

## BIOLOGICAL MONITORING OF ORGANIC SUBSTANCES IN WORKERS AT A HAZARDOUS WASTE INCINERATOR OF CATALONIA, SPAIN

M. Carmen Agramunt<sup>1</sup>, Jose L. Domingo<sup>1</sup>, Marta Schuhmacher<sup>1</sup>, Mercedes Gomez<sup>1</sup>, Juan M. Lobet<sup>1</sup> and Lutz Müller<sup>2</sup>

<sup>1</sup>Laboratory of Toxicology and Environmental Health, "Rovira i Virgili" University, San Lorenzo 21, 43201 Reus, Spain

<sup>2</sup>MPU GmbH, Department of Analytical Laboratory, 10829 Berlin, Germany

### Introduction

Although incineration is a frequently used technology for hazardous waste (HW) treatment, the potential environmental and public health impact of hazardous waste incinerators (HWI) has become and continues being a subject of concern. The construction of the first, and up till now the only HWI in Spain, finished in 1999. A pre-operational monitoring program was established during the construction of the plant in order to evaluate its impact on the environment and public health<sup>1-4</sup>. The program also included the assessment of internal exposure of workers to a number of organic and inorganic substances.

HWI workers are potentially exposed to various chemicals, some of them organochlorine compounds such as dioxins and furans, with a well known toxicity. Human biological monitoring is an important tool in occupational medicine to establish the levels of internal exposure to harmful substances taken up from the occupational environment<sup>5</sup>. Baseline concentrations of a number of metals and organic compounds were determined in blood and urine of the HWI workers before operation of the plant<sup>6</sup>. In the present paper, we show the results of a monitoring study, which was carried out on the HWI workers after two years of regular operations in the plant. Results were compared with the baseline levels<sup>6</sup> and with those obtained one year after operation of the new facility<sup>7</sup>.

### Methods and Materials

Twenty-one men and 7 women (25-37 years) were included in the study. They were divided into three groups according to the workplace and task: group I, incinerator operators, boiler maintenance, control panel, furnace maintenance and waste gas washing operators (n = 22); group II, laboratory workers (n = 3), and group III, management and office workers (n = 3). To evaluate the exposure to organic substances in plasma and urine, the 28 individual samples were pooled in 6 samples (4, 1 and 1 samples for the Groups I, II and III, respectively), which were mixed by equal volume per subject. The criteria used for pooling was the specific workplace together with the sex, and age of the subject. Information about each participant was obtained using a questionnaire which includes data about sex, age, health status, lifestyle, potential environmental exposure sources, dietary habits, as well as smoking and drinking habits. Details of the workers are shown in Table 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).

# HUMAN EXPOSURE I

**Table 1.** Details of the workers in the HWI.

	Incinerator	Laboratory	Administration
Number of subjects	22	3	3
Women/men	1/21	3/0	3/0
Age (years, mean $\pm$ SD)	28.5 $\pm$ 3	32 $\pm$ 4	26.7 $\pm$ 2
Smokers/non smokers	12/10	1/2	1/2

The analytical determination of PCDD/Fs, PCBs and HCB was performed in accordance to European guideline VDI 3499 (1993). The clean-up procedure and fractionation of the crude extract was carried out by adsorption chromatography as a multi-step-clean-up with silicagel and alumina columns. The cleaned extracts were analyzed by HRGC/HRMS. The urinary analyses of DCPs, TCPs and PCP were performed using the NIOSH-method No. 8001 (1994). The urine was undergone an acid hydrolysis and chlorophenols (CLPs) were extracted and derivatized. The derivates were analyzed by HRGC/HRMS. Quantification was carried out using  $^{13}\text{C}$ -marked CLP as internal standard. Urinary analysis of 1-HP was carried out using the "DFG, Analyses of Hazardous Substances in Biological Materials (1990)" method.

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. Multiple regression analyses were carried out to evaluate which independent variables could best explain the variations in the plasma and urine levels of the different chemicals. The current results were also compared with those of the previous studies<sup>6,7</sup>.

## Results and Discussion

The levels of HCB, PCBs and PCDD/Fs in plasma of the HWI workers for the 1999, 2000 and 2001 studies are summarised in Table 2. PCDD/F levels ranged from 7.4 to 11.8 pg I-TEQ/g lipid while the baseline PCDD/F concentrations ranged from 13.4 to 84.0 pg I-TEQ/g lipid. The median PCDD/F levels show a continued and notable decrease: 23.7, 18.1 and 10.4 ng I-TEQ/kg lipid for the 1999, 2000 and 2001 studies, respectively. Dietary intake is the major route of PCDD/F exposure for the general population. When recent data on PCDD/F levels in food samples (unpublished data) and dietary information of the workers were examined, a strong correlation with the current plasma concentrations could be observed.

The concentrations of HCB, PCBs and PCDD/Fs in plasma of the HWI workers classified according to the workplace are shown in Table 3 (1999, 2000 and 2001). In plant workers (Group I), significant differences between the year of collection of the samples (1999, 2000 and 2001) were found.

Table 4 shows the urinary levels of DCPs, TCPs and PCP, as well those of 1-HP. It can be seen that the current CLP concentrations are similar to the baseline levels<sup>1</sup>. On the other hand, the concentrations of CLPs and 1-HP in urines of the HWI workers are also shown according to the respective workplace (Table 5). Significant differences in plant workers (Group I) were again noted depending on the year of collection of the samples (1999, 2000 and 2001). However, no differences according to the workplace were found.

According to the results of the current survey, after two years of regular operation of the facility, no signs of significant exposure to the organic substances here analyzed result evident. Therefore, under the present conditions, no health risks for the workers at the HWI can be noted. Additional surveys will be performed in order to detect any potential occupational risk for these workers.

**Table 2.** Plasma levels of HCB, PCBs and PCDD/Fs in HWI workers. Results for 1999, 2000 and 2001.

	1999	2000	2001	Ratio of concentration 1999/2000	Ratio of concentration 2000/2001
HCB	104.1	107.1	164.0	1.0	0.7
2,4,4'-Tri-PCB28	14.9	1.4	2.8	10.6	0.5
2,2',5,5'-Tetra-PCB52	6.7	0.9	1.3	7.4	0.7
2,2',4,5,5'-Penta-PCB101	7.6	1.8	1.8	4.2	1.0
2,2',3,4,4',5'-Hexa-PCB138	127	124.3	76.5	1.0	1.6
2,2',4,4',5,5'-Hexa-PCB153	173	89.7	105.0	1.9	0.9
2,2',3,4,4',5,5'-Hepta-PCB180	169	119.7	89.5	1.4	1.3
PCDD/Fs	23.7	16.1	10.4	1.5	1.5

Results are given as median values and expressed in m g/kg lipid, with the exception of PCDD/Fs that are expressed in ng I-TEQ /kg lipid.

**Table 3.** Plasma levels of HCB, PCBs and PCDD/Fs in HWI workers classified according to the workplace. Results for 1999, 2000 and 2001.

	Workers					Workers			
	Year	Plant	Laboratory	Administration		Year	Plant	Laboratory	Administration
HCB	1999	134	182	223	2,2',3,4,4',5'-Hexa-PCB138	1999	150 <sup>a</sup>	164	134
	2000	84	179	179		2000	114 <sup>b</sup>	129	91
	2001	143	159	359		2001	93 <sup>b</sup>	130	120
	p	NS	—	—		P	<0.05	—	—
2,4,4'-Tri-PCB28	1999	18.5 <sup>a</sup>	22.4	13.2	2,2',4,4',5,5'-Hexa-PCB153	1999	213 <sup>a</sup>	228	188
	2000	2.5 <sup>b</sup>	1.8	1.6		2000	79 <sup>b</sup>	179	119
	2001	3.1 <sup>b</sup>	3.2	4.7		2001	65 <sup>b</sup>	94	89
	p	<0.001	—	—		p	<0.001	—	—
2,2',5,5'-Tetra-PCB52	1999	10.7 <sup>a</sup>	11.9	6.4	2,2',3,4,4',5,5'-Hepta-PCB180	1999	228	203	91
	2000	1.5 <sup>b</sup>	1.1	0.6		2000	113	170	110
	2001	1.3 <sup>b</sup>	1.6	1.9		2001	89	110	86
	p	<0.001	—	—		p	NS	—	—
2,2',4,5,5'-Penta-PCB101	1999	9.1 <sup>a</sup>	9.9	6.9	PCDD/Fs	1999	26.4 <sup>a</sup>	31.1	30.5
	2000	2.1 <sup>b</sup>	1.8	1.5		2000	16.8 <sup>a</sup>	16.4	17.8
	2001	1.9 <sup>b</sup>	2.1	2.6		2001	9.4 <sup>b</sup>	11.7	10.4
	p	<0.01	—	—		p	<0.01	—	—

Results are expressed in m g/kg lipid, with the exception of PCDD/Fs that are expressed in ng I-TEQ /kg lipid. NS: No significant differences.

Different superindices (a,b) mean significant differences at  $p < 0.05$ .

## References

- Schuhmacher M., Granero S., Llobet J.M., de Kok, H.A.M. and Domingo J.L. (1997) Chemosphere 35, 1947.
- Schuhmacher M., Domingo J.L., Llobet J.M., Müller L., Sünderhauf W. and Jager J. (1998) Chemosphere 36, 2581.

# HUMAN EXPOSURE I

**Table 4.** Urinary levels of chlorophenols and 1-hydroxypyrene (1-HP) in HWI workers. Results for 1999, 2000 and 2001

	1999	2000	2001	Ratio of concentration 1999/2000	Ratio of concentration 2000/2001
2,4-Chlorophenol	5.7	5.2	5.0	1.1	1.0
2,5-Chlorophenol	66.1	121.3	181.8	0.5	0.7
2,4,5-Trichlorophenol	0.4	2.6	1.0	0.2	2.6
2,4,6-Trichlorophenol	0.9	0.7	0.4	1.3	1.8
Pentachlorophenol	0.5	1.9	1.1	0.2	1.7
1-HP	— <sup>a</sup>	— <sup>b</sup>	— <sup>c</sup>	—	—

Results are presented as mean values (mg/g creatinine).

<sup>a</sup>Only nine workers showed concentrations above the detection limit (0.1 mg/l). <sup>b</sup> Only three samples showed concentrations above the detection limit. <sup>c</sup>Only two samples showed concentrations above the detection limit.

**Table 5.** Urinary levels of chlorophenols and 1-hydroxypyrene (1-HP) in HWI workers classified according to the workplace. Results for 1999, 2000 and 2001.

	Workers					Workers			
	Year	Plant	Laboratory	Administration		Year	Plant	Laboratory	Administration
2,4-Chlorophenol	1999	2.8 <sup>a</sup>	6.6	22.5	2,4,6-Trichlorophenol	1999	1.1 <sup>a</sup>	1.05	0.3
	2000	4.3 <sup>b</sup>	3.9	9.8		2000	0.6 <sup>b</sup>	1.2	0.4
	2001	3.4 <sup>ab</sup>	6.5	9.7		2001	0.9 <sup>b</sup>	1.0	1.4
	p	<0.05	—	—		p	<0.05	—	—
2,5-Chlorophenol	1999	19.2 <sup>a</sup>	108.7	321.5	Pentachlorophenol	1999	0.5 <sup>a</sup>	0.14	0.51
	2000	80.7 <sup>b</sup>	127.7	277.2		2000	1.9 <sup>b</sup>	1.9	1.7
	2001	85.2 <sup>b</sup>	177.9	571.8		2001	1.1 <sup>b</sup>	1.0	1.4
	p	<0.001	—	—		p	<0.01	—	—
2,4,5-Trichlorophenol	1999	0.5	0.2	0.3	1-HP	1999	<0.04-1.1	<0.04-11.2	<0.04-0.2
	2000	3.5	1.0	0.6		2000	<0.04-0.3	0.2	<0.04
	2001	0.3	0.7	0.5		2001	<0.04-0.2	<0.04	<0.04
	p	NS	—	—		p <sup>o</sup>	—	—	—

Results are expressed as mean values (mg/g creatinine). For 1-HP, detection limit was 0.04 mg/g creatinine.

- Schuhmacher M., Domingo J.L., Llobet J.M., Lindström G. and Wingfors H. (1999) *Chemosphere* 38, 1123.
- Domingo J.L., Schuhmacher M., Granero S. and Llobet J.M. (1999) *Chemosphere* 38, 3157.
- Ewers U., Krause C., Schulz C. and Wilhelm M. (1999) *Int Arch Occup Environ Health* 72, 255.
- Domingo J.L., Schuhmacher M., Agramunt M.C., Müller L. and Neugebauer F. (2001) *Int Arch Occup Environ Health* 74, 263
- Schuhmacher M., Domingo J.L., Agramunt M.C., Bocio A. and Müller L. (2002) *Int Arch Occup Environ Health*. In press.