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PRECIPITATION CHEMISTRY IN THE VELIKA MORAVA CATCHMENT

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Abstract

Bulk precipitation chemistry on a daily basis was studied for seven years (1998-2004) at three meteorological stations (Smederevska Palanka, Kraljevo, Niš) in the Velika Morava catchment. Samples were analyzed for the anions Cl^-, NO_3^- and SO_4^{2-}, and for the cations Na^+, NH_4^+, K^+, Mg^{2+} and Ca^{2+} in addition to pH and conductivity measurements. The most abundant ion was SO_4^{2-}, followed in descending order by $Ca^{2+} > NH_4^+ > Mg^{2+} > Cl^- > Na^+ > NO_3^- > K^+$. A significant wet deposition of sulfate of 58-134 $mmol.m^{-2}.yr^{-1}$ was calculated caused by heating emission during combustion of low-quality sulfur-rich lignite.

Introduction

Precipitation is an efficient pathway for removing the gases and particles from the atmosphere playing a significant role in controlling their concentration. Determination of chemical composition of rainwater provides an understanding of the source types that contribute to precipitation chemistry, and enhances the understanding of the local and regional dispersion of pollutants and their potential impacts on ecosystems through deposition processes [1]. Sulfur dioxide (SO_2) is considered the main atmospheric pollutant of anthropogenic origin. The main pathway of the sulfate removal from the atmosphere is rain scavenging. The aim of this paper was to evaluate the natural composition of precipitation and to identify possible sources that contribute to precipitation chemistry of the Velika Morava catchment.

Results and Discussion

The precipitation collection and its analyses were conducted by the Republic Hydrometeorological Service of Serbia following the recommendation of the WHO [2]. The amount of precipitation varied considerably from year to year in the different regions with a minimum of 297 mm (in 2000) and a maximum of 822 mm (in 2004) which corresponded to 47% and 123% respectively to the values of the 30 years averages (1961-1990). The pH values of colleted precipitation covered a wide range from acidic (minimum of 3.3) to alkaline (maximum of 9.5). Approximately 50% of the rain events had pH between 6.0 and 7.0, indicating highly alkaline nature of rainwater at the catchment area with mean values of 6.1 (Smederevska Palanka and Kraljevo) and 6.3 (Niš) due to extensive neutralization of acidity. The neutralizing agents are primarily ammonia, soil dust and fly ash components (predominantly, $CaCO_3$, $MgCO_3$, oxides, silicates). The quality control for the entire database was checked for each rain sample by calculating the cation and anion balance (ID, ion difference in %)

$$\text{Ion Difference (\%)} = 100 \cdot (CE - AE) / (CE + AE)$$

where AE is the sum of anion equivalents (μeL^{-1}) and CE is the sum of cation equivalents (μeL^{-1}). Linear regression of cation sum on anion sum for the sets of samples considered in this study gave r^{2} values of 0.90-0.95 indicating that the quality of the data was good. The mean monthly concentrations for each analyzed species have been calculated as volume-weighted mean (VWM) by taking into account the event rainfall.

The annual level of SO_4 (155-394 μeq.L^{-1}) was high and comparable with concentration for sites to the time before the unification of Germany and the reorganization in the other countries of Eastern Europe [3]. Regarding the same period the annual mean concentrations of SO_2 registered at those sites were in the range of 14-54 μg.m^{-3} with maximum in winter months (November-February, exceeding permissible limits of 150 μg.m^{-3} for averaging 24 hour period) and a slightly decline since 2001 due to combustion of low-quality lignite with high sulfur and/or salt and ash content. The emissions of SO_2 were estimated to 396 kt in Serbia in 2003 [4]. The second abundant element was Ca (98- 449 μeq.L^{-1}) indicating its anthropogenic origin emitted by human activities such as traffic, cement factory work and fly ash through short and intermediate range transport phenomena. The latter from sulphur-rich lignite burned contains 12–28% CaO on average which quantity was estimated at around 6,6x10^{6} t.y^{-1} [4]. The good correlation (r^{2}=0.90) of calcium in precipitation with chloride is a hint at lignite burning as well as the dilution effect of the precipitation amount on their concentrations. The nitrate concentration in rain exhibited interannual changes (between 5 and 85 μeq.L^{-1}) with decreasing trend probably due to restructing of industry, a reduction of stock farming and a reduction in the numbers of animals. On the other hand, ammonium concentration (6-92 μeq.L^{-1}) showed increasing trend mostly due to the volatilization of NH_3 from soils having pH values grater than 6.0. The annual wet deposition was calculated as the product of ion concentration (μeq.L^{-1}) and amount of precipitation (mm) over the sampling time (Fig. 1).

Conclusion

In general, VWM concentrations were not statistically distinct among sampling sites. The heating emission situation in Serbia was characterized by combustion of low-quality lignite with high sulfur generating significant SO_4^{2-} fluxes from 58 to 134 mmol.m^{-2}.yr^{-1} during high precipitation levels.

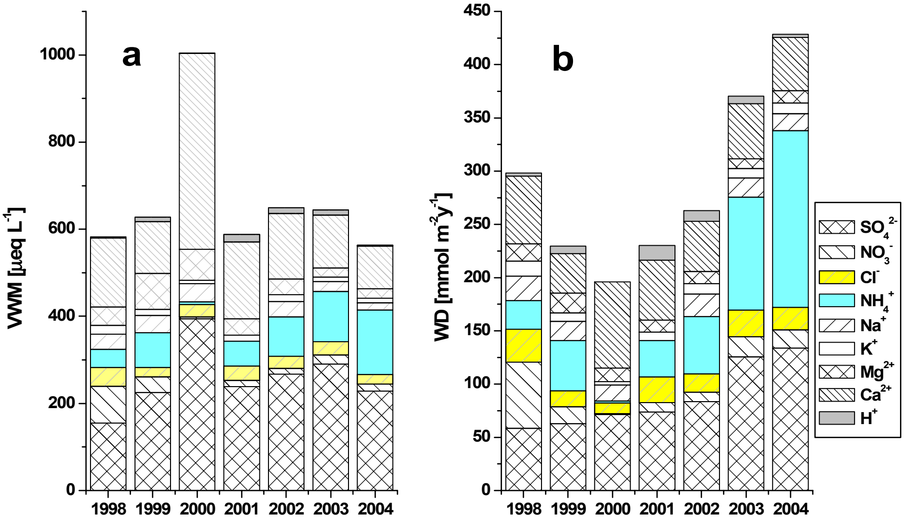

Fig. 2. (a) Annual average volume weighted mean concentration in precipitation for seven years (1998-2004) and (b) Annual wet deposition in the Velika Morava catchment

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