

Volcanic influence on sulfate aerosols from Mexico City

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Sulfate aerosols influence the physical and chemical properties of the terrestrial atmosphere by changing the radiative energy budget and by increasing the acidity of rain. Small radii sulfate particles can also penetrate deep into lung and cause serious damages for the human health. Uncertainties remain in the sources and formation pathways of sulfate aerosols in different environments. The oxygen and sulfur isotope compositions of sulfates could be used as key tracers to address better constrain the fate and sink of sulfates in terrestrial environments both in present and past geological time. The multiple isotope measurements to access the mass independent isotopic fractionations of oxygen and sulfur isotopes add valuable constraints on the oxidation pathways for O-isotopes and sources of sulfates for S-isotopes.

Here, we present a new data set of oxygen and sulfur isotope composition of sulfate aerosols monitored over the past 25 years in Mexico City. Sulfate aerosols were sampled from 1989 to 2013 throughout the city with high-volume samplers (1.133 m³/min) and collected on glass fiber filters. Fresh volcanic ash samples were collected directly after the recent eruptions of the Popocatepetl volcano during the 1997-2013 period. The oxygen isotopic composition was measured at the University of Washington with the pyrolysis method coupled with a gas bench interface for sub-micromole material. The sulfur isotope compositions were analyzed at the IPGP with a SF₆ extraction line. The coupled measurements of anthropogenic and volcanic sulfate aerosols in the Mexico City area provide information on the regional sulfur cycle.

Sulfate aerosols from Mexico City (mostly anthropogenic in origin) have a mass-independent signature in oxygen and sulfur isotopes (up to +1.75‰ in $\Delta^{17}\text{O}$ and in sulfur isotopes up to + 0.28‰ and down to - 1.20‰ in $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ respectively), whereas the volcanic sulfates are mass dependent ($\Delta^{17}\text{O}$, $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}\approx 0$). This disparity is an indication for the different routes of sulfate production and provides a means to differentiate between primary and secondary sulfates.

For urban sulfate aerosols, the $\Delta^{17}\text{O}$ values suggest that the ozone contribution is near to 9% in the global dioxide sulfur oxidation including O_3 , H_2O_2 and O_2 -TMI oxidation pathways which is in agreement with chemical models and previous studies. The oxidation pathways seem to be seasonally variable due to the significant change in $\Delta^{17}\text{O}$ values for the wet and dry season; the TMI-catalyzed O_2 oxidation pathway may be significant for the dry season. Finally we observed a volcanic signature in the isotope compositions of sulfates inside the city which may confirm the volcanic influence in Mexico-City aerosols.