EC-146: Sulphur distribution in two tree species: cellular, annual and long-term variability

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Work carried out at ID21 on 28th June 2007 to 3rd July 2007

Samples:

The study site lies at 1100-1200 m altitude on the N side of the Valsugana valley (45º 58' 37" N, 11º 39' 28" E), NE Italy. Trees were sampled using increment corers from living trees and segments collected from felled trees of known provenance. Within the sampling area is the Grotta di Ernesto, a cave site where a record of S concentrations has been obtained from a speleothem. The woodland is managed, but consists of conifers mixed with beech on south-facing slopes; we sampled the two most common conifers: Norway spruce (*Picea abies* (L.) Karst) and Silver fir (*Abies alba* Miller). Dendrochronologies were constructed from the 0.5-2 mm-thick annual rings so that the age of all samples was known

Experimental:

Synchrotron work complemented ICP-MS analysis of acid leachates of wood. The synchrotron technique was used to generate high-resolution time series of S and to map the distribution of elements on a micro-scale. Acetone-treated wood samples were cut into thin laths (ca. 4 mm thick) and smooth surfaces manually prepared with a scalpel and mounted on a sample holder. The specimens were placed in the ID-21 beamline microscope chamber operated at a pressure of 10^{-5} mbar. X-ray fluorescence emission (K lines) from S was optimized by using 2.5 keV monochromatic synchrotron radiation. Cell walls were visible in images of secondary X-rays specific to O, Na, Mg, Al, Si, P and S, generated from depths of up to 10 μm. Given the incident beam angle of 37° and the porous nature of the samples, there was some directional bias in element intensities related to variable absorption of the secondary X-rays. Scans were run with a beam size of 100 μm (pinhole) and 10 second dwell time, and maps were constructed with a focused beam approximately 0.5 or 2 μm diameter and dwell time of 5 seconds. Scan intensities were normalised using an Io detector to correct for the small decrease in the incoming synchrotron beam flux over several hours. XANES scans were run using a 300 μm diameter beam by adjusting excitation energies from 2.45 to 2.53 keV at 0.00018 keV intervals each with 9 second count times. Peak responses at 2.474, 2.4765 and 2.482 keV provided a natural contrast to construct maps of $S^{0 \text{ to } +0.5}$, S^{+2} and $S^{+5 \text{ to } +6}$ species.

Summary of outcomes:

Bulk analyses of *Abies* demonstrate that S concentrations were higher in the second half of the 20th century, but with some high outliers possibly reflecting particulate impurities. X-ray synchrotron analyses confirmed the observed time trend, which is similar to that of a nearby stalagmite, and reflects an atmospheric pollution record mediated by storage in the soil and ecosystem. S and P were found to be localized in the inner cell wall (c. 2 μm wide), local thickenings of which probably account for some outlying high values of S in synchrotron studies. S occurs as a mixture of oxidation states (0 to +0.5, +2, +5 and +6) which are consistent in space and time. The results indicate that

wood older than a few years contains archive-quality S, but that robust conclusions require multiple replicate analyses.

Publication:

Fairchild, I.J., Loader, N.J., Wynn, P.M., Frisia, S., Thomas, P.A., Lageard, J.G.A., de Momi, A., Hartland, A., Borsato, A., La Porta, N. and Susini, J. 2009 Sulfur fixation in wood mapped by synchrotron X-ray studies: implications for environmental archives. *Environmental Science and Technology,* 43, 1310–1315.