Isotope dynamics of sulfate oxygen in forest catchments differing 10 times in pollution inputs

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Processes controlling the behavior of sulfur and oxygen isotopes in environmental sulfates are de-coupled. Atmospheric oxidation of SO_2 causes only relatively small fractionations in sulfur isotopes, but it causes large fractionations in the oxygen isotope values. The $\delta^{18}O$ value of sulfate is completely determined by the oxidation mechanism and the prevailing conditions.

We investigated temporal trends in the isotope composition of sulfate oxygen in two forested catchments in the Czech Republic (Central Europe) similar in elevation, temperature and precipitation totals. JEZ was situated mere 5 km from large coal-fired power stations, LIZ was situated in a relatively unpolluted area 150 km from the power stations. There was a unique 10-fold pollution gradient between the sites, with JEZ receiving as much as 130 kg S ha^{-1} yr^{-1}, and LIZ receiving about 13 kg S ha^{-1} yr^{-1}. At both sites, we monthly monitored $\delta^{18}O$-SO_4 values of spruce canopy throughfall, open-area precipitation and surface runoff over a two-year period. Our objective was to compare the $\delta^{18}O$-SO_4 time-series at the two contrasting sites and to evaluate their dependence on the relative magnitude of dry and wet deposition.

In both catchments, $\delta^{18}O$-SO_4 decreased in the order: open-area precipitation > throughfall > runoff. Mean $\delta^{18}O$-SO_4 values were 13.1, 10.3, and 8.6 per mil (JEZ), and 14.2, 11.3 and 9.0 per mil (LIZ) for open-area precipitation, throughfall and runoff, respectively. All differences were statistically significant at the 0.05 level. The $\delta^{18}O$-SO_4 values of throughfall exhibited a clear-cut sinusoidal pattern at both sites, with maxima in summer and minima in winter. The sinusoid parallelled $\delta^{18}O$-H_2O values, which were off-set by minus 18 per mil. Sulfate in throughfall was predominantly formed by heterogeneous oxidation of SO_2, a process that incorporates oxygen from ambient water into the sulfate molecule. Wet-deposited sulfate did not show systematic $\delta^{18}O$ trends, suggesting formation mainly by homogeneous oxidation. Sulfur mass balances independently showed that throughfall contained 84 % of dry-deposited SO_2-S at JEZ, but only 54 % at LIZ. There appeared to be a quantitative discrepancy between the oxygen data and the S mass balance data: The nearly 50 % contribution of wet-deposited sulfate to LIZ throughfall should smear out the sinusoidal pattern, while it did not. Processes controlling these patterns merit further study. For example, sulfate in horizontal deposition might be formed by a different mechanism than sulfate in rainfall.