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Monitoring Metals near a Hazardous Waste Incinerator. Temporal Trend in Soils and Herbage

N. Ferré-Huguet · M. Nadal · M. Mari · M. Schuhmacher · M. A. Borrajo · J. L. Domingo

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Abstract In recent years, incineration has been demonstrated to be a commercially available technology for hazardous waste (HW) disposal (Richter and Johnke, 2004). However, because of the potential adverse effects of toxic emissions, waste incinerators are still an important cause for concern for the public. In spite of that, compliance with current EU emissions has vastly reduced the probability of adverse health effects (Glorennec et al., 2005). With respect to metals, a number of studies have shown that these elements are emitted by industrial, medical and municipal waste incinerators (Schumacher et al., 1997; Rimmer et al., 2006). Filter ash is an especially problematic residue because it contains high metal concentrations (Lisk et al., 1989). After combustion in modern HW incinerators (HWIs), metals contained in HW are mainly collected in bottom and fly ash, with only small quantity of metals being discharged from the stack as particulate matter or vapor (Jung et al., 2004). However, the atmospheric emission of these elements is a matter of concern.

Between 1996–1998 a new HWI was constructed in Constantí (Tarragona County, Catalonia, Spain). During the period of the construction of the facility a preoperational monitoring program for metals and dioxins and furans (PCDD/Fs) was established. It included monitoring of these pollutants in soils and herbage. The baseline survey was finished in 1998, just before the HWI began regular operations (Llobet et al., 2000). In accordance with the surveillance program on the environmental impact of the new facility, in 2001 and 2003 soil and herbage samples were again collected at the same sampling points in which samples had been collected in the baseline survey (Nadal et al., 2005). To continue with this monitoring program, samples of soil and herbage were again (2004–2005) collected and metal levels were recently determined. The purpose of the present study was to establish the temporal trend of metal concentrations in the vicinity of the HWI in relation to the previous (including the baseline) surveys. A second objective of this study was to assess the health risks due to metal exposure for the population living near the facility.

N. Ferré-Huguet · M. Nadal · M. Mari · M. Schuhmacher · J. L. Domingo (✉)
Laboratory of Toxicology and Environmental Health, ''Rovira i Virgili'' University, San Lorenzo 21, 43201, Reus, Catalonia, Spain
e-mail: joseluis.domingo@urv.cat

M. Schuhmacher · M. A. Borrajo
Department of Chemical Engineering, School of Chemical Engineering, ''Rovira i Virgili'' University, Sescelades Campus, 43007 Tarragona, Catalonia, Spain

Materials and Methods

The area under study is within a radius of 8.0 km around the HWI. To determine the temporal trend in the levels of metals in the vicinity of the facility, 40 soil and 40 herbage samples were collected at the same points in which samples were taken in the previous surveys. A wide description of the HWI and surroundings, the prevailing winds in the area, and the characteristics of sampling were previously reported (Llobet et al., 2000; Nadal et al., 2005). Thirty samples corresponded to rural areas, while the remaining 10 samples were collected in urban zones.

In April 2004, 40 topsoil samples were collected. These were bulk samples representing an area of approximately 1 m^2 at each sampling site. Samples were dried at room

Table 1 Mean concentrations of a number of elements (μg/g ± SD) in soil and herbage samples collected in the vicinity of the HWI, and percentages of temporal variation

Soil	1998	2003	2004	% Temporal variation (2003–2004)	% Temporal variation (2003–2004)
As	6.71 ± 2.18	8.54 ± 3.71	7.37 ± 2.80	–13.7	9.8
Be	0.40 ± 0.23	0.56 ± 0.28	0.63 ± 0.21	12.5	57.5***
Cd	0.26 ± 0.17	0.22 ± 0.15	0.22 ± 0.09	0.0	–15.4
Cr	16.01 ± 5.01	21.64 ± 11.27	19.06 ± 6.78	–11.9	19.1*
Hg	0.16 ± 0.11	0.08 ± 0.22	ND	–	–
Mn	280.4 ± 84.5	320.5 ± 126.4	304.5 ± 99.9	–5.0	8.6
Ni	15.16 ± 4.66	29.87 ± 11.92	16.51 ± 3.46	–4.7***	8.9
Pb	41.46 ± 32.58	40.07 ± 24.83	37.55 ± 17.67	–6.3	–9.4
Sn	0.22 ± 0.18	0.19 ± 0.34	0.16 ± 0.16	–15.8	–27.3**
Tl	0.12 ± 0.03	0.16 ± 0.11	0.15 ± 0.06	–6.3	25.0
V	18.94 ± 5.34	29.24 ± 17.03	26.73 ± 8.17	–8.58	41.13***
Herbage	1998	2003	2005	% Temporal variation (2003–2005)	% Temporal variation (1998–2005)
As	0.11 ± 0.04	0.07 ± 0.06	0.08 ± 0.04	14.3	–27.3
Be	ND	ND	ND	–	–
Cd	0.05 ± 0.01	0.02 ± 0.02	0.02 ± 0.01	–	–60.0
Cr	0.23 ± 0.17	0.32 ± 0.21	ND	–	–
Hg	0.23 ± 0.09	ND	0.03 ± 0.02	–	–87.0**
Mn	37.7 ± 15.4	49.3 ± 16.1	43.9 ± 13.0	–10.9	16.5
Ni	0.59 ± 0.25	0.58 ± 0.34	0.42 ± 0.32	–27.6	–28.8**
Pb	1.03 ± 1.21	0.63 ± 0.54	0.46 ± 0.22	–27.0	–55.3
Sn	0.12 ± 0.03	0.11 ± 0.17	0.07 ± 0.03	–36.4	–41.7
Tl	ND	ND	ND	–	–
V	0.19 ± 0.13	0.38 ± 0.17	0.06 ± 0.08	–84.2**	–68.4**

ND: not detected. Significant differences at: $^{*}P < 0.05$; $^{**}P < 0.01$; $^{***}P < 0.001$

temperature and sieved through a 2 mm mesh screen to get a homogeneous grain distribution. In April 2005, herbage samples [*Piptatherum paradoxum* (L.)] were collected at the same 40 sampling points by cutting at a height of approximately 5 cm from the soil. Samples were immediately stored in a double aluminum fold and dried at room temperature until analyses. In both surveys, no sign of rain was noted during the 20 days prior to the sampling.

Total concentrations of arsenic (As), beryllium (Be), cadmium (Cd), chromium (Cr), lead (Pb), manganese (Mn), mercury (Hg), nickel (Ni), thallium (Tl), tin (Sn), vanadium (V) and zinc (Zn) were determined in soil and herbage samples. Approximately 0.5 g of dried soil or herbage was digested with 5 mL of nitric acid (65% Suprapur, E. Merck, Darmstadt, Germany) in hermetic teflon bombs. They were kept at room temperature for 8 h, and heated at 80°C for 8 additional hours. Further methodological details were recently reported (Segura-Muñoz et al., 2004; Mari et al., 2007). Depending on each specific element, metal concentrations were measured by inductively coupled plasma spectrometry (ICP-MS, Perkin Elmer Elan 6000), or atomic-absorption spectrophotometry with graphite-furnace atomization (AAS, Varian, Spectra A-30). Blank and control samples, as well as reference materials (for soils, loamy clay, RTC US, CRM 052, and for herbage, Lobster Hepatopancreas, NRC Canada, TORT-2), were used to check the accuracy of the instrumental methods.

For calculations, if the level of an element was under its respective limit of detection (LOD), the concentration was assumed to be one-half of that limit. To evaluate the differences in metal concentrations, data for soils and herbage were analyzed by one-way analysis of variance (ANOVA), or by the Kruskal-Wallis test, respectively, depending on whether data followed a normal distribution.

Results and Discussion

Table 1 shows the concentrations of As, Be, Cd, Cr, Hg, Mn, Ni, Pb, Sn, Tl and V in soil and herbage samples collected in 2004 and 2005, respectively, near the HWI. Hg was only detected in four soil samples, whereas Mn and Tl presented the maximum and minimum mean levels (304.5 and 0.15 μg/g, respectively). In herbage, As was detected only in a relatively low number of samples located far from the facility (northwest direction and urban zones), whereas Be, Cr and Tl levels were below their respective detection limits. No significant Pearson correlation between soil and

Table 2 Metal concentrations (μg/g) in soil and herbages samples collected near the HWI (Catalonia, Spain) in 2004 and 2005

	Soil			Herbage		
	Urban	Rural	*P*	Urban	Rural	*P*
As	6.28 ± 4.03	7.74 ± 2.23	< 0.05	0.11 ± 0.05	0.07 ± 0.03	< 0.05
Be	0.49 ± 0.17	0.68 ± 0.20	< 0.01	ND	ND	–
Cd	0.22 ± 0.14	0.22 ± 0.07	NS	ND	0.02 ± 0.01	–
Cr	15.42 ± 7.4	20.27 ± 6.22	NS	ND	ND	–
Hg	ND	ND	–	0.05 ± 0.03	ND	NS
Mn	238.1 ± 89.80	326.6 ± 94.4	< 0.05	44.38 ± 14.6	43.78 ± 12.70	NS
Ni	14.01 ± 3.74	17.34 ± 2.98	NS	0.60 ± 0.45	0.36 ± 0.25	< 0.05
Pb	41.02 ± 24.08	36.39 ± 15.3	NS	0.48 ± 0.19	0.45 ± 0.23	NS
Sn	0.28 ± 0.23	0.12 ± 0.10	< 0.05	0.07 ± 0.03	0.07 ± 0.03	NS
Tl	0.12 ± 0.06	0.16 ± 0.06	NS	ND	ND	–
V	24.75 ± 12.60	24.40 ± 6.22	< 0.05	0.06 ± 0.08	0.06 ± 0.09	NS

ND: not detected; NS: not statistically significant ($P > 0.05$)

herbage concentrations could be found for any of the elements.

Data corresponding to previous surveys performed in the same zone (Llobet et al., 2000; Nadal et al., 2005), as well as the respective percentage of variation, are also shown in Table 1. In soils, a significant reduction of Sn levels was observed between 1998 and 2004. In contrast, the levels of Be, Cr and V in soils were found to be significantly higher in samples collected in 2004 than in those collected in 1998. These increases could be due not only to the emissions of the HWI, but also to the effects of other potential emission sources of metal pollution in the same area (Hallenbeck et al., 1993). The results of the 2004 study show that, in general terms, the metal concentrations in soils diminished between 2003 and 2004. However, the differences reached the level of statistical significance only for Ni.

The concentrations of metals in soils collected in 2004 were similar to the levels recently found in other industrial and urban zones of Tarragona County (Nadal et al., 2004; Mari et al., 2007). Possible explanations for the differences found in metal concentrations after certain periods of time are rather complex, and could be due to a number of reasons. An important factor, which can affect metal emissions from HWI and the subsequent deposition to soils and herbage, is the amount and chemical composition of burned materials (Morselli et al., 2002). Moreover, other factors, such as heavy traffic and agricultural activities, may also be important (Hallenbeck et al., 1993). Likewise, the presence of chemical/petrochemical industries in the surroundings of the HWI might also be another important factor (Nadal et al., 2005).

With respect to concentrations in herbage, all detected metals (excepting Mn) showed lower concentrations in the 2005 study than in the baseline survey. However, the level of statistical significance for the differences was only reached for Hg, Ni and V. Although between 2003 and 2005 the concentrations of all elements (excepting As) decreased, the differences were only significant for V (Table 1). The most remarkable finding was the continued reduction in metal levels, which was observed in all samples independently of the distance of the sampling point to the HWI. This reduction would be an indicator of the general finding in recent years of decreasing atmospheric concentrations of an important number of metals.

The concentrations of the analyzed elements in soil and vegetation samples, according to the area of collection, are summarized in Table 2. Data are presented according to two zones: rural (located at distances between 500 and 4,000 m from the stack) and urban (located at distance greater than 4,000 m from the stack). In soils, As, Be, Mn and V concentrations were significantly higher in the rural area, whereas Sn showed a higher level in the urban zone. In herbage, significant higher levels of As and Ni were reported in sampling points far away the facility (urban area).

The current data concerning metal concentrations in soils and herbage collected in the vicinity of HWI are similar to those found in various industrial and urban areas of Spain (Schuhmacher et al., 1997; Granero and Domingo, 2002). The comparison of the results of the present study with recent results from international surveys shows that the current metal levels in soils are usually lower. Recently, Rimmer et al., (2006) measured the levels of a series of metals in soil samples collected near a municipal solid-waste incinerator (MSWI) in the UK. All metal concentrations (As, Cd, Cr, Hg, Ni and Pb) were higher than those found in the present study. The current mean Pb and Cd concentrations in soil samples collected in the vicinity of the HWI are also lower than those found in forest soils from Mexico City (Morton-Bermea et al., 2002), whereas similar levels of Pb were found in vegetable garden soils from Hangzhou, China (Wuzhong et al., 2004). With respect to vegetation, higher mean concentrations of a

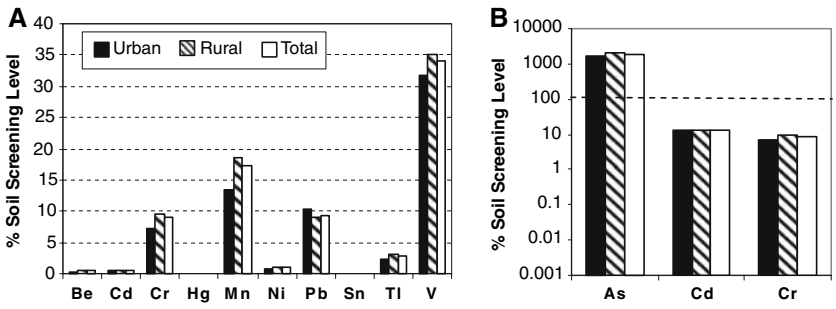

Fig. 1 Non-carcinogenic (A) and carcinogenic (B) risks for subjects living near the HWI of Tarragona (Catalonia, Spain). Comparison between metal concentrations in soils and the Preliminary Remediation Goals

number of heavy metals (As, Cd, Cr, Hg and Pb) were recently reported in edible vegetables cultivated in agricultural soil in Zhengzhou, China (Liu et al., 2006).

On the other hand, metal concentrations in soils in the vicinity of the HWI were compared with those established as Preliminary Remediation Goals (PRG) in residential areas by the US EPA (2004) (Fig. 1). With respect to non-carcinogenic risks, none of the elements exceeded the safe value of 100% (Fig. 1A). Since the levels of most metals were slightly higher in the urban area, health risks were consequently higher in populated areas. However, the differences (in percentage) between both areas were not statistically significant. Among the analyzed metals, V showed the highest percentage of soil screening level, although the risk was approximately 3-times lower than the safe value. With respect to cancer risks (Fig. 1B), As was the only carcinogenic element exceeding the 100% soil screening level. The concentrations of As in soils can vary enormously depending on their geological origin. According to local geological studies, the area under current evaluation belongs to the quaternary period. Consequently, it could be expected that the natural composition of soils would show high As values. In addition, since PRGs are very conservative in comparison to the levels found in soils worldwide, these concentrations may be easily exceeded.

Metal intake through ingestion and inhalation was calculated for adults and children living in the vicinity of the HWI. The criteria for calculations were obtained from Granero and Domingo (2002): a soil intake, an inhalation rate, and a body weight of 50 mg/day, 20 m^3/day and 70 kg for adults, and 200 mg/day, 10 m^3/day and 15 kg for children, respectively. A particulate matter concentration of 52 $\mu g/m^3$ was considered. The predicted oral daily exposure to metals together with the oral reference dose (RfD_o), are summarized in Table 3. For all elements, the hazard quotient (HQ), calculated by dividing the oral exposure by the RfD_o, did not exceed the safe value of 1. The predicted inhalation exposure is also shown in Table 3. Cancer risks due to ingestion and inhalation of carcinogenic elements were also calculated for adults and children living in urban and rural areas near to the HWI. It was noted that As ingestion would slightly exceed the recommended value of 10^{-6} (3.4×10^{-6} and 1.3×10^{-5} for adults and children, respectively). As has been observed, the concentrations of this metal in soils are above the PRG established by the US EPA (2004). Excepting As, only Cr inhalation might mean a very slight increase in the number of cancer cases in adults (2.5×10^{-6}). Since it is included in the range 10^{-4}–10^{-6}, this level can be considered allowable in risk assessment.

The current data indicate that the HWI of Constantí does not result in a significant source of metal pollution in the area. The surveillance program has determined that the levels of most elements (with the potential exception of As)

Table 3 Predicted oral and inhalation daily exposures (mg/kg day) to metals from soils for adults and children living in the vicinity of the HWI of Tarragona (Catalonia, Spain)

	RfD_o (mg/kg day)	Ingestion		Inhalation	
		Adults	Children	Adults	Children
As	3.00E-04	5.26E-06	9.83E-05	5.47E-08	1.28E-07
Be	2.00E-03	4.50E-07	8.40E-06	4.68E-09	1.09E-08
Cd	5.00E-04	1.57E-07	2.93E-06	1.63E-09	3.81E-09
Cr	3.00E-03	1.36E-05	2.54E-04	1.42E-07	3.30E-07
Hg	3.00E-04	1.79E-08	3.33E-07	1.86E-10	4.33E-10
Mn	2.40E-02	2.18E-04	4.06E-03	2.26E-06	5.28E-06
Ni	2.00E-02	1.18E-05	2.20E-04	1.23E-07	2.86E-07
Pb	3.50E-03	2.68E-05	5.01E-04	2.79E-07	6.51E-07
Sn	6.00E-01	1.14E-07	2.13E-06	1.19E-09	2.77E-09
Tl	6.60E-05	1.07E-07	2.00E-06	1.11E-09	2.60E-09
V	1.00E-03	1.91E-05	3.56E-04	1.99E-07	4.63E-07

do not add relevant health risks for the population living in the vicinity of the facility. However, a continued monitoring of As would be desirable.

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