

An estimation of isotope mass balance of biogeochemical sulphur cycle in forest regions

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Introduction

Sulphur is one of the main element in the biosphere and transformations of sulphur in the nature shows cycling character where variations in red-ox is crucial factor of isotope effects observed.

The biospheric part of S cycling is poorly understood and air pollutions may complicate the picture (Jędrysek *et al.*, 2002). Therefore, spruce needles (*Picea abies*) at the area of Lower Silesia (SW Poland) was selected for our investigations. The SW part of Lower Silesia is called "Black Triangle". Although considerable decrease in pollution (about 87% for dust and 74% for SO₂) between 1990-2000 has been noted, this region is still under anthropogenic SO₂ and dust impact (WIOŚ, 2002).

Trees assimilate sulphur from two sources: 1) sulphate dissolved in water 2) atmospheric SO₂ (Jensen 1963, Chukhrov *et al.*, 1975, Carlson and Forrest, 1982, Mayer *et al.*, 1995). The sulphur assimilated is turned to three sulphuric amino acids: cysteine, cystin (formed from oxygenation of cysteine) and methionine. Under natural condition, main portion of the assimilated sulphur comes from sulphate uptake through roots (Krouse *et al.*, 1991). Under SO₂ anthropogenic impact, assimilated sulphur comes from atmospheric SO₂ (Rennenberg 1984) and coniferous (especially spruce) show tendency to uptake every quantity of accessible sulphur (Turner and Lambert, 1980).

Under strong anthropogenic impact, assimilation of high amount of sulphur may be balanced by sulphur H₂S emission from plants. This process is controlled by following environmental conditions: concentration of SO₂, light intensity, humidity and age of needles (DeCormis 1968, Wilson *et al.*, 1978, Hällgren and Fredriksson, 1982, Rennenberg 1984, Kałużny 2002, Jędrysek *et al.*, 2002). Under humid conditions (fog, precipitation) H₂S may be easily dissolved and oxidised to SO₄²⁻ (Jędrysek *et al.*, 2002) but some portion of isotopically light H₂S is emitted to the atmosphere.

Results and Discussion

Concentrations of SO_4^{2-} in spruce needles analysed varied out from 0,0001 to 0,0646 wt.%, with average value about 0,014 %. This values are typical for conifers (Turner et al., 1977, Manninen et al., 1997). Also concentration of organic sulphur (average value about 0,1 %) are comparable to data obtained by other authors (Krouse et al., 1991, Staniaszek 1992, Gebauer et al., 1994, Giesemann et al., 1995).

The $\delta^{34}\text{S}(\text{SO}_4^{2-})$ value varied from 4,19 to 11,9 ‰ (average about 8 ‰). Correlation of isotopic composition with altitude are noticed: higher $\delta^{34}\text{S}(\text{SO}_4^{2-})$ value corresponds to higher altitudes. Generally, isotopic data of sulphate in spruce needles show smaller variations as compared to sulphate in precipitation in neighbouring areas (Grescheova *et al.*, 1998, Jędrysek 2000).

Isotopic composition of organic sulphur varied out from 0,03 to 9,16 ‰. It clear correlates with altitude and show relatively small $\delta^{34}\text{S}(\text{S-org})$ value variations as compared to $\delta^{34}\text{S}(\text{SO}_4^{2-})$ value (Fig. 1). The difference between $\delta^{34}\text{S}$ value of sulphate and organic sulphur ($\Delta^{34}\text{S}(\text{SO}_4^{2-}-\text{S-org})$) varied from -1,12 to 7,57 ‰, with average 3,70 ‰.

The oxidation state of sulphur is the main factor controlling isotope fractionation in the atmosphere-biosphere-pedosphere system. S^{2-} -bearing compounds are depleted in ^{34}S as compared to S^0 or SO_4^{2-} -bearing compounds (Chukhrov et al., 1975, Toran and Harris 1989). Both $\delta^{34}\text{S}(\text{S-org})$ and $\delta^{34}\text{S}(\text{SO}_4^{2-})$ value increase with altitude (Fig. 1). Plants preferentially assimilate ^{32}S isotope, thus the residual sulphur is ^{34}S enriched. Therefore, the higher $\delta^{34}\text{S}(\text{SO}_4^{2-})$ value of higher altitudes could be explained by on increasing uptake of SO_2 from the atmosphere and consequently increasing emission of H_2S . Consequently, the residual SO_4^{2-} in needles become ^{34}S enriched (Fig. 2).

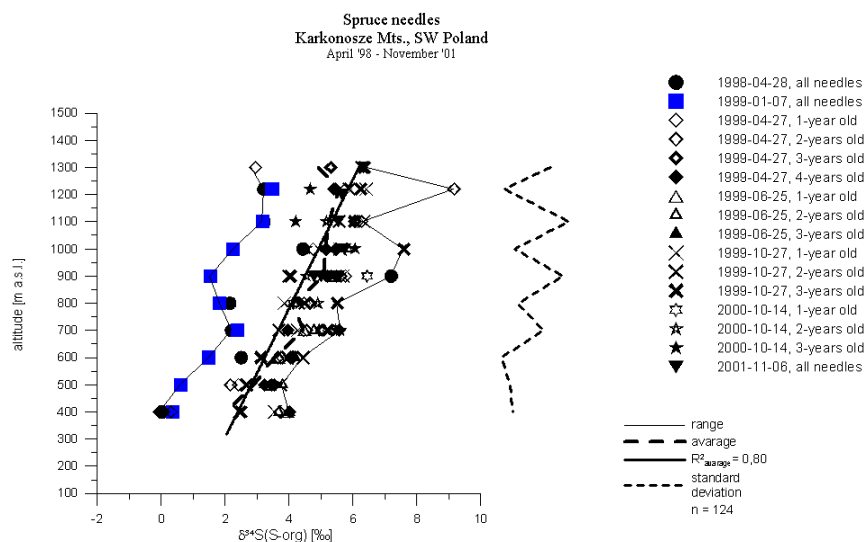


Fig. 1. Isotopic composition of organic sulphur in spruce needles (Karkonosze Mts.).

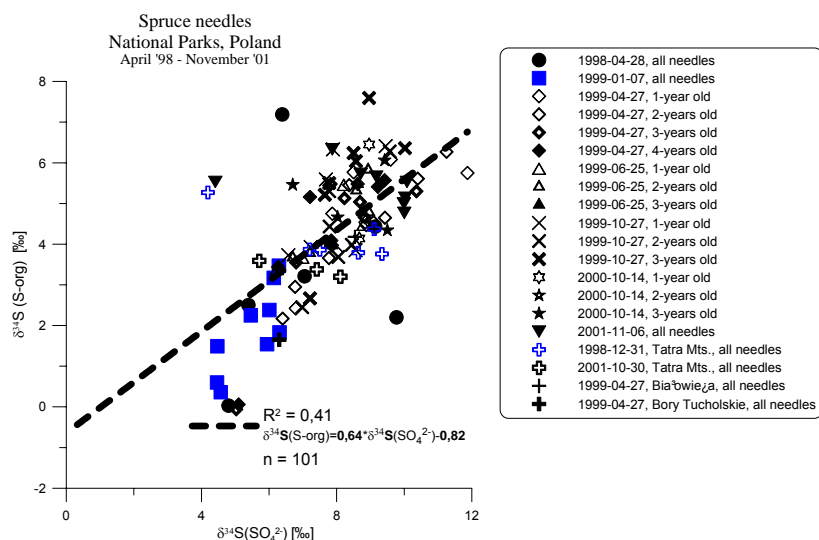


Fig. 2. Isotopic ratio of organic and inorganic sulphur in spruce needles (Karkonosze Mts.).

Isotope mass balance (SO_4^{2-} - H_2S - SO_2 system)

The difference in sulphur isotopic composition of SO_4^{2-} and H_2S under isotope equilibrium ($\Delta^{34}\text{S}(\text{SO}_4^{2-} - \text{H}_2\text{S})$), at temperature 25°C is $-63,36$ ‰ (Robinson 1973). Likewise, the $\Delta^{34}\text{S}(\text{SO}_4^{2-} - \text{SO}_2)$, at temperature 25°C , is $-12,41$ ‰ (Sakai 1968). At lower temperatures larger differences of isotopic composition at this systems are expected. Thus, the difference in $\delta^{34}\text{S}$ value in SO_4^{2-} - H_2S system should be about 70 ‰. The average difference of isotopic composition of inorganic and organic sulphur ($\Delta^{34}\text{S}(\text{SO}_4^{2-} - \text{S-org})$) is 3,70 ‰. This evidence isotopic disequilibrium or open S-system. Any change in intensity of H_2S emission should be isotopically detectable (at precision of isotopic analysis about

0,1 ‰). Therefore, isotopic study in the atmosphere seasonal and diurnal variations of SO₂ and H₂O would allow to describe individual factors controlling emission of hydrogen sulphide and to calculate an isotopic mass balance of H₂S emitted and amount of sulphur stored (in the form of SO₄²⁻) by forest complexes.

Conclusions

1. Higher value $\delta^{34}\text{S}(\text{SO}_4^{2-})$ and $\delta^{34}\text{S}(\text{S-org})$ with higher altitude result from an intensive assimilation SO₂ from atmosphere from the plant and probably growing emission H₂S to atmosphere.
2. Plants can not prevent to uptake of any portion of sulphur in the form of SO₂ through stomata. After assimilation SO₂ is oxidised and accumulate in the form of sulphate in spruce needles.
3. Coniferous forests can be a significant source of H₂S to the atmosphere.
4. Coniferous forests may play significant role in purification of the atmosphere from SO₂.

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