Biological monitoring of organic substances in workers of a hazardous waste incinerator

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Introduction

In recent years, incineration has been one of the most frequently used technologies for hazardous waste treatment. However, health risks and the potential environmental impact of hazardous waste incinerators (HWI) are still issues of major concern. The reason is the association of stack emissions of semivolatile and volatile compounds from HWI with their potential adverse health effects. Some compounds of special interest are polychlorinated dibenzo-p-dioxins (PCDDs) and dibenzofurans (PCDFs). In relation to this, HWI workers can be potentially exposed to PCDD/Fs, polychlorinated biphenyls (PCBs) and other pollutants with a well-known toxicity.

Since 1999, the only HWI in Spain has been operating in Constantí (Tarragona, Catalonia). It has a burning furnace that operates at a temperature of 1100ºC and can burn 30,000 tons of hazardous waste per year[1]. The purpose of the present survey was to determine after four years of regular operations in the facility, the concentrations in blood and urine of the HWI workers of a number of organic substances directly related with HWI and to which workers could be exposed. Human biological monitoring evaluates the degree of internal exposure to a defined environmental or occupational pollutant of individuals or population groups[2, 3]. The results of the current study have been compared with the baseline levels[1].

Methods and Materials

Sixteen men and 6 women who participated in the baseline study were included. They were divided into three groups according to the workplace and task: group I, plant workers (n=17), group II, laboratory workers (n=3), and group III, administration workers (n=2). To evaluate the exposure to organic substances in

plasma and urine, the 22 individual samples were pooled in 6 samples (4, 1, and 1 samples for the groups I, II, III, respectively), which were mixed by equal volume per subject. The criteria used for pooling was previously reported[9]. Information about each participant was obtained using the same questionnaire that reported in the baseline study[1].

Plasma analyses of hexachlorobenzene (HCB), polychlorinated biphenyls (PCB 28, 52, 101, 138, 153 and 180) and polychlorinated dibenzo-p-dioxins and furans (PCDD/Fs) were carried out. Moreover, the levels of di-, tri- and penta-chlorophenols (DCPs, TCPs and PCP), as well as those of 1-hydroxypyrene (1-HP) were measured in urines (6 pooled samples)[1].
The analytical determination of PCDD/Fs, PCBs and HCB in plasma was performed in accordance with European guideline VDI 3499 (1993). The extraction and clean-up procedures, as well as the analytical determination (HRGC/HRMS) of these compounds were carried out as recently reported[1]. Quantitative determinations were performed using internal standards. The urinary analyses (HRGC/HRMS) of DCPs and TCPs were performed using NIOSH Method No. 8001 (1994), while Henschler Method (1981) was used for PCP. Finally, analysis of 1-HP was carried out using the appropriate method from the method collection "DFG Analysis of Hazardous Substances in Biological Materials"[5]. Extraction and analyses of these substances were performed as previously reported[1].

Statistical significance of the data was computed by the Kruskal-Wallis and the Mann-Whitney U-test. A probability of 0.05 or less was considered as significant. The current results were compared with baseline concentrations of organic compounds in blood and urine of the workers at the HWI[6].

Results and Discussion
The levels of HCB, PCBs and PCDD/Fs in plasma of the HWI workers for the 1999 and 2003 studies are summarised in Table 1. PCDD/F levels ranged from 4.4 to 8.1 pg I-TEQ/g lipid while the baseline PCDD/F concentrations ranged from 13.4 to 84.0 pg I-TEQ/g lipid. In general, the mean levels of these organic substances showed notable decreases. The concentrations of PCDD/Fs decreased from 26.7 to 6.0 ng I-TEQ/kg lipid for the 1999 and 2003 studies, respectively. The 2003 levels are lower than those of some recent studies corresponding to non-exposed populations: 30 and 42.7 ng I-TEQ/kg lipid[6,7]. However, they are similar to those reported for workers of a municipal waste incinerator, 10.4 pg I-TEQ/g lipid[8].

Table 1. Plasma levels of HCB, PCBs and PCDD/Fs in HWI workers. Results for 1999 and 2003

	Mean		Ratio of concentration
	1999	2003	1999/2003
HCB	152.0	49.8	3.1
2,4,4'-Tri-PCB28	18.5	0.31	59.7
2,2',5,5'-Tetra- -PCB52	10.4	<0.25	-
2,2',4,5,5'-Penta-PCB101	9.0	<0.25	-
2,2',3,4,4',5'-Hexa-PCB138	151	22.1	6.8
2,2',4,4',5,5'-Hexa-PCB153	213	52.6	4.0
2,2',3,4,4',5,5'-Hepta-PCB180	209	58.0	3.6
PCDD/Fs	26.7	6.0	4.6

Results are expressed in µg/kg lipid, with the exception of PCDD/Fs that are expressed in ng I-TEQ /kg lipid.

The concentrations of HCB, PCBs and PCDD/Fs in plasma of the HWI workers classified according to the workplace are shown in Table 2 (1999 and 2003 data). In plant workers (Group I), a significant decrease between the baseline levels and those obtained 4 years after was found. Some of these levels are similar to those concerning studies of non-exposed populations[9].

Table 3 summarises the urinary levels of DCPs, TCPs and PCP, as well those of 1-HP. It can be seen that only 2,5-chlorophenol and PCP were detected in 2003. These concentrations were lower than baseline levels[1].The concentrations of CLPs and 1-HP in urines of the HWI workers are also shown according to the respective workplace (Table 4). Significant decreases in plant workers (Group I) were noted for PCP. However, the remarkable decrease of 2,5-chlorophenol was not statistically significant. On the other hand, the levels of administration workers were higher than the rest. Finally, in relation to the urinary levels of 1-HP, only one sample was above detection limit.

Table 2. Plasma levels of HCB, PCBs and PCDD/Fs in HWI workers classified according to the workplace. Results for 1999 and 2003.

	Workers	Years 1999	Years 2003		Workers	Years 1999	Years 2003
HCB	Plant	134[a]	40[a]	2,2',3,4,4',5'-Hexa-PCB138	Plant	150[a]	20[b]
	Laboratory	182	65		Laboratory	164	68
	Administration	223	75		Administration	134	47
2,4,4'-Tri-PCB28	Plant	18.5[a]	0.3[b]	2,2',4,4',5,5'-Hexa-PCB153	Plant	213[a]	50[ba]
	Laboratory	22.4	0.4		Laboratory	228	20
	Administration	13.2	0.3		Administration	188	30
2,2',5,5'-Tetra- -PCB52	Plant	10.7	-	2,2',3,4,4',5,5'-Hepta-PCB180	Plant	228[a]	59[b]
	Laboratory	11.9	-		Laboratory	203	41
	Administration	6.4	-		Administration	91	72
2,2',4,5,5'-Penta-PCB101	Plant	9.1	-	PCDD/Fs	Plant	26.4[a]	6.0[b]
	Laboratory	9.9	-		Laboratory	31.1	6.4
	Administration	6.9	-		Administration	30.5	5.2

Different superscripts (a,b) mean significant differences at $p < 0.05$. Results are expressed in µg/kg lipid, with the exception of PCDD/Fs that are expressed in ng I-TEQ /kg lipid.

Table 3. Urinary levels of chlorophenols and 1-hydroxypyrene (1-HP) in HWI workers. Results for 1999 and 2003.

	1999	2003	Ratio of concentration 1999/2003
2,4-Chlorophenol	5.7	-	-
2,5-Chlorophfenol	66.1	1.8	36.7
2,4,5-Trichlorophenol	0.4	-	-
2,4,6-Trichlorophenol	0.9	-	-
Pentachlorophenol	0.5	0.14	3.6
1-HP	-[a]	-[b]	-

Results are presented as mean values (µg/g creatinine).
[a]Only nine workers showed concentrations above the detection limit (0.1 µg/l). [b]Only one sample showed concentrations above the detection limit.

According to the results of the present survey performed four years after of regular operations in the facility, no evidence of significant exposure to the organic substances here analyzed has been found. Most current concentrations are lower than

the respective baseline levels. In summary, we can conclude that under the present occupational conditions, no additional health risks for the workers at the HWI can be noted.

Table 4. Urinary levels of chlorophenols and 1-hydroxypyrene (1-HP) in HWI workers classified according to the workplace. Results for 1999 and 2003.

		Years				Years	
	Workers	1999	2003		Workers	1999	2003
2,4-Chlorophenol	Plant	2.8	-	2,4,6-Trichlorophenol	Plant	1.1	-
	Laboratory	6.6	-		Laboratory	0.15	-
	Administration	22.5	-		Administration	0.3	-
2,5-Chlorophfenol	Plant	19.2 [a]	1.92 [a]	Pentachlorophenol	Plant	0.5 [a]	0.1 [b]
	Laboratory	108.7	0.4		Laboratory	0.1	0.07
	Administration	321.5	2.75		Administration	0.4	0.4
2,4,5-Trichlorophenol	Plant	0.5	-	1-HP	Plant	<0.04-1.1	<0.04-0.2
	Laboratory	0.2	-		Laboratory	<0.04-11	<0.04
	Administration	0.3	-		Administration	<0.04-0.2	<0.04

Results are expressed as mean values (µg/g creatinine). For 1-HP, detection limit was 0.04 µg/g creatinine. Different superscripts (a,b) mean significant differences at $p < 0.05$.

Acknowledgements

This study was financially supported by GRECAT SA, Spain.

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