Fairchild, IJ, Loader, NJ, Wynn, PM, Frisia, S, Thomas, PA, Lageard, JGA, 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 (Washington), 43 (5). pp. 1310-1315. ISSN 0013-936X

DOI: https://doi.org/10.1021/es8029297

Publisher: American Chemical Society

Version: Accepted Version

Sulfur Fixation in Wood Mapped by Synchrotron X-ray Studies: Implications for Environmental Archives

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There is a shortage of archives of sulfur that can be used to investigate industrial or volcanic pollution in terrestrial catchments, but the role of S as a nutrient, coupled with sparse published evidence, suggests that trees are promising targets. We focused on two conifer species (*Picea abies* (L.) Karst and *Abies alba* Miller) from an Alpine site in NE Italy. 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 (ca. 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.

Introduction

Environmental archives are valuable in assessing the impact of ongoing episodes of pollution as well as identifying events of the past which document specific environmental forcings valuable for improving earth system models The most straightforward archives of sulfur are ice cores, which provide an overview of volcanic events in the same hemisphere in addition to documenting the long-range effects of pollution (*1*). Reconstruction of industrial emissions from documentary evidence (*2*), in agreement with ice cores (*3*), shows that atmospheric sulfur pollution reached a peak in the late 20th century. However, ice cores reflect a clean boundary layer at remote and/or elevated locations, and more specific information is required on lower altitude environments where more severe pollution occurred, from more local sources (*4*, *5*). Archived soils have demonstrated a record of environmental pollution in the Anthropocene (*6*), but they are by definition a limited resource. In certain circumstances, peat can serve as an archive (*7*), but S remobilization destroys the integrity of the signal in other cases. More generally, detailed monitoring of catchments has shown that they tend to store the pollutants (*8*) such that S outputs may not decline until years to decades later (*9*). Hence, an atmospheric input signal will be modified in any archive that derives from S stored in soil and biomass. This is the pattern we found in a wooded catchment in NE Italy within a study demonstrating that speleothems (calcareous deposits in karst caves) can act as S-archives (*4*). In the current study, using this same site above the cave Grotta di Ernesto, we present the first interproxy (speleothem-tree) comparison of S archives at a given location.

Woody tissues have provided a firm foundation for studies of past climates through study of tree-ring width, relative latewood density, and carbon, hydrogen, and oxygen isotopic composition (*10*−*12*), and so it is natural also to look to the forests to provide records of environmental pollution. The results have been mixed, because the initial signal of elemental uptake from the environment is often overwhelmed by migration of elements in resins/sap (*13*−*15*), buffered in the soil or rapidly recycled in less durable plant organs. Although S has only rarely been determined in dendrochemical studies, a study in Sweden has demonstrated higher wood S levels in *Picea abies* when fertilized (*16*), and there is sparse evidence (*17*−*19*) indicating that pollution records may be constructed. Particular impetus is provided by a recent report on coniferous trees from Japan (*20*) that uses a combination of elemental and S isotopic data to demonstrate a contrasting impact of 20th century pollution on urban and rural sites. However, no study has yet demonstrated the spatial patterning of S occurrence on a microscale to demonstrate the mode of its fixation. Neither has the issue of signal strength and replication been examined. This is important, since it has proved necessary to use replicated tree samples in all dendroclimatological applications (*10*−*12*) and previous dendrochemical studies on metals also show significant intersample variability (*13*−*15*) that may limit their wider interpretation. Both issues are addressed in this report.

One reason for the lack of study of S in trees concerns analytical difficulties. Reference *20* generated high-quality data but used a laborious technique requiring large samples (100 g). Other workers have been limited by analytical

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constraints such as the volatilization of S during standard dendrochemical protocols by bulk analysis and interference effects with molecular oxygen that make it difficult to determine by mass spectrometry at low levels. In this study, we have chosen to use a combination of two techniques by which S can be robustly determined in order to generate a critical mass of data on its variation in space and time in woody tissues. First, we analyzed powdered wood samples using inductively coupled mass spectrometry (ICPMS) at high mass resolution to eliminate the oxygen interference. Second, we explored the same samples using synchrotron radiation. Synchrotron studies have provided valuable information on the localization of metals in wood (*21, 22*) and the distribution and oxidation state of S in timber from a marine shipwreck (*23*), in soil humic substances (*8, 24, 25*), and in living plant matter (*26*). Here we compare the pattern of 20th century S variability in two conifer species from solution-based analyses with high-resolution synchrotron micro-X-ray fluorescence (μ-XRF) scans. We also determine the oxidation states and localization of S using a combination of X-ray absorption near-edge structure (XANES) measurements and μ-XRF-mapping to provide new lines of evidence to assess the value of trees as recorders of environmental S variability.

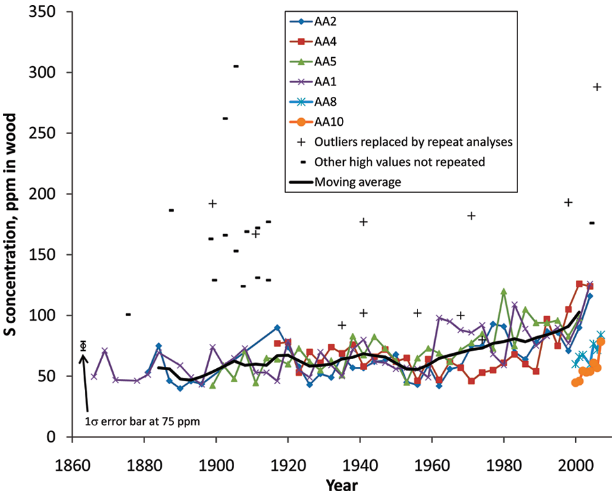

FIGURE 1. ICP-MS analyses of powdered resin-extracted *Abies* wood samples (AA numbers refer to different trees sampled). The moving averages do not include the outlying values. See text for discussion of trend and of outlying high values.

Experimental Section

Sampling. The study site lies at 1100−1200 m altitude on the N side of the Valsugana valley (45° 58′ 37″ N, 11° 39′ 28″ E), NE Italy. Trees were sampled using increment corers from living trees and segments collected from felled trees of known provenance. More detailed information is provided in ref *27* and in the Supporting Information. Within the sampling area is the Grotta di Ernesto, a cave site where a record of S concentrations (*4*) 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.

Inductively Coupled Mass Spectrometry (ICP-MS) Analysis. This technique was used to generate definitive absolute concentrations of S. Samples for solution-based analyses were pretreated with a 9:1 Aristar-grade acetone:deionized water treatment for 48 h at room temperature and rinsed thoroughly with hot and then cold deionized water and dried (following ref *28*) to remove the potentially mobile resinous component and any surface bound mobile (soluble) sulfur. Subsequent sample treatment methods were developed from those in refs *14* and *29−31*. Segments were cut by scalpel and hand-ground to a fine powder, 8 mg of which was digested in 0.25 mL of concentrated Aristar-grade HNO_3 for 48 h at room temperature. Solutions were diluted with deonized water to 12.5 mL, and the supernatant from centrifugation was analyzed by high mass-resolution ICP-MS using an Axiom instrument at Kingston University, UK (instrument configuration as described in ref *4*). Blank corrections were made using 2% v/v HNO_3 solutions, and although solutions were strongly brown-colored, negligible matrix effects on S sensitivity were found when tested using standard additions. Results were compared with inorganic standards. Standards tested as unknowns had an uncertainty of 5% of the analysis at 10 ppb S in solution; this represents a maximum uncertainty for wood solutes with higher S concentrations, and hence variations greater than 5% are attributed to sample inhomogeneity.

Synchrotron Studies. This technique was used to generate high-resolution time series of S and to map the distribution of elements on a microscale. Acetone-treated wood samples (as described above) 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 at the European Synchrotron Research Facility (more details are in ref *4*). 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 s dwell time, and maps were constructed with a focused beam approximately 0.5 or 2 μm diameter and dwell time of 5 s. Scan intensities were normalized 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 at 0.00018 keV intervals each with 9 s 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.

Results and Discussion

Time Series from Bulk Analyses. Annual growth is divided into early- and late-wood, referring to the wide, thin-walled cells formed early in the growth season and the narrower, thicker-walled compact cells in the late summer, respectively (*11*). Most work was focused on *Abies*, the bulk analysis of which showed to be richer in S than *Picea* (Supporting Information, Figure S2).

Because some differences were found between the mean composition of early- and late-wood (Supporting Information, Figure S2), three-year-aggregated samples were used to generate time series. Samples from four *Abies* were studied, supplemented by two new samples for 21st century growth (Figure 1). The data show an increase in S composition in the late 20th century, but with considerable noise, including variation between individual trees. One specific issue is the presence of outlying high values (Figure 1), all of which were confirmed by reanalysis of the sample solution on the same day. However, when samples were freshly prepared from dissolution of powders, the reanalyses all lay within the main data trend. The implication is that the sample powders are inhomogeneous, with rare localized particles or regions rich in S. At present we cannot conclude whether these are

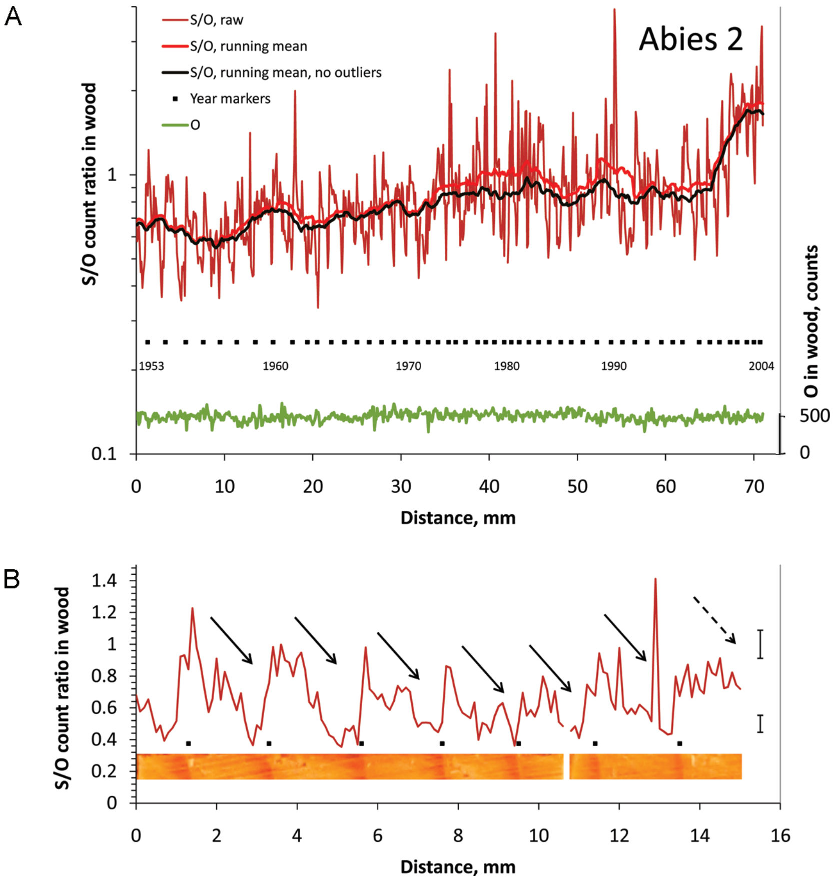

FIGURE 2. (a) Synchrotron line scan of sample *Abies* 2 at 100 μm resolution. Year markers indicate the top of the late wood of the year in question; the sample stopped growing after 2004. Two 40-point running means are calculated of which one excludes outlying points defined as where S/O count ratios were more than 50% higher than the initial running mean; points where O was <0.67 times its running mean were also excluded from this calculation. Rising S trends are shown, with an additional lift in the last six growth years. (b) An enlargement of years 1953−1960 together with an image of sample laths. Arrows illustrate falling trend of S/O during the growth season. Error bars are from counting statistics (see Supporting Information).

endogenous or exogenous in nature; however, this emphasizes the elemental variability at both inter- and intrasample level and the need for replicated analyses and possibly independently replicated extractions when developing robust elemental time series based upon tree rings. Excluding the outliers, the trend of values (Figure 2) shows a distinct rise from the 1960s onward, a period when S emissions were high (*2*). The last two 3-year samples show an additional upward trend. This upward trend in S is replicated in the annually sampled *Abies* tree cores collected in 2007 (AA8 and AA10), albeit at somewhat lower concentrations which likely reflects the importance of site effects: local soil geochemistry and physical/genetic differences in plant tolerance and elemental uptake. Similarly, enrichments in S in the outer growth (10−12 years) of *Picea abies* were found in the study of ref *19*.

Synchrotron Scans and Images. These analyses allowed the variation in S concentration to be examined at higher spatial resolutions. A restriction on quantitative analysis arises from the preferential absorption of secondary X-rays on one side of the wood cells, because of the directionality of the incident beam. Hence, one wall generates more counts than the opposite wall (Supporting Information, Figure S3). In order to remove this bias during the creation of time series, the spatial scale used (100 μm beam diameter and 100 μm step) aggregated several wood cells. A further desirable feature of quantitative microanalysis is to ratio a trace element to a major element to eliminate the effects of minor flaws in the sample surface. We thus present results for S as S/O ratios.

Two multidecadal synchrotron time series for *Abies* samples were created (Figure 2a; Supporting Information Figures S4 and S5). In each scan, there is much high-frequency variation on an annual scale, typically by a factor of at least two. Figure 2b illustrates the typical pattern of falling S/O ratios during each growth season (consistent with the bulk ICPMS data of Supporting Information Figure S2 showing lower S in late wood), interrupted by irregular behavior and outlying high values. About 7% of data are such outliers (defined as more than 50% above 40-point moving average of data). Exclusion of these points gives a smoother representation of longer-term trends (Figure 2a, Supporting Information Figure S5), and although the two samples differ in detail, both show elevated levels of S since 1970. The synchrotron results also confirm the presence of higher S concentrations in the last 6 years of growth (1993−1999 and 1998−2004 for the two different samples).

Oxidation states of S were calibrated using the linear relationship with the excitation energy corresponding to the absorption edge (*25*, *26*) and are shown in Figure 3. Clear peaks at energies of 2.474, 2.4764, and a double peak at 2.4815 and 2.4825 correspond to S oxidation states of 0 to +0.5, +2, and +5 and +6, respectively. Qualitatively the patterns are similar in each of the 300 μm diameter regions studied in the two tree species.

The distribution of elements was mapped at high magnification in a cell wall from the 1985 growth in sample *Abies* 2. The location of the studied area is shown in Figures 4a and 4b. The cell wall is displayed by a broadband of higher O counts up to 8 μm wide in Figures 4g and 4i. The pattern of S distribution is similar for each of the three mapped oxidation states (Figures 4c, 4e, 4j) and is also similar to P (Figure 4f) in defining a narrower zone up to 2 μm wide, which diminish

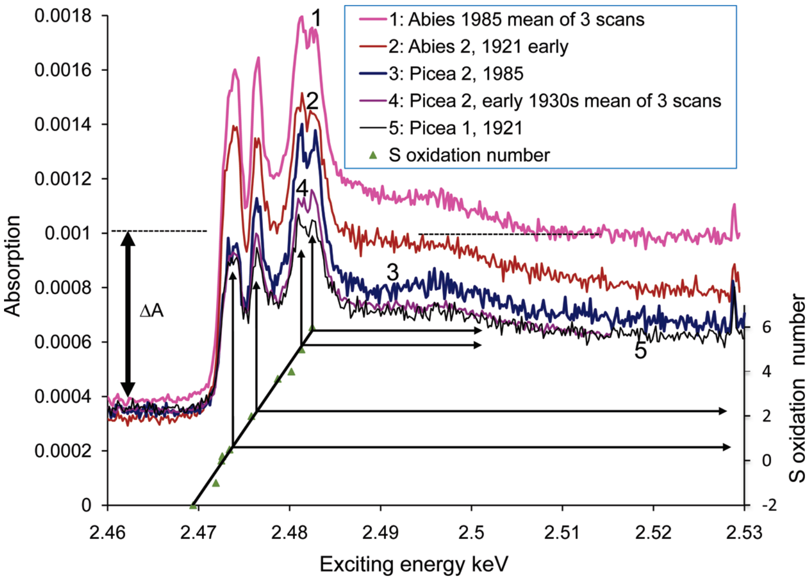

FIGURE 3. Summary of XANES scans (300 μm beam). The difference in absorption when excited at energies lower and higher than the absorption edge is proportional to the total abundance of S (shown as ΔA for the *Abies* 1985 line as an example). Hence the S concentrations can be seen to be in the expected order of young *Abies* > older *Abies* > young *Picea* > older *Picea*. The peaks in the absorption spectrum correspond to excitation at the absorption edge for specific oxidation states as shown by the calibration line for humic substances from ref *29* at the same experimental beamline. The distribution of oxidation states of S is similar for all samples.

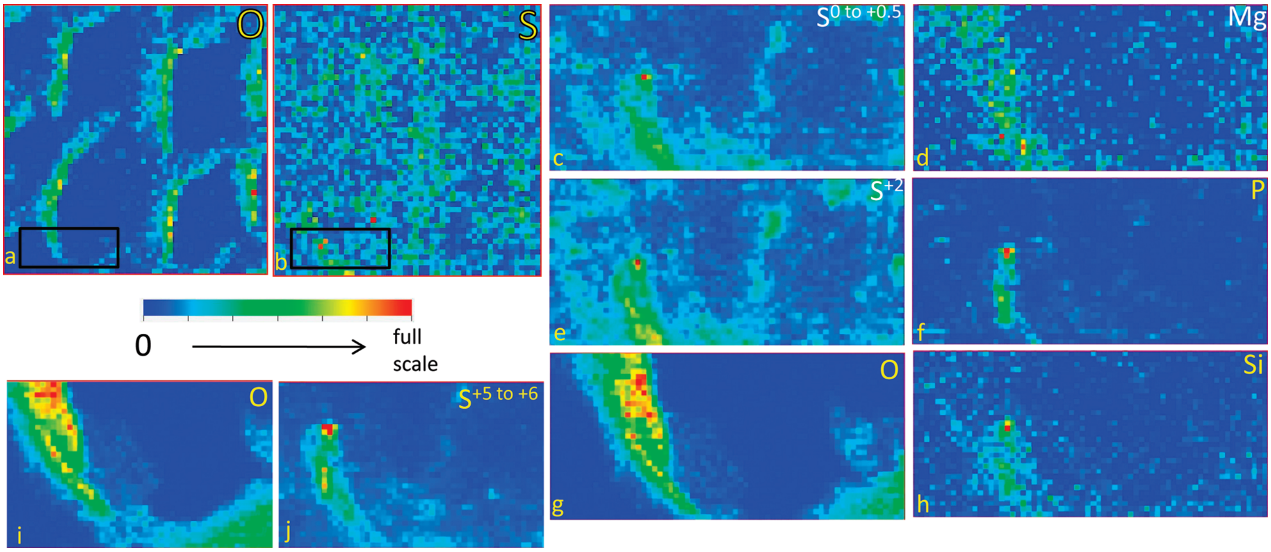

FIGURE 4. Maps of cell walls in the 1985 late wood of sample *Abies* 2. (a) O map and (b) S map of 100 by 100 μm area with 2 μm pixels imaging secondary X-rays. (c−j) Maps of elemental species as labeled using secondary X-ray images (0.5 μm pixels) from the boxed area in b; the area is slightly smaller and displaced in i and j. See Supporting Information for scale quantification.

toward the top of the image. In contrast Mg (Figure 4d) shows a much more diffuse distribution, corresponding to the whole cell wall region. The Si map (Figure 4h) appears to represent a combination of those patterns expressed by Mg and P.

S Fixation in Woody Tissues. Sulfur is supplied to the catchment overwhelmingly as sulfate (*4*), in part released from host carbonate rocks but predominantly from atmospheric sources that, in the late 20th century, were dominated by aerosols derived from anthropogenic pollutants. Only parts of conifers, notably pine needles, are supplied with S directly from the atmospheric source. In contrast, nutrients for growth of woody tissues are predominantly derived from soil−waters. S plays an important physiological role in regulating the redox state of plant tissues (*32*) where it is known to be present in a variety of forms (*19, 26*) including disulfides and thiols such as cysteine (oxidation state +0.2 to +0.5), sulfoxides such as methionine sulfoxide (+2), sulfonates (e.g., cysteinic acid, +5), and ester and inorganic sulfates (+6). Our results for both tree species demonstrate that S representing these oxidation states is present together within a narrow region in the center of the cell wall. A mathematical deconvolution yields results in 66 ± 2% for oxidation states 0 to +0.5, 15 ± 1% for +2 and 19 ± 1% for states +5 to +6 with no resolvable difference between the samples (further details in Supporting Information). The S-rich zones correspond to the primary cell wall (*33*) in which proteins (necessarily P- and S-bearing) define the architecture of the cell; later growth of cellulose, hemicellulose, and lignin thickens and strengthens the cell, but S incorporation is nonessential. We can therefore demonstrate that the bulk of the S forms structural entities within the wood, even during a period of enhanced S supply in the late 20th century. This implies that wood S should be more reliable as an indicator of environmental pollution than those elements that are not structurally fixed (*14, 15*).

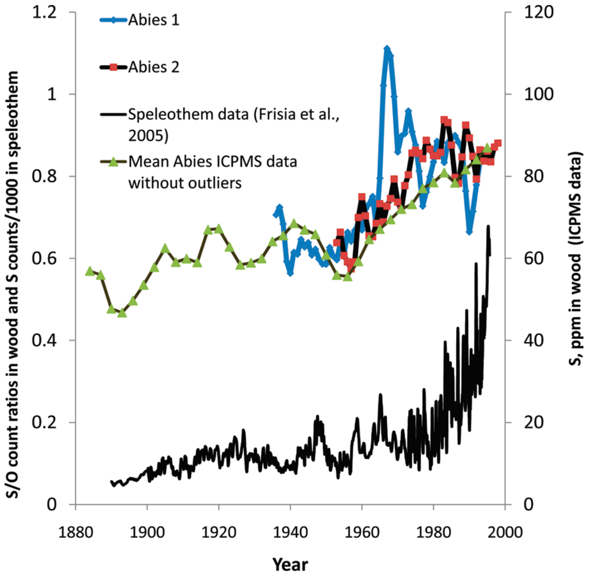

FIGURE 5. Summary of secular trends in S concentration reported in this paper compared with the S concentrations recorded by a speleothem from Grotta di Ernesto (*4*) in the same study area.

Nevertheless, both ICPMS and μ-XRF analyses have shown the outer six years of tree growth (the last six years of growth before it was felled) are enriched in S, although it has not been mapped in this study. This zone of enrichment in S may correspond to a difference between outer sapwood and inner heartwood because elemental differences are commonly found across this boundary in other studies (*22, 34*), but such a morphological distinction is unclear in the studied trees. An additional feature is the annual variability in S (Figure 2b), which is anticipated from the tree's physiology (*19*). Our pattern of S decrease throughout the growth season in *Abies alba* contrasts with a lower-resolution laser-ablation ICMPS study on *Picea abies* (*19*) where S tended to be lower in the middle of the growth season.

Interpretation of Pollution Records from Trees. On a longer time scale, the century-scale pattern of variability of wood S is broadly congruent between the different analyses presented here (Figure 5) but with variations between individual trees. The trees share with the nearby stalagmite record (Figure 5) the overall increasing trend in the 20th century but with a more immediate (earlier) response of the trees to the high emissions of the 1960s and 1970s. Both types of record display high S to 1995. S emissions in western European countries have been declining since 1980 (*2*), and the difference between the emissions data and archive response can be attributed to storage and recycling of S within the soil and associated biomass. The studies of refs *8* and *35* from southern Germany in particular (which agree with our own unpublished data at our study site) specifically demonstrates that the $\delta^{18}O$ composition of sulfate is reset from the atmospheric inputs. S in soil−waters and cave dripwaters has a $\delta^{18}O$ composition which arises from (1) assimilation in reduced form into organic molecules and (2) reoxidation in the presence of the local meteoric water which determines the $\delta^{18}O$ signature. The sulfate leaves the catchment primarily as seepage through to the underlying karstic system. The extent of similarity of tree and speleothem records (Figure 5) reflects the soil as a medium for storage and transformation of S.

An additional means of obtaining pollution records would be via the $\delta^{34}S$ composition because it is a powerful means of distinguishing pollution sources (*3, 5, 6, 20*) and there is only a limited degree of fractionation of sulfur isotopes during assimilation and subsequent reoxidation (*8*). Sulfur isotope analysis of wood could provide more reliable archives than concentration records alone, but we currently lack methods for quantitative extraction of the S in the small samples typically available for palaeostudies. Notwithstanding the pioneering study of Kawamura et al. (*20*), new methods of time-resolved or microscale extraction of S would be needed to develop this approach widely. As an alternative, we should examine the issue of replicability as a means of improving reliability of S analyses.

Replication and Its Statistical Requirements. We have demonstrated spatial and temporal variability of S in *Abies* on different scales. How do these bear on its capabilities as an archive? Promising characteristics are that S is fixed in the inner cell wall, and that it is present as a consistent mixture of different oxidation states in various growth layers; also there is a consistent increase in S in the period 1950−2000. However, there are issues of concern related to the identification of intertree differences in decadal patterns and the frequent presence of outlying high values in both ICPMS and μ-XRF data (Figures 1 and 2). The latter are not associated with any reduction in the O counts and so do appear to be analyses of tree cell wall: therefore, they may represent localized thickening of primary cell walls or living (and so comparatively sulfur-rich) axial cells associated with primary and traumatic resin canals. In contrast, the ICPMS outliers (Figure 1) are from 8 mg (16 mm^3) samples of three years growth and, since they are not reproducible in repeat dissolutions, could be explained by single inclusions of inorganic sulfate particles on the decimicron-scale that may not have been encountered in the synchrotron traverses. These problems have been identified only through replication, and in the same manner as single tree-ring series cannot be used to reconstruct past climate; so too is a single dendrochemical series unable to reconstruct adequately the environmental history of a region. We consider below what degree of replication might be required.

In contrast to many previous dendrochemical studies we have endeavored to replicate the elemental profiles through analysis of multiple trees. Using the data of Figure 1, corrected for the outliers as described earlier, it is possible to calculate the expressed population signal (EPS) for our data set (*36*). This statistic provides a measure of mean intersample correlation and has been used extensively in dendroclimatology. The EPS primarily explains the common signal preserved between increments and describes the degree to which trees respond in a similar manner. The expressed population signal does not take into account absolute differences between series, a factor which must be considered in dendrochemistry if tree-ring chemical composition is to be used as a proxy for environmental pollution; so to provide an estimate of intertree differences the mean standard deviation between increments is presented. Calculation of the EPS on the four sulfur series in Figure 1 yields a value of 0.64 ($n = 29$ increments per tree). Series with an EPS value >0.85 are normally regarded as providing an acceptable degree of common forcing. The value obtained from these data fall below this "threshold" value. If we assume additional series contain an equivalent degree of interseries coherence, then a total of 13 trees would be required for an EPS of >0.85. The mean interblock standard deviation for the 1920−2000 series was 13 ppm with a range from 5 to 29 ppm. The mean record produced displays an increasing trend from ca. 50 ppm to 100 ppm over this period, and therefore, while the common signal may be low, with four trees analyzed as 3-year blocks, the trend is nevertheless significant and the level of intertree variability would suggest that these trees provide useful information on sulfur variability through time.

As is the case for speleothem analysis (*37*), the most promising technique for the rapid generation of the large data series that would be required to meet the above replication requirements is laser-ablation ICPMS. Previous work has demonstrated its technical feasibility (*19*), but a key feature would be to perform the analysis using a sufficiently high mass resolution to eliminate interferences at the low concentrations likely to be encountered.

Acknowledgments

The study was funded by NERC (funding reference NE/C511805/1 to IJF and NE/B501504 to NJL), ESRF project ec146, and project AQUAPAST of the Trentino province. We thank members of the Forest Service of the Provincia Autonoma di Trento for their assistance in locating material, and Kim Jarvis and Kathryn Linge for assistance at the NERC ICP-MS facility at Kingston University. We are grateful to the three journal reviewers for their perceptive and helpful comments.

Supporting Information Available

(1) Additional details of the dendrochronology carried out prior to sample selection and analysis; (2) additional detailed line scan and representative lower magnification maps and other experimental details from synchrotron studies, (3) explanation of the deconvolution used to calculate proportions of S in different oxidation states from the XANES work. This information is available free of charge via the Internet at http://pubs.acs.org.

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ES8029297