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Interrogating trees for isotopic archives of atmospheric sulphur deposition and comparison to speleothem records

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ABSTRACT

Palaeorecords which depict changes in sulphur dynamics form an invaluable resource for recording atmospheric pollution. Tree rings constitute an archive that are ubiquitously available and can be absolutely dated, providing the potential to explore local- to regional-scale trends in sulphur availability. Rapid isotopic analysis by a novel "on-line" method using elemental analyser isotope ratio mass spectrometry (EA-IRMS) is developed, achieving sample precision of <0.4‰ using sample sizes of 40 mg wood powder. Tree cores from NE Italy show trends in pollution, evidenced through increasing concentrations of sulphur towards the youngest growth, and inverse trends in sulphur isotopes differentiating modern growth with light sulphur isotopes (+0.7‰) from pre-industrial growth (+7.5‰) influenced by bedrock composition. Comparison with speleothem records from the same location demonstrate replication, albeit offset in isotopic value due to groundwater storage. Using EA-IRMS, tree ring archives form a valuable resource for understanding local- to regional-scale sulphur pollution dynamics.

1. Introduction

Changes in atmospheric sulphur aerosols over time represent a principal driver of climatic variability and an essential forcing mechanism for climate modelling (e.g. Charlson et al., 1991; Shindell et al., 2003). The varying flux of sulphur to the atmosphere modulates climate on a range of timescales. Inventories of anthropogenic sulphur emissions to the atmosphere have identified clear trends of increasing regional pollution levels prior to the introduction of clean-up technologies fitted to power stations and industry. The subsequent onset of reductions in sulphur loading to the atmosphere depends upon location and emissions policy. Whereas in many European countries, sulphur emissions peaked in the 1970s (Smith et al., 2001, 2011; Vestreng et al., 2007), newly emerging industrial nations are struggling to curb emissions and in many cases have yet to reach peak emissions status (Schreifels et al., 2012; Su et al., 2011). However, understanding the spatial patterns of sulphur emissions and their possible impact upon environmental status is not straightforward. The extraction of sulphur from palaeoarchives is difficult, and fraught with poor analytical resolution. Many types of archive are also frequently distal from points of emission and they rarely respond rapidly to direct changes in atmospheric composition.

Trees take up nutrients from the environment to store them in annual growth rings, producing archives of environmental change which respond rapidly to external biogeochemical cycling (Watmough et al., 1999). However, until recently sulphur concentrations contained within tree rings have only been explored by few environmental scientists owing to difficulties associated with the extraction of a robust signal and uncertainties regarding post-depositional mobility (e.g. Barrelet et al., 2006; Fairchild et al., 2009; Novak et al., 2009; Pyatt, 1975; Tendel and Wolf, 1988). Stable isotopes of sulphur render the sulphur isotopic content of palaeoarchives one of the most important diagnostic signatures available, but their extraction from tree ring archives remains limited (e.g. Giesemann et al., 2005; Kawamura et al., 2006; Yang et al., 1996). Here, we present an analytical technique using on-line combustion of wood powders using elemental analyser to extract sulphur from woody tissues for isotope ratio analysis. We compare records of tree sulphur with established speleothem sulphur archives obtained from the same location and address the ability of trees to record regional pollution dynamics. The rapidity and precision of the technique, coupled with absolute dating of widely-available tree ring archives, should help achieve

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understanding of regional pollution dynamics through sensitive, high resolution records of atmospheric sulphur variability.

2. Sulphur cycling in trees

2.1. Pollutant impact upon forested environments

The role of air pollutants on tree growth, or as triggers to forest decline is recognized in many areas of high atmospheric pollutant load (e.g. Muzika et al., 2004; Rinne et al., 2013). However, it is difficult to isolate precise cause-and-effect relationships, due to synergistic relationships between pollutant types and background natural environmental stresses including soil moisture, trace metal contents, frost, stand structure, and pathogens (McLaughlin and Bräker, 1985). Effects of pollution can be either through direct uptake of gaseous atmospheric pollutants, or through acid deposition which alters soil pH and mobilises trace elements in concentrations toxic to plant species (Tendel and Wolf, 1988). The trace elemental content of tree rings and foliage is one such indicator of pollutant stress, which has provided variable measures of success in determining environmental pollution status and pollutant dispersion patterns (e.g. Baes and McLaughlin, 1984; Guyette and Cutter, 1994; Siegwolf et al., 2001).

2.2. Sulphur concentrations within tree rings

Where trees have been exposed to twentieth century increases in atmospheric SO_2 pollution and catchment acidification, transient increases in the sulphur concentration profiles of tree rings have been noted and concluded to reflect levels of fossil fuel consumption in the surrounding areas (Giesemann et al., 2005; Kawamura et al., 2006; Tendel and Wolf, 1988; Pyatt, 1975). Analysis undertaken by synchrotron radiation (X-ray fluorescence emission (Sulphur K lines) using 2.5 keV monochromatic radiation) in Fairchild et al. (2009) identifies some of the highest resolution trends in sulphur concentration using tree cores taken from NE Italy (the same cores which are re-analysed for sulphur isotopic composition as a part of this study). These are interpreted to represent limited pre-1960 sulphur inputs, commensurate with a dominant control from the pre-industrial atmosphere, and a post-1960 increase in tree ring sulphur concentration, attributed to the onset of industrialisation and enhanced loading of sulphur emissions to the atmosphere. Peaks in sulphur concentration are frequently seen to occur in the most recent growth of tree ring time-series (out of phase with the expected peak in emissions to the atmosphere on a national scale), and have previously been interpreted to reflect either: storage of sulphur in the soil and biomass during biogeochemical cycling, thereby de-coupling conditions of atmospheric pollution from those recorded in the trees (Fairchild et al., 2009); or as sulphur storage within the outer active zone of tree growth during formation of woody tissues (Barrelet et al., 2006; Fairchild et al., 2009; Ulrich et al., 2009). Synchrotron radiation has also highlighted the immobile nature of sulphur (beyond the outer active zone) as compounds fixed within the primary cell wall structures, minimizing the concern over element translocation between tree rings (Fairchild et al., 2009; Sandström et al., 2005). There is also understanding of variability in sulphur concentration across an annual cycle linked to biogeochemical cycling and seasonality of incorporation into early wood/late wood cell structures (Barrelet et al., 2006; Fairchild et al., 2009). However, multiple sources of sulphur to trees (gaseous uptake; soil/groundwater; geological substrate), and physiological effects of variable root depth accessing sulphur reserves of differing composition (Yang et al., 1996), and bioaccumulation of trace elements in the active region of tree growth (Barrelet et al., 2006; Ulrich et al., 2009), have lead to uncertainty in attributing concentration profiles to time-resolved records of twentieth century atmospheric pollutant status.

2.3. Sources of sulphur to trees

Plants which utilize soil as their growth medium receive sulphur inputs from two distinct sources: either as uptake of nutrients from soil and groundwater via root systems; or through the direct uptake of constituent gases from the atmosphere via foliage (Fig. 1) (Krouse, 1977; McLaughlin and Bräker, 1985; Xiao et al., 2012). Due to the large range in isotopic values between sulphur inputs to the atmosphere (European pollution −3 to +9‰ (Mayer, 1998); marine aerosol +21‰ (Rees et al., 1978); volcanic emissions ~0‰; continental and intertidal biogenic emissions 0 to −30‰ (Nielson, 1974)), tree ring archives of sulphur form a powerful diagnostic tool for understanding past atmospheric variability where processes of fractionation during uptake and biogeochemical cycling can be accounted for. The soil/groundwater system receives sulphur inputs from precipitation and weathering of bedrock. Subsequent biogeochemical cycling serves to control speciation, concentration and availability of sulphur compounds throughout the system. Biogeochemical cycling through forest environments involves processes of assimilation (the uptake and incorporation of sulphate into plants), mineralisation (the conversion of organic sulphur compounds back into sulphate), adsorption/desorption (binding/release of sulphur compounds by inorganic means) and oxidation (e.g. Krouse et al., 1991; Likens et al., 2002; Mayer et al., 1995; Mitchell et al., 1998, 2001). Sulphur isotope fractionation does not occur during adsorption/desorption (Van Stempvoort et al., 1990), and is restricted to just 1–2‰ during assimilation and mineralisation such that there is a slight preference for ^{32}S incorporation into the reaction products (Krouse et al., 1991; Mitchell et al., 2001; Thode et al., 1991). However, where reducing conditions persist within soils and groundwaters, dissimilatory sulphate reduction carries a distinctive isotopic fractionation, such that residual sulphate becomes enriched in ^{34}S (e.g. Chambers and Trudinger, 1979). Where the depth of the plant root system is invariant through time (Yang et al., 1996) uptake of sulphate and storage within woody tissues thereby forms a good representation of environmental conditions, unless redox conditions are strongly reducing. Two pathways to incorporation determine whether the assimilated sulphur is stored in reduced format (the reductive pathway), or as sulphate, (the sulphation pathway). In higher plants, the sulphation pathway is of minor significance (Leustek and Saito, 1999). The dominant presence of reduced sulphur has been demonstrated by Fairchild et al. (2009) within the woody tissues of conifers *Abies alba* and *Picea abies*, using X-ray absorption and near edge structure (XANES) analysis, and suggested to form the majority of the sulphur signal incorporated into tree ring archives.

Where the foliage of plants is directly exposed to the atmosphere, direct atmospheric uptake of SO_2 with little accompanying isotopic fractionation creates a sulphur signature similar to that of the atmosphere (Trust and Fry, 1992). After diffusion through the stomata, SO_2 dissolves and the majority is metabolised ultimately to produce organic sulphur compounds (Kaiser et al., 1993). Poor permeability of the leaf cuticle to atmospheric sulphate means dissolved sulphate is predominantly assimilated through the root system, whilst SO_2 is the dominant form of sulphur assimilated through foliage (Jędrysek and Kałużny, 2002). Uncertainty remains regarding the relative contribution of sulphur within foliage obtained from either direct atmospheric uptake, or groundwater sources, although foliage from rooted plants has been used successfully to directly reflect seasonality in air pollution (e.g. Xiao et al., 2012) and to reflect atmospheric uptake of SO_2 in pine needles (e.g. Gebauer et al., 1994). Where vegetation is

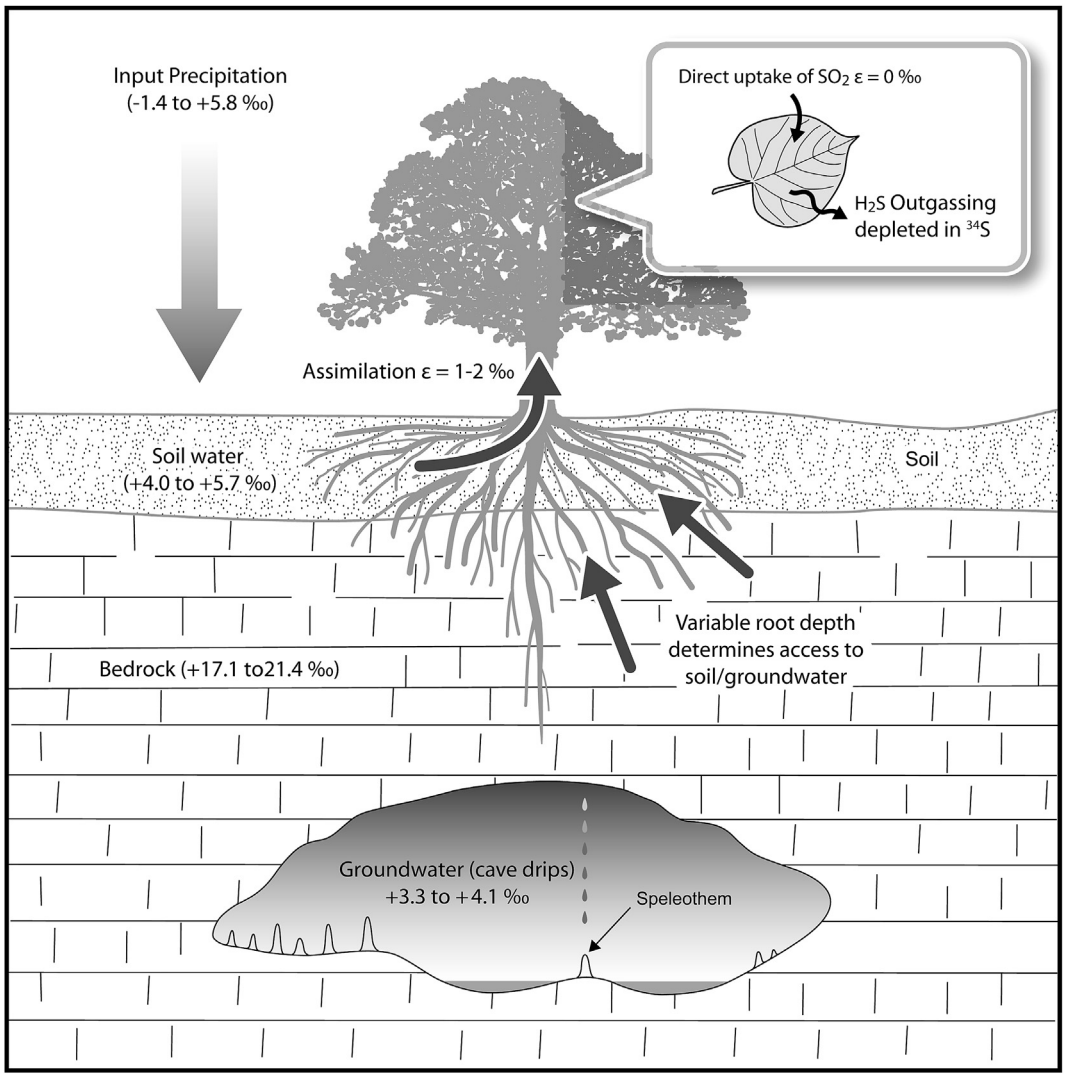

Fig. 1. Sources of sulphur to tree ring records of environmental change and associated isotopic fractionations. Isotopic values of precipitation, soil water, ground water and bedrocks are sourced from Wynn et al. (2013) monitoring undertaken between 2005 and 2007.

subjected to high concentrations of atmospheric SO_2 (Jędrysek and Kałużny, 2002) or other forms of biotic/abiotic environmental stress (Bloem et al., 2005) sulphur compounds may be emitted from foliage as hydrogen sulphide gas (H_2S) to play a key role in plant defence systems. The direct effect of H_2S release upon residual sulphur isotopic composition in the foliage is to cause ^{34}S enrichment within vegetation compared to input values (Trust and Fry, 1992).

2.4. Sulphur isotope records in tree rings

The isotopic composition of sulphur incorporated into annual ring structures will therefore represent a weighted balance between 1) the amount of sulphur assimilated from soil/groundwater stores, reflecting atmospheric deposition, biogeochemical cycling, bedrock weathering and fractionation during assimilation, 2) that incorporated through direct gaseous uptake through foliage and 3) the amount of H_2S emitted as a function of physiological stress, causing ^{34}S enrichment in residual leaf sulphur (Fig. 1). As direct gaseous uptake of SO_2 through foliage appears to be less important in determining the sulphur composition of tree rings than soil/groundwater stores when sulphur supply to the root system is high (Rennenberg, 1984), stable sulphur isotopes of tree rings have the potential to fingerprint sources of sulphur contained within soil and groundwater systems and identify changing pollution dynamics throughout the twentieth century. However, measurement of sulphur isotopes in woody tissues has been limited by low sulphur concentrations. Measurements have therefore been restricted to hyper-concentrating species or using large quantities of sample materials. Yang et al. (1996) studied *Tamarix aphylla*, achieving annual resolution of analysis from 1 g of wood powder. Through the use of reaction bombs to dissolve large volumes of material (minimum 5–8 g) resolution of one sample per 5 years was obtained by Giesemann et al. (2005) and Kawamura et al. (2006). Both latter studies obtained isotopic evidence supportive of tree rings providing suitable archives of atmospheric sulphur pollution. This highlights the potential for tree ring archives of sulphur isotopes to be used as a readily available, sensitive record of local atmospheric change if methods can be improved to enhance spatial resolution of analysis, optimise analytical precision, and increase sample throughput.

3. Methods

3.1. Site and sample description

Environmental background to the field site and details of samples collected in the vicinity of Ernesto Cave (NE Italian Alps, 1167 m a.s.l, 45° 58′ 37″ N, 11° 39′ 28″ E) are provided within Fairchild et al. (2009) and Lageard et al. (2007).

Grotta di Ernesto is a shallow cave site developed within the dolomitized Jurassic limestone in which extensive *in-situ* monitoring of cave atmosphere (Frisia et al., 2011), hydrology (Miorandi et al., 2010), and drip water and speleothem geochemistry (Borsato, 1997, 2007; Fairchild et al., 2000; Frisia et al., 2003, 2008; Hartland et al., 2012; Huang et al., 2001; Wynn et al., 2008, 2010, 2013), make this an ideal site to compare cave speleothem records of twentieth century environmental change with terrestrial records from tree ring dendrochemistry. Soils in the area are up to 1 m thick (calcareous brown forest soils; Rendzic Leptosol, pH 6.5–7.7) and overlie Jurassic dolomitized limestones with blocks of red marly limestones. They support a mixed conifer-deciduous forest in which the main species are *Fagus sylvatica*, *Picea abies* and *Abies alba*. Vegetation growth is well managed and dominated by deforestation events in the 19th and 20th centuries, thereby limiting longevity of available tree ring records. Sulphur pollution at the site has been documented in Wynn et al. (2010) and attributed to industrial activity within the nearby Valsugana valley, transported up to 4000 m altitude by strong vertical air mixing (Gabrielli et al., 2006). The sulphur biogeochemical cycle, traced from precipitation input to speleothem host, has been described within Wynn et al. (2013). Samples were collected within a 4 km radius of the cave site using 5 and 12 mm diameter increment borers and standard dendroecological procedures were used to produce absolutely dated records and mean ring-width chronologies. Thirty individual trees were used to build a master chronology for sample cores collected from *Abies alba* (see Fairchild et al. (2009), Supplementary information). Of the collected cores, two trees (Abies 1, cambial age 160; and Abies 2, cambial age 90) underwent preliminary investigation for sulphur concentration and intra-cellular speciation (Fairchild et al., 2009) as a background to developing a method for extracting sulphur isotopes from the same samples. In sampling the trees, no oils, polish wax or lubricant was used to reduce potential contamination from sulphur-containing compounds.

Wood powders were extracted by carefully drilling 5-year blocks of dated rings to yield a well-mixed, representative sample of approximately 40 mg for sulphur isotope analysis. On a sub-section of the conifer samples, a cold resin extraction was conducted using a 9:1 high purity (Aristar grade) acetone:water mixture for 48 h, followed by multiple washes with hot and cold deionised water to remove the potentially mobile resinous component and any surface bound mobile (soluble) sulphur.

3.2. Mass spectrometer analysis

All samples were analysed by continuous-flow-isotope-ratio mass spectrometry using an Isoprime 100 mass spectrometer linked to an Elementar Pyrocube analyser at the University of Lancaster, Lancaster Environment Centre. Combustion of 30–40 mg of wood powder in tin capsules at 1030 °C and 70 s oxygen pulse, yielded product N_2, CO_2 and SO_2 for analysis. CO_2 and SO_2 gases were trapped using a Thermal Programmed Desorption (TPD) system inherent to the Elementar pyrocube. The large retention capacity of the CO_2 TPD column, a programmed temperature increase and full use of the diluter, controlled the release of large volumes of CO_2 gas without overloading the source electronics. Capture and focus of product SO_2 within the TPD allowed determination of $^{34}S/^{32}S$ (expressed as $\delta^{34}S$) where whole-wood sulphur contents were approximately 0.01%. $\delta^{34}S$ values were corrected to V-CDT (Vienna-Canyon Diablo Troilite) using international standards NBS-127 and SO5 (assumed values of +21.1 and +0.5‰ respectively) (Halas and Szaran, 2001). Within-run replication of international standards and in-house $BaSO_4$ gave $\delta^{34}S$ precisions of <0.3‰ (1 Standard Deviation, analysed in batches of $n = 4$). Standard materials prepared as a bulk volume of homogenised wood powder yielded internal precisions of <0.5‰ (1 SD, analysed in batches of $n = 4$ in each analysis sequence), and no sample size dependence. Duplicate samples had a mean difference of 0.41‰, (range 1.1‰–0.1‰) ($n = 13$), with only four duplicate analyses exceeding 0.5‰ difference. Analytical differences between samples, which had received resin extraction, were within error of standard material precisions. To validate the direct EA method of wood powder analysis, a bulk quantity of wood powder was prepared and analysed by both on-line EA combustion and offline combustion using Eschka's reagent (e.g. Kester et al., 2001). 5 g aliquots of wood powder were mixed with Eschka's reagent in porcelain crucibles and combusted in a muffle furnace at 850 °C for two hours. The combusted product was rinsed with de-ionised water and filtered to remove solid residues. The eluent was acidified to pH 2 using HCl and boiled to remove any remaining dissolved inorganic carbon. Sulphate was precipitated as barium sulphate with the addition of excess barium chloride. Repeated centrifugation and washing with de-ionised water concentrated the product barium sulphate for analysis. Barium sulphate produced as an end product of the Eschka digestion was analysed by EA ($\delta^{34}S = 3.7$‰, SD = 1.5‰, $n = 3$) and found to be comparable to those analyses of the same material undertaken by direct EA combustion ($\delta^{34}S = 3.9$‰, SD = 0.4‰, $n = 5$). Elemental sulphur concentrations were calculated using the pyrocube Thermal Conductivity Detector (TCD) and calibrated to a known mass of sulphanilamide. EA blanks yielded no significant sulphur signal when run using empty tin capsules. The performance of direct analysis by Pyrocube EA is compared in Table 1 to other published methods concerning the extraction of sulphur concentrations and isotopic values from tree rings.

4. Results

Sulphur concentrations and isotope signatures obtained from the two tree cores (*Abies alba*) in the Italian Alps are displayed in Fig. 2 and compared to speleothem proxy records from the area.[1] Values are reported as 5-yearly increments between 1875 and 2004, with the heartwood-sapwood boundary located around 1985. The first 50 years of growth were omitted from analyses due to possible presence of juvenile effects in the sulphur isotope series as observed in other tree ring parameters (Loader et al., 2013; McCarroll and Loader, 2004; Young et al., 2012). Concentrations range between 88 and 196 ppm $\delta^{34}S$ signatures are reported between +0.7 and +7.5‰, significantly lower than those contained within the surrounding bedrock ($\delta^{34}S = +19.7$‰, range = 4.3‰, $n = 14$) and show an overall inverse trend between concentration and isotopic values.

5. Discussion

5.1. Sulphur isotopes in tree ring archives as an indictor of industrialisation

Prior to the onset of industrialisation, sulphur inputs to the atmosphere are restricted largely to marine aerosols, volcanic eruptions, and background contribution from vegetation and soil emissions. Soils and groundwaters receive additional contributions from bedrock weathering. Concentrations of sulphur would thus be low, and the sulphur isotopic composition of soils under aerobic conditions would closely reflect that of the atmosphere, with a minor component from constituent bedrock. The sulphur concentrations presented in Fig. 2 replicate those obtained from the same samples in Fairchild et al. (2009) and represent a limited pre-1960 sulphur input, commensurate with a dominant control from the pre-industrial atmosphere, and a post-1960 increase in tree ring sulphur concentration, attributed to the onset of industrialisation and enhanced loading of sulphur emissions to the atmosphere as SO_2 aerosols. Despite the record extending to 2004 however, there is little evidence of the well-documented decline in European sulphur emissions to the atmosphere, post-1970 (e.g. Smith et al., 2011; Vestreng et al., 2007) and catchment acidification reversal (e.g. Alewell, 2001; Gislason and Torssander, 2006; Sucker and von Wilpert, 2011) imprinting on the tree ring record. The broad antipathetic trend seen in Fig. 2 between sulphur isotopes and concentrations indicates the lightest sulphur isotopic compositions are commensurate with enhanced sulphur concentrations stored within the tree rings. This shows the post-1960 source of sulphur to be predominantly from industrial pollution (range of sulphur isotopic values in precipitation from industrialised countries in the Northern hemisphere −3 to +9‰; Mayer, 1998). Sulphur isotopes appear to stabilise at minimum values during the 1980s, suggesting a pollution maxima in sync with measured atmospheric loads from western European countries. A limited return to pre-industrial isotopic values would appear to signify continuing high levels of pollution being experienced at this locale, dominating the atmospheric sulphur load until late into the twentieth century.

Based on contemporary sulphur cycling at the field site monitored between 2005 and 2007 (discussed extensively in Wynn et al. 2013), isotope systematics would appear to support incorporation of sulphur into the tree ring record with only minimal delay. Sulphur isotopic values of input precipitation, soil and groundwaters are detailed in Fig. 1. Soil waters support $\delta^{34}S$ values of +4.0

[1] Data used in compiling Fig. 2 are stored at the British Atmospheric Data Centre (BADC). http://badc.nerc.ac.uk.

Table 1
Comparison of published analytical techniques used to extract sulphur isotopes and concentrations from tree rings.

Sample preparation technique	Isotope analytical technique	Mass wood powder required	Precision between sample preparations	Spatial resolution	Technique for determination of sulphur concentration	References
Hand drilling	Pyrocube elemental analyser (wood powder)	~40 mg	<0.5‰ ($n = 4$; 1 SD)	5 years, analysed from 5 mm diameter tree core	Simultaneous pyrocube elemental analysis	This study
Parr bomb combustion	Thermal decomposition of $BaSO_4$ to SO_2	8 g aliquots	Not quoted	5 years, extracted from tree cross section	Dionex ion chromatography	Kawamura et al., 2006
	Thermal decomposition of $BaSO_4$ to SO_2	~1 g	Not quoted	Annual, extracted from tree cross section	XRD analysis	Yang et al., 1996
	Carlo Erba NA 1500 elemental analyser ($BaSO_4$)	Not stated	Not quoted	5 years, extracted from tree cross section	Automatic S analyser (LECO SC132)	Giesemann et al., 2005
Eschka digestion	Pyrocube elemental analyser ($BaSO_4$)	~5 g	1.5‰ ($n = 3$; 1 SD)	Bulk homogenized powder	Gravimetric analysis	This study

to +5.7‰. Whilst the common precipitation input has a weighted average sulphur isotopic value of +1.2‰ (range −1.4 to +7.3‰), the enrichment in recipient soil waters can be attributed largely to processes of net assimilation, whereby lighter isotopes are preferred during uptake of sulphate into vegetation, enriching the remaining soil water sulphate in ^{34}S by 1–2‰ (e.g. Krouse et al., 1991; Mitchell et al., 2001; Thode et al., 1991). Despite the short time difference between monitored isotopic values in the soil waters and timing of tree core collection, the youngest growth recorded in the tree rings supports an isotopic value of approximately 2‰ and close to that expected from soil water assimilation and fractionation during uptake into vegetation. On the basis that sulphur isotopes provide evidence for a rapid response of tree ring records to atmospheric forcing and a high pollutant load in this locale which has prevailed since the 1980s, the peak of sulphur concentration in the most recent growth is likely the result of a biophysical process of trace element concentration enhancement beneath the bark (Barrelet et al., 2006), rather than a delayed peak in atmospheric pollution due to biogeochemical sulphur cycling.

5.2. Tree-Speleothem comparison

Replication of proxy records engenders strength in interpretation. This can be replication within the same type of host material (e.g. multiple tree cores, ice cores, speleothems), but real merit in understanding environmental processes is afforded through

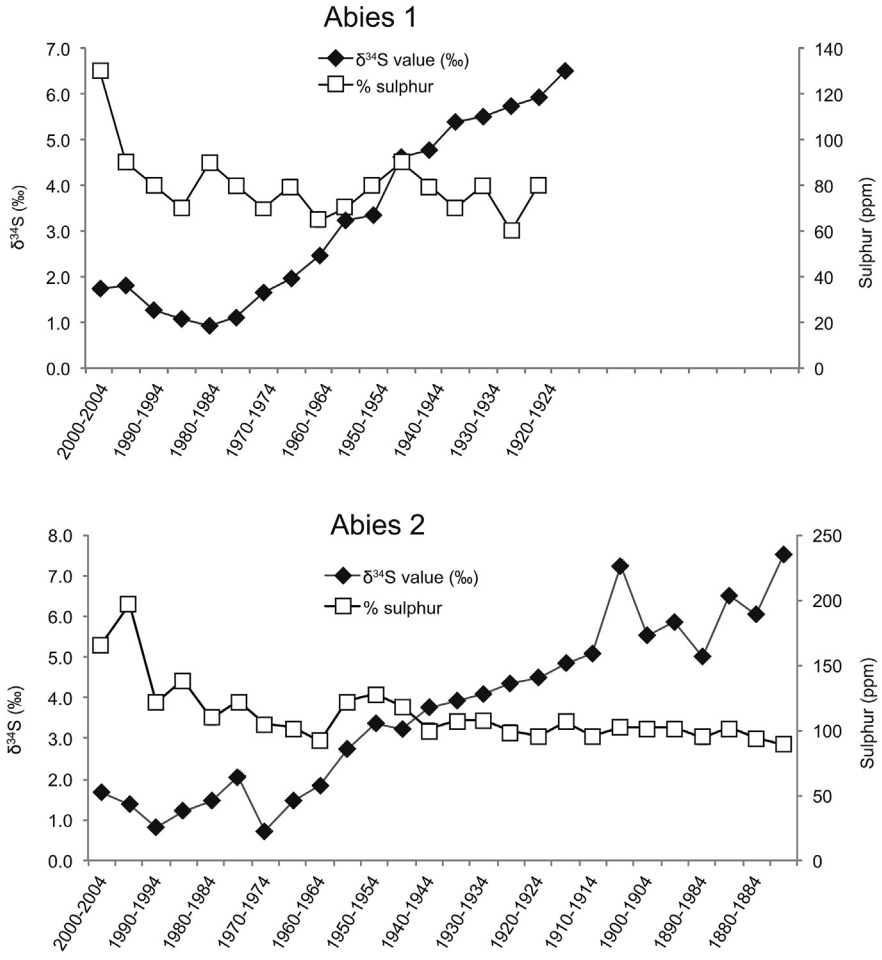

Fig. 2. Sulphur isotopes and concentrations in *Abies alba* from Ernesto Cave, NE Italy.

consideration of different archives, which develop at the same location. Records of sulphur concentration and isotopic change within both speleothems (ER78) and trees (Abies 2) are depicted in Fig. 3.

Sulphur isotopes within speleothem calcite, extracted from Grotta di Ernesto within the locale of tree sampling, were analysed by secondary ionization mass spectrometry and presented within Wynn et al. (2010). The controls on speleothem sulphur composition were found to be determined not only by atmospheric input, but also by biogeochemical cycling through vegetation, soils and groundwaters (Wynn et al., 2013). Despite a common atmospheric input and soil water status, each drip site delivering trace elements to the site of speleothem growth was found to have a unique sulphate composition, based on the extent of aquifer residence time, mixing with stored water and redox status encountered along the drip water flow pathway. The nature of the record contained within the associated speleothems was thereby determined by the subtleties of aquifer hydrology, as well as atmospheric forcing. Despite these additional controls on sulphate biogeochemical cycling, the sulphur record imprinted in the speleothem maintained a close resemblance to known trends in atmospheric sulphur loading, albeit lagged by approximately 15–20 years (Wynn et al., 2013).

As both speleothem and tree ring records derive their dominant water/nutrient source from common soil/ground water environs, similarities in the characteristics of both records would be expected. Both archives depict a low pre-1960 background sulphur concentration, enriched in ^{34}S due to the relatively greater input of sulphur from bedrock dissolution. The antipathetic trend between sulphur isotopes and concentrations is also common to both types of records. Neither record shows a dominant acidification reversal common to many catchments across Europe, due to biophysical processes of concentration enhancement in tree ring archives, and extensive delays due to storage effects in the case of speleothems.

However, an absolute difference in isotopic values from equivalent dates in each archive identifies subtleties in biogeochemical cycling. The tree ring record contains lighter sulphur isotope signatures than the speleothem archive. This offset is of variable magnitude, reaching up to 10‰ in some instances (Fig. 3). Whilst up to 2‰ of the difference between speleothem and tree ring record may be accounted for through processes of assimilation. Remaining differences are likely due to varying proportions of soil/groundwater feeding trees and speleothems respectively. Processes occurring at depth in the epikarst which are largely beyond the root zone and capable of inducing ^{34}S enrichment in speleothem forming drip waters include bedrock dissolution, sulphate reduction and mixing with groundwater of differing isotopic signature. Under contemporary conditions (monitoring between 2005 and 2007, Wynn et al., 2013), the influence of bedrock dissolution was limited to just 2.1% of total drip water sulphur load (accounting for just 0.5‰ enrichment in ^{34}S between soil and drip waters), and stored groundwater was deduced to be isotopically depleted in ^{34}S, not enriched. Processes of intense redox cycling were detected in the drip waters of speleothem ER78 which enrich the $\delta^{18}O_{SO_4}$ due to equilibrium fractionation between sulphate and water, but maintain $\delta^{34}S_{SO_4}$ due to the closed system and maintenance of isotope balance (Wynn et al., 2013). Thus, at this particular site, the process

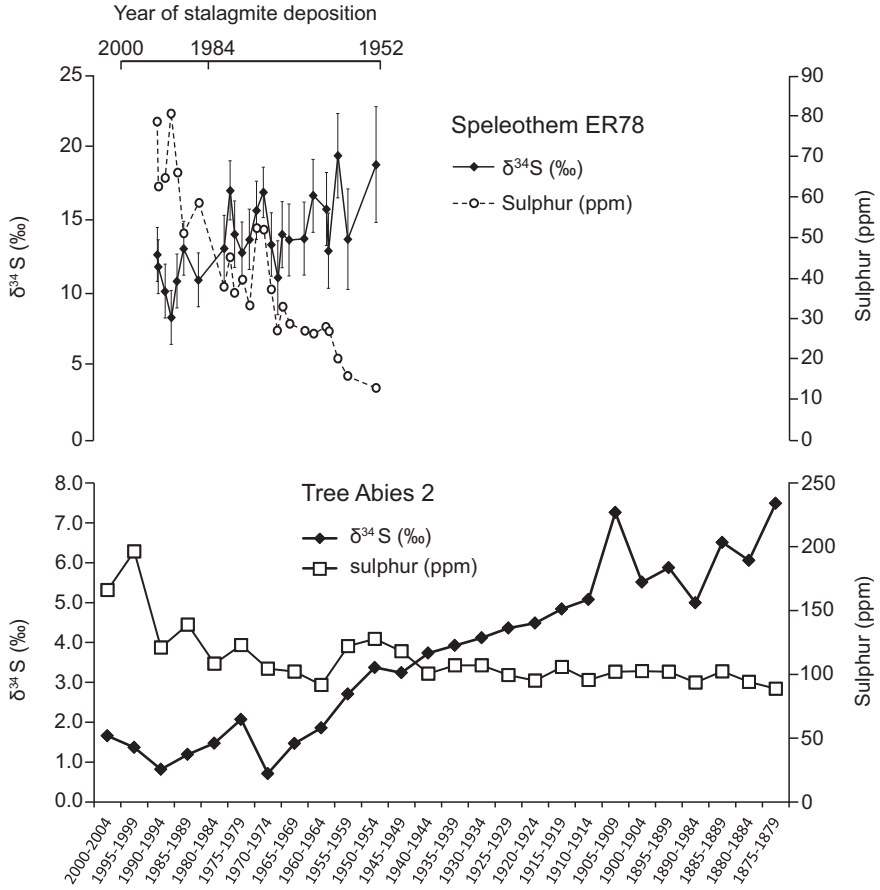

Fig. 3. Records of sulphur loading to both speleothem ER78 and tree ring archives (Abies 1) of environmental change collected from the same field site at Ernesto cave in NE Italy. Data for speleothem ER78 are originally published in Wynn et al. (2010) and analysed by secondary ionisation mass spectrometry; The age model for ER78 during the most recent 150 years was developed using trace element patterns, ^{14}C dating and laminae counting from the speleothem growth surface, known to be actively growing when collected in the yr 2000 (Smith et al., 2009).

of assimilation, acquisition of sulphate additional to that present in the soil waters, and the influence of redox cycling, cannot account for more than 2.5‰ of ^{34}S enrichment compared to the tree ring archives. The only remaining influence upon sulphur isotopic values of both speleothem and tree ring records, concerns the storage times associated with the epikarst/soil water respectively. Enhanced storage due to karst hydrology is known to impart extensive delays to atmospheric signals reaching the recipient speleothem (Wynn et al., 2013). For representation of atmospheric sulphur forcing within speleothems, this delay has been calculated at Ernesto cave to be 15–20 years (based on an offset between national atmospheric load and cave drip water chemical composition (Frisia et al., 2005). However, trees which are predominantly shallow rooted are likely to extract the majority of nutrients from the soil zone, where a faster rate of biogeochemical cycling and limited storage component diminishes any delay between atmospheric deposition and incorporation into the tree ring record. Part of the offset between speleothems and trees, must thereby be associated with the magnitude of storage delay imparted between atmosphere-speleothem and atmosphere-tree. On this basis, the tree records presented appear to be responding rapidly to the changing sulphur load, to the extent that the most recent tree ring $\delta^{34}S$ values from the year 2004 are close to those expected from soil water inputs. Placing an absolute value on the time-lag between atmospheric forcing and tree response however, is impossible without long-term records of soil water sulphate concentration. The speleothem is lagged by 15–20 years dependent upon additional storage and mixing within the epikarst. At the time of sampling in the year 2000, the speleothem was still responding to the peak of atmospheric sulphur loading experienced during the 1980's.

Variable amounts of bedrock dissolution, redox cycling and karst storage, as well as fractionation induced through vegetation assimilation, thereby appear responsible for the isotopic offset between proxy records and the relative enrichment in speleothem ^{34}S. The speleothems formed within the cave environment effectively contain a record which is duplicated within the trees growing in the same location. However, compared to speleothem archives which have the added complication of epikarst processes dominating the delivery of nutrients, shallow rooted trees perhaps offer a more responsive and better source defined archive of atmospheric sulphur loading. Soil, vegetation and groundwater characteristics are thereby fundamental in dictating tree and speleothem chemical composition in response to atmospheric change.

6. Conclusion

Sulphur isotopic analysis of wood powders by elemental analyser has relied on trap and purge technology to concentrate product SO_2 gases into sample peaks large enough for integration. This has enabled high resolution, high throughput analysis of tree ring archives depicting environmental change in sulphur dynamics, with a particular focus on atmospheric pollutant loading to the atmosphere and ensuing catchment acidification. Reported trends in sulphur concentration and isotopic composition within tree ring archives depend heavily upon background environmental conditions. Primarily these include precursor soil/bedrock sulphur content and isotopic signature, as well as the nature and extent of soil biogeochemical cycling, and tree physiology determining depth of root penetration and possible bio-accumulation effects within young woody tissues. A comparison of speleothem and tree ring sulphur series demonstrates similarity between the two archives. However, compared to tree ring archives which draw water and nutrients predominantly from the soil zone, speleothems have the added complication of deeper epikarst processes which induce an isotopic offset between the two archives at this locale due to storage. We suggest the high degree of analytical precision afforded by the methods described, as well as the potential for replication between trees and other proxies of environmental change, support the further exploration and interrogation of tree rings as precise archives of regional variability in environmental sulphur, forced not only through atmospheric pollutant loading but potentially also through volcanic activity. Such a precisely dated record can be used to locate the source of past volcanic eruptions, and provide an independent continental dataset of sulphur forcing for climate modelling. We believe replicated sulphur concentration and isotopic analysis obtained from tree rings at sub-annual resolution provides the best possibility of building a reliable record of sulphur forcing and its impact upon climate during the past millennium.

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