Sulphur diagenesis in freshwater peatlands

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Introduction

Freshwater peatlands are distributed world-wide, from boreal regions to the tropics. Their total area has been estimated as 5.2×10^6 km^2. Peatland deposits have been identified as net sinks for atmospheric sulphur (Howarth *et al.*, 1992). However, the question of whether or not the storage of sulphur in peat is permanent has rarely been addressed. We studied early diagenesis of sulphur in 9 freshwater peat bogs using annual S accumulation rates and vertical changes in S isotope composition. Despite site differences in atmospheric S inputs, we found similar vertical patterns in S accumulation rates and δ^{34}S values, respectively, in 7 bogs indicating a high degree of openness toward buried S.

Samples and techniques

Six study sites are located in the industrialized North-east of the United States, a seventh, Marcell Bog, is situated in unpoiluted northern Minnesota. Two sites sampled in the Czech Republic have similarly contrasting annual S inputs, Bozi Dar Bog in North Bohemia is part of one of the most polluted regions in Europe, while Jezerni slat is located in a pristine area of South Bohemia. Big Run Bog, West Virginia and Tamarack Swamp, Pennsylvania are runoff-water fed peatlands with continuous *Sphagnum* growth in which the coring device reached bottom silts. At Cranesville Swamp, West Virginia and Marcell Bog, Minnesota the peat depth exceeded the maximum depth sampled. Tub Run Bog, West Virginia and Allegheny Mining Bog, Maryland receive devated S inputs due to the proximity of coal mines. In both the entire shallow peat profile was sampled. McDonalds Branch Swamp, New Jersey is groundwater fed. Total S was determined in 2cm thick peat-core sections using a LECO Analyzer. The profiles were dated by means of ^{210}Pb activity measurements based on the constant rate of supply model. Total S for δ^{34}S determinations was extracted by combustion with Eschka's mixture and isotope measurements were performed on a Finnigan MAT 251 mass spectrometer.

Results and discussion

Sulphur accumulation rates Deposition dates of 2cm peat increments were calculated based on their ^{210}Pb activities. The number of years per section increased in a smooth, non-linear fashion with depth. Sulphur accumulation rates showed a rather uniform development over time: profiles at Big Run, Cranesville, Tamarack, Marcell, Tub Run and Jezerni slat were characterized by a subsurface peak followed by a steady decrease with depth. This steady decrease in S accumulation rates started between 19 and 58 years after sedimentation at a depth of 6 to 18 cm Any systematic trends in S accumulation rates reflect bulk sedimentation rates, actual S deposition rates and diagenetic processes. Maxima in S accumulation rates were found between years 1932 and 1971, i.e. at times pre-dating maximum levels in regional atmospheric S deposition (*c.* 1980). Therelore both the increasing (near-surface) and the decreasing (deeper) trend in S accumulation rates were ascribed to diagenetic processes. Increasing S accumulation rates with depth may result from a selective release of other peat macroelements higher than the release of S. Decreasing S accumulation rates may result from disproportionally high remobilization of buried S, accompanying peat maturation.

The near-surface negative δ^{34}S shift At all studied depths 80–95 % of total S was present as organic C-bonded S, with reduced inorganic, sulphate and ester-bonded S pools relatively small (Novak and Wieder, 1992). A striking feature of S isotope profiles was the near-surface negative δ^{34}S shift (Fig. 1). It has been interpreted as resulting from bacterial sulphate reduction known to discriminate against ^{34}S Thc termination of the shift at a depth of 4 to 12 cm was likely caused by a decreasing degree of openness toward residual sulphate, or an outright cessation of bacterial activity. There was no correlation between the magnitude of the negative δ^{34}S shift and the age of its deepest layer: at Big Run a 7 per mil isotope shift was effected over 13 years, at Cranesville 3 per mil over 33 years, at Tamarack 2.5 per mil over 38 years, at Marceli 4.5 per mil over 11 years, at Tub Run 13 per mil over 26 years, at Jezerni slat
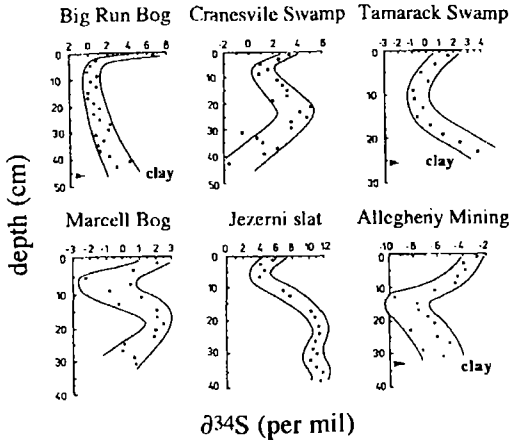
FIG. 1. Sulphur isotope composition in peat profiles.

2 per mil over 91 years, at McDonalds Branch 12 per mil over 14 years. A positive correlation of these two variables would be expected if repeated bacterial sulphate reduction (associated with a negative isotope shift) following hydrologically controlled periodical reoxidation of S^{-2} (no isotope effect) played a major role in internal S cycling in the bog.

The mid-depth positive $\delta^{34}S$ *shift* A mid-depth positive $\delta^{34}S$ shift followed the near-surface negative $\delta^{34}S$ shift at 7 sites indicating a different degree of openness toward the lighter isotope ^{32}S and the heavier isotope ^{34}S. Alternatives considering both influx and export of individual S species have been discussed by Novak *et al.* (1994). We proposed preferential volatilization of ^{32}S as the quantitative control of the mid-depth positive $\delta^{34}S$ shift. This mechanism is unrelated to bacterial S reduction and results entirely from decomposition of organic matter releasing S-containing gases. At most sites the mid-depth positive $\delta^{34}S$ shift overlapped with decreasing S accumulation rates.

The second negative $\delta^{34}S$ *shift* At three sites (Cranesville, Marcell, Bozi Dar) the mid-depth positive $\delta^{34}S$ shift was reversed back to lower $\delta^{34}S$ values in the deepest layers. Sites which lack this reversal (Big Run, Tamarack, Allegheny Mining) were characterized by a shallow peat deposit. At sites with deeper peat the time span of the mid-depth positive $\delta^{34}S$ shift was strikingly similar: 170 years at Cranesville, 185 years at Jezerni slat, and 193 years at Bozi Dar. This might indicate a diagenesis-related termination of the mid-depth positive $\delta^{34}S$ shift. The onset of a second negative shift may reflect the reached maturation stage of the substrate. Various mechanisms, including disproportional diffusion of ^{32}S and ^{34}S could account for the second negative $\delta^{34}S$ shift. Importantly, even at depths below 24–40 cm diagenesis did not proceed under closed-system conditions typified by no net isotope fractionation.

Conclusions

Two lines of evidence suggested that a certain portion of S buried in present-day peat bogs does not survive early diagenetic processes. A sequence of two isotope signals, a near-surface negative and a mid-depth positive $\delta^{34}S$ shift was invariably present at 7 study sites. Decreasing S accumulation rates with increasing depth overlapped with the interval of the mid-depth positive $\delta^{34}S$ shift leading to a scenario of preferential volatilization of the lighter isotope ^{32}S from the substrate. Within at teast 40 cm below peat surface S was found to be vertically mobile decades to centuries after its burial.

References

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