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Long-term Resistance of Spruce to SO₂ requires Mobilization of Cations

By

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Summary

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Oxidative detoxification of atmospheric SO₂ inside the needles of spruce yields sulfuric acid. Protection of needle cells against acidification requires the uptake of cations. At the boundary between apoplasm and symplasm cations can either be exchanged against protons or taken up together with anions, which on degradation (e.g. malate) or reduction (e.g. nitrate) yield hydroxyl ions. Cations are supplied from the root system by the transpiration stream. As long as transferable cations become available, low atmospheric levels of SO₂ can be tolerated for long times while sulfate accumulates in the plant.

Introduction

In spruce only part of SO₂ taken up by needles via open stomata is detoxified by reduction and incorporation of reduced sulfur into amino acids and other organic compounds. SO₂ which is not reduced will be oxidized to sulfuric acid (DITTRICH & al. 1991, GASCH & al. 1988). Neutralization of this acid requires mobilization of cations by the plant.

Protection against cellular acidification by the sulfuric acid formed from SO₂ is possible in several ways (Figure 1):

1. Sulfuric acid could be exported from the needles via the phloem to the roots and excreted into the soil. Release of protons by roots is a well-known phenomenon. GARSED & READ 1977 have demonstrated excretion of ³⁵S from ³⁵SO₂ into the root environment. Only about 20 % of radioactivity was excreted into the

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nutrient solution. Herbaceous plants are known to be able to transport sulfate via the phloem, but in contrast to GARSEED & READ, excretion of sulfate anions has not been observed by KAISER & al. 1992. In herbaceous plants sulfate anions may accumulate in the root system. In spruce, however, sulfate accumulates in needles (KAISER & al. 1991).

2. Base may be mobilized for neutralization. Reduction of nitrate yields base in the form of hydroxyl ions and ammonia. Ammonia is toxic to cells at elevated concentrations. Detoxification of ammonia occurs during growth by incorporation of its nitrogen into amino acids which form proteins. However, spruce uses ammonium as a main nitrogen source. The concentration of nitrate in the xylem sap was very low (0.012 ± 0.014 mM, annual mean). In needles, nitrate is often too low to be detectable.

3. Organic acids may be degraded to compensate for the acidification caused as a consequence of SO_2 uptake. However, such degradation, if it occurs at all, cannot prevent acidification during exposure of spruce over prolonged periods of time. Organic acids take part in and are required for metabolism.

4. Long-term compensation of the acid resulting from SO_2 uptake is possible by cation-proton exchange first across the plasmalemma of cells which have taken up SO_2 , but finally between soil and the root system. While protons are excreted into the soil, cations are taken up in exchange. They are transported to the needles together with counterions which may circulate in the xylem/phloem transport system. In the needles, cation-proton exchange between apoplast and symplast provides the basis for neutralization of sulfuric acid inside the mesophyll cells. This meets the demand for electrical neutrality and maintenance of pH-values. Excess sulfate is sequestered in the vacuoles (DITTRICH & al. 1991, KAISER & al. 1991). Thus, transport of cations in the xylem sap plays an important role in the protection against cellular acidification.

Materials and Methods

Samples were taken from spruce trees in the Botanical garden of the University of Würzburg. Four twigs of a tree (fresh weight 20 to 50 g) were collected 1.50 - 2.0 m above ground every week from December 1990 to December 1991. The twigs were sealed in polyethylene bags and stored on ice for a maximum period of 3 h until xylem sap was obtained. Twigs were stripped of their bark from the cut end for about 1 cm in order to avoid contamination by phloem sap. The bark was sealed with thin plastic film. A twig was locked in a pressure chamber with the cut end protruding. The end of the shoot was fitted with a 3 cm long piece of silicone tube. The xylem water potential was determined by measuring the pressure required for moistening the cut end of the twig by xylem sap. The pressure was then increased by 0.1 MPa per minute. Exuding sap (800 - 900 μl) was collected with a syringe and stored at -18°C .

Cations (Na^+ , Mg^{2+} , K^+ , Ca^{2+} , Al^{3+} , Mn^{2+} , Fe^{2+} , Cu^{2+} , Zn^{2+}), total S and P were determined in the xylem sap with an Inductively Coupled Plasma Atomic Emission Spectrophotometer (Model JY 70 PLUS, Jobin-Yvon).

Anions (Cl^- , NO_3^- , HPO_4^{2-} , SO_4^{2-} , malate²⁻, oxalate²⁻) and amino acids were determined by High Pressure Liquid Chromatography.

Results and Discussion

Concentrations of cations and anions measured in xylem sap are shown in Table 1. It should be noted that concentrations of the measured ions changed depending on changes in weather conditions. However, no major differences in cation concentrations were observed in the different seasons of a year.

pH values of the xylem sap ranged from 5.2 to 6.9 (mean: 6.14 ± 0.46). During the summer pH values were generally lower than during the winter. Main cations were K^+ , Ca^{2+} and Mg^{2+} . Na^+ levels were very low. As should be expected, iron, zinc, aluminum, manganese and copper were minor components of xylem sap. Nonetheless, it is remarkable that aluminum could be found in the xylem sap of spruce trees which grow on the slightly alkaline soils of Würzburg.

Alkaline amino acids could be found in the xylem sap, but their levels were very low (0.0045 ± 0.0061 mM arginine, 0.00010 ± 0.00068 mM lysine, 0.0047 ± 0.0077 mM histidine).

Because bicarbonate and several organic anions could not be measured with our HPLC-devices, the equivalents of measurable anions did not match the total equivalents of cations (Table 1).

Malate concentrations were almost as high as chloride concentrations which changed much during the year. Phosphate levels were lower than malate and chloride levels, but nonetheless appreciable. Sulfate concentrations were low, but higher than nitrate concentrations which showed large fluctuations. Concentrations of acidic amino acids changed much during the observed period. Aspartate concentrations were high, whereas glutamate levels were low.

The main information contained in Table 1 is that the total concentration of cation equivalents in the xylem sap is about 5 mEq l^{-1} . Potassium and magnesium which can be taken up by mesophyll cells contribute about half to this. Another major contributor is calcium whose possible role in the neutralization of airborne sulfuric acid remains unclear. Cytosolic calcium activities are tightly controlled, they are in the submicromolar range. Anions not accounted for in the determinations amount to about 0.6 mEq l^{-1} . A major organic anion is malate. On full degradation, organic anions yield CO_2 , which may escape into the atmosphere, water and hydroxyl ions. On removal of CO_2 from bicarbonate, hydroxyl ions also remain. As an alternative to the formation of base in the cells, cations of the xylem sap may be exchanged for H^+ of the mesophyll cells where sulfuric acid has been formed. This neutralizes sulfuric acid in the mesophyll, but acidifies the leaf apoplasm. Cations readily available for cation/proton exchange are potassium and magnesium. They occur in the xylem sap at a total concentration of about 2.7 mEq l^{-1} . If calcium is also included, this figure would increase to about 4.7 mEq l^{-1} . Interestingly, cation concentrations did not change dramatically during the course of a year even though the rate of water transport in transpiration changed much with the season (Fig. 2).

Degradation of organic anions for purposes of base formation is limited because organic anions serve vital functions in cellular metabolism. They cannot be exhausted without detrimental effects on the organism. Cations, on the other hand,

are needed for growth. If they are removed from the xylem sap for the neutralization of airborne sulfuric acid, sulfate formation competes with growth for cations. It is well known that SO_2 immissions decrease growth. Also, cation/proton exchange shifts the burden of acidification from mesophyll cells to other parts of the organism. Finally, protons released into the apoplasmic space in exchange for cations, which enter the mesophyll, should reach the roots via the xylem/phloem circulation system. At the level of the roots, they may be excreted into the soil in exchange for cations of the soil. It is known that cation uptake from the soil occurs as cation/proton exchange. There is potassium accumulation together with sulfate in needles of spruce growing in the Ore Mountains (KAISER & al. 1991). However, it is still completely unknown, how the neutralization of sulfuric acid, which is formed from SO_2 in the needles and requires cations, is coordinated with cation uptake by the root/mycorrhiza system of spruce trees. A main problem of SO_2 tolerance of trees such as spruce is how to obtain the cations which are needed as counterions of sulfate, and how to remove the protons of sulfuric acid.

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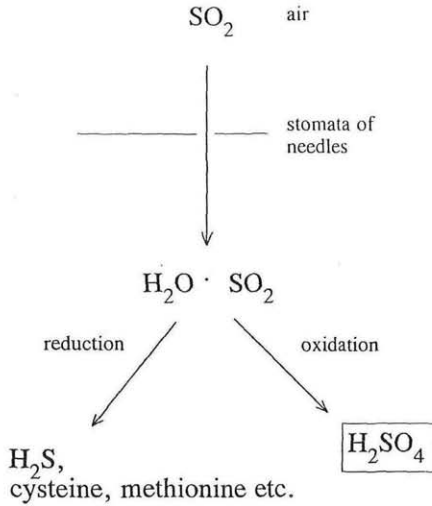


Fig. 1. Uptake and detoxification of SO₂ by leaves.

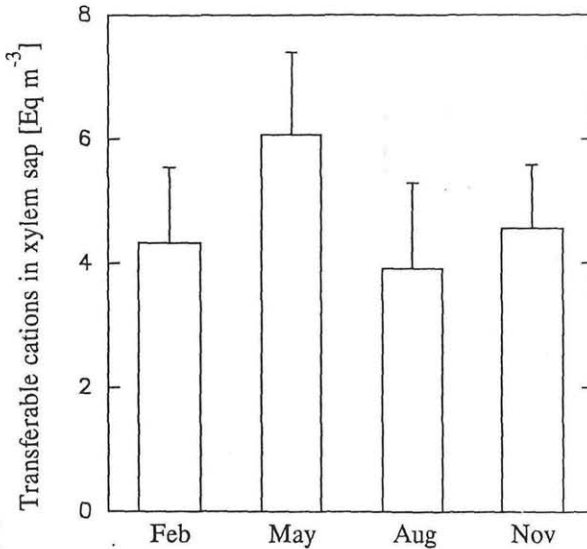


Fig. 2. Mean total concentration of cations in the xylem sap of healthy spruce trees at the Botanical garden of the University of Würzburg (calculation after SLOVÍK & al. 1992).

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Table 1. Concentrations of cations and anions in the xylem sap. Data are averages of 200 determinations during the course of one year (\pm SD).

pH	6.14 \pm 0.46
Total phosphorus (ICP measurements)	0.29 \pm 0.21 mM
Total sulfur (ICP measurements)	0.19 \pm 0.0097 mM
Nonmetal cations: (HPLC measurements)	
Alkaline amino acids: arginine	0.0045 \pm 0.0061 mM
lysine	0.00010 \pm 0.00068 mM
histidine	0.0047 \pm 0.0077 mM
Metal cations: (ICP measurements)	
potassium	2.3 \pm 0.97 mM
calcium	1.0 \pm 0.38 mM
magnesium	0.19 \pm 0.089 mM
sodium	0.071 \pm 0.041 mM
iron	0.026 \pm 0.061 mM
zinc	0.013 \pm 0.012 mM
aluminium	0.0027 \pm 0.0067 mM
manganese	0.0017 \pm 0.0014 mM
copper	0.00075 \pm 0.00065 mM
total metal cations	4.8 \pm 1.8 mEq l ⁻¹
Anions: (HPLC measurements)	
chloride ⁻	0.97 \pm 1.1 mM
HPO ₄ ²⁻	0.29 \pm 0.20 mM
sulfate ²⁻	0.081 \pm 0.052 mM
nitrate ⁻	0.012 \pm 0.014 mM
malate ²⁻	0.83 \pm 0.93 mM
oxalate ²⁻	0.0069 \pm 0.0092 mM
Acidic amino acids: glutamate	0.013 \pm 0.014 mM
aspartate	0.82 \pm 0.77 mM
Total cations	4.8 mEq l ⁻¹
Total anions	4.2 mEq l ⁻¹
Anion deficit	0.60 mEq l ⁻¹

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