

Thallium Content in Zagreb Air

J. Hršak, A. Škrbec, I. Balagović, K. Šega

Institute for Medical Research and Occupational Health, Ksaverska c. 2, 10000 Zagreb, Croatia

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Thallium is present in raw materials and can significantly increase environmental exposure on local and regional level (IPCS, 1996). It is present in the air in relatively small amounts and in most countries it is not included in general monitoring practice. Thallium is mainly released in the air by mineral smelters, power-generating plants, and cement plants (ATSDR, 1992). Deterioration of building material could be considered as a significant source of thallium contamination in urban areas. The main source of thallium is the re-dispersion of dust from the contaminated soil as a disperse pollution source, covering an entire city. The only cement plant in Zagreb was the main source of thallium and was shut down approximately 15 years ago, so we can assume that no significant new deposition occurred during the last decade. The contribution of two large power plants with 200 meter smokestacks as point sources which disperse the pollution over vast areas may be considered negligible. Croatian legislation (Ordinance, 1996) prescribes only the limit value for a monthly amount of thallium in deposited matter (a large particle fraction); there are no limit values for thallium concentrations in the ambient air (suspended particulate matter). In order to get an insight into thallium levels in the Zagreb environment, thallium content in total suspended particulate matter, and its content in deposited matter was investigated for three consecutive years at two urban sites.

MATERIALS AND METHODS

Thallium monitoring was performed at two measuring sites, one representing the city centre with high traffic density and large number of individual heating systems mainly using natural gas and the other situated in the northern, residential part of the town with moderate traffic density and plenty of green areas. Monitoring lasted for three consecutive years (January 1998-December 2000). In order to detect thallium levels in the air, 24-hour samples of total suspended particles were collected on membrane filters (Millipore HOK63169B) from approximately 250 m³ of air. Samples of deposited matter were collected at the same locations once a month using the Bergerhof-type (Measurement of Dustfall, 1972) deposit gauge. After weighing and drying samples were digested in nitric acid, the residue evaporated, dissolved in 5.0 mL 1 mol nitric acid, and the thallium content was determined by flame atomic absorption spectrometry.

RESULTS AND DISCUSSION

Thallium content levels in suspended particulate matter are shown in Table 1. The concentrations are similar to those measured in some other cities (Bowen 1979; Valerio et al. 1988).

Table 1. Thallium content in suspended particulate matter (ng/m³).

	City centre			Residential		
	1998	1999	2000	1998	1999	2000
N	156	192	185	194	327	363
Mean	4.91	1.02	0.62	1.12	0.81	0.74
SD	3.96	0.53	0.45	0.92	0.75	0.94
50 th percentile	3.69	0.92	0.64	1.05	0.61	0.59
25 th percentile	1.67	0.67	0.34	0.51	0.29	0
75 th percentile	6.76	1.34	0.76	1.62	1.14	1.08
Minimum	0	0	0	0	0	0
Maximum	18.78	2.62	2.17	5.04	5.85	8.90

N - number of samples

SD - standard deviation

Unlike with other heavy metals, the distribution of thallium could not be approximated, either to normal, or to log normal or gamma distribution. This is why median, lower and upper quartile concentrations are shown in addition to the mean concentration. No significant correlations were found between daily concentrations measured at the different sampling sites. The concentrations showed no significant seasonal dependence. Negative yearly trend of thallium concentrations could be perceived at both locations. These results suggest that concentrations of thallium in the air depend on local sources only.

Thallium content levels in deposited matter (Table 2), was relatively low, keeping around the recommended limit value (LV) of 2 µg/m²/day, but much lower compared to the limit value of 10 µg/m²/day stipulated by the Ordinance on Recommended and Limit Air Quality Values (Ordinance, 1996).

Deposited thallium showed no significant seasonal dependence and no correlation between the sampling locations. Again, there is a negative yearly trend of thallium content in deposited matter at both locations. These results corroborate the conclusion that thallium concentration levels depend on local sources only. Monthly averages of thallium content in suspended particulate matter were calculated (Table 3) in order to correlate these values to the results of thallium content in dustfall. No significant correlations were found.

It should be noted that in the near vicinity of the sampling site located in the city centre, roof hydro-insulation was replaced during the end of July and most of the

Table 2. Thallium content in deposited matter ($\mu\text{g}/\text{m}^2/\text{day}$).

	City centre			Residential		
	1998	1999	2000	1998	1999	2000
January	-	1.92	1.42	1.43	1.85	0.31
February	-	1.91	2.74	1.51	2.00	0.86
March	3.52	4.18	1.08	1.40	1.35	2.13
April	4.84	3.08	1.69	2.99	1.63	2.37
May	2.12	1.60	0.98	1.45	3.14	1.64
June	3.23	2.27	1.29	1.79	1.60	0.80
July	4.71	1.75	3.26	2.37	1.70	1.20
August	10.07	2.89	1.23	2.40	1.51	0.95
September	3.86	1.94	1.60	2.28	1.54	1.23
October	0.98	2.28	1.75	1.26	2.34	0.76
November	2.15	2.12	0.46	2.12	3.14	0
December	0.92	1.11	2.28	1.09	0.77	1.42
Mean	3.64	2.25	1.65	1.84	1.88	1.14

Table 3. Average monthly thallium concentrations in suspended particulate matter (ng/m^3).

	City centre			Residential		
	1998	1999	2000	1998	1999	2000
January	5.23	1.24	0.99	1.09	1.01	1.15
February	7.01	0.81	0.56	1.74	0.42	0.90
March	4.70	1.06	0.64	0.99	1.04	0.66
April	4.04	1.23	0.65	1.15	0.73	0.58
May	2.47	1.01	0.44	1.21	0.56	0.60
June	0.55	0.67	0.55	0.55	0.53	0.58
July	2.51	0.86	0.67	0.36	0.46	0.54
August	3.83	0.67	0.55	1.36	0.62	0.56
September	1.66	0.89	0.74	1.35	1.01	0.57
October	1.45	0.99	0.63	1.31	0.88	1.00
November	1.79	1.27	0.62	2.18	1.00	1.24
December	1.17	0.93	0.59	1.22	0.71	0.56

August. Elevated concentrations during this period clearly indicate the influence of the local source.

Mass concentrations of thallium in total suspended particulate matter in Zagreb air were relatively high and showed similar with the levels measured in some other cities. Thallium content in deposited matter was much lower than the limit value defined in the Ordinance on Recommended and Limit Air Quality Values. It could be concluded, that the likeliest major source of thallium is dust dispersed from the soil in which thallium had been depositing as an emission product from the cement plant shut down 15 years ago. No correlations were found between thallium concentrations measured at different locations, as well as no correlations between deposited and suspended thallium content, which suggests that the environmental pollution with thallium was strictly dependent on local sources.

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