

AN ASESMENT OF OCCUPATIONAL EXPOSURE TO ORGANIC SUBSTANCES IN A HAZARDOUS WASTE INCINERATOR

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Introduction

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.¹ Biological monitoring is also useful to evaluate temporal changes in individuals environmentally or occupationally exposed to a defined contaminant. In 1996, the construction of a hazardous waste incinerator (HWI) was initiated in Constantí (Tarragona County, Catalonia, Spain). Regular operations began in 1999. This facility was the first and, up until now, the only HWI in Spain. Before starting regular operations, a surveillance program was designed to assess the impact of a number of organic substances on the workers. Baseline data were obtained.² Since then, we have annually measured in the workers of the HWI the concentrations of those substances that were also determined in the baseline survey.³⁻⁵ The aim of the present study was to measure, after approximately 6 years of regular operations in the HWI, the concentrations in blood and urine of the organic substances, and to establish the temporal variation of these compounds in relation to the baseline survey and the previous monitoring studies.

Materials and Methods

Nineteen workers (15 men and 4 women) participated voluntarily in this study. Individuals were divided into three groups according to their respective workplace. Group I (plant workers) included 12 subjects; Group 2 (laboratory workers) included 5 individuals, and Group 3 (administration workers) included 2 subjects. Most of the volunteers which took part in the present survey also participated in the baseline and subsequent studies. However, due to usual changes in the staff, some of them had to be replaced by new workers in order to keep the number of samples. Fifty mL of blood of each participant were centrifuged to get plasma. Urine samples were also collected. To determine the concentrations of organic substances in plasma: hexachlorobenzene (HCB), polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs), polychlorinated biphenyls (PCBs) No. 28, 52, 101, 138, 153, and 180, and in urine (2,4- and 2,5-dichlorophenol, 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). These samples were differentiated according to the workplace: plant, laboratory and administration (4, 1 and 1 composite samples, respectively), and were mixed by equal volume per subject.

The analytical determination of PCDD/Fs, PCBs and HCB in plasma was performed in accordance with the US EPA method 1625. Samples were homogenized and subsequently extracted (liquid/liquid extraction). 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. Finally, the cleaned extract was analyzed by HRGC/HRMS. The toxic equivalents (TEQ) of the analyzed PCDD/F were calculated according to the international NATO/CCMS system. For the analysis of chlorophenols in urine, the samples were spiked with ¹³C₁₂-marked chlorophenols. This was followed by an acid hydrolysis and an extraction with dichloromethane. The extract was analyzed by HRGC/HRMS using a non-polar column of a DB1-type. 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. The extract was analyzed by HPLC/Fluorescence and a Microsphere RP18 EC reverse phase column.

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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 analyses of data.

Results and Discussion

Table 1 shows the levels of HCB, PCBs and PCDD/Fs in plasma of HWI workers during the period 1999-2005. The ratios corresponding to 1999/2005 and 2004/2005 are also given. Concentrations of HCB decreased notably since the baseline survey (ratio 1999/2005: 2.1). However, the difference did not reach the level of statistical significance ($p>0.05$). 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. 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 evident.

Table 1. Plasma levels (mean values) of HCB, PCBs and PCDD/Fs in HWI workers. 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 ^{abcd}	115.4 ^{abc}	181.7 ^{ad}	225.5 ^a	49.8 ^{bcd}	61.3 ^{cd}	71.0 ^d	2.1	0.9
PCB28	18.5 ^a	2.2 ^{bde}	3.4 ^{be}	2.1 ^{be}	0.3 ^{ce}	1.3 ^d	2.4 ^e	7.7	0.5
PCB52	10.4 ^{ae}	1.3 ^{be}	1.5 ^{be}	0.4 ^{ce}	<0.25	0.2 ^{de}	0.8 ^e	13.0	0.3
PCB101	9.0 ^a	2.0 ^{be}	2.0 ^{bce}	0.9 ^{cde}	<0.25	0.6 ^{de}	1.5 ^e	6.0	0.4
PCB138	151 ^a	89.0 ^{ab}	74.0 ^{bd}	50.1 ^{bd}	22.1 ^c	76.3 ^b	48.0 ^d	3.1	1.6
PCB153	213 ^a	125.4 ^{ab}	103.8 ^b	103.9 ^b	52.6 ^c	40.0 ^c	110.8 ^b	1.9	0.4
PCB180	209 ^{abd}	121.7 ^{abd}	92.0 ^{acd}	198.5 ^{bd}	58.0 ^c	76.9 ^{cd}	114.8 ^d	1.8	0.7
PCDD/Fs	26.7 ^a	16.9 ^{ad}	10.0 ^{bd}	10.3 ^{bd}	6.0 ^{cd}	7.7 ^{bcd}	10.4 ^d	2.6	0.7

Values not showing a common superscript (a, b, c, d, e) are significantly different according to the non-parametric Mann-Whitney U-test ($p>0.05$).

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. The current mean PCDD/F concentration was also lower than those found in some studies concerning blood of workers in MSW/medical incinerators,^{6,7} while are similar to those reported in other studies.⁸

Table 2. Urinary levels (mean values) of chlorophenols and 1-hydroxypyrene (1-HP) in HWI workers. 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 1999/05	Ratio 2004/05
2,4-Dichlorophenol	5.7 ^a	5.2 ^{bcd}	5.0 ^{abd}	2.4 ^{ab}	ND	7.5 ^{cd}	6.7 ^{ad}	0.9	1.1
2,5-Dichlorophenol	66.1 ^a	121.3 ^{bc}	181.8 ^{bc}	96.8 ^b	ND	181.7 ^{cd}	93.4 ^{bd}	0.7	1.9
2,4,5-Trichlorophenol	0.4 ^a	0.7 ^a	0.4 ^{ab}	0.1 ^c	ND	0.2 ^{bc}	0.2 ^{bc}	2	12
2,4,6-Trichlorophenol	0.9 ^a	2.6 ^{bc}	1.0 ^{bd}	0.5 ^{ad}	ND	2.7 ^{bcd}	ND	-	-
Pentachlorophenol	0.5 ^a	1.9 ^b	1.1 ^c	0.9 ^{abc}	0.3 ^a	1.4 ^{bc}	0.5 ^a	1	2.8
1-HP	ND	ND	ND	ND	ND	0.2	ND	-	-

Values not showing a common superscript (a, b, c, d, e) are significantly different according to the non-parametric Mann-Whitney U-test ($p>0.05$).

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

	HCB			PCB28			PCB52			PCB101			PCB138			PCB153			PCB180			PCDD/Fs		
	P	L	A	P	L	A	P	L	A	P	L	A	P	L	A	P	L	A	P	L	A	P	L	A
1999	134 ^{abc}	182	223	18.5 ^{ac}	22.4	13.2	10.7 ^a	11.9	6.4	9.1 ^a	9.9	6.9	150 ^a	164	134	213 ^a	228	188	228 ^{abd}	203	91	26.4 ^a	31.1	30.5
2000	84 ^{abc}	179	179	2.5 ^{bc}	1.8	1.6	1.5 ^{bd}	1.1	0.6	2.1 ^{bd}	1.8	1.5	79 ^{abe}	129	91	114 ^{ab}	179	119	113 ^{abd}	170	110	16.8 ^{ad}	16.4	17.8
2001	143 ^{ac}	159	359	3.1 ^{bc}	3.2	4.7	1.3 ^{bd}	1.6	1.9	1.9 ^{bcd}	2.1	2.6	65 ^{bce}	94	89	93 ^b	130	120	89 ^{acd}	110	86	9.4 ^{bcd}	11.7	10.4
2002	150 ^a	346	408	2.0 ^{bc}	2.4	2.6	0.4 ^{cd}	0.5	0.5	0.9 ^{cd}	1.1	0.9	41 ^{ce}	77	59	87 ^b	151	125	176 ^b	278	209	9.2 ^{bd}	13.5	11.6
2003	40 ^{bc}	65	75	0.3 ^{bc}	0.4	0.3	ND	ND	ND	ND	ND	ND	20 ^{de}	68	47	50 ^b	20	30	59 ^{cd}	41	72	6.0 ^c	6.4	5.2
2004	59.0 ^c	87.3	44.2	1.3 ^{bc}	1.3	1.3	0.2 ^{cd}	0.4	0.3	0.5 ^d	1.3	0.5	68 ^{bce}	127	60	38 ^b	61	29	71 ^{cd}	119	61	8.2 ^{bcd}	9.2	4.4
2005	50.5 ^c	74	150	2.8 ^c	1.5	1.7	1.1 ^d	ND	ND	1.8 ^d	0.8	0.8	41 ^e	55	71	94 ^b	120	170	97 ^d	130	170	11.5 ^d	6.8	9.5
p	<0.05	-	-	<0.001	-	-	<0.001	-	-	<0.01	-	-	<0.01	-	-	<0.01	-	-	<0.05	-	-	<0.05	-	-

P: Plant; L: Laboratory; A: Administration

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 according to the non-parametric test U de Mann-Whitney.

Table 4. Concentrations (mean values) of organic compounds in urine of workers at the HWI according to their specific workplaces.

	2,4-Dichlorophenol			2,5-Dichlorophenol			2,4,5-Trichlorophenol			2,4,6-Trichlorophenol			Pentachlorophenol			1-Hydroxipirene		
	P	L	A	P	L	A	P	L	A	P	L	A	P	L	A	P	L	A
1999	2.8 ^a	6.6	22.5	19.2 ^a	108.7	321.5	0.5 ^{ab}	0.2	0.3	1.1 ^a	0.2	0.3	0.5 ^a	0.1	0.5	<0.04	<0.04	<0.04
2000	4.3 ^{bc}	3.9	9.8	80.7 ^{bc}	127.7	277.2	0.6 ^a	1.2	0.4	3.5 ^b	1.0	0.6	1.9 ^b	1.9	1.7	<0.04	0.2	<0.04
2001	3.4 ^{abc}	6.5	9.7	85.2 ^{bd}	177.9	571.8	0.3 ^{ac}	0.7	0.5	0.9 ^{ab}	1.0	1.4	1.1 ^b	1.0	1.4	<0.04	<0.04	<0.04
2002	1.5 ^{ab}	2.6	5.7	48.4 ^{be}	101.6	285.8	0.2 ^c	0.1	0.1	0.7 ^a	0.3	0.1	0.6 ^{ab}	2.7	0.6	<0.04	<0.04	<0.04
2003	ND	ND	ND	1.92 ^{ac}	0.40	2.75	ND	ND	ND	ND	ND	ND	0.1 ^{ab}	0.1	0.4	<0.04	<0.04	<0.04
2004	6.1 ^{cd}	3.7	17.0	153.4 ^{cd}	115.6	360.8	0.2 ^{bc}	0.4	0.2	3.4 ^b	0.3	0.3	1.7 ^b	1.1	0.6	<0.04	<0.04	0.2
2005	8.4 ^d	3.6	3.1	104.7 ^{cb}	45.1	96.8	0.2 ^{ac}	0.3	0.3	ND	0.5	1.0	0.5 ^{ab}	0.5	ND	<0.04	<0.04	0.4
p	<0.05	-	--	<0.05	-	-	<0.05	-	-	<0.05	-	-	<0.05	-	-	-	-	-

P: Plant; L: Laboratory; A: Administration

ND: not detected. Results are expressed in µg/g creatinine. For values corresponding to plant workers, different letters (a, b, c, d) indicate significant differences according to the non-parametric test U de Mann-Whitney.

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Table 2 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 levels of organohalogenated compounds in plasma of the HWI workers classified according to the specific workplace are summarized in Table 3. A similar annual tendency to that found for all HWI workers (Table 1), was also noted 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.

The urinary levels of chlorophenols and 1-hydroxypyrene in the HWI workers classified according to the specific workplace are summarized in Table 4. 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. With respect to the remaining 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).

In summary, the results of the current (2005) 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.

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