SULPHUR ISOTOPE DYNAMICS IN PRESENT-DAY ATMOSPHERIC DEPOSITION, FOREST CANOPY, FOREST SOIL AND CATCHMENT DISCHARGE

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The forest ecosystems of the northern Czech Republic are slowly recovering from four decades of air pollution unmatched elsewhere. 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 SO_2 emissions from coal-burning power stations decreased from 820 to 490 thousand tons yr^{-1}, i.e., by 40 %. Norway spruce die-back which in the northern Czech Republic affected an area of 400 km^2 in the mid-1970's was mostly ascribed to direct kill by atmospheric SO_2 levels (up to 3 400 µg m^{-3}). To better understand transport pathways of atmogenic S at the catchment level, we monitored S isotope composition at Jezeří (490–924 m a. s. l.) and Načetín (780 m a. s. l.), two sites situated in the Krušné hory Mts., northern Czech Republic. The $\delta^{34}S$ 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. The $\delta^{34}S$ of total soil sulphur was measured at three depth levels at 15 locations within the two catchments.

Sulphur concentrations and $\delta^{34}S$ 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. Mean $\delta^{34}S$ ratios increase in the order: soil water 30 cm (tensionless) < soil water 70 cm (tensionless) < surface discharge < soil water 90 cm (suction) < soil water 30 cm (suction) < soil water 10 cm (tensionless) < soil water 0 (tensionless) cm < spruce throughfall < beech throughfall < bulk deposition. These differences reflect (i) mixing of various sulphur sources, and (ii) isotope fractionation. Bulk deposition (mean $\delta^{34}S$ of 7.9 ‰ at Načetín, 7.7 and 7.0 ‰ at two sites within Jezeří) is dominated by high-$\delta^{34}S$ 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 $\delta^{34}S$ ratios (around 2 ‰). The $\delta^{34}S$ ratios of spruce throughfall (5.9 ‰ at Načetín and 5.5 ‰ at Jezeří) are intermediary between those of wet and dry deposition. The $\delta^{34}S$ of beech throughfall (7.3 ‰) is close to that of bulk deposition due to smaller leaf surface area of broadleaves compared to spruce needles. Isotope fractionation associated with mineralization of organic matter appears to be responsible for the isotope shift toward lower $\delta^{34}S$ ratios in soil water ($\delta^{34}S$ at a depth of 70 cm averaged 4.6 ‰) relative to the incoming atmospheric sulphate (5.9 ‰). Consequently, soil water sulphate is, to a large extent, secondary sulphate whose S was cycled through an organic S pool. The total amount of S stored in the soil at Jezeří (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). The $\delta^{34}S$ ratios of total soil S systematically increase from the topsoil to the mineral soil averaging 2.2, 3.3 and 4.6 ‰ in in the 0+A, Bv and B/C horizons, respectively, in Eutric Cambisol; 2.7, 4.2 and 3.8 ‰ in 0+A, Bv and B/C, respectively, in Dystric Cambisol, and 2.8, 6.7 and 6.4 ‰ in 0+A, Bsv and B/C, respectively, in Cambic Podzol. This vertical isotope shift was attributed to mineralization-related isotope fractionation rather than to mixing of atmogenic and bedrock S. Mean $\delta^{34}S$ ratio for the bulk Jezeří soil was 3.9 ‰. Annual mass-weighted mean $\delta^{34}S$ of surface discharge from Jezeří was 4.9, 4.6 and 4.3 ‰ in 1993, 1994 and 1995, respectively. $\delta^{34}S$ of surface discharge was thus higher than $\delta^{34}S$ of the bulk soil S pool but lower than $\delta^{34}S$ 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 $\delta^{34}S$ measurements of atmospheric inputs started. An admixture of groundwater bearing the isotope signature of bedrock S cannot explain $\delta^{34}S$ of the discharge since whole-rock $\delta^{34}S$ is relatively high (5.8 ‰). 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.