

Adam KAŁUŻNY, Mariusz JĘDRYSEK and Dariusz STRĄPOĆ

**STABLE ISOTOPE GEOCHEMISTRY OF ORGANIC AND INORGANIC
SULPHUR IN SPRUCE NEEDLES (SW POLAND, KARKONOSZE MTS.)**

INTRODUCTION

Europe is one of the world's largest acid rain regions, especially the region called Black Triangle (the region of SE Germany, NW Czech Republic and SW Poland) is the most heavily contaminated region in Europe (Jędrysek 2000). Despite decreasing trends in pollution, the sulphur deposition are still the most important acidifying factor for the hydrosphere, pedosphere and biosphere in the Black Triangle.

It is clear from numerous observations (Gebauer *et al.* 1994, Bruckner *et al.* 1993) that trees cannot prevent a passive uptake of considerable amounts of gaseous and aerosol compounds including SO₂, because these substances diffuse through the stomata. In polluted regions, nearly all sulphate in spruce needles originates from atmospheric SO₂ (*e.g.* Horn *et al.* 1989, Gebauer *et al.* 1994). The subject of this study was to investigate isotope ratios of organic and inorganic sulphur in spruce needles to assess the anthropogenic impact reflected from atmospheric SO₂.

MATERIALS AND METHODS

Spruce needles (*Picea abies*) was carried out at the northern slope of Karkonosze Mts., along a transect from Piechowice (400 m a.s.l.) to near Wielki Szyszak Mt. (1300 m a.s.l.). Samples was collected from April 1998 to November 2001. Moreover, spruce needles were collected from region of lower anthropogenic impact (Tatra Mts., Białowieski National Park and Bory Tucholskie National Park) for comparative analysis (Strąpoć 2002).

Needles were according to their different age classes and the S-isotope data of the individual age classes show similar trends as the total classes (Jędrysek *et al.* 2002). Needles were washed to remove dust, through intensive shaking in redistilled water, dried in vacuum and weighed. Sulphate was removed from

^{1,2} *Institute of Geological Sciences, University of Wrocław, Cybulskiego 30, 50-205 Wrocław, Poland, e-mail: ¹morion@ing.uni.wroc.pl, ²plum@ing.uni.wroc.pl*

³ *Indiana University, Department of Geological Sciences, Bloomington, dstrapoc@indiana.edu*

needles during a 24 hours washing in 0.01N NH_4Cl using magnetic stirring (Mynard *et al.* 1987). Afterwards the needles were washed again in double distilled water and no trace of sulphate was visible on AgNO_3 addition. To obtain the organic sulphur fraction the sulphate-free sample was dried in vacuum, and weighed for Parr Bomb combustion (Siegfriedt *et al.* 1951). The solution was filtered and BaSO_4 was precipitated. The precipitated BaSO_4 was rinsed with distilled water, dried, weighed, powdered in an agate mortar, preheated at 550°C (2 minutes) and weighed again in order to calculate the concentration of sulphur compounds.

For sulphur isotope analysis, 10 mg of BaSO_4 were mixed with 100 mg of V_2O_5 and 100 mg of pure quartz (Yanagishawa and Sakai 1983). The mixture was placed at the bottom of quartz glass tubes together with preheated pure copper wire situated 2 cm above the reaction mixture, and attached to the vacuum preparation line. The tube was heated at 450°C for about 10 minutes to remove any volatile contaminants. Afterwards, the temperature was raised to 950°C . The obtained SO_2 was frozen in a liquid nitrogen trap and then cryogenically cleaned using dry ice-ethanol mixture.

Sulphur isotope analyses were carried out using a Varian MAT CH7 mass spectrometer with a modified detection system in Wrocław and, a Finnigan MAT 251 in Göttingen. The precision was generally better than 0.1 ‰ for sulphur isotope analysis. The $\delta^{34}\text{S}$ value is given in the conventional way, in reference to CDT international standards.

RESULTS AND DISCUSSION

Concentration of sulphate from needles varied from 0.0001 (detection limit) to 0.0646 wt %, with average about 0.014 wt %. This values are typical (Turner *et al.* 1977, Manninen *et al.* 1997). Concentration of organic sulphur for respective samples are about eight times higher then concentration of inorganic sulphur. It was also observed at not polluted reference regions (Tatra Mts., Białowiecki National Park and Bory Tucholskie National Park).

$\delta^{34}\text{S}(\text{SO}_4^{2-})$ value varied form 4.19 do 11.9 ‰ (average about 8 ‰) with higher value at higher altitude. For organic sulphur $\delta^{34}\text{S}$ varied form 0.03 to 9.16 ‰. The difference in sulphur isotope ratios between sulphate and organics varied from – 1.12 to 7.57 ‰ with average 3.70 ‰.

Generally, the highest SO_4^{2-} concentrations are at the altitudes 500-700 and 1000 m a.s.l. The main source of pollution in the lower part of the transect is probably the international road Jelenia Góra–Jakuszyce. At the 1000 m a.s.l. there are no local anthropogenic factor. The high SO_4^{2-} concentration corresponding to the zone of thermal inversion and higher condensation of moisture. Probably gasses (SO_2) were transported by wind for a long distance. More detailed information on

the source will be probably to find by means of mineralogical and isotopic studies of the dust deposited on the needles.

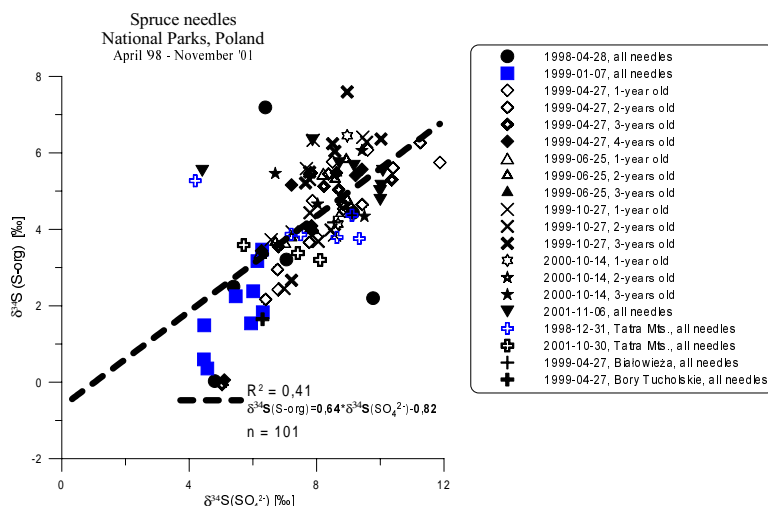


Fig. 1. Isotopic ratios of organic and inorganic sulphur in spruce needles (SW Poland, Karkonosze Mts.).

Isotopic composition of sulphur in plant are controlled by redox reactions in the atmosphere-biosphere system. In general, of isotope equilibrium condition, compounds on lower oxidation state are ^{34}S -depleted as compared to S^{+6} or S^{+4} -bearing compounds. A positive correlation between isotopic data and the altitude, could be explained by more efficient assimilation SO_2 from the atmosphere. Plants use a pool of sulphate in needles, consequently residual sulphate become enriched in ^{34}S , consequent new formed organic sulphur are enriched in ^{34}S too (Fig. 1). Moreover, observed ^{34}S enrichment in needles could be explain by H_2S emission (Jędrysek *et.al.* 2002) Efficiency of H_2S emission from plants are determined mainly by sulphur supply and light intensity (Wilson *et al.* 1978). Under humid conditions, ^{34}S -depleted H_2S are oxidized to ^{34}S -depleted SO_4^{2-} . Thus, high SO_2 stress at strong radiation and at humid environment result may in higher concentration of ^{34}S deplete SO_4^{2-} in forests highly populated by spruce.

Additional studies on concentration and isotope ratio of organic and inorganic sulphur in plant and concentration and isotope ratio of atmospheric sulphur dioxide may enable to calculate isotopic mass balance of S system in forested areas. This calculations could explain how much of atmospheric pollution (generally SO_2) may be accumulate and redistributed in the SO_4^{2-} form by coniferous forests.

CONCLUSIONS

1. Average differences in $^{34}\text{S}/^{32}\text{S}$ ratios in the SO_4^{2-} - S_{org} system are rather constant (about 3,70 ‰).

2. Higher value $\delta^{34}\text{S}$ (SO_4^{2-}) and $\delta^{34}\text{S}$ (S-org) at higher altitudes arise from more intensive assimilation SO_2 by tree and probability increase of emission of H_2S through stomata.
3. Coniferous forest plays an important role in elimination of SO_2 from the atmosphere.

Acknowledgements: This study was supported by: 2022/W/ING/02, 1017/S/ING/02-IX grants.

REFERENCES

- BRUCKNER G., GEBAUER L. and SCHULZE E-D., 1993: Uptake of $^{15}\text{NH}_3$ by *Picea abies* in closed chamber experiments., *Isotopenpraxis Environ. Health Stud.*, **29**, 71-76.
- GEBAUER G., GIESEMANN A., SCHULZE E-D. and JÄGER H-J., 1994: Isotope ratios and concentrations of sulphur and nitrogen in needles and soils of *Picea abies* stands as influenced by atmospheric deposition of sulphur and nitrogen compounds., *Plant and Soil*, **164**, 267-281.
- HORN R., SCHULZE E-D. and HANTSCHER R., 1989, Nutrient balance and element cycling in healthy and declining Norway spruce stands., *Ecol. Studies*, **77**, 444-455
- JĘDRYSEK M.O., 2000: Oxygen and sulphur isotope dynamics in the SO_4^{2-} of an urban precipitation., *Water, Air and Soil Pollution*, **117**, 15-25
- JĘDRYSEK M.O., KAŁUŻNY A., HOEFS J., 2002: Sulphur and oxygen isotope ratios in spruce needles as a tracer of atmospheric pollution., *Jour.Gephysical Research – Atmospheres*, **107**(D18), pp. ACH5-1 – ACH5-12
- MANNINEN S., HUTTUNEN S. and PERÄMÄKI P., 1997: Needle S fractionations and S to N ratios as indices of SO_2 deposition., *Water, Air and Soil Pollution*, **95**, 277-298
- MYNARD D.G., KALRA Y.P. and RADFORD F.G., 1987: Extraction and determination of sulphur in organic horizons of forest soils., *Soil Sci. Soc. Amer.*, **53**(3), 801-806.
- SIEGFRIEDT R.K., WIBERLEY J.S., MOORE R.W., 1951: Determination of sulphur after combustion in a small oxygen bomb., *Anal. Chem.*, **23**, 1008-1011.
- STRAPOĆ D., 2002: Geochemiczny obieg siarki w biosferze na przykładzie igieł świerka w wybranych Parkach Narodowych Polski. MSc Thesis
- TURNER J., LAMBERT M.J. and GESSEL S.P., 1977: Use of foliage sulphate concentrations to predict response to urea application by Douglas-fir., *Can. J. For. Res.*, **7**, 476-480
- WILSON L.G., BRESSEN L.G. and FILNER P., 1978: Light-dependent emission of hydrogen sulfide from plants. *Plant Physiol.*, **61**, 761-67
- YANAGISHAWA F. and SAKAI H., 1983: Thermal decomposition of barium sulfate – vanadium pentoxide – silica glass mixtures for preparation of sulfur dioxide in sulfur isotope ratio measurements. *Anal. Chem.*, **55**, 985-987.