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EXPRESS LETTER

Controls on sulfur content in tree rings of Norway spruce and European beech at a heavily polluted site

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Search for a biogeochemical archive of past sulfur pollution is motivated by the need to predict ecosystem health. Sofar, no indicator of local-scale S pollution has existed, while long-range transport of S can already be studied using polar ice records. One archive of S pollution in temperate climate zones could be annual growth rings of trees. However, S concentration patterns in tree rings of most species have been unknown because of negligible S accumulation in wood. We modified a wet chemistry procedure to increase the recovery of S from tree rings, and report time series of S concentrations in six trees from an acidified, spruce die-back affected area of Central Europe. Beech tree rings, despite 4 times lower atmospheric S inputs, exhibited twice higher S concentration in wood than spruce. The period of peak industrial S pollution of the 1980s did not result in enhanced S accumulation in tree rings of either species. Physiological processes rather than S abundance in the ecosystem regulate S storage in tree rings.

Keywords: sulfur, tree rings, spruce, beech, pollution

INTRODUCTION

The second half of the 20th century was characterized by an unprecedented increase in atmospheric pollution by industrial sulfur emissions in many countries. Central Europe, and in particular the northern Czech Republic, eastern Germany and southern Poland, experienced massive forest decline due to acidification, with most damage to high-elevation spruce ecosystems (Mayer *et al*., 2001). Atmospheric sulfur deposition was as much as 160 kg ha^{-1} yr^{-1} in the late 1980s (Novak *et al*., 2005), a value unmatched elsewhere, with the exception of industrialized parts of China (Vogt *et al*., 2007).

The response of forests to high ambient-air concentrations of SO_2 and H_2SO_4 has been evaluated by analyzing sulfur in soil, grasses, mosses, tree needles and leaves (e.g., Gebauer *et al*., 1994, Novak *et al*., 1996, Koptsik and Alewell, 2007). These concentrations can be compared with other continental proxies of sulfur pollution, such as speleothems (Wynn *et al*., 2008). However, very few studies reported time series of S concentrations in wood biomass, due to the fact that the amount of S in tree rings is extremely low (Yang *et al*., 1996, Giesemann *et al*., 2005, Kawamura *et al*., 2006). Sofar, it has been unclear whether S concentrations in tree rings in spruce-die back areas reflect the changing availability of anthropogenic sulfur, and thus can be used as an archive of past environmental change.

Previous studies showed that high atmospheric SO_2 input results in elevated S concentration in leaves, mainly in the form of sulfate (Giesemann *et al*., 2000). Similarly, S concentration in organic soil horizons under spruce canopy is positively correlated with the atmospheric S inputs along an east-west pollution gradient across Europe (Novak *et al*., 2001). We hypothesized that the degree of sulfate assimilation and storage of sulfur in annual growth rings of hardwoods would parallel temporal changes in industrial S emissions in Central Europe. We measured S concentrations in tree rings of three Norway spruce and three European beech trees from a forest die-back affected site in the northern Czech Republic. The biomass data were complemented with a year-long monitoring of atmospheric S deposition into both stands. Our objective was to evaluate whether trees were passive stores of assimilated sulfur. If so, the species receiving higher S input from atmospheric deposition would display the greatest enrichment of S in annual growth rings.

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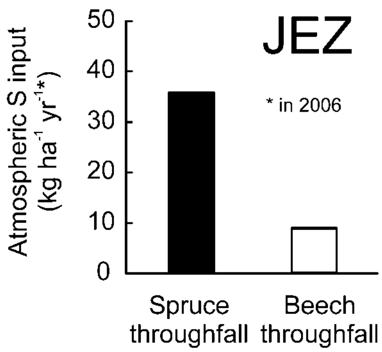

Fig. 1. Atmospheric deposition to spruce and beech stands.

STUDY SITE

The small mountain-slope catchment Jezeri (JEZ; 50°38′ N, 13°29′ E) is situated in an industrial part of the northern Czech Republic. The hydrochemical fluxes have been monitored on a monthly basis for the past 30 years (Paces, 1985). The JEZ catchment (490–924 m a.s.l.) overlooks a coal basin with 11 coal fired power plants, in operation mostly since the 1950s. Between 1970 and 1996, spruce died back on 63% of the catchment's area, with only small patches of young vigorous trees surviving. A mature beech stand at the foot of the mountain (26% of the catchment's area) remained undamaged. While the two-mica orthogneiss in bedrock contains practically no sulfur, the catchment has been recently characterized by annual S export via stream discharge three times higher than atmospheric S deposition (Novak *et al*., 2000). The net export of S was interpreted as release of older anthropogenic sulfur that had accumulated in the soil in the years of peak pollution (1980s). Groscheova *et al*. (1998) showed that along the JEZ slope, a sharp gradient in S isotope composition of atmospheric deposition exists, in addition to an altitudinal gradient in S inputs. The mean annual temperature is 6.0°C, and the mean annual precipitation is 940 mm. The soils are mainly distric cambisols.

METHODS

Three *Picea abies* (Norway spruce) and *Fagus sylvatica* (European beech) trees were harvested in the spring of 2007. The spruce and beech stands were sampled at an elevation of 830 and 500 meters, respectively. Since all mature spruce at JEZ perished following the pollution-related defoliation of the 1970s, we were only able to study individual spruce trees 57 years old. Beech was 100 years old. Five-cm thick trunk segments were taken to the laboratory. Full concentric segments of 5 consecutive tree rings were separated by a cutter, homogenized in a planetary mill and dried at 60°C. Pooling of full tree rings made it possible to recover enough material for the Eschka digestion. Six grams of pulverized wood were used for the Eschka digestion rather than 1 g recommended by Chakrabarti (1978). A mixture of Mg and Na_2CO_3 (wt. ratio 2:1) was added to the sample for thermal decomposition at 800°C. $BaSO_4$ was precipitated by an addition of 10% $BaCl_2$ solution at pH of 2.5. The gravimetric sulfur determination was based on 1–6 mg of $BaSO_4$ (reproducibility better than ±5 ppm S).

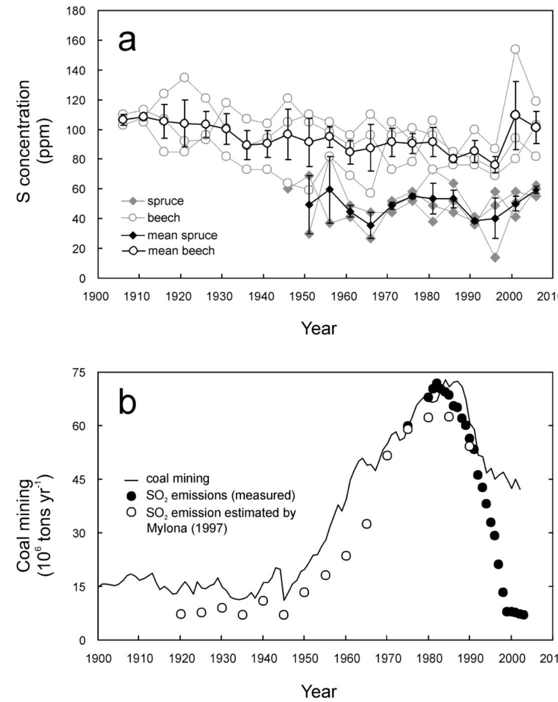

Fig. 2. (a) Sulfur concentration in tree rings, means and standard errors are given; (b) Historical sulfur pollution in the Czech Republic (Kopacek and Vesely, 2005).

Sulfur in the tree canopy throughfall is a mixture of dry deposited SO_2, and wet-deposited SO_4. For the hydrological year 2006, S input fluxes into the spruce and beech stands at JEZ were evaluated based on replicated sampling of precipitation. Cumulative water samples were taken monthly in a network of 9 samplers in a 10 × 10 m grid underneath closed spruce and beech canopy, respectively. Deposition samplers were polyethylene funnels (area of 122 cm^2) fitted to 1 L bottles placed 120 cm above ground. In winter, plastic vessels (area of 380 cm^2) with polyethylene bags replaced the funnels to collect snow. Sulfate concentration in precipitation was determined on a Shimadzu LC6A liquid chromatograph. Annual S fluxes were calculated from monthly sulfate concentrations and water fluxes.

Results

Annual S deposition into JEZ forests was measured in the last year before the trees were harvested. Sulfur input was 36.0 and 9.0 kg ha^{-1} yr^{-1} into the spruce and beech stand, respectively (Fig. 1). In 2006, spruce was receiving 4 times more atmospheric S than beech. In contrast, average S concentration in beech tree rings (94.7 ppm) was nearly twice that measured in spruce tree rings (49.8 ppm; Fig. 2a). As also seen in Fig. 2a, neither species exhibited any temporal trend in tree-ring S concentration. Based on calculations of S input in each of the stands, there is an apparent discrepancy regarding the amount of S contained within the 2006 annual growth ring of the two tree species. Despite spruce receiving the higher S input, this species contains the lower S concentration. We will first discuss processes affecting atmospheric S deposition into the two tree stands, and then evaluate further ecosystem processes affecting S availability to trees.

Discussion

Atmospheric sulfur deposition is influenced by both the surface roughness of the vegetation (depending on plant species), and elevation. Spruce needles have a higher surface area than beech leaves, and are exposed to air pollution also in winter. Power plant stacks emit about 98% S in the form of SO_2, and 2% S in the form of SO_4. Partial oxidation of SO_2 to sulfate occurs in the atmosphere. It has been shown that in the vicinity of the point sources of pollution up to 70% of total S deposition via conifer canopy throughfall occurs as dry-deposited SO_2, and only 30% as wet deposited SO_4 (Novak *et al.*, 1996). In contrast, the relatively small surface area of foliage in deciduous forests captures less SO_2, and both the dry and total deposition into beech stands are smaller compared to spruce. Previous studies at JEZ showed that total S deposition in spruce stands was even more than 4 times higher relative to beech throughfall (Novak *et al.*, 2000). Higher elevation of the spruce stand compared to the beech stand at JEZ also contributed to higher S inputs into spruce. More rainfall at a higher elevation brings more S, compared to the valley (Groscheova *et al.*, 1998).

Hydrogeochemical catchment-level mass balances, and isotope comparisons of atmospheric and bedrock S have shown that old pollutant sulfur at JEZ is largely stored in the soil (Novak *et al.*, 2005). Now, in an era of decreasing pollution, this S is gradually released from the catchments via runoff. Sulfur is an essential nutrient for the trees, and, in principle, can be taken up from both the atmosphere, and the soil (Cram *et al.*, 1997). There are three reasons why spruce wood at JEZ could have higher S concentrations than beech wood: (i) S-richer atmospheric input; (ii) S-richer soil (itself a consequence of higher atmospheric S input); and (iii) a shallower root system which may more easily tap into the anthropogenic S pool stored predominantly in the topmost organic soil horizons. Yet, as seen from a comparison of Figs. 1 and 2a, the opposite is true: four times lower atmospheric S inputs in the beech stand were accompanied by twice higher S content in wood, compared to the spruce stand. It follows that the abundance of reactive S species in the environment is not the main control of the levels of S in spruce and beech wood.

Figure 2b shows temporal changes in S pollution in the Czech Republic between 1900 and 2007. Soft coal mined in the northern Czech Republic contains as much as 3 wt. % of sulfur, which until the installation of desulphurization units in power plants in the 1990s was largely released into the environment by the process of combustion. Both soft coal production and SO_2 emissions peaked in the 1980s. Since then, the SO_2 emission rates decreased by more than 90%. The large maximum in pollution is not seen in the tree ring S content (Fig. 2a). Tree rings from the relatively unpolluted years 1905 (beech) and 1950 (spruce) contain the same amount of S as those from the highly polluted 1980s. This was surprising because two previous studies showed higher S contents under higher pollution in the tree rings of juniper and oak (Guyette *et al.*, 1989; Giesemann *et al.*, 2005). We conclude that spruce and beech tree rings in a highly acidified ecosystem do not record past pollution levels.

Data in Figs. 1 and 2 collectively indicate that post-depositional mobility of S among tree rings cannot be the only factor determining S storage in the wood of spruce and beech. Post-depositional mobility of S among tree rings could explain the absence of S peaks at times of maximum pollution, but cannot explain the higher overall S contents in beech wood than in spruce wood.

Conclusions

Our study suggests that foliar uptake of atmospheric S is not the main control of S abundance in tree rings of *Picea abies* and *Fagus sylvatica* in the stressed ecosystems of Central Europe. It has ruled out the predominance of S uptake from the soil in combination with post-depositional immobility of S among tree rings. Sulfur content in the soil at the tree rooting depth increased for most of the 20th century, but this increase was not seen in tree rings. It appears that physiological processes control S accumulation rates in the tree rings of Norway spruce and European beech, the two most common tree species in the polluted regions of Central Europe. These processes are species-specific.

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