

CORRELATION BETWEEN METALLIC AND ACIDIC COMPONENTS IN DEPOSITED MATTER

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ABSTRACT

The paper presents the results of the monitoring of acidic components (fluoride, chloride, nitrate, sulphate) and heavy metals (lead, cadmium, thallium) in total deposited matter at three measuring sites in Šibenik and one site in an unpolluted area. Research was carried out during six years (1999-2004). Samples of the deposited matter were collected by the Bergerhoff method. Total deposited matter was determined gravimetrically. Acidic anions were analysed using ion chromatography. Metallic components were determined by atomic absorption spectrometry. The correlation between measured pollutants varied and it depended on the measuring site and investigated pollutants.

Key Words: Heavy metals, fluoride, chloride, nitrate, sulphate

1. INTRODUCTION

Deposited matter are solid or liquid particulates in the atmosphere in excess of 10-20 µm in diameter (Noller, 1981), which settle on the ground and contaminate soil, plants and materials, but do not affect people and animals directly. Climatic conditions are important in determining the effects of deposited particulate emissions on plants, water and animals. Light rains may cause particle deposition from the atmosphere on vegetation, whereas heavy rains may partially wash off dusts from vegetation to soil. In arid regions, the dusts may accumulate on vegetation and be ingested by grazing animals. It is very important to know the quantity of deposition, especially the content of toxic substances such as acidifying ions and heavy metals, lead, cadmium and thallium.

2. MATERIALS AND METHODS

In the period 1999 to 2004, monthly samples of atmospheric depositions were collected using the Bergerhoff-type deposit gauge (VDI, 1972) at three sampling sites in Šibenik (A,B,C) and at a site in an unpolluted area (K) of the island of Žakan in Kornati National Park (Figure 1). Measuring sites were selected at a distance from emission sources (such as aluminium plant destroyed during the war in 1991, and a plant for electrode and ferroalloy production which stopped operating under decision of the Croatian Government), population density and meteorological parameters.



Figure 1 – The position measurement sites

The total deposition was determined gravimetrically. Samples were analysed for acidifying ions (fluoride, chloride, nitrate and sulphate) using an ion chromatograph (Dionex DX-120) and for heavy metals (lead, cadmium and thallium) using a flame atomic absorption spectrometer (SOLAAR 969 AAS).

3. RESULTS AND DISCUSSION

Air quality in Croatia is currently assessed by comparing annual mean values with recommended (RV) and limit (LV) values stipulated by the Law on Air Quality Protection in Croatia and the Ordinance on Recommended and Limit Air Quality Values (Ordinance, 1996). The Law on Air Quality (Law, 1995) in Croatia should be in accordance with EU laws.

Overall monthly values of total deposited matter ranged from 8 to 511 mg/(m²d) during the entire measuring period and at all sampling sites. Annual values are shown in Figure 2. They were below the recommended value 200 mg/(m²d)

according to the Law on Air Quality Protection in Croatia and the Ordinance on Recommended and Limit Air Quality Values.

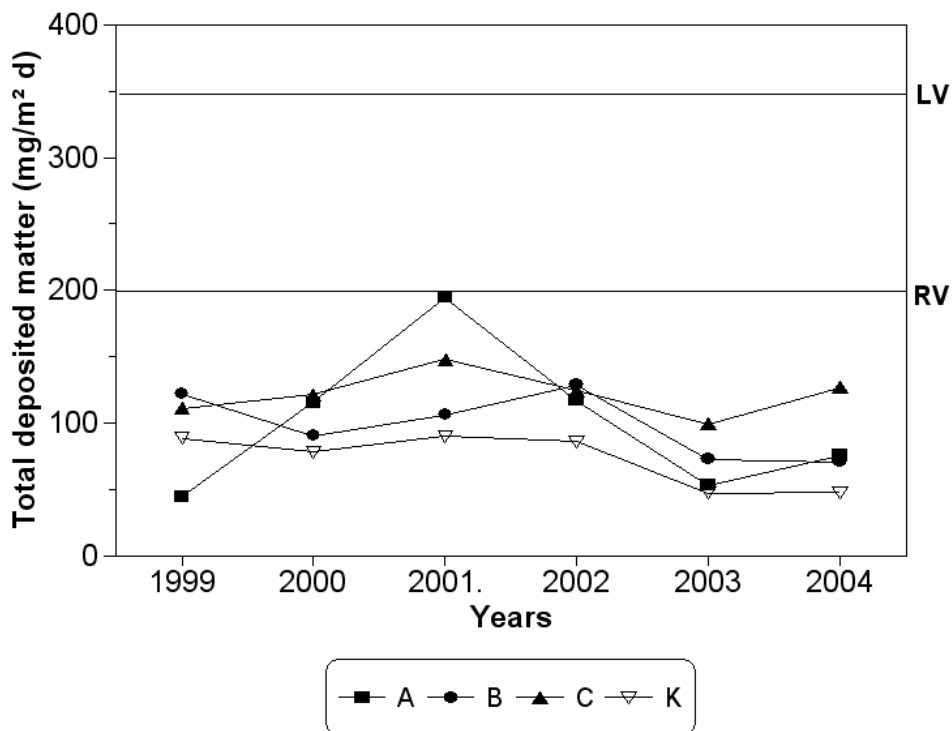


Figure 2 - Annual values of total deposited matter in Šibenik from 1999 to 2004

Monthly lead content in total deposited matter ranged from 0 to 215 $\mu\text{g}/(\text{m}^2\text{d})$. Annual values are shown in Figure 3. All results were below the recommended value 100 $\mu\text{g}/(\text{m}^2\text{d})$.

Overall monthly cadmium content in total deposited matter for the same period ranged from 0 to 2.11 $\mu\text{g}/(\text{m}^2\text{d})$. Annual values are shown in Figure 4 and they were below the recommended value 2 $\mu\text{g}/(\text{m}^2\text{d})$.

Overall monthly thallium content in total deposited matter ranged from 0 to 14.77 $\mu\text{g}/(\text{m}^2\text{d})$. Annual values are shown in Figure 5, and until 2001 they were below the recommended value 2 $\mu\text{g}/(\text{m}^2\text{d})$ at three measuring sites (A, B, K). During 2001, the annual mean concentrations of thallium were above recommended value, but below limit value (10 $\mu\text{g}/\text{m}^2\text{d}$) at all measuring sites. In 1999 and 2000 at the measuring site C, and in 2002 at the measuring sites A and B the annual mean concentrations of thallium exceeded recommended value (Figure 5). Figure 5 clearly shows that concentrations of thallium decrease during 2003 and 2004.

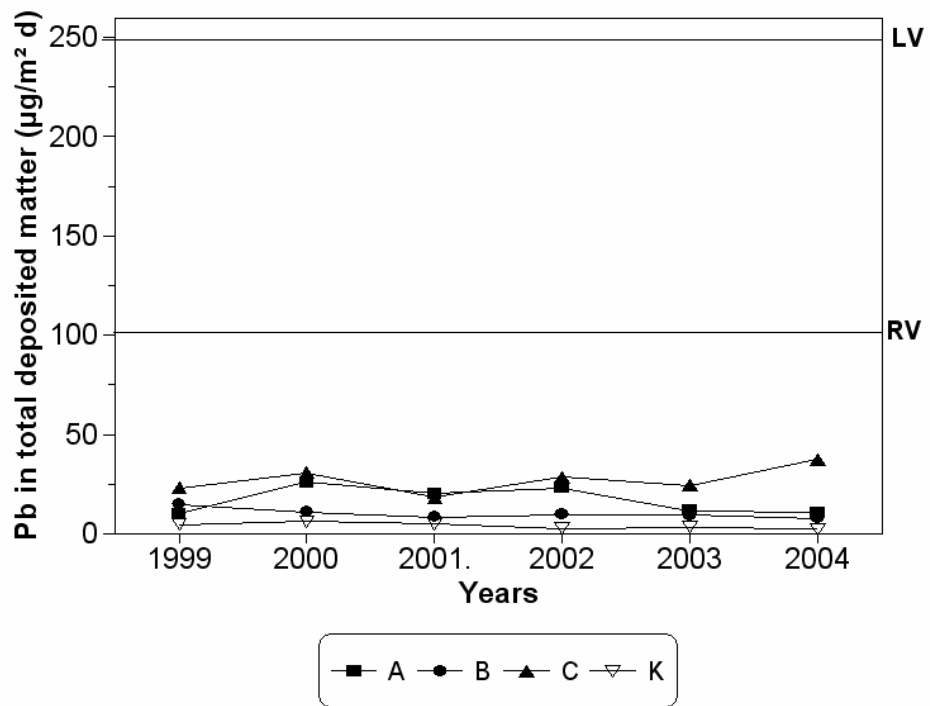


Figure 3 - Annual values of lead in total deposited matter in Šibenik from 1999 to 2004

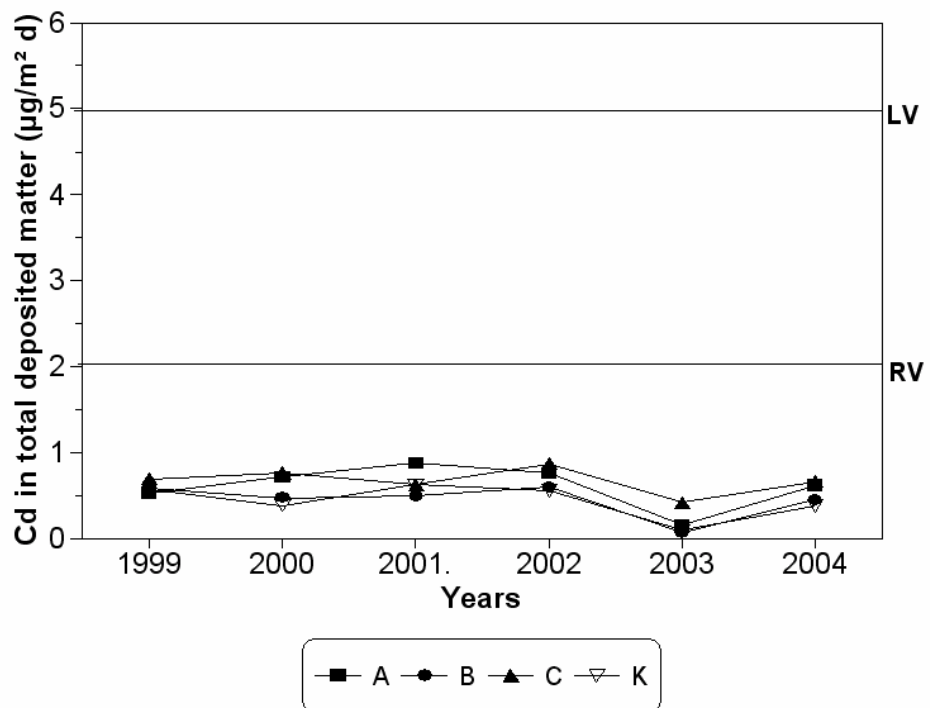


Figure 4 - Annual values of cadmium in total deposited matter in Šibenik from 1999 to 2004

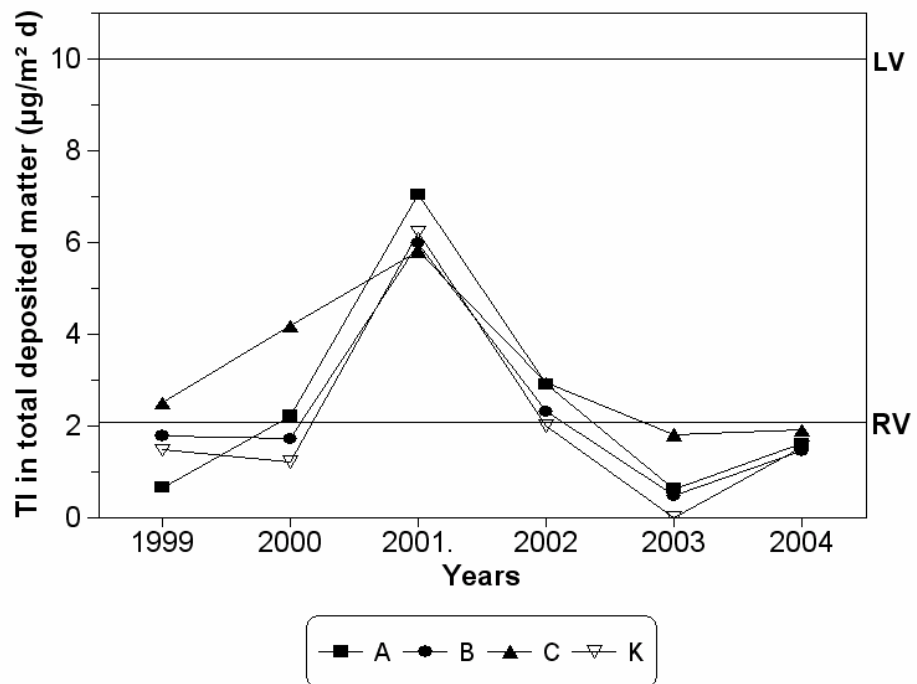


Figure 5 - Annual values of thallium in total deposited matter in Šibenik from 1999 to 2004

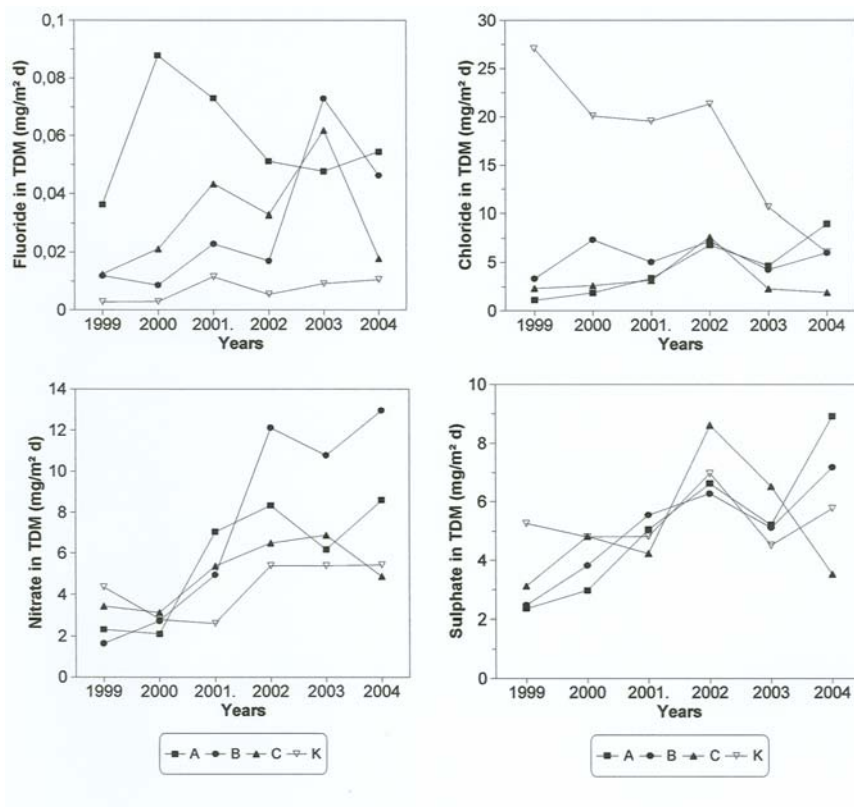


Figure 6 - Annual values of fluorides, chlorides, nitrates and sulphates in total deposited matter in Šibenik from 1999 to 2004

Overall monthly fluorides in total deposited matter ranged from 0 to 0.18 mg/(m²d), chlorides from 0 to 85.56 mg/(m²d), nitrates from 0 to 74.29 mg/(m²d) and sulphates from 0 to 24.13 mg/(m²d). Annual values for acidifying ions are shown in Figure 6. It should be noted that the Croatian Ordinance does not define recommended or limit values for acidifying ions.

The correlation coefficients between acidifying ions and heavy metals for the entire measurement period are presented in Table 1.

Table 1 – Significant correlation coefficients between acidic components and heavy metals in total deposited matter

Measuring site	Correlated components	F ⁻	Cl ⁻	NO ³⁻	SO ₄ ²⁻
A N=54	Pb	0.558**	0.111	0.465**	0.132
	Cd	0.297*	0.133	0.284*	0.303*
	Tl	0.338**	0.057	0.351**	0.102
B N=67	Pb	0.359**	0.374**	0.110	0.306**
	Cd	0.066	0.710**	0.121	0.424**
	Tl	0.059	0.126	0.007	0.123
C N=64	Pb	0.025	0.226	0.203	0.144
	Cd	0.114	0.132	0.234*	0.031
	Tl	0.074	0.201	0.332**	0.243*
K N=57	Pb	0.033	0.104	0.297*	0.188
	Cd	0.238*	0.155	0.018	0.032
	Tl	0.026	0.015	0.115	0.022

* - P<0.05

** - P<0.01

N – number of samples

Before the war in Croatia in 1991, the air pollution in the Šibenik area resulted mostly from fluoride emissions from the light-metal factory and the measuring site A was chosen in this part of the town. At the same measuring site a significant correlation (P <0.01; P<0.05) was found between fluorides and lead, cadmium and thallium. Correlation between lead, cadmium and thallium with chlorides, and lead and thallium with sulphates was not significant. At the measuring site B (long distance from the light-metal factory) a significant correlation (P<0.01) was found between lead with fluorides, chlorides and sulphates and between cadmium with chlorides and sulphates. At the measuring site C (city centre) a significant correlation was found between cadmium and nitrates (P<0.05), and thallium with nitrates (P<0.01) and sulphates (P<0.05). At the measuring site K (the island of Žakan) a significant correlation was found only between lead and nitrates and cadmium and fluorides (P<0.05).

The correlation between measured pollutants varied and it depended on the measuring site and investigated pollutants. Significant higher correlations indicated that the pollutants might originate from the same source. No significant correlation may indicate that other components were involved in the deposition, such as sodium,

potassium, calcium, ammonia etc., which can react with measured metals and acidic components.

4. CONCLUSION

During the six-year period of measurement, the total deposited matter at all measuring sites was relatively low and below the recommended value (200 mg/m²d). Acidifying ions (fluorides, chlorides, nitrates, sulphates) were relatively high (Hršak, 2003), but for them no recommended or limit values are set by the Croatian Ordinance.

Over the six-year measuring period, lead and cadmium content in total deposited matter was found to be low and below the recommended value (100 µg/m²d for lead and 2 µg/m²d for cadmium) at all sampling sites.

Thallium content in total deposited matter was below the recommended value (2 µg/m²d) until 2001 at all measuring sites, except at measuring site C where it was above the recommended value in the years 1999 and 2000. During 2001, thallium content in total deposited matter exceeded the recommended value at all measuring sites, and in 2002 it remained above the recommended value at the measuring sites A and B. Finally, during 2003 and 2004, thallium content dropped below the recommended value at all measuring sites.

The correlation between measured pollutants varied and it depended on measuring site and investigated pollutants. Significant higher correlations indicated that the pollutants might originate from the same source. No significant correlation may indicate that other components were involved in the deposition, such as sodium, potassium, calcium, ammonia etc., which can react with measured metals and acidic components.

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