TRENDS OF LEAD, MANGANESE AND CADMIUM CONCENTRATIONS IN ZAGREB AIR

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ABSTRACT

This paper presents trends of annual mean values for lead, manganese and cadmium concentrations in TSPM, in PM_{10} and $PM_{2.5}$ particles and their comparison with the Croatian limit values, European Union (EU) limit values and World Health Organization (WHO) Guidelines for Europe. The obtained data showed a decreasing trend of lead in TSPM, especially during the last ten years when consumption of lead-free gasoline increased. In 1997, the annual mean lead concentrations in TSPM were 0.5 $\mu g/m^3$, which is the EU limit value and WHO guideline for Europe. Since 1999 the concentrations fell down and they were below 0.25 $\mu g/m^3$.

The annual mean values of manganese in TSPM were very low during the whole period of measuring and they were below 0.15$\mu g/m^3$, which is WHO guideline for Europe.

The trend of cadmium in TSPM slowly decreased and the concentrations were below 0.005 $\mu g/m^3$ (WHO guideline for Europe) during the whole period of measurement except in 1989 in the city centre.

The heavy metal concentrations measured in PM_{10} and $PM_{2.5}$ particles show very high percentages: 88-92% in the case of lead, 60-72% in the case of manganese and 82-97% in the case of cadmium, all were in $PM_{2.5}$ particles.

INTRODUCTION

The monitoring of lead and manganese concentrations in total suspended particulate matter (TSPM) started in Zagreb in 1971. Since 1984 the measurements performed at two measuring sites located in the city centre and in the northern part of the town, have also included cadmium concentrations in TSPM. The monitoring of lead, manganese and cadmium concentrations in PM_{10} and $PM_{2.5}$ particles has started in the northern part of the town in 1999.

MATERIALS AND METHODS

Twenty-four-hour mass concentration samples of TSPM were collected on membrane filters from about 200 m^3 of air, while PM_{10} and $PM_{2.5}$ samples were also collected on membrane filters from about 100 m^3 of air.

Mass concentrations of TSPM, PM_{10} and $PM_{2.5}$ samples were determined gravimetrically. Detection limit values were 2.0 $\mu g/m^3$ for TSPM and 1.0 $\mu g/m^3$ for PM_{10} and $PM_{2.5}$ [1].

Mass concentrations of metals lead, cadmium and manganese in TSPM, PM_{10} and $PM_{2.5}$ were determined by the atomic absorption spectrophotometric method (AAS). Detection limit values for Pb and Mn were 0.0005 $\mu g/m^3$ and for Cd were 0.00005 $\mu g/m^3$.

CROATIAN AND EUROPEAN AIR QUALITY LIMIT VALUES

The recommended and limit values for lead, cadmium and manganese in TSPM in Croatia are shown in Table 1 [2].

Averaging period	Pollutant	RV	LV	Average over
Calendar year	Lead in TSPM	1	2	24 hour
Calendar year	Cadmium in TSPM	0.01	0.04	24 hour
Calendar year	Manganese in TSPM	1	2	24 hour

Table 1 – Recommended (RV) and limit (LV) values for lead, cadmium and manganese in TSPM ($\mu g/m^3$) in Croatia

Table 2 shows WHO Air Quality Guidelines for lead, cadmium and manganese for Europe [3] and Table 3 shows the limit values for lead in TSPM in the European countries [4].

Averaging period	Pollutant	LV ($\mu g/m^3$)
Calendar year	Lead	0.5
Calendar year	Cadmium	0.005
Calendar year	Manganese	0.15

Table 2 – Guidelines for Air Quality, WHO

Averaging period	LV ($\mu g/m^3$)	Date by which limit value is to be met
Calendar year	0.5	From 1 January 2001

Table 3 –Limit value for lead in the European countries

From the Tables 1, 2 and 3 it can be seen that the Croatian limit values are more tolerant than the European ones, and that Croatian regulations should be in agreement with the European standards.

RESULTS AND DISCUSSION

The trends of annual mean values for lead in TSPM in Zagreb air, measured at two sites located in the city centre (densely populated area) and in the northern part of the town (sparsely populated housing area) for the period 1971-2002 are shown in Figure 1.

Figure 2 shows the same trends for manganese in TSPM at the same measuring sites, for the same measuring period.

The measurements of cadmium in Zagreb air started in 1984. Figure 3 shows the trends of annual mean values for Cd in TSPM at the same measuring sites for the period 1984-2002.

As can be seen from the obtained data, the annual mean concentrations of lead in TSPM ranged between 0.4 and 1.4 $\mu g\ m^3$ in the period 1971-1991, but since 1991, over the past ten years, a strong decreasing trend could be observed resulting from an increased consumption of lead-free gasoline in Croatia. The annual mean concentrations of lead in TSPM in 1997 were below 0.5 $\mu g/m^3$, which is in accordance with the EU limit value and WHO guideline for Europe. Since 1999 the concentrations have fallen down and were kept below 0.25 $\mu g/m^3$.

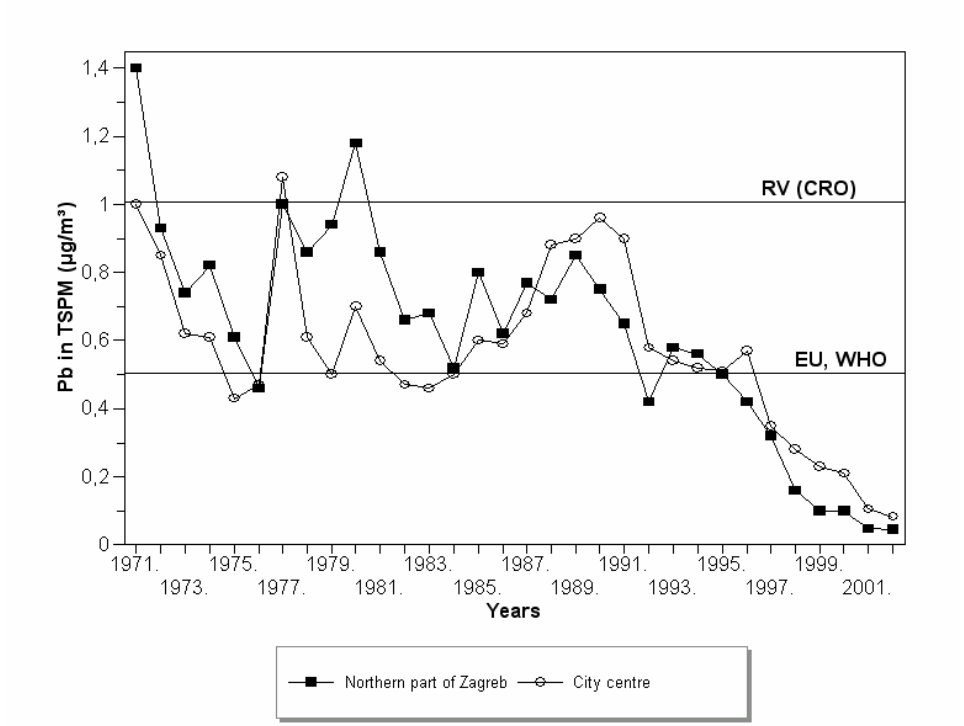

Figure 1 – Trends of annual mean values for lead in TSPM in Zagreb air for the period 1971-2002

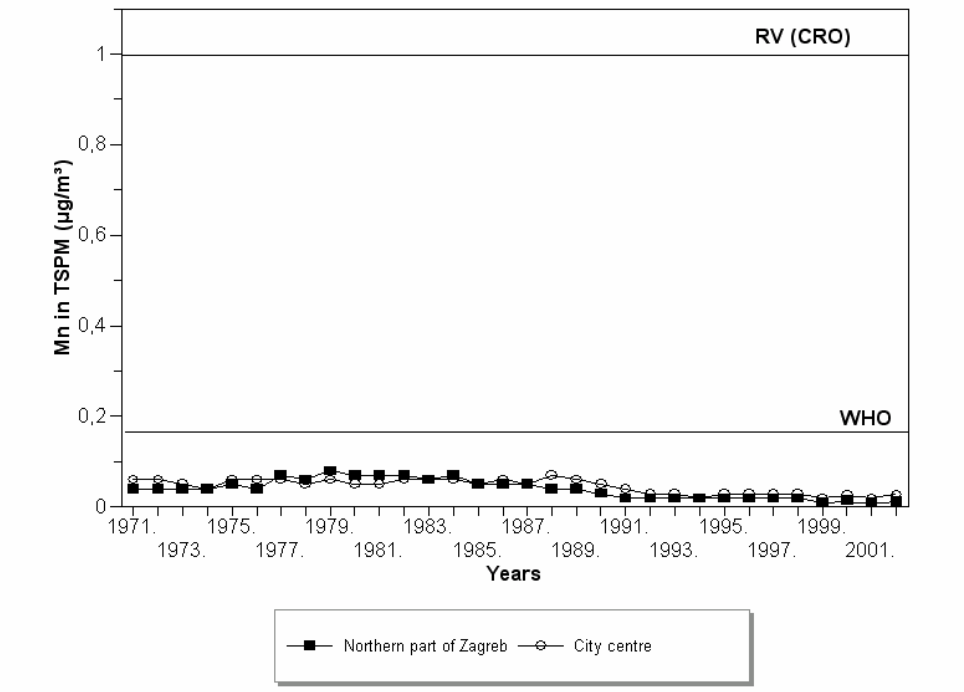

Figure 2 – Trends of annual mean values for magnese in TSPM in Zagreb air for the period 1971-2002

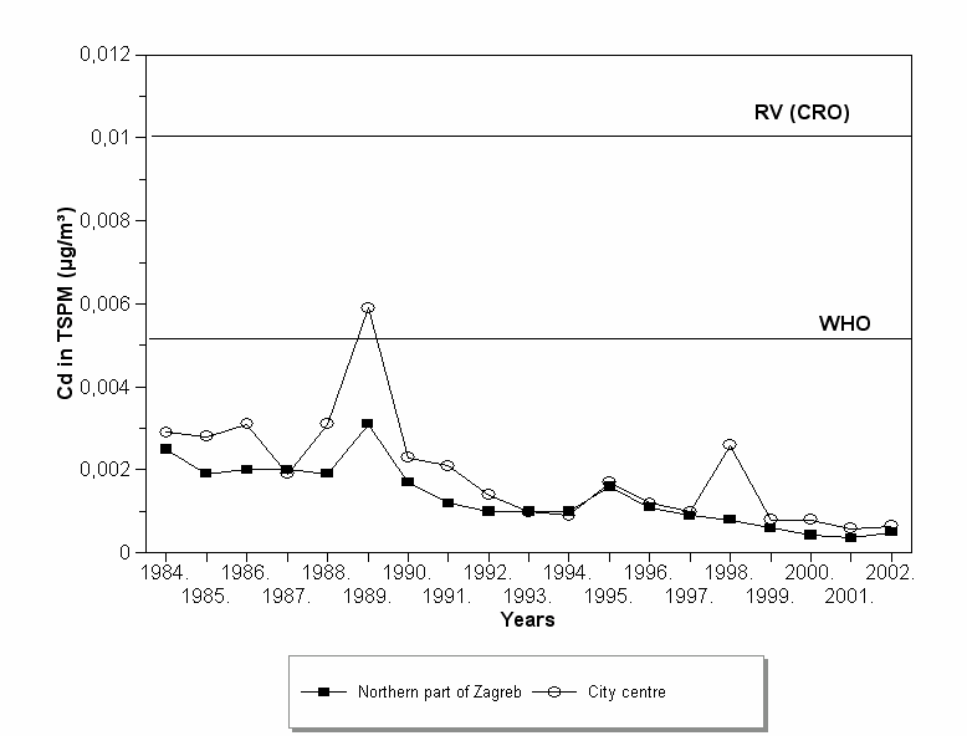

Figure 3 – Trends of annual mean values for cadmium in TSPM in Zagreb air for the period 1971-2002

The obtained results showed that the annual mean values for manganese in TSPM were very low during the whole period of measurement, and were kept below 0.15 µg m^3 which is in agreement with the WHO guideline for Europe. It is shown in Figure 2.

The trend of cadmium in TSPM slowly decreased during the monitoring. Over the whole measuring period, the concentrations were below the Croatian recommended limit value of 0.01 µg/m^3 and below 0.005 µg m^3 (WHO guideline for Europe) except for 1989 in the city centre.

The annual mean values of lead in PM_{10} and $PM_{2.5}$ in the northern part of the town, for the period 1999-2002, are shown in Figure 4. The data for manganese are shown in Figure 5 and for cadmium in Figure 6.

The data for heavy metal concentrations in PM_{10} and $PM_{2.5}$ particles showed very high percentage of metals in smaller $PM_{2.5}$ particles. The percentage was 88-92% in lead, 60-72% in manganese and 82-97% in cadmium.

The heavy metals concentrations in PM_{10} and $PM_{2.5}$ particles were very low during the whole measuring period and for lead and cadmium showed a slowly decreasing trend.

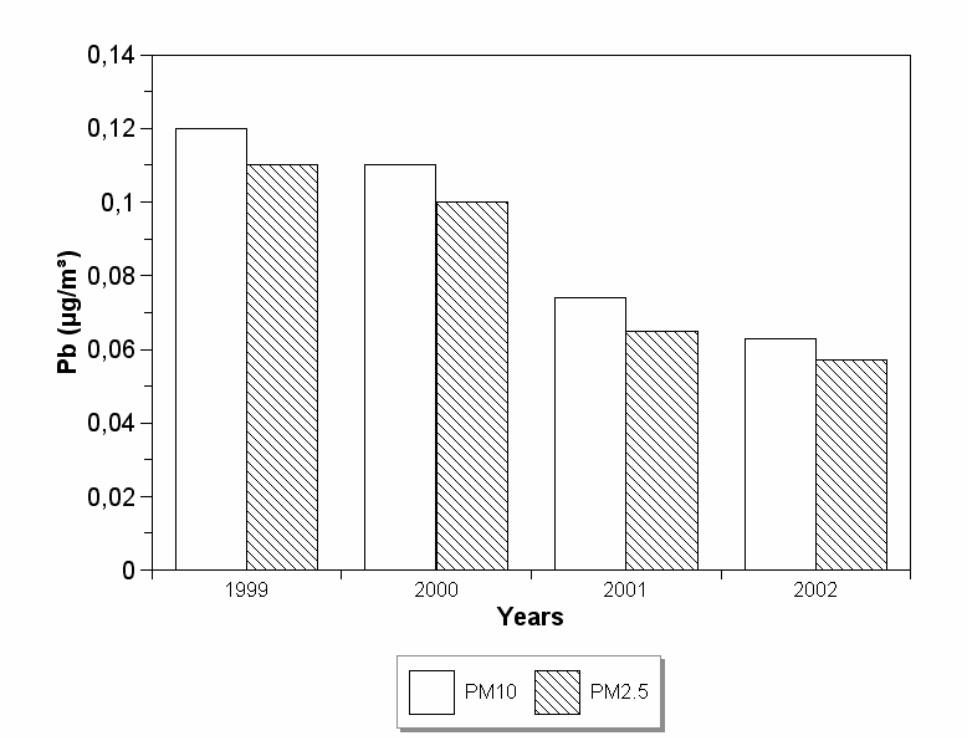

Figure 4 - Annual mean values of lead in PM_{10} and $PM_{2.5}$ in the northern part of Zagreb for the period 1999-2002

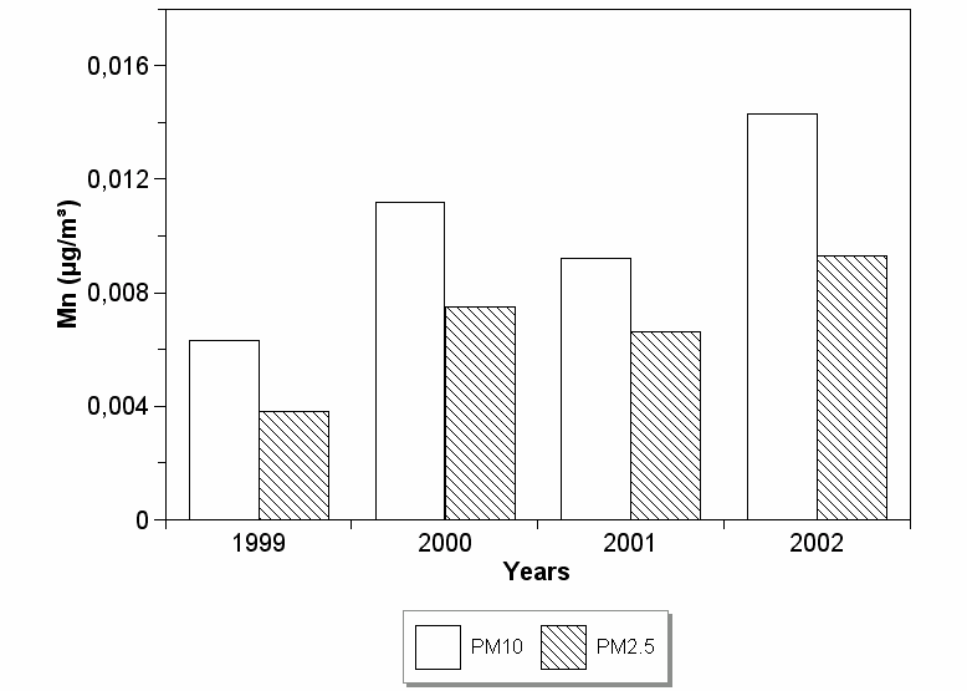

Figure 5 - Annual mean values of magnese in PM_{10} and $PM_{2.5}$ in the northern part of Zagreb for the period 1999-2002

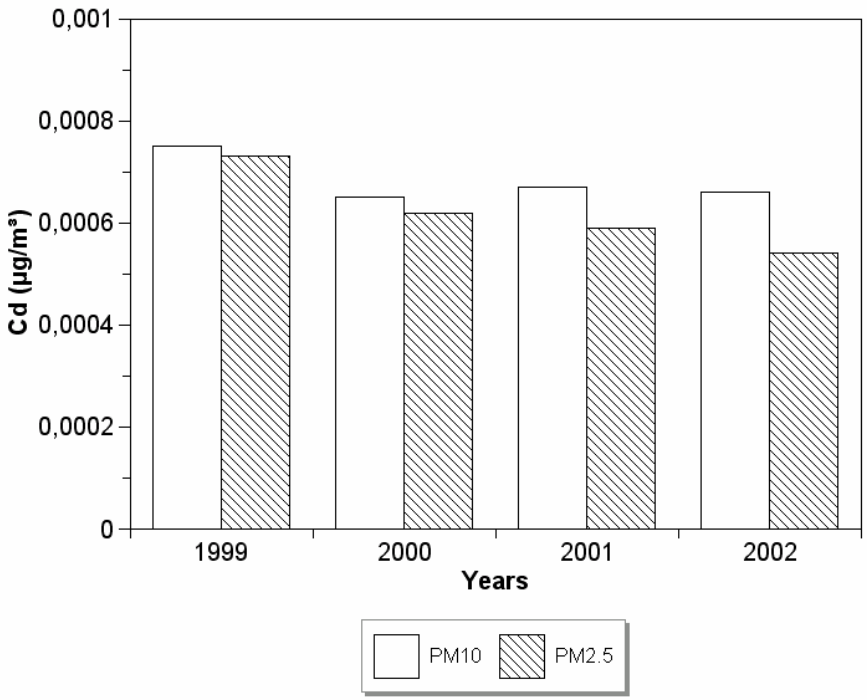

Figure 6 - Annual mean values of cadmium in PM_{10} and $PM_{2.5}$ in the northern part of Zagreb for the period 1999-2002

CONCLUSION

The results for lead, manganese and cadmium monitoring in TSPM in Zagreb, the capital of Croatia, indicate that the concentrations of those metals in TSPM were not high. During the past ten years concentrations were below the Croatian recommended limit value, limit values in EU and WHO guideline for Europe.

The Croatian limit values are more tolerant than the European ones and they should be brought in agreement with the European standards.

LITERATURE

[1] Bešlić, I., Šega, K.: Gravimetric determination of suspended particulate matter concentrations – requirements for the accurate measuring parameters. Proceedings of the Third Scientific Symposium "Air protection 01", Šibenik, Croatia 2001, pp. 323-327 (in Croatian).
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