium was only detected in one (<1 km from the MSWI) of the four samples, with a concentration of 0.08 ng m⁻³. The spatial analysis showed no differences with respect to the distance to the plant. In general terms, the concentration of metals in all air samples were similar to those recently reported around other MSWIs in Catalonia, Spain (Mari et al., 2008; Vilavert et al., 2009).

The profiles of PCDD/F congeners in air were similar in the four sites here studied. The PCDD/F patterns were also very similar to those found in the soil samples collected at the same sites, being the heaviest congeners the most abundant (OCDD, 1,2,3,4,6,7,8-HpCDD and OCDF). On the other hand, 2,3,7,8-TCDD and 1,2,3,4,7,8,9-HpCDF were minority congeners, with levels below their corresponding detection limits in all samples. Total PCDD/F concentrations in air ranged from 0.008 pg WHO-TEQ m⁻³, in Arenys de Mar, to 0.015 pg WHO-TEQ m⁻³ in the MSWI. The results were similar to those observed in other industrial and urban areas in Catalonia (Mari et al., 2008; Vilavert et al., 2009). The PCDD/F profiles of each ambient air sample are depicted in Fig. 1, together with the mean profile of six stack MSWI emission measurements. PCDD/F emissions from the facility were periodically collected

Table 1

Concentrations of micropollutants (metals, PCDD/Fs and PCBs) in soil samples collected around the MSWI of Mataró (Catalonia, Spain).

	MSWI	<1 km	>1 km	Arenys de Mar
As	3.92	0.81	2.19	0.92
Cd	0.30	0.09	0.10	0.05
Co	5.87	7.89	1.83	8.39
Cr	11.1	12.1	4.17	11.8
Cu	26.8	8.40	10.7	12.3
Hg	0.11	ND	ND	ND
Mn	385	462	136	648
Ni	4.93	3.81	3.02	3.63
Pb	35.7	10.3	26.1	14.5
Sb	ND	ND	ND	ND
Sn	2.06	0.83	0.64	0.99
Ti	0.21	0.21	0.06	0.25
V	43.3	67.3	14.4	75.0
Zn	97.8	90.1	29.6	75.3
2,3,7,8-TCDD	0.05	ND	ND	0.05
1,2,3,7,8-PeCDD	0.29	ND	0.09	0.25
1,2,3,4,7,8-HxCDD	ND	ND	0.1	ND
1,2,3,6,7,8-HxCDD	0.12	ND	0.29	0.10
1,2,3,7,8,9-HxCDD	0.14	ND	0.13	ND
1,2,3,4,6,7,8-HpCDD	1.20	1.20	6.20	1.30
OCDD	7.40	9.50	45.0	7.80
2,3,7,8-TCDF	ND	ND	ND	ND
1,2,3,7,8-PeCDF	ND	ND	0.22	0.09
2,3,4,7,8-PeCDF	0.09	ND	0.11	0.10
1,2,3,4,7,8-HxCDF	0.08	ND	0.14	0.10
1,2,3,6,7,8-HxCDF	ND	ND	0.08	ND
1,2,3,7,8,9-HxCDF	ND	ND	ND	ND
2,3,4,6,7,8-HxCDF	0.11	ND	0.17	0.09
1,2,3,4,6,7,8-HpCDF	0.51	0.51	1.90	0.60
1,2,3,4,7,8,9-HpCDF	ND	ND	ND	ND
OCDF	0.50	0.59	1.20	0.57
Total WHO-TEQ	0.14	0.46	0.35	0.41
PCB#28	ND	200	130	110
PCB#52	ND	69.0	65.0	42.0
PCB#101	ND	81.0	200	34.0
PCB#118	ND	36.0	91.0	24.0
PCB#153	34.0	500	1000	89.0
PCB#138	26.0	290	550	67.0
PCB#180	39.0	660	1300	72.0
Σ PCBs	167	1840	3340	438

Units: PCDD/Fs, PCBs: ng kg⁻¹; metals: mg kg⁻¹; ND: not detected.

Limit of detection: Hg: 0.05 mg kg⁻¹; 2,3,7,8-TCDD: 0.04 ng kg⁻¹; 1,2,3,7,8-PeCDD, 1,2,3,4,7,8-HxCDD, 1,2,3,6,7,8-HxCDD, 1,2,3,7,8,9-HxCDD, 2,3,4,7,8-PeCDF, 2,3,4,7,8-PeCDF, 1,2,3,6,7,8-HxCDF, 1,2,3,7,8,9-HxCDF: 0.08 ng kg⁻¹; 2,3,7,8-TCDF: 0.25 ng kg⁻¹; 1,2,3,4,7,8,9-HpCDF: 0.17 ng kg⁻¹; PCB#28, #52#101, #118: 17 ng kg⁻¹.

Table 2
Concentrations of micropollutants (metals, PCDD/Fs and PCBs) in air samples collected around the MSWI of Mataró (Catalonia, Spain).

	MSWI	<1 km	>1 km	Arenys de Mar
As	2.50	0.20	5.09	9.09
Cd	0.50	0.23	0.27	0.38
Co	0.46	0.35	0.17	0.40
Cr	ND	ND	ND	ND
Cu	34.7	52.9	32.9	26.9
Hg	ND	ND	ND	ND
Mn	19.3	15.4	6.92	13.9
Ni	4.46	6.43	3.30	5.70
Pb	19.4	10.9	1.75	11.3
Sb	3.46	3.87	1.62	2.80
Sn	8.11	6.79	3.27	6.12
Ti	ND	0.08	ND	ND
V	7.97	14.0	8.15	11.8
Zn	NA	NA	NA	NA
2,3,7,8-TCDD	ND	ND	ND	ND
1,2,3,7,8-PeCDD	ND	0.002	0.005	0.002
1,2,3,4,7,8-HxCDD	0.003	0.002	0.003	0.003
1,2,3,6,7,8-HxCDD	0.008	0.004	0.008	0.005
1,2,3,7,8,9-HxCDD	0.006	0.004	0.006	0.006
1,2,3,4,6,7,8-HpCDD	0.063	0.054	0.070	0.052
OCDD	0.195	0.133	0.171	0.148
2,3,7,8-TCDF	0.006	0.008	0.007	0.004
1,2,3,7,8-PeCDF	0.006	0.005	0.006	0.002
2,3,4,7,8-PeCDF	0.015	0.010	0.008	0.005
1,2,3,4,7,8-HxCDF	0.011	0.008	0.006	0.004
1,2,3,6,7,8-HxCDF	0.008	0.004	0.004	0.003
1,2,3,7,8,9-HxCDF	ND	0.001	0.002	0.002
2,3,4,6,7,8-HxCDF	0.012	0.007	0.005	0.005
1,2,3,4,6,7,8-HpCDF	0.024	0.021	0.016	0.016
1,2,3,4,7,8,9-HpCDF	ND	ND	ND	ND
OCDF	0.039	0.028	ND	ND
Total WHO-TEQ	0.015	0.010	0.013	0.008
PCB#28	10.1	19.5	11.6	3.67
PCB#52	11.6	10.8	4.27	1.33
PCB#101	2.11	4.02	2.47	ND
PCB#118	ND	ND	ND	ND
PCB#153	1.93	3.72	1.92	ND
PCB#138	0.95	2.14	1.10	ND
PCB#180	ND	0.96	ND	ND
Σ PCBs	28.2	42.1	22.9	9.20

Units: PCDD/Fs: pg m^{-3} ; PCBs: ng m^{-3} ; metals: ng m^{-3} ; ND: not detected; NA: not available.

Limit of detection: Cr: 0.47 ng m^{-3} ; Hg: 0.19 ng m^{-3} ; 2,3,7,8-TCDD: $9.69 \text{ E-07 ng m}^{-3}$; 1,2,3,7,8-PeCDD: $2.25 \text{ E-06 ng m}^{-3}$; 1,2,3,7,8,9-HxCDF: 1.5E-05 ng m^{-3} ; 1,2,3,4,7,8,9-HpCDF: $1.4 \text{ E-05 ng m}^{-3}$; PCB#118, #180: 0.8 ng m^{-3} .

(four times a year) by means of high-volume sampling devices, according to the UNE-EN 1948-1 norm referred to "Sampling from stationary source emissions". Total PCDD/F concentrations in the emission samples ranged between 0.0022 and $0.0159 \text{ ng l-TEQ m}^{-3}$, being clearly below the maximum guideline ($0.1 \text{ ng l-TEQ m}^{-3}$). Some differences may be observed between emission and immission profiles, especially regarding the percentages of some PCDD/F congeners. In fact, OCDD was substituted by 1,2,3,4,6,7,8-HpCDD as the predominant compound in waste incineration emissions, in agreement with recently published data (Gao et al., 2009). This would be a first indication that other natural or anthropogenic sources contribute to the burden of PCDD/Fs in environmental compartments.

The concentrations of PCBs in air samples collected around the MSWI of Mataró were between 9.20 and 42.1 pg m^{-3} (control site and <1 km of the facility, respectively). The ambient air samples showed an opposite pattern with respect to the soil samples, being the lightest congeners more abundant in air (especially PCB#28 and #52). As commented above, these expected results would be related to the physical-chemical characteristics of the congeners, as the lightest are more abundant in the gas phase, and the heaviest tend to be sorbed to particles (Schuhmacher et al., 2004). On the other hand, PCB#118 could not be detected in any of the samples, while PCB#180 was only detected in the sample collected at >1 km of the facility. In any case, the four samples showed lower PCB levels than those recently found by Nadal et al. (2009) in urban areas of Tarragona (Catalonia), and by Mari et al. (2008) around another MSWI in S. Adrià de Besòs (Barcelona, Catalonia, Spain).

3.3. Human health risks

The results of the estimation of total heavy metal, PCDD/F and PCB exposure for individuals living in the four sites studied around the MSWI of Mataró are summarized in Table 3. With respect to metals, the direct exposure for the diverse elements varied from 1.31×10^{-7} to $1.62 \times 10^{-4} \text{ mg kg}^{-1} \text{ d}^{-1}$ (Hg and V, respectively). Soil ingestion was the main pathway of exposure for all metals, ranging between 61% and 74%, except for Cd, whose major exposure pathway was dermal absorption (50%). Moreover, air inhalation was the minor route of exposure for heavy metals (0.3–14%).

The results of the estimated risks for all metals are summarized in Table 4. The carcinogenic risks were only evaluated for those elements whose slope factor has been established (EPA, 2009a).

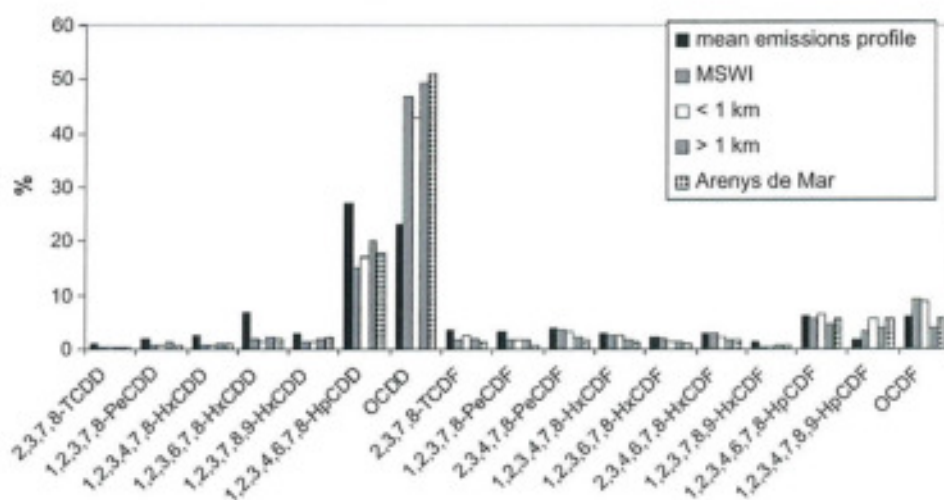


Fig. 1. PCDD/F congener profiles of emission and immission samples collected around the MSWI of Mataró.

This is the case of As ingestion, and As, Cd and Cr inhalation. In Spain, the acceptable excess of cancer risks is 1 out of 100 000 for lifetime exposed individuals. All the carcinogenic results were below 10^{-5} , which means a non-significant carcinogenic risk. Regarding the non-carcinogenic risks, the HQ of all elements was below the unity, considered the safe threshold. Among them, inhalation of As presented the highest value (0.30), corresponding to the control site (Arenys de Mar).

It has been largely stated that dietary intake is the most important exposure pathway to some chemical pollutants such as metals and POPs (Martí-Cid et al., 2008a; Peralta-Videa et al., 2009). Martí-Cid et al. (2008b) recently determined metal exposure through food intake for the Catalan population. A dietary intake of 3.5, 0.14, 0.14 and $0.85 \mu\text{g kg}^{-1} \text{d}^{-1}$ was calculated for As, Cd, Hg and Pb, respectively. These values are one- to threefold higher than those corresponding to environmental exposure. According

to those results, in the case of As, Cd, Hg and Pb the dietary exposure would range from 94% (Pb) to more than 99% (As) of the total exposure. Therefore, it is clear that the dietary intake is, by far, the main contributor to the carcinogenic and non-carcinogenic risks of metal exposure for the population living near the MSWI of Mataró.

With regard to PCDD/Fs, total exposure was very similar in the four studied sites, with a mean value of $4.2 \times 10^{-6} \text{ ng WHO-TEQ kg}^{-1} \text{d}^{-1}$. No correlation was found between the degree of exposure and the distance to the facility. Inhalation was the main pathway of exposure for PCDD/Fs in all sites (73%), followed by dermal contact (14%) and soil ingestion (13%). For PCBs, the same pattern of exposure was observed (79%, 14% and 7% for inhalation, dermal contact and soil ingestion, respectively). The carcinogenic risks were calculated using the US EPA oral slope factors (EPA, 2009a) of $0.13 \text{ ng}^{-1} \text{ kg d}$ for TCDD equivalents, and $2 \times 10^{-6} \text{ ng}^{-1} \text{ kg d}$ for PCBs (assuming a high-risk scenario). In

Table 3
Heavy metal ($\text{mg kg}^{-1} \text{d}^{-1}$), PCDD/F ($\text{ng WHO-TEQ kg}^{-1} \text{d}^{-1}$) and PCB ($\text{ng kg}^{-1} \text{d}^{-1}$) exposure for individuals living in the surroundings of the MSWI of Mataró.

	Pathways of exposure	MSWI	<1 km	>1 km	Arenys de Mar
As	Soil ingestion	6.13E-06	1.26E-06	3.42E-06	1.44E-06
	Dermal contact	6.53E-06	1.34E-06	3.65E-06	1.53E-06
	Air inhalation	6.84E-07	5.38E-08	1.39E-06	2.49E-06
	Total exposure	1.33E-05	2.65E-06	8.46E-06	5.46E-06
Cd	Soil ingestion	4.73E-07	1.48E-07	1.59E-07	7.70E-08
	Dermal contact	1.68E-07	5.27E-08	5.66E-08	2.73E-08
	Air inhalation	1.38E-07	6.32E-08	7.34E-08	1.03E-07
	Total exposure	7.79E-07	2.64E-07	2.89E-07	2.07E-07
Cr	Soil ingestion	1.73E-05	1.88E-05	6.51E-06	1.84E-05
	Dermal contact	6.15E-06	6.69E-06	2.31E-06	6.55E-06
	Air inhalation	6.37E-08	6.37E-08	6.37E-08	6.37E-08
	Total exposure	2.35E-05	2.56E-05	8.88E-06	2.50E-05
Co	Soil ingestion	9.16E-06	1.23E-05	2.86E-06	1.31E-05
	Dermal contact	3.25E-06	4.38E-06	1.02E-06	4.65E-06
	Air inhalation	1.26E-07	9.63E-08	4.64E-08	1.09E-07
	Total exposure	1.25E-05	1.68E-05	3.93E-06	1.79E-05
Cu	Soil ingestion	4.19E-05	1.31E-05	1.68E-05	1.93E-05
	Dermal contact	1.49E-05	4.66E-06	5.96E-06	6.85E-06
	Air inhalation	9.51E-06	1.45E-05	9.00E-06	7.38E-06
	Total exposure	6.63E-05	3.23E-05	3.18E-05	3.35E-05
Hg	Soil ingestion	1.77E-07	7.81E-08	7.81E-08	7.81E-08
	Dermal contact	6.28E-08	2.77E-08	2.77E-08	2.77E-08
	Air inhalation	2.55E-08	2.55E-08	2.55E-08	2.55E-08
	Total exposure	2.65E-07	1.31E-07	1.31E-07	1.31E-07
Ni	Soil ingestion	7.69E-06	5.94E-06	4.71E-06	5.67E-06
	Dermal contact	2.73E-06	2.11E-06	1.67E-06	2.01E-06
	Air inhalation	1.22E-06	1.76E-06	9.05E-07	1.56E-06
	Total exposure	1.16E-05	9.81E-06	7.29E-06	9.24E-06
Pb	Soil ingestion	5.57E-05	1.61E-05	4.08E-05	2.26E-05
	Dermal contact	1.98E-05	5.71E-06	1.45E-05	8.04E-06
	Air inhalation	5.32E-06	2.99E-06	4.81E-07	3.11E-06
	Total exposure	8.08E-05	2.48E-05	5.58E-05	3.38E-05
V	Soil ingestion	6.77E-05	1.05E-04	2.25E-05	1.17E-04
	Dermal contact	2.40E-05	3.73E-05	8.00E-06	4.16E-05
	Air inhalation	2.18E-06	3.83E-06	2.23E-06	3.23E-06
	Total exposure	9.39E-05	1.46E-04	3.27E-05	1.62E-04
Zn	Soil ingestion	1.53E-04	1.41E-04	4.62E-05	1.18E-04
	Dermal contact	5.43E-05	5.00E-05	1.64E-05	4.18E-05
	Air inhalation	na	na	na	na
	Total exposure	2.07E-04	1.91E-04	6.26E-05	1.60E-04
PCDD/Fs	Soil ingestion	2.19E-07	7.18E-07	5.51E-07	6.46E-07
	Dermal contact	2.33E-07	7.65E-07	5.87E-07	6.89E-07
	Air inhalation	4.02E-06	2.71E-06	3.51E-06	2.07E-06
	Total exposure	4.47E-06	4.19E-06	4.65E-06	3.41E-06
PCBs	Soil ingestion	2.61E-04	2.87E-03	5.22E-03	6.84E-04
	Dermal contact	5.56E-04	6.12E-03	1.11E-02	1.46E-03
	Air inhalation	2.71E-02	4.04E-02	2.20E-02	8.79E-03
	Total exposure	2.79E-02	4.94E-02	3.83E-02	1.09E-02

na: Not analyzed.

Table 4
Carcinogenic and non-carcinogenic risks (unitless) derived from exposure to metals, PCDD/Fs and PCBs for the population living around the MSWI of Mataró.

	Pathways of exposure	MSWI	<1 km	>1 km	Arenys de Mar
Carcinogenic risk					
As	Soil ingestion	3.94E-06	8.10E-07	2.20E-06	9.26E-07
	Dermal contact	4.20E-06	8.63E-07	2.34E-06	9.86E-07
	Air inhalation	4.41E-06	3.47E-07	8.99E-06	1.61E-05
	Total carcinogenic risk	1.35E-05	6.32E-06	1.64E-05	2.22E-05
Cd	Air inhalation	3.73E-07	1.71E-07	1.98E-07	2.77E-07
Cr	Air inhalation	1.34E-06	1.34E-06	1.33E-06	1.34E-06
PCDD/Fs	Soil ingestion	1.22E-08	4.00E-08	3.07E-08	3.60E-08
	Dermal contact	1.30E-08	4.26E-08	3.27E-08	3.84E-08
	Air inhalation	2.29E-07	1.54E-07	2.00E-07	1.18E-07
	Total carcinogenic risk	2.54E-07	2.37E-07	2.63E-07	1.93E-07
PCBs	Soil ingestion	2.24E-10	2.46E-09	4.47E-09	5.86E-10
	Dermal contact	4.76E-10	5.25E-09	9.53E-09	1.25E-09
	Air inhalation	6.62E-09	9.86E-09	5.36E-09	2.15E-09
	Total carcinogenic risk	7.32E-09	1.76E-08	1.94E-08	3.98E-09
Non-carcinogenic risk					
As	Total non-cancer risk	1.22E-01	1.49E-02	1.86E-01	3.00E-01
Cd	Total non-cancer risk	1.28E-03	4.02E-04	4.32E-04	2.09E-04
Cr	Total non-cancer risk	1.01E-02	1.07E-02	5.17E-03	1.06E-02
Co	Total non-cancer risk	1.15E-01	1.12E-01	4.00E-02	1.23E-01
Cu	Total non-cancer risk	1.42E-03	4.44E-04	5.68E-04	6.53E-04
Hg	Total non-cancer risk	1.10E-03	6.50E-04	6.50E-04	6.50E-04
Ni	Total non-cancer risk	5.21E-04	4.03E-04	3.19E-04	3.84E-04
Pb	Total non-cancer risk	2.16E-02	6.22E-03	1.58E-02	8.76E-03
V	Total non-cancer risk	1.83E-02	2.85E-02	6.10E-03	3.18E-02
Zn	Total non-cancer risk	6.90E-04	6.36E-04	2.09E-04	5.31E-04
PCDD/Fs	Total non-cancer risk	1.45E-02	1.10E-02	1.34E-02	8.59E-03

turn, the inhalation unit risks (IUR) considered were 3.8×10^{-2} and $5.7 \times 10^{-7} \text{ ng}^{-1} \text{ m}^3$, for TCDD equivalents and PCBs, respectively. The cancer risk ranged 1.67×10^{-7} – 2.46×10^{-7} and 2.94×10^{-9} – 1.32×10^{-8} for PCDD/Fs and PCBs, respectively. As it can be seen, the maximum level of risk assumable according to the Spanish legislation (10^{-5}) was not exceeded in any case. The non-carcinogenic risks (Hazard Quotient) for PCDD/Fs were established by comparing the exposure to PCDD/Fs with the tolerable daily intake (TDI) established by the World Health Organization ($1\text{--}4 \text{ pg WHO-TEQ kg}^{-1} \text{ d}^{-1}$). The HQ for PCDD/Fs comprised values between 8.59×10^{-3} and 1.45×10^{-2} , below the maximum value of 1, which is considered as safe. For PCBs, the HQ could not be calculated since Reference Doses have not been established yet for these compounds.

It has been demonstrated that dietary intake is the main pathway of exposure to PCDD/Fs for the general population, with a contribution up to 95% (Schechter et al., 2006; Martí-Cid et al., 2008a). Recently, PCDD/Fs and PCBs have been determined in foodstuffs widely consumed in Catalonia (Spain) to establish the dietary intake for the population of this Spanish region (Llobet et al., 2008). According to that study, for the Catalan population the dietary exposure to PCDD/Fs and PCBs was $3.7 \times 10^{-4} \text{ ng WHO-TEQ kg}^{-1} \text{ d}^{-1}$ and $11.5 \text{ ng kg}^{-1} \text{ d}^{-1}$, respectively. Consequently, the results indicate that the direct (or environmental) exposure in the area under study only accounts for 1.2% and 0.3% of the total exposure to PCDD/Fs and PCBs, respectively.

Since 1994, when the MSWI of Mataró started its regular operations, a biomonitoring study has been running to establish the internal dose, and thus human exposure to heavy metals, PCDD/Fs and PCBs. Those pollutants have been measured since then in plasma of two groups of inhabitants of Mataró (Gonzalez et al., 1998, 2000). The first group was considered as exposed population, since the distance from their homes to the plant was from 0.5 to 1.5 km. The second group was considered as control, since the participants lived at between 3 and 4 km from the facility. In addition, from the third survey on, an additional control group was added. The purpose of the new group was to specifically evaluate the cau-

sality between the increase of PCDD/F levels observed during the period 1995–1997 and the emissions from the MSWI. This third group was composed by residents of Arenys de Mar and, therefore, outside the area under direct influence of the facility. For all three groups, similar trends were observed in the levels of PCDD/Fs in plasma, indicating that the increase of PCDD/F body burden was associated to the dietary intake, rather than to the presence of the MSWI. The growing trend of PCDD/F levels in blood was observed until 2002, when it was reversed. These results agree with the decrease noted in PCDD/F concentrations in food (Martí-Cid et al., 2008a). On the other hand, PCB levels in plasma have decreased from the first survey in the exposed and non-exposed groups, indicating again that the main pathway of exposure is not related to the facility. A similar decreasing trend for PCBs in foodstuffs has been also observed in recent years (Llobet et al., 2008). For metals, no clear trends were observed for the different groups.

4. Conclusions

The results of the current surveillance program have shown that the environmental levels of all analyzed pollutants are low in comparison with other areas with similar characteristics. Therefore, the current data indicate that the MSWI of Mataró is not being a significant source of heavy metals, PCDD/Fs and PCBs in the area. It is also interesting to note that the environmental results agree with the trends observed in the biological surveys, which showed similar trends in the exposure of PCDD/Fs and PCBs of subjects living near and far from the facility. On the other hand, it has been observed that the behavior of metals, not only in environmental, but also in biological samples, is very variable and consequently difficult to control. Finally, it can be stated that the MSWI of Mataró does not add relevant/significant health risks for the population living in the vicinity of the facility. In spite of this, in order to verify the proper operation of the facility, a continued monitoring is clearly desirable.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.chemosphere.2010.06.016.

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