Sulphur Isotope Dynamics in Two Mountaintop Forest Catchments in the Black Triangle, Central Europe

Martin Novák1 (novak@cgu.cz), James W. Kirchner2 (kichner@geomorph.berkeley.edu) & Hana Groscheová1 (grosche@cgu.cz)

1 Czech Geological Survey, Klárov 3, 118 21 Prague 1, Czech Republic.

2 Department of Geology and Geophysics, University of California, Berkeley, California 94720 4767, U.S.A.

The forest ecosystems of the northern Czech Republic are slowly recovering from four decades of air pollution unmatched elsewhere (Cerny´, 1995). Between 1987 and 1996 the production of local soft coal containing 1-3 wt % of S decreased from 72 to 44 million tons yr⁻¹, i.e., by 39 %, while SO₂ emissions from coal-burning power plants decreased from 820 to 490 thousand tons yr⁻¹, i.e., by 40 %. S deposition measured in three forested catchments in the northern Czech Republic decreased from 1994 to 1995 despite higher precipitation totals in 1995. This contrasts with an increase in S deposition in nine catchments monitored in less polluted parts of the country over the same two-year period. Norway spruce die-back that in the northern Czech Republic affected an area of 400 km² in the mid-1970's was mostly ascribed to direct kill by atmospheric SO₂ levels (up to 3 400 mg m⁻³). The results of reforestation efforts are mixed: in winter 1995/96 spruce seedlings and young trees perished on an area of 1300 ha.

To better understand transport pathways of atmogenic S at the catchment level, we monitored S isotope composition at Jezeri (490-924 m a.s.l.) and Nacetin (780 m a.s.l.), two sites situated near the Czech-German border in the Krus–ne hory Mts., northern Czech Republic. ³⁴S ratios were determined monthly for bulk deposition, spruce and beech throughfall, surface discharge and soil water (0-90 cm below surface) over a period of three years 1993-1996. To collect soil water, zero tension lysimeters were used for the depths of 0, 10, 30 and 70 cm, and suction lysimeters for the depths of 30 and 90 cm. ³⁴S of total soil sulphur was measured at three depth levels at 15 locations within the two catchments.

³⁴S ratios were determined in a total of 298 samples. Both S pools and S fluxes in forest ecosystems of the northern Czech Republic exhibit distinct isotope signatures. When data for the two sites are combined (the distance between Jezeri and Nacetin is 17 km) mean ³⁴S ratios increase in the order: soil water 30 cm (zero tension) < soil water 70 cm < surface discharge < soil water 90 cm < soil water 30 cm (suction) < soil water 10 cm < soil water 0 cm < spruce throughfall < beech throughfall < bulk deposition. These
differences reflect (1) mixing of various sulphur sources, and (2) isotope fractionation. Bulk deposition (mean $^{34}$S of 7.9 per mil at Nacetin, 7.7 and 7.0 per mil at two sites within Jezeri) is dominated by high-$^{34}$S wet deposition. In contrast, canopy throughfall intercepts a large amount of dry-deposited SO$_2$, which in the northern Czech Republic is characterized by relatively low $^{34}$S ratios (around 2 per mil). $^{34}$S ratios of spruce throughfall (5.9 per mil at Nacetin and 5.5 per mil at Jezeri) are intermediary between those of wet and dry deposition. $^{34}$S of beech throughfall (7.3 per mil) is close to that of bulk deposition due to smaller leaf surface area of broadleaves compared to spruce needles. Isotope fractionation associated with mineralisation of organic matter appears to be responsible for the isotope shift toward lower $^{34}$S ratios in soil water ($^{34}$S at a depth of 70 cm averaged 4.6 per mil) relative to the incoming atmospheric sulphate (5.9 per mil). Consequently, soil water sulphate is, to a large extent, secondary sulphate whose S was cycled through an organic S pool. This type of data should be considered when calculating mean residence time of S in the catchments, and in scenarios of an acidification reversal. In addition to distinct isotopic signatures, individual S fluxes exhibit a seasonality in both magnitude and $^{34}$S (cf. Novak et al., 1995). The total amount of S stored in the soil at Jezeri (261 ha; 0 - 65 cm) was estimated to be 194 tons, that is 13 times more than the amount of S deposited on its surface in a single year (56 kg ha$^{-1}$ yr$^{-1}$ in 1994). $^{34}$S ratios of total soil S systematically increase from the topsoil to the mineral soil averaging 2.2, 3.3 and 4.6 per mil in in the 0+A, Bv and B/C horizons, respectively, in Eutric Cambisol; 2.7, 4.2 and 3.8 per mil in 0+A, Bv and B/C, respectively, in Dystric Cambisol, and 2.8, 6.7 and 6.4 per mil in 0+A, Bsv and B/C, respectively, in Cambic Podzol. The shift to higher $^{34}$S in deeper soil horizons was similar to 16 less polluted sites throughout the Czech Republic (Novak et al., 1996) and was previously attributed to mineralisation-related isotope fractionation rather than to mixing of atmogenic and bedrock S. Mean $^{34}$S ratio for the bulk Jezeri soil was 3.9 per mil. Annual mass-weighted mean $^{34}$S of surface discharge from Jezeri was 4.9, 4.6 and 4.3 per mil in 1993, 1994 and 1995, respectively. $^{34}$S of surface discharge was thus higher than $^{34}$S of the bulk soil S pool but lower than $^{34}$S of all types of present-day atmospheric deposition. A considerable proportion of S in the discharge must be derived from "old" soil S accumulated before $^{34}$S measurements of atmospheric inputs started. An admixture of groundwater bearing the isotope signature of bedrock S cannot explain $^{34}$S of the discharge since whole-rock $^{34}$S is relatively high (5.8 per mil). Over the observation period (1993-1996), yearly discharge (on average 17 tons of S) would suggest a potential minimum turnover time for the bulk soil S in the catchment to be 11.4 years.

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References


