LONG-TERM BIOLOGICAL MONITORING OF PCDD/Fs AND OTHER ORGANIC SUBSTANCES IN WORKERS OF A HAZARDOUS WASTE INCINERATOR

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Introduction

The incineration of hazardous waste is a strategic way of disposal when that type of waste cannot be recycled or reused[1]. The European Union (EU) establishes strict operating conditions and technical requirements on waste incineration and co-incineration plants to reduce their environmental impact. Nevertheless, hazardous waste incinerators (HWIs) generate an important concern among the population living around since they are potential sources of a wide range of chemical pollutants, which may affect the surrounding environment and have harmful effects on the human health. Among all the pollutants potentially emitted by the HWI stacks, most evaluations have focused on three classes of substances: heavy metals, volatile, and semivolatile compounds, and very especially polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs). These chemicals are characterized by their toxicity to humans and animals, ability to bioaccumulate through the food chain, and persistence in the environment[2].

The first HWI in Spain, and up till now the only one, is located in Constantí (Catalonia). Before the plant started its regular operations (1999), a wide environmental and biological monitoring program was implemented to evaluate its potential impact for the surrounding environment and the health of the local population[3-7]. In parallel, an industrial hygiene program was initiated to assess the occupational exposure of the HWI workers to a number of chemical pollutants, including heavy metals, PCDD/Fs, as well as other organic compounds[8,9]. Since then, the levels of the same substances determined in the baseline survey, have been also annually analyzed to detect possible changes linked to the plant operations[10,11]. We here present updated information on the body burdens of organic compounds in plasma and urine from the workers of the HWI, according to data from the most recent sampling (2014). The results are compared with those obtained in the baseline (1999) and previous (2009-2013) surveys.

Materials and methods

Thirty-three subjects (21 men and 12 women) participated in the current study. They belonged to different working areas: plant (18 workers), laboratory (6 workers), and management/administrative (9 workers). The individual samples of plasma and urine were pooled into six "composite" samples corresponding to plant (4 samples), laboratory (1 sample) and management/administration (1 sample). Blood and urine samples were mixed by equal volume per subject. Blood samples were drawn from each participant in thoroughly cleaned glass bottles. Approximately 50 ml were centrifuged to get plasma. Moreover, urine samples were also collected and centrifuged. Plasma analysis of hexachlorobenzene (HCB), polychlorinated biphenyls (2,4,4'-Tri-PCB28, 2,2',5,5'-Tetra-PCB52, 2,2',4,5,5'-Penta-PCB101, 2,2',3,4,4',5'-Hexa-PCB138, 2,2',4,4',5,5'-Hexa-PCB153, 2,2',3,4,4',5,5'-Hepta-PCB180) and PCDD/Fs were performed by high-resolution mass chromatography coupled to high-resolution mass spectrometry (HRGC/HRMS), in accordance with the US EPA method 1625. In turn, in urine samples, the analysis of 2,4- and 2,5-dichlorophenol (DCP), 2,4,5- and 2,4,6-trichlorophenol (TCP), and pentachlorophenol (PCP) were also performed by HRGC/HRMS, following the NIOSH 8001 method, while the 1-hydroxypyrene (1-HP) levels were determined by HPLC/fluorescence using the appropriate method from the German DFG method for the collection and analysis of hazardous substances in biological materials[12].

For calculations, when a result was below the limit of detection (LOD), the value was assumed to be one-half of that limit (ND = 1/2 LOD). The normality of the variables and the homogeneity of the variances were analyzed by means of the Shapiro-Wilks and Levene tests, respectively. The statistical software SPSS (version IBM Statistics 19) was used for the analyses. A probability lower than 0.05 ($p<0.05$) was considered as significant.

Results and discussion

The concentrations of organochlorinated compounds found in six plasma pool samples are summarized in Table 1. In turn, Table 2 shows the mean values obtained in the current survey (2014), as well as in the baseline (1999) and previous (2009, 2010, 2011, 2012, and 2013) studies. The current mean concentrations were 9.73 μg/kg lipid for HCB, 0.41 μg/kg lipid for PCB28, 0.19 μg/kg lipid for PCB101, 36.2 μg/kg lipid for PCB138, 13.6 μg/kg lipid for PCB153, and 43.2 μg/kg lipid for PCB180. The concentrations of PCB52 were below the LOD (<0.15 μg/kg lipid) in all samples. The levels of PCDD/Fs ranged between 1.21 and 4.53 ng I-TEQ/kg lipid, with a mean concentration of 2.71 ng I-TEQ/kg lipid.

The current concentrations of six individual PCB congeners (PCB28, PCB101, PCB138, PCB153, and PCB180) were similar to those found in the immediately precedent studies ($p>0.05$). As in the 2012 and 2013 surveys, PCB52 could not be detected in any sample (<0.15 μg/kg de lipid). A significant reduction of the levels of all the analyzed compounds was found ($p<0.05$), in comparison with the values of the baseline study (1999). In the present survey, the mean concentration of PCDD/Fs was 2.71 ng I-TEQ/kg lipid, being lower than that reported in the last surveys (4.4, 4.6, 5.5 and 3.1 ng I-TEQ/kg lipid, in 2010, 2011, 2012 and 2013, respectively). However, the decrease of PCDD/Fs in plasma was only significant with respect to data from 1999 and 2009, while no significant changes were noted from 2010 onwards. Since food ingestion is the main pathway of exposure to these pollutants for the general population[6], the reduction in the plasma concentrations of PCDD/Fs agrees well with the decrease noted in the dietary exposure to PCDD/Fs for the population living in the surrounding area[6]. Furthermore, the concentrations of PCDD/Fs in plasma of workers were similar or even lower than those found for non-occupationally exposed populations living in the same area[13], as well as in other zones in Spain[14,15].

Table 1. Concentrations of organochlorinated compounds in plasma from workers of the HWI of Constantí.

	Mean	Median	St. Dev.	Min	Max
HCB	9.73	9.55	4.88	3.30	18.0
PCB28	0.41	0.42	0.19	0.10	0.62
PCB52	<0.15	-	-	-	-
PCB101	0.19	0.15	0.12	0.10	0.39
PCB138	36.2	36.5	17.1	13.0	59.0
PCB153	13.6	14.0	6.37	4.70	23.0
PCB180	43.2	42.0	19.7	18.0	68.0
PCDD/Fs	2.71	2.41	1.30	1.21	4.53

Concentrations are given in □g/kg lipid, excepting those of PCDD/Fs, which are expressed in ng I-TEQ/kg lipid.

Table 2. Mean values of organochlorinated compounds in plasma from workers of the HWI in the baseline (1999), previous (2009-2013), and current (2014) surveys of the biological monitoring program.

	1999	2009	2010	2011	2012	2013	2014	%variance	
								99/14	13/14
HCB	152^{a}	18.3^{bc}	15.6^{bcd}	10.8^{bd}	19.3^{bc}	16.0^{c}	9.73^{d}	-94	-39
PCB28	18.5^{a}	0.4^{b}	0.6^{b}	0.8^{cd}	0.6^{bd}	0.49^{b}	0.41^{b}	-98	-16
PCB52	10.4^{a}	ND	ND	0.3^{b}	ND	ND	ND	-	-
PCB101	9.0^{a}	0.3^{bc}	0.2^{b}	0.5^{cd}	0.4^{bd}	0.26^{b}	0.19^{b}	-98	-26
PCB138	151^{a}	20.5^{b}	45.8^{b}	42.2^{b}	22.9^{b}	19.3^{b}	13.6^{b}	-91	-29
PCB153	213^{a}	46.5^{b}	20.1^{b}	18.5^{b}	54.0^{b}	50.2^{b}	36.2^{b}	-94	-42
PCB180	209^{a}	53.2^{b}	57.8^{b}	51.2^{b}	68.2^{b}	61.8^{b}	43.2^{b}	-79	-30
PCDD/Fs	26.7^{a}	4.7^{b}	4.4^{bc}	4.6^{bd}	5.5^{bc}	3.1^{c}	2.71^{cd}	-90	-12

Concentrations are given in □g/kg lipid, excepting those of PCDD/Fs, which are expressed in ng I-TEQ/kg lipid. ND: Not detected. Different superscripts (a,b,c) indicate significant differences ($p<0.05$) according to the Mann–Whitney U or Anova tests.

The concentrations of organochlorinated compounds found in the six urine pool samples are summarized in Table 3. In 2014, the mean concentration of 2,4-dichlorophenol in urine of the HWI workers was 0.70 μg/g de creatinine, ranging between 0.21 and 2.40 μg/g creatinine. The 2,5-dichlorophenol showed a mean value of 1.15 μg/g creatinine, with minimum and maximum values of 0.67 and 2.70 μg/g creatinine, respectively. The concentration of 2,4,6-trichlorophenol was 3.94 μg/g creatinine, while that of 2,4,5-trichlorophenol was 0.18 μg/g creatinine. Pentachlorophenol mean value was 0.06 μg/g creatinine (range: <0.03-0.15 μg/g creatinine). Finally, the concentrations of 1-hydroxypyrene were between <0.10 and 0.29 μg/g creatinine, with a mean value of 0.14 μg/g creatinine. In general terms, the levels of organochlorinated compounds found in urine samples of the HWI workers were similar to those observed in other studies for non-occupationally exposured populations[16,17].

Table 3. Concentrations of organochlorinated compounds in urine from workers of the HWI of Constantí.

	Mean	Median	St. Dev.	Min	Max
2,4-Dichlorophenol	0.70	0.43	0.84	0.21	2.40
2,5-Dichlorophenol	1.15	0.87	0.71	0.62	2.70
2,4,5-Trichlorophenol	3.91	2.46	4.59	0.13	13.0
2,4,6-Trichlorophenol	0.18	0.09	0.17	0.03	0.47
Pentachlorophenol	0.06	0.03	0.04	0.03	0.15
1-Hydroxypyrene	0.20	0.16	0.13	0.10	0.47

Concentrations are given in □g/g creatinine.

Table 4. Mean values of organochlorinated compounds in urine from workers of the HWI in the baseline (1999), previous (2009-2013), and current (2014) surveys of the biological monitoring program.

	1999	2009	2010	2011	2012	2013	2014	%variance	
								99/14	13/14
2,4-Dichlorophenol	5.7^{a}	ND	0.4^{b}	1.7^{a}	0.2^{bd}	0.1^{b}	0.7^{cd}	-88	526
2,5-Dichlorophenol	66^{a}	2.0^{bc}	4.5^{ac}	2.8^{ac}	0.7^{b}	1.8^{bc}	1.2^{b}	-98	-35
2,4,5-Trichlorophenol	0.4^{a}	0.2^{bc}	0.2^{ac}	0.2^{ac}	ND	ND	3.9^{a}	877	-
2,4,6-Trichlorophenol	0.9	1.2	0.2	0.5	0.3	0.1	0.2	-80	56
Pentachlorophenol	0.5^{a}	ND	0.4^{ac}	0.3^{ac}	0.1^{b}	0.1^{bc}	0.1^{b}	-87	-46
1-Hydroxypyrene	ND	ND	ND	0.1	0.2	0.1	0.2	-	38

Concentrations are given in □g/g creatinine. ND: Not detected. Different superscripts (a,b,c) indicate significant differences ($p<0.05$) according to the Mann–Whitney U or Anova tests.

The concentrations of organochlorinated compounds in urine in the current study were higher than those found one year before (2013) (Table 4). However, the increase was only significant for the 2,4-dichlorophenol ($p>0.05$). On the other hand, the concentrations of 2,5-dichlorophenol and pentachlorophenol suffered a non-significant decrease ($p>0.05$), while the temporal trend of the 2,4,5-trichlorophenol could not be evaluated because this chemical was not detected in urine in the survey performed in 2013. In general terms, the urine concentrations of all the organochlorinated compounds were significantly lower than those observed in the baseline survey, with the only exception of 2,4,5-trichlorophenol, whose levels significantly raised with time ($p>0.05$).

In conclusion, despite the slight increase observed in the levels of some specific organochlorinated compound in urine with respect to the survey of 2013, a clear decreasing tendency in the concentrations of most chemical pollutants in samples of both biological monitors, plasma and urine, was observed when comparing with data from the baseline study (1999). Furthermore, the current concentrations of those organochlorinated compounds were even relatively low when compared with values from the scientific literature for non-occupationally exposed populations. In summary, after 15 years of continuous operation, the impact of the plant on its workers seems to be low, in terms of human exposure to the organic compounds here studied.

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