

## Rainwater chemical composition at two sites in Central Mexico

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### Abstract

Chemical analyses were performed on rainwater samples collected at the National Autonomous University of Mexico (UNAM) in Mexico City and at a wooded site, Rancho Viejo (RV) in the State of Mexico, for the periods 1994–2000 and 1994–1999, respectively. At UNAM, rainwater was collected for the entire rainy season period each year, while at RV, technical considerations limited collection to weekends only. The results showed large variations in rainwater chemical composition in most years, mainly because of the variability of meteorological conditions and also because of changes in source emissions. Sulfates and  $\text{NH}_4^+$  showed higher annual volume-weighted mean concentrations (VWMC) in both sites. At UNAM, the maximum annual VWMC for  $\text{SO}_4^{2-}$  occurred in March and the minimum in July and August. Lower concentrations of almost all ions were found at RV; however, the  $\text{H}^+$  concentration was higher at this site. The pH in Mexico City, calculated from the annual VWMC of  $\text{H}^+$ , was 4.95, which is a little higher than pH values reported in some other countries. Despite the fact that sulfate and  $\text{NO}_3^-$  concentrations were lower at RV, the pH was lower. Air-mass back trajectories were calculated for individual concentrations of  $\text{SO}_4^{2-}$ ,  $\text{H}^+$ ,  $\text{NH}_4^+$ ,  $\text{Ca}^{2+}$ , and  $\text{Mg}^{2+}$ , observed at each sampling site for weekend data. At RV, sulfate concentrations were higher when air-mass back trajectories indicated a wind flow from Mexico City and Toluca at 1000 MAGL (meters above ground level) and 3000 MAGL. The hydrogen ion exhibited the same behavior. Calcium and  $\text{Mg}^{2+}$  concentrations were also higher when the wind blew from urban areas at 1000 and 3000 MAGL. At UNAM,  $\text{H}^+$  concentration was lower and  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  were higher when wind blew from the northern sector of the city at 1000 and 3000 MAGL. In UNAM, the  $\text{NO}_3^-/\text{SO}_4^{2-}$  and  $\text{NH}_4^+/\text{SO}_4^{2-}$  ratios were 0.5 and 1.09 in 1994 and 0.86 and 1.64 in 2000, respectively, indicating a decrease in  $\text{SO}_2$  emissions resulting from the change of fuel oil to gas fuel. The  $\text{SO}_4^{2-}/\text{Ca}^{2+}$  ratio was significantly lower at the UNAM site (1.82) compared to RV (5.36), and the  $\text{SO}_4^{2-}/\text{H}^+$  ratio was significantly higher at the UNAM site (6.77) compared to RV (2.01). The Spearman's rho correlation between ionic concentrations indicated a positive correlation in most cases ( $p < 0.05$ ) for data from UNAM and RV. The multiple regression correlation analysis to predict

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$\text{H}^+$  concentration in Mexico City showed that  $\text{NO}_3^-$ ,  $\text{NH}_4^+$ ,  $\text{SO}_4^{2-}$ , and  $\text{Ca}^{2+}$  contributed 23.2%, 20.9%, 8.0%, and 6.1%, respectively, to the  $\text{H}^+$  prediction, while  $\text{Cl}^-$  plus  $\text{Na}^+$  plus  $\text{K}^+$  only contributed 2.2%, and  $\text{Mg}^{2+}$  did not contribute. Sea-salt contribution to rainwater chemical composition was negligible with any wind direction at both levels. Excess sulfate (non-sea-salt sulfate) represented 98.7% of the total sulfate in rainwater collected during weekends at RV and 98.6% for weekend and annual rain samples at UNAM.

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## 1. Introduction

Although the chemical composition of wet precipitation has been studied in many countries for more than 30 years, such investigations remain important because anthropogenic emissions of some gases and aerosols in the atmosphere are continuously increasing. Air pollutant emissions are increasing rapidly in Asia, and the opposite is the case in Europe and North America (Higashino et al., 1997). Lee et al. (2000) reached the same conclusion, stating that the fast-growing economy in East Asia resulted in increased emissions of  $\text{SO}_2$  and  $\text{NO}_x$ . According to Galloway (1995), future emissions of these pollutants in Asia will be equal to or even greater than the combined emissions of Europe and North America by 2020. Emissions from fossil fuel combustion have produced an environmental acidification of rain (Higashino et al., 1997; Lee et al., 2000; Terada et al., 2002). As a consequence, there has been damage to terrestrial, aquatic, and biological systems. Regarding ammonia, its concentration has increased substantially over the past years (Walker et al., 2000). The geographical extent to which precipitation chemistry is affected by industrial emissions has produced transboundary pollution with the associated ecological and political problems (Lee, 1993; Tuncer et al., 2001). Herut et al. (2000) performed chemical analyses of rain samples collected during five winter seasons and studied the variation of rain chemistry in relation to natural and anthropogenic sources and transport of the constituents. Civerolo and Rao (2001) reported a space–time analysis of precipitation-weighted  $\text{SO}_4^{2-}$  concentration data across the USA.

Several studies of temporal trends in precipitation chemistry in different regions have been published. Dillon et al. (1988) reported a 10-year trend for sulfate, nitrate, and hydrogen deposition in Central Ontario. Fay et al. (1989) published observed and modeled trends of sulfate and nitrate in precipitation in eastern North America. Puxbaum et al. (1998) concluded that sulfate and hydrogen concentrations have decreased with well-defined significant trends in central Austria in a 10-year trend study of the precipitation chemistry. Other studies of trends for nitrate and ammonium concentrations have been conducted (Erisman et al., 1989; Lynch et al., 1995; Avila, 1996). In the present study, the chemical composition of precipitation and temporal variability were determined in a highly polluted urban area and in a rural area from 1994 to 2000. The aim was to examine the long-term temporal variability of rainwater chemical composition in Mexico City and Rancho Viejo and its relationship to governmental policies of anthropogenic gas emissions.

## 2. Materials and methods

### 2.1. Sampling sites

One sampling site was chosen in Mexico City (Fig. 1). The rain collector was located on the roof of the Atmospheric Sciences Center building at the campus of the National Autonomous

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