

# **Biochemical Parameters as Biomarkers for the Early Recognition of Environmental Pollution on Scots Pine Trees. II. The Antioxidative Metabolites Ascorbic Acid, Glutathione, $\alpha$ -Tocopherol and the Enzymes Superoxide Dismutase and Glutathione Reductase**

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Field investigations with Scots pine trees (*Pinus sylvestris* L.) were performed in eastern Germany, where ambient SO<sub>2</sub>, NO<sub>x</sub> and O<sub>3</sub> concentrations differed significantly in 1992–99 at three sites, namely Neuglobsow (yearly mean SO<sub>2</sub> in 1992: 9 µg m<sup>-3</sup>), Taura (yearly mean SO<sub>2</sub> in 1992: 54 µg m<sup>-3</sup>) and Rösa (yearly mean SO<sub>2</sub> in 1992: 73 µg m<sup>-3</sup>). To investigate the effects of SO<sub>2</sub>, NO<sub>x</sub> and O<sub>3</sub> on antioxidants (superoxide dismutase, ascorbic acid, glutathione, glutathione reductase,  $\alpha$ -tocopherol) and pigments including chlorophyll fluorescence as well as visible damage symptoms in the form of needle yellowing and tip necroses, needles of the 1st and 2nd age class from young and mature trees were collected at the sites every October. Eight years after the start of the field study in 1992, the ambient SO<sub>2</sub> concentrations had decreased significantly at Neuglobsow (yearly mean SO<sub>2</sub> in 1999: 4 µg m<sup>-3</sup>), Taura (yearly mean SO<sub>2</sub> in 1999: 5 µg m<sup>-3</sup>) and Rösa (yearly mean SO<sub>2</sub> in 1999: 5 µg m<sup>-3</sup>). NO<sub>x</sub> and O<sub>3</sub> differed less at the three sites and showed no temporal variations. Whole needle glutathione continuously decreased, although concentrations were higher in needles of the 1st and 2nd age class from the polluted sites Taura and Rösa than the unpolluted site Neuglobsow. The activities of glutathione reductase exhibited the same site-related differences and temporal variations and were correlated with concentrations of oxidized glutathione (GSSG). In contrast, the activities of the enzyme superoxide dismutase and the concentrations of whole needle ascorbic acid remained unchanged over the period. Only at the end of the investigation period did the concentrations of oxidized ascorbic acid (dehydroascorbate) increase in six-month-old needles at the polluted sites Taura and Rösa. Despite the clear decreases in SO<sub>2</sub>, the visible symptoms of needle tip necroses remained unchanged, especially at the polluted sites Taura and Rösa, although the needles contained higher pigment concentrations than needles from the unpolluted sites. The results of measurements with antioxidants as biomarkers for SO<sub>2</sub>-mediated stress in pine needles show that the adult Scots pine trees at the polluted sites suffered from greater oxidative stress than the needles from the less polluted site.