Bull Environ Contam Toxicol (2010) 85:628–631
DOI 10.1007/s00128-010-0142-6

Zinc Levels in Suspended Particulate Matter in Zagreb Air

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Received: 18 January 2008 / Accepted: 28 October 2010 / Published online: 25 November 2010

Abstract Monitoring of zinc in total suspended particulate matter (TSPM) started in Zagreb, Croatia in 1972 at two measuring sites, located in the city centre and in the northern part of the city. Monitoring of zinc concentrations in PM_{10} started in the northern part of the city in 2003. The obtained data show a decreasing trend of zinc in TSPM. Over the past 3 years, the measurement of zinc in PM_{10} particles has been performed, and the obtained data, in comparison to zinc in TSPM, have shown that 82%–93% of zinc was in the small PM_{10} particles.

Keywords Heavy metals · City areas · Total suspended particulate matter · PM_{10}

In nature, zinc occurs only rarely in its metallic state and the vast majority of environmental samples contain the element only in the form of zinc compounds.

Zinc levels of 0.01–0.30 µg m^{-3} are given for background concentrations and up to 1.00 µg m^{-3} for urban and industrial areas. Zinc concentrations of 0.0003–0.027 µg m^{-3} were found over the Atlantic Ocean, <0.0004–0.3 µg m^{-3} in European urban areas (WHO 2001). Deposition of airborne zinc is strongly dependent on particle size and meteorological factors, primarily wind speed and humidity. Wet deposition predominates with estimated values for zinc removal from air of 60%–90%.

The transport and distribution of atmospheric zinc vary according to the size of particles and the properties of the zinc compounds concerned. Zinc adsorbed on particles with low densities and diameters can be transported over long distances (WHO 2001).

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Materials and Methods

The monitoring of zinc concentrations in total suspended particulate matter (TSPM) started in Zagreb in 1972 at two measuring sites located in a densely populated area in the city center, and in a sparsely populated housing area in the northern part of the city. Zinc monitoring in PM_{10} particles started in the northern part of the city in 2003. The location of measuring sites is shown in Fig. 1.

Twenty-four-hour mass concentration samples of total suspended particulate matter were collected on membrane filters of about 200 m^3 of air, while PM_{10} samples were also collected on membrane filters of about 100 m^3 of air.

Mass concentrations of total suspended particulate matter and PM_{10} samples were determined gravimetrically. Detection limit values were 2.0 µg m^{-3} for total suspended particulate matter and 1.0 µg m^{-3} for PM_{10} (Hršak et al. 2000).

Mass concentration of zinc in total suspended particulate matter and in PM_{10} samples was determined by atomic absorption spectrophotometry (AAS). The detection limit for Zn was 0.0005 µg m^{-3} (Christian and Feldman 1970).

Until the end of 2005, air quality in Croatia was assessed by comparing annual means with recommended (RV) and limit (LV) values stipulated by the national Air Protection Act of 1995 (Air Protection Act 1995) and the Ordinance on Recommended and Limit Air Quality Values (Ordinance 1996). The 1995 Air Protection Act defines three categories of air quality:

1st category – clean air (the concentration levels of air pollution are below RV)

Fig. 1 Location of measuring sites

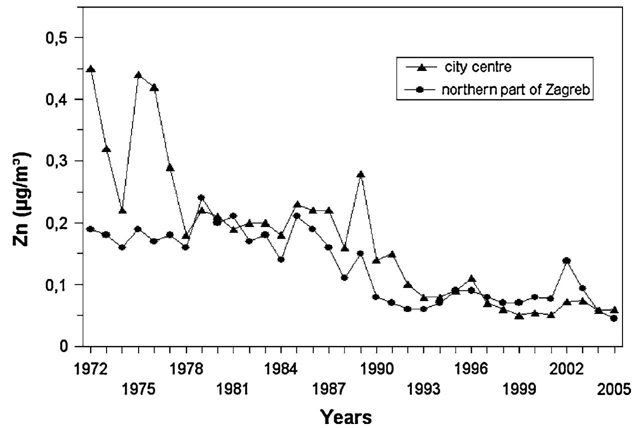

Fig. 2 Trends of annual values for zinc in total suspended particulate matter in Zagreb

2nd category – moderately polluted air (the concentration levels of air pollution are over RV and below LV)
3rd category – polluted air (the concentration levels of air pollution are over LV)

It also defines RV and LV in total suspended particulate matter for Pb, Mn and Cd, but not for Zn and the categorization of Zagreb air with the respect to the levels of zinc can not be provided.

The new Air Protection Act (Air Protection Act 2004) and the new Ordinance on Limit Values of Pollutants in the Air (Regulation 2005) have started with the enforcement in 2006. Croatian regulations are in agreement with the European standards.

Following the European Council Directives, the 2005 Ordinance on Limit Values of Pollutants in the Air gives limit values (LV) for PM_{10} and for metals Pb, Mn, Cd, As and Ni in PM_{10}, and the "margin of tolerance", that is, the percentage of the limit value by which this value may be exceeded. Limit values for zinc are not given.

Results and Discussion

Figure 2 shows the trends of annual values for zinc in total suspended particulate matter in Zagreb air measured at two sites located in the city center (densely populated area) and in the northern part of the city (sparsely populated housing area) for the period 1972–2005. The annual mean concentrations of zinc in total suspended particulate matter ranged between 0.045 and 0.45 µg m^{-3} during the measuring period.

A strong decreasing trend can be observed from 1972 to 1978 in the city centre. During that period coal for heating in the city centre was replaced by gas. A light decreasing trend can be observed from 1978 until now in the city centre and for the whole measuring period in the northern part of the city.

Figure 3 shows daily concentrations of zinc in total suspended particulate matter in 1976 and 2004, measured in the northern part of the city. These data show a significant decrease in 24-hour mass concentrations of zinc in total suspended particulate matter in 2004 in comparison with the 1976 measurements.

Table 1 shows annual mean values and the range of zinc concentrations in total suspended particulate matter and in PM_{10} in the northern part of the city for 2003–2005.

The obtained data show that 82% of zinc was in small PM_{10} particles in 2005, 86% of zinc was in PM_{10} in 2003 and as much as 93% in 2004. These data are in agreement with conclusions in literature that zinc in the atmosphere is primarily bound to aerosol particles.

Figure 4 shows daily concentrations of zinc in total suspended particulate matter and in PM_{10} at the same measuring site in 2004. The size of particle is determined by the source of zinc emission. A major proportion of zinc released from industrial processes is adsorbed on particles that are small enough to be in the respirable range (PM_{10}) (WHO 2001). From Fig. 4 it can be seen that the daily variations of zinc concentrations in total suspended particulate matter and in PM_{10} in 2004 are similar.

Zinc is essential element in the environment and there are few literature reports about the levels of zinc in the air. The toxicity of zinc will depend on environmental conditions and habitat types, thus any risk assessment of the potential effects of zinc on organisms must take into account local environmental conditions.

The essential nature of zinc, its relatively low toxicity in humans, and the limited sources of human exposure suggest that normal, healthy individuals not exposed to zinc in

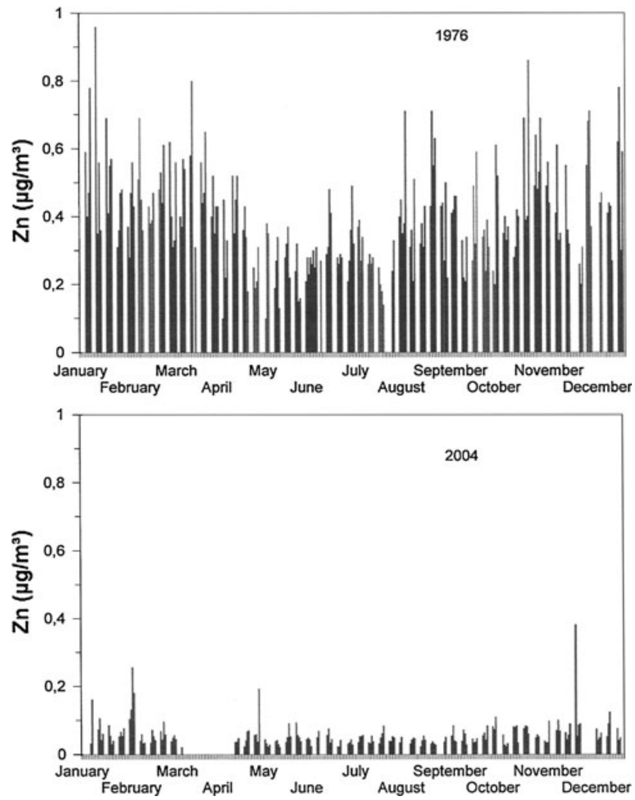

Fig. 3 Daily concentrations of zinc in total suspended particulate matter in 1976 and 2004 measured in the northern part of the city

Table 1 Annual mean values and range of zinc concentrations (µg m^{-3}) in TSPM and in PM_{10} for the period 2003–2005

Year	Zn in TSPM		Zn in PM_{10}	
	C	Range	C	Range
2003	0.093	0.012–0.713	0.080	0.011–0.199
2004	0.057	0–0.560	0.053	0–0.505
2005	0.045	0.004–0.176	0.037	0.005–0.194

C Annual mean values

the workplace are at potentially greater risk from the adverse effects associated with zinc deficiency than from those associated with normal environmental exposure to zinc.

Natural background zinc concentrations usually go up to 0.3 µg m^{-3} in the air. Increased levels can be attributed to anthropogenic sources.

Air zinc levels in Belgium have also shown a decreasing trend. In 1980–1990, they were 0.15–0.38 µg m^{-3} in rural areas and small towns, 0.14–0.21 µg m^{-3} in large cities, and 0.50–1.27 µg m^{-3} in industrial areas. By 1992–1993 they fell to 0.07–0.10, 0.1–0.17 and 0.39–1.02 µg m^{-3}, respectively (Cleven et al. 1993).

In the Netherlands, yearly average zinc levels in the air varied between 0.06 and 0.08 µg m^{-3} in 1990. By 1992,

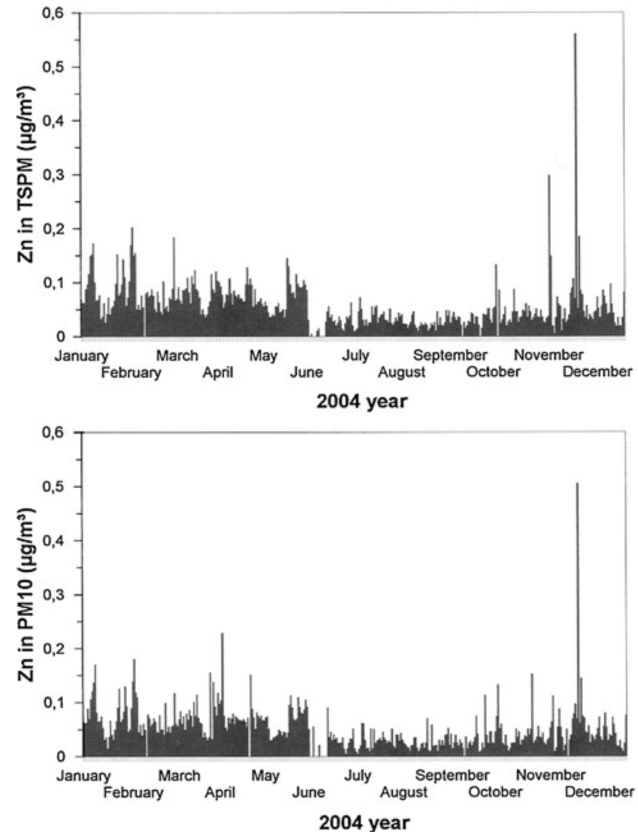

Fig. 4 Daily variations of zinc concentrations in total suspended particulate matter and in PM_{10} in 2004 are similar

the averages decreased to 0.043–0.057 µg m^{-3} (Cleven et al. 1993; European Commission 2008).

In Zagreb, the capital of Croatia, with about one million inhabitants, air zinc levels in total suspended particulate matter were 0.45 µg m^{-3} in the city centre and 0.24 µg m^{-3} in the northern part of the city at the beginning of monitoring in the 1970s.

In 2005, annual mean values were 0.050 µg m^{-3} in the city centre and 0.045 µg m^{-3} in the northern part of the city.

Annual mean values of zinc in PM_{10} particles ranged from 0.08 µg m^{-3} in 2003 to 0.037 µg m^{-3} in 2005.

Zinc monitoring in total suspended particulate matter in Zagreb showed that its concentrations were not high and kept within the natural background concentrations of total zinc. The obtained data showed a decreasing trend for zinc in total suspended particulate matter. According to the Air Protection Act (2004) the monitoring of TSPM finished in 2005.

The obtained data of zinc measurements in PM_{10} respirable range particles, 2003–2005, in comparison with zinc in total suspended particulate matter, showed that 82%–93% of zinc was in the small PM_{10} particles. Monitoring of zinc in PM_{10} particles is ongoing.

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