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Influence of Waste Dump Remediation on the Levels of Mercury in the Air

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Abstract Mercury concentrations in air were measured at three measuring sites in the vicinity of a waste dump Jakuševec in Zagreb, Croatia over a 4-year period, from the beginning to the end of remediation. Measurements at the beginning of the remediation show that the concentrations of mercury at all three measuring sites were relatively high. Annual mercury mass concentrations in 2001 were between 17 and 445 ng m^{-3}. Annual mercury averages in 2004 ranged from 8 to 10 ng m^{-3}. Mercury variations were analysed with regard to the meteorological conditions. The results of this investigation show that in regard to mercury, the remediation was successful.

Keywords Air pollution · Atmospheric mercury · Meteorological parameters · Seasonal variations

Mercury (Hg) is emitted in the atmosphere as elemental, inorganic, and organic mercury, in the form of vapour and aerosols. The sources may be natural or anthropogenic. Natural sources are volcanic eruptions and mercury evaporation from ground or water. The main anthropogenic mercury sources are fossil fuel combustion, different industrial processes (Dommergue et al. 2002; Wängberg et al. 2003), waste treatment, and waste incineration (de la Rosa et al. 2006). Mercury is present in the soil, water, plants, and in almost all human food (Schroeder and Munthe 1998). It readily evaporates at room temperature. With the exception of lead, mercury is the oldest known toxic element. In human body it can disturb its normal function and transiently or permanently damage body organs. Mercury can reach into the human body through the gastrointestinal tract, skin or respiratory system. Breathing of mercury vapours and small particles is the main path of mercury intake.

The waste dump Jakuševec is located in the southeast part of Zagreb, Croatia (~700,000 inhabitants), on the right bank of the River Sava, and it poses a risk to groundwater pollution and to the health of people living in nearby settlements. Preliminary measurements at the location showed that mercury concentrations in air were relatively high (Čačković et al. 2000; Hršak et al. 2001). In order to protect the environment and human health, remediation of the waste dump started in 2001. This investigation presents the results of mercury measurements in air at three measuring sites in the vicinity of the waste dump Jakuševec over a 4-year period. The measurements were carried out in order to find if remediation successfully reduced mercury air pollution.

Materials and Methods

Mercury samples were collected at three sites. Measuring site S1 was located several hundred meters southwest from the waste dump, at a football playground of FC Sava in the village Jakuševec. Measuring site S2 was located on the western edge of the waste dump, while measuring site S3 was on the northern edge of the waste dump (see Fig. 1). Measurements were taken over the period 2001–2004.

24-h samples were collected by sucking small volumes of air through membrane filter Sartorius (diameter 37 mm, pore sizes 0.8 μm). The filter is a collective medium for mercury aerosols. Mercury vapours were collected in glass bubblers filled with absorption solution. Absorption solution was the mixture of 1% potassium permanganate

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Fig. 1 Position of the measuring sites

solution and 1 mol L^{-1} sulphuric acid solution, in the ratio 1:1 (ISO 6978 1992). Analysis of samples included measurements of particulate mercury collected on membrane filter and the analysis of mercury vapours collected in bubblers. Membrane filter with particle sample was put in absorption solution to dissolve mercury compounds. In the absorption solution mercury was oxidised to Hg(II) ion. The rest of permanganate was reduced with hydroxylamine hydrochloride ($NH_2OH \bullet HCl$). Mercury ions were then reduced with tin (II) chloride, $SnCl_2$, to elemental mercury. Mercury vapours released in this reaction were conducted in the stream of purified air through a cell of atomic absorption spectrometer (AAS). Mercury was analysed with flameless atomic absorption spectrometry, and the intensity of absorbance was measured at 253.7 nm. Hg vapours were analysed in the same way as aerosols. The limit of detection of the method was 0.13 ng mL^{-1}, which approximately corresponds to mercury concentration in air of 3 ng m^{-3}. The accuracy of the method was determined by adding known amounts of Hg standard solution in the absorption solution and on membrane filters. The recovery tests were carried out at three levels (0.05, 0.10 and 0.20 ng of mercury). Average fortified recoveries ranged from 95.5 to 100.9%.

Mercury in the atmosphere is mostly in a vapour form, and only about 5% is associated with particles (Schroeder and Munthe 1998). Valente et al. (2007) found that particulate mercury usually occurred in concentrations about a hundred times lower than vapour mercury while in the study of Pyta et al. (2009) the contribution of particulate mercury in the total mercury was between 4.6 and 14.4%. In our study, mercury concentrations in aerosol were usually low and close to the detection limit of the method. For this reason, we calculated the sum of values obtained by aerosol analysis and by vapour analysis, and this sum presents total mercury concentration in the air.

Meteorological data in the form of 24-h averages (average daily temperature, relative humidity and pressure) were obtained from the national Meteorological and Hydrological Service.

Results and Discussion

Table 1 presents summary statistics of mercury mass concentration at all three measuring sites in the vicinity of the waste dump Jakuševec. Over the whole measuring period, 24-h mercury concentrations varied from below the detection limit of 3 ng m^{-3} to 853, 745, and 7,613 ng m^{-3} at measuring sites S1, S2, and S3, respectively. The average annual values obtained in the first year of measurements (17 ng m^{-3} at S2, 35 ng m^{-3} at S1, and 445 ng m^{-3} at S3) were significantly higher than values observed in the last year of measurements (annual averages between 8 and 10 ng m^{-3}). The highest daily value for the whole measuring period was also observed in the first year of measurements (7,613 ng m^{-3} at S3).

Preliminary measurements carried out before remediation showed that air temperature had the main influence on Hg concentrations (Hršak et al. 2001), and higher concentrations were observed in the summer months. Characteristic seasonal variations were found due to greater mercury evaporation at higher temperatures. In this study, linear (Pearson) correlation coefficients were calculated between air temperature, relative humidity, pressure, and mercury concentrations at S1, S2 and S3 (Table 2). Statistically significant positive correlation was found between mercury concentrations at S1 and S2 over the whole measuring period ($r = 0.24$, $P < 0.001$), and the strongest correlation was observed during the first year ($r = 0.54$, $P < 0.001$). A weak positive correlation between mercury concentration and temperature was also observed at both sites. This correlation was the most pronounced over the second year. At measuring site S3, which was the most exposed to the remediation, statistically significant negative correlation was found only between mercury levels and atmospheric pressure.

Mercury concentrations at all three sites and meteorological data in the form of 24-h averages, were also subjected to the factor analysis in order to define virtual variables which will describe their interdependence. Factors were based on principal component extraction and rotated by normalized varimax method. Three significant factors were extracted (Fig. 2). The total variance explained by three factors accounted 65%. The first factor separates temperature and relative humidity, e.g. good weather conditions but not connected with mercury levels,

Table 1 Descriptive statistics of 24-h mercury mass concentrations (ng m^{-3}) in the vicinity of the waste dump Jakuševec

Year of measurement	Measuring site	*N*	Mean	Median	Minimum	Maximum	Standard deviation
1	S1	358	35	15	n.d.	853	70
	S2	353	17	13	n.d.	186	15
	S3	330	445	23	n.d.	7,613	1,180
2	S1	365	10	8	n.d.	68	7
	S2	363	11	9	n.d.	120	11
	S3	350	15	9	n.d.	98	17
3	S1	360	20	9	n.d.	521	38
	S2	361	21	9	n.d.	745	59
	S3	363	22	9	n.d.	783	52
4	S1	365	10	8	n.d.	49	9
	S2	360	9	6	n.d.	97	9
	S3	358	8	6	n.d.	48	7
Overall	S1	1448	19	10	n.d.	853	41
	S2	1437	14	9	n.d.	745	32
	S3	1401	116	10	n.d.	7,613	601

n.d. values were lower than the detection limit of the method (3 ng m^{-3})

Table 2 Correlation coefficients (*r*) between Hg concentrations at S1, S2 and S3 and some meteorological parameters over the period 2001–2004

	S2	S3	*t*	RH	*P*
S1	0.24*	0.01	0.18*	−0.07	−0.03
S2		0.00	0.15*	−0.09	0.02
S3			−0.03	−0.02	−0.13*
t				−0.44*	−0.31*
RH					−0.06

* Statistically significant correlations ($P < 0.001$)

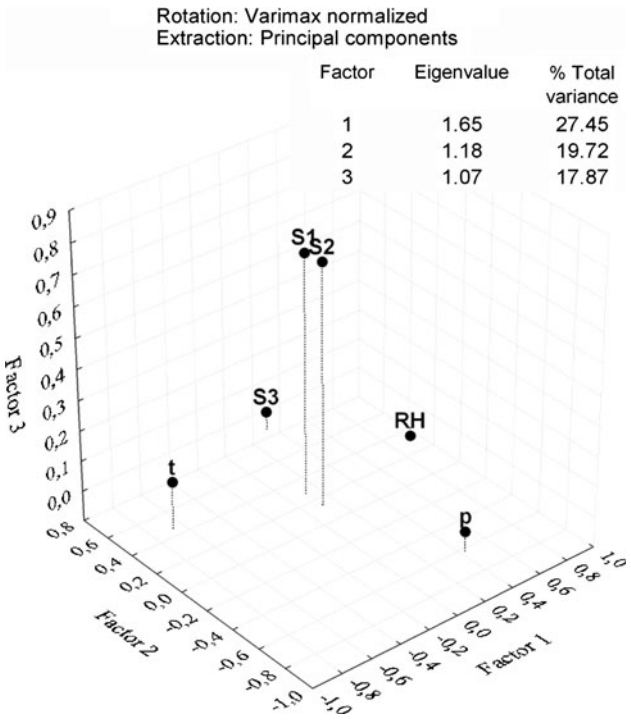

Fig. 2 3D plot of factor loadings (daily Hg concentrations at S1, S2 and S3 and some meteorological parameters)

as it was found in previous investigations (Hršak et al. 2001). The second factor describes the relationship between high mercury concentration at S3 and low air pressure. Low atmospheric pressure is usually connected with air masses mixing and with windy and rainy weather. During such weather conditions the strong winds probably blew before the storms. They carried dust from the waste dump surface causing high Hg concentrations in air at S3. The third factor describes relationship between mercury concentrations at S1 and S2, which are both approximately at the same distance from the centre of the remediation surface and closer to the local population.

Figure 3 shows the variations of minimum, maximum, and average monthly Hg concentrations at measuring sites S1, S2, and S3 over the whole measuring period. Figure 4 shows mercury concentrations measured over three winter and three summer months at all three locations. Mercury concentrations did not show characteristic seasonal pattern during the remediation. Variations of daily, monthly, and annual concentrations depended on the dynamic and type of remediation processes and on the composition of the deposited waste at different parts of the surface. The highest mercury concentrations were measured in March, April, and May of 2001 when remediation works were the most intense. After that period, Hg concentrations slowly

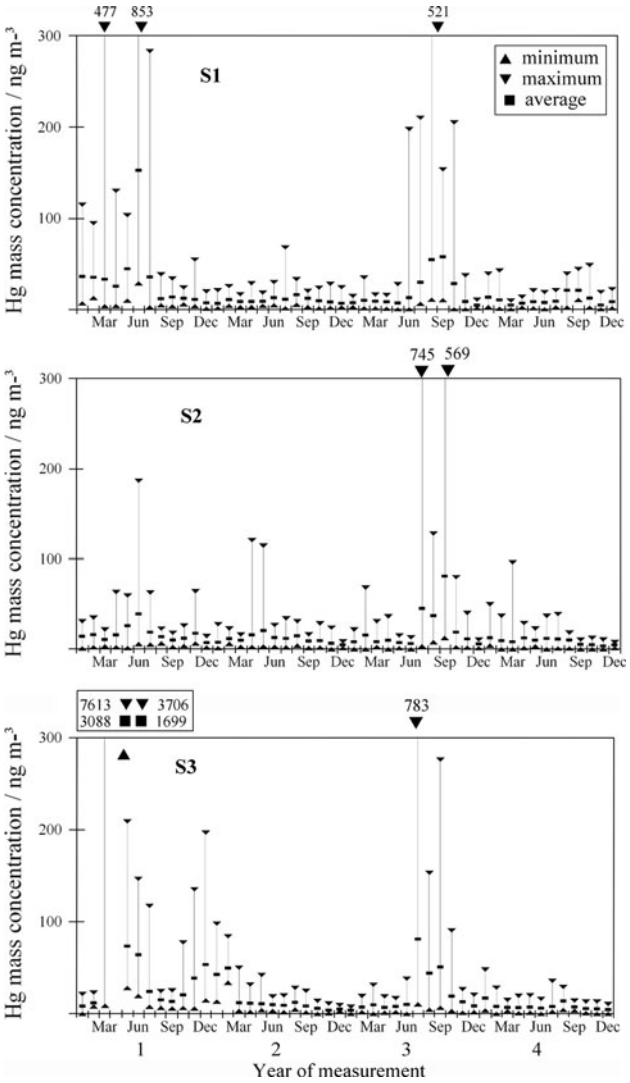

Fig. 3 Variations of minimum, maximum, and average monthly Hg concentrations at measuring sites S1, S2 and S3 over the whole measuring period

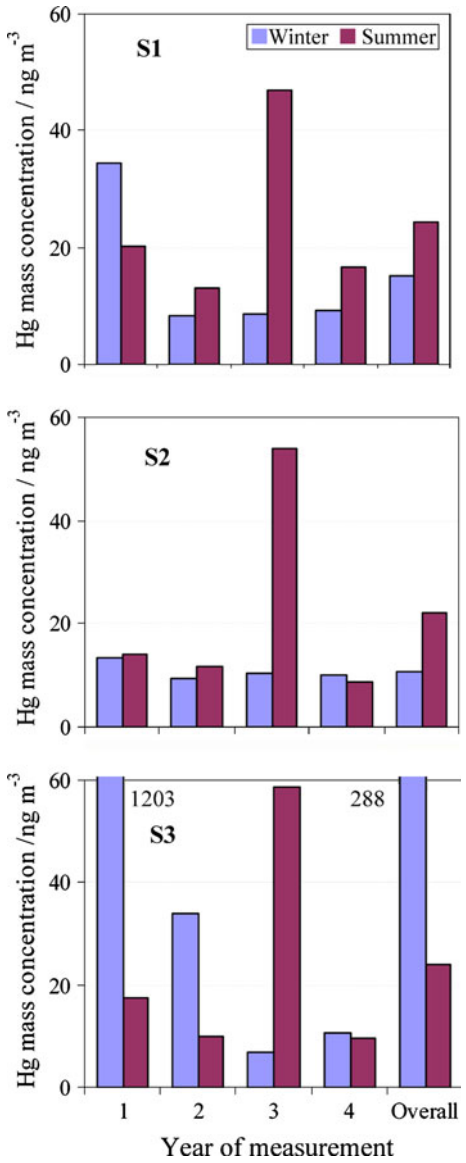

Fig. 4 Mercury concentrations measured at all three locations during three winter and three summer months

decreased. High mercury levels were also recorded in the second part of the third measuring year, when some remediation processes were renewed. During the third year of measurement, the remediation in the northern part of the waste dump was completed, and measuring site S3 was removed from the northern to the eastern edge of the waste dump. From July to October 2003 (warmer months), mercury concentrations were elevated and their monthly averages ranged from 21 to 80 ng m^{-3}. Figure 3 and Table 1 clearly show that the highest daily mercury concentration in the fourth year was much lower than in previous years.

World Health Organization (WHO 2000) established a guideline value for inorganic mercury vapour of 1 μg m^{-3} as an annual average. In our measurements this value was not trespassed for all 4 years. However, our investigation raises a question should daily mercury values be included in air quality standards (for example as a number of exceedings over the year) because such occasionally high daily values (more than 7,500 ng m^{-3}) probably have an influence on human health and environment.

Mercury concentrations measured in this study were compared with similar measurements at different locations in the world. Valente et al. (2007) reported about atmospheric mercury measurements from many remote, rural and urban areas in the world. These authors compared their own results with earlier measurements, which, in average, ranged between 1.7 in rural to 5.2 ng m^{-3} in urban or near-source areas for gaseous elemental mercury, and between 0.021 and 0.185 ng m^{-3} for particulate mercury. At four

remote EMEP stations 5-year average of total gaseous mercury (TGM) for the period 1999–2002 was between 1.6 and 1.8 ng m^{-3} (Wängberg et al. 2007). Slemr and Scheel (1998) found that TGM at Wank mountain in Germany decreased about 7% per year over the period 1990–1996, and annual means ranged between 1.822 and 2.973 ng m^{-3}. In a rural area in Poland TGM concentrations were below 2.5 ng m^{-3} in the summer and between 3 and 7 ng m^{-3} in the winter (Zielonka et al. 2005) while in a rural site of central southern England mean annual value was 1.68 ng m^{-3} (Lee et al. 1998). Measurements of TGM in suburban industrial area in France located near chlor-alkali plant and municipal waste incinerator showed that hourly averages ranged between 0.1 and 37.1 ng m^{-3} with an average 3.4 ng m^{-3}. Hg concentrations showed variability due to the influence of local anthropogenic sources (Dommergue et al. 2002). In French urban areas waste incineration is the major source of mercury. Atmospheric mercury concentrations near a chlor-alkali plant in Bohus, Sweden, varied between 0.15 and 270 ng m^{-3} (Wängberg et al. 2003). In an urban area in Poland (Gliwice) average monthly mercury concentrations ranged between 4.1 and 9.1 ng m^{-3}, and the highest concentrations were observed in months with low temperature and precipitation (Pyta et al. 2009). Mercury concentrations in air were continuously measured in the Idrija region, Slovenia, with the world's second largest Hg mine. In that area, Hg concentrations decreased significantly in the last decade, especially after the mine was shut down. Mercury air levels swooped from more than 1,000 ng m^{-3} to below 10 ng m^{-3} (Kotnik et al. 2005). There are several papers discussing high mercury concentrations still present in soils and waters near abandoned mines (Gemici and Tarcan 2007; Hojdová et al. 2008).

In general, mercury concentrations in air at all three sites near the waste dump Jakuševec significantly decreased from 2001 to 2004. At measuring sites S1 and S2 (more distanced from the remediation processes) a weak positive correlation was found between air temperature and Hg concentrations. Measuring site located near the remediation surface (S3) exhibited a different behaviour. The results show that in regard to mercury the remediation was successful. However, occasionally high daily mercury concentrations showed that continuous measurements are necessary during such remediation processes. Values measured in this study are one of the highest reported for Europe over the last decade, and may be compared to the levels measured near the closed mining areas (e.g. Kotnik et al. 2005). High daily peaks of Hg concentrations may be expected in other countries during similar remediation processes. Such levels present a risk for the health of workers on the waste dump and on the health of local population.

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