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Characterization of sulfur deposition over the period of industrialization in Japan using sulfur isotope ratio in Japanese cedar tree rings taken from stumps

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Abstract We characterized the sulfur deposition history over the period of industrialization in Japan based on the sulfur isotope ratio ($\delta^{34}S$) in tree rings of Japanese cedar (*Cryptomeria japonica* D. Don) stumps. We analyzed and compared $\delta^{34}S$ values in the rings from two types of disk samples from 170-year-old stumps that had been cut 5 years earlier (older forest stand) and from 40-year-old living trees (younger forest stand) in order to confirm the validity of using stump disks for $\delta^{34}S$ analysis. No differences in $\delta^{34}S$ values by age were found between the sample types, indicating that stump disks can be used for $\delta^{34}S$ analysis. The $\delta^{34}S$ profile in tree rings was significantly correlated with anthropogenic SO_2 emissions in Japan ($r = -0.76$, $p < 0.05$) and, thus, tree rings serve as a record of anthropogenic sulfur emissions. In addition, the values did not change largely from pre-industrialization to the 1940s (+4.2 to +6.1‰). The values before the 1940s are expected to reflect the background sulfur conditions in Japan and, thus, disks containing rings formed before the 1940s contain information about the natural environmental sulfur, which is useful for biogeochemical studies.

Keyword Air pollution · Dendrochemistry · Heartwood formation · Sulfur isotope · Tree ring

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Introduction

Tree growth in the form of rings incorporates information on the ambient climatic and chemical environments in a way that allows accurate dating of historical environmental events over wide geographical ranges, making tree rings a valuable resource in the fields of dendrochronology, dendroclimatology, and dendrochemistry (Watmough 1999; Grudd et al. 2002; Sano et al. 2013). Likewise, concentrations or isotopic compositions of elements in each ring can be used to reconstruct the ambient environmental conditions present during the growth that produced the tree rings (McCarroll and Loader 2004; Leavitt 2010; Savard 2010). For example, $\delta^{18}O$ patterns in rings can reveal past precipitation patterns (Treydte et al. 2006; Sano et al. 2013), and the concentration and isotope ratio of Pb can be related to air pollution records (Bellis et al. 2002). In the case of sulfur, tree rings have been utilized for the reconstruction of sulfur deposition history based sulfur concentration (Barrelet et al. 2008; Fairchild et al. 2009) and isotope ratio (Kawamura et al. 2006; Thomas et al. 2013; Wynn et al. 2014).

The history of sulfur deposition varies by region, and amounts and sources of sulfur emissions have been changing since the Industrial Revolution. In the 1970s, North America and Europe were the main sulfur emitters in the world, but sulfur emissions later shifted toward Asia, especially China (Smith et al. 2011; Stern 2005). In Japan, industrialization began in the late 19th century and high sulfur emissions occurred in the 1960s to 1970s, as in North America and Europe (Okita et al. 1997; Smith et al. 2011). Increased sulfur deposition caused acidification of terrestrial ecosystems (Prietzel et al. 2004; Johnson et al. 2013; Oulehle et al. 2013; Robison et al. 2013) and additionally changed the cycling and dynamics of sulfur (Mayer et al. 2001; Prietzel et al. 2004; Tejnecký et al. 2013) and the other elements (Prietzel et al. 2004; Åkerblom et al. 2013; Palmer et al. 2013). Thus, sulfur deposition history needs to be evaluated in order to accurately assess and predict the impact of human activities on ecosystems.

The sulfur isotope ratio (δ^{34}S) value is specific to the source of sulfur, such as sea salt sulfate (20.3‰). The δ^{34}S values in plants may accurately reflect the value of environmental sulfur (e.g., Krouse 1977; Xiao et al. 2012) because little fractionation occurs during uptake (Monaghan et al. 1999; Tcherkez and Tea 2013). Sulfur is primarily absorbed from the soil in the form of sulfate and assimilated mainly in the leaves; assimilation products are transported through phloem. However, less is known about sulfur metabolism in woody plants than in herbaceous plants. Although research of δ^{34}S in tree rings has been limited, historical changes in δ^{34}S values in tree rings have been used in several studies to estimate sources of atmospheric sulfur (Kawamura et al. 2006; Thomas et al. 2013; Wynn et al. 2014). However, until now, the oldest sequential profile of δ^{34}S in tree rings dates to the late 1880s (Wynn et al. 2014) and no profile completely before industrialization has been reported.

In order to obtain samples for analysis of sulfur concentrations and isotope ratios in tree rings over a long time period, it is desirable to cut large trees and take disks from the trunks. However, it is often difficult to obtain the desired samples from target forests because large trees are valuable resources. In these cases, some researchers have taken drill core samples, but these core samples do not provide a sufficient amount of material for δ^{34}S analysis. To analyze δ^{34}S in tree rings, large amounts of sample (e.g., 8 g, Kawamura et al. 2006) are typically needed because of low sulfur concentrations in tree rings, although a new method has allowed analysis using small amount of sample (less than 40 mg, Wynn et al. 2014). Disk samples collected from previously cut tree stumps is another option; however, it is necessary to confirm that contamination after cutting does not affect the δ^{34}S value.

The aims of this study are to confirm the validity of using disks from old stumps for sulfur analysis and to assess long-term sulfur deposition using samples including tree rings formed before the industrialization of Japan. We used samples collected from two forest stands of Japanese cedar (*Cryptomeria japonica* D. Don) from the same area in central Japan: disks obtained from 170-year-old stumps that had been cut 5 years earlier and from 40-year-old living trees. By comparing the results from the two types of disks, we also evaluated the effects of age and heartwood formation, which are possible factors affecting the δ^{34}S values in tree rings.

Materials and methods

Sampling

Sampling was conducted in a forested mountain area at the Inabu site (35°12′ N, 137°31′ E) located about 60 km northeast of Nagoya city in central Japan and 30 km from a plain region. The mean annual precipitation and temperature from 1981 to 2010 at Inabu (AMeDAS Inabu Station, Japan Meteorological Agency) were 1964 mm and 11.5 °C, respectively. The soil at Inabu is Dystric Cambisol and the bedrock is granite. Disk samples were taken from two forest stands of Japanese cedar, one 170 years old and another 40 years old, located 2.3 km apart. Sampling was conducted in 2012 in the older forest stand from stumps of trees that had been cut down in 2007; over 10 cm was removed from the stumps to remove the decayed upper surface, and a disk sample was collected from three trees. In the younger forest stand, trees were cut at about 0.5 m from the ground in 2013, and three disk samples were collected from the exposed trunks. From each forest stand, disk samples were obtained from trees located at the upper, middle, and lower areas of the slope. Although stump disk samples taken at the upper and lower positions of the slope had worm holes in some of the outer rings, the disk samples had freshness similar to the disks taken from living trees. The sapwood-heartwood boundary in both types of disks was identified visually. Detailed information about the samples is summarized in Table 1.

Since no observation data for atmospheric SO_2 concentration at Inabu are available, we used national annual mean atmospheric SO_2 concentration data for reference (Fig. 1). To evaluate $\delta^{34}S$ value in the current atmospheric depositions, throughfall samples were collected in the months of April and August 2010 by placing a polyethylene bottle (20 L) set with a funnel (30 cm diameter) in the younger forest stand.

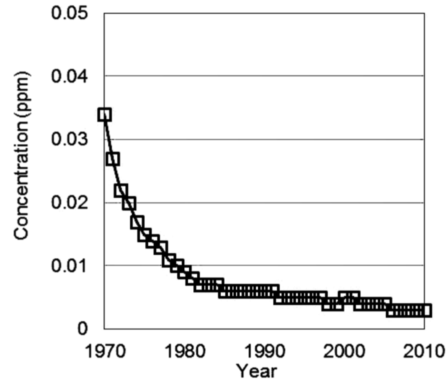

Fig. 1 Annual mean air SO_2 concentration based on nationwide data in Japan. Data from the Ministry of the Environment, Government of Japan 2012

Analysis

Disk samples from the 170-year-old forest stand were divided into 5-year increments from the bark toward the pith using a chisel. From the stump at the lower position of the slope, 32 samples of 5-year increment rings were taken, and at the innermost part, a ring sample covering 10 years including the pith (1838–1847) was taken to obtain a sample of adequate size. For the other stump disks taken from middle and upper positions of the slope, 15 samples were prepared from each tree (1933–2007). The outer 20 years of rings (1988–2007) of the stump taken at the upper position were unified into one sample, as the amount of sample required for analysis was not obtained from several worm holes. In the case of living trees, rings were divided into one 6-year increment sample and seven 5-year increment samples. A 6-year increment sample was taken at the outermost edge of the disk (2008–2013) in order to align the sample age between the disks from the two forest stands. The samples were then sonicated in deionized water for about 30 s, and the process was repeated three times. After drying for 48 h at 80 °C, the samples were ground using a power mill.

To measure sulfur concentration in rings, 0.1 g of ground sample was digested in 15 ml of 69 % HNO_3 and 0.5 ml of 30 % H_2O_2 using a graphite block acid digestion system (Ecopre, Actac). After filtration using 0.45 μm filter paper, sulfur concentration was determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES, IRIS ICAP, Nippon Jarrell Ash).

To measure $\delta^{34}S$, a requisite amount (determined by the sulfur concentration of each sample) of ground sample, ranging from 5 to 15 g, was placed in a 200 or 300 ml beaker and 69 % HNO_3 (UGR grade, Kanto Chemical) was added until the sample became saturated (about 50–80 ml). In a capped Erlenmeyer flask, the sample was heated at 120 °C and gradually raised to 200 °C. After the samples became almost uniformly brown liquid, the Erlenmeyer flask was decapped, 5 ml of 30 % H_2O_2 (UGR grade, Wako) and 69 % HNO_3 were added, and the mixture was heated at 180 to 200 °C. This procedure was repeated until the liquid became transparent and vigorous foaming due to the addition of H_2O_2 stopped. Finally, the sample was evaporated to dryness and dissolved in 30 % H_2O_2. After filtration through a 0.45 μm filter, 5 % $BaCl_2$ solution was added to the sample to precipitate $BaSO_4$.

Table 1 Samples collection and characteristics of trees in two forest stands.

Forest type	Older forest stand			Younger forest stand		
Sample type	Stump			Living tree		
Slope position	Upper	Middle	Lower	Upper	Middle	Lower
Tree age (years)	170			40		
Cut down date	2007			2013/11		
Collection date	2012/12			2013/11		
Boundary age of sap/heartwood (years)	25 (1983)	21–23 (1985–87)	24–27 (1981–84)	11 (2003)	15–16 (1998–99)	14–15 (1997–98)

For the throughfall samples, preparation of samples for $\delta^{34}S$ determination was conducted in a similar manner. Briefly, the sample was filtered through a 0.45 μm filter, followed by $BaSO_4$ precipitation by adding $BaCl_2$ solution. The $BaSO_4$ precipitate was collected on a 0.45 μm filter, and the filter was transferred to a crucible and combusted in an electric muffle furnace at 275 °C for 15 min with sufficient oxygen supply. Then, the sample was combusted at 750 °C for 30 min. The $BaSO_4$ powder residue in the crucible was used to measure $\delta^{34}S$.

The $\delta^{34}S$ values (reported relative to Vienna Canyon Diablo Troilite, VCDT) of $BaSO_4$ were measured using an EA-IRMS (Flash HT connected to Delta V Plus isotope ratio mass spectrometer via Conflo IV, Thermo Fisher Scientific) at the Research Institute for Humanity and Nature, Japan. Calibration and normalization were performed by analyzing three international reference materials: IAEA-S1, IAEA-S2, and IAEA-S3. The analytical precision (±SD) was ±0.4‰. To test the repeatability of the $\delta^{34}S$ analysis, including sample preparation, five replicate samples of acid digestion were assayed in two specimens, heartwood and sapwood in a disk from living tree.

Statistical analysis

We used the *t* test to determine the significance of differences in mean $\delta^{34}S$ values between samples from cut stumps and living tree in each age range among the analysis samples. The combined samples from the outer edge of the cut stump were not included in the statistical analysis. Thus, the *t* test was conducted on sample sets corresponding to the years 1973–1977, 1978–1982, and 1983–1987. The annual SO_2 emission values were combined to reflect the tree ring sample year spans; the mean of each set was taken and used for analysis. The relationship between the long-term $\delta^{34}S$ profile of the disk from the stump at lower position on the slope and SO_2 (Okita et al., 1997) was analyzed using the Pearson correlation (*r*). All statistical analyses were conducted using R ver. 2.15.1 (R Core Team 2012). Significance was set at $p < 0.05$ for all analyses.

Results

Sulfur concentration

Sulfur concentration in the stump disks showed a distinct decreasing trend from the outermost ring sample, and the values became constant starting around the boundary between sapwood and heartwood (Fig. 2a). In contrast, the sulfur concentrations in disks from living trees seemed to be constant without any marked differences between sapwood and heartwood (Fig. 2b). Consistent patterns between sulfur concentration and slope position were not observed for either forest stand type (Fig. 2). Figure 3 shows the profile of the mean sulfur concentration of three samples from each forest stand type from different positions on the slope (upper, middle, and lower). Clear differences between forest stand types were observed.

$\delta^{34}S$ values in tree rings and throughfall

Based on a lower standard deviation (±SD) obtained from five replicate analyses (±0.3‰) than the analytical precision (±0.4‰), the sample preparation method used in this study is judged to be adequate for $\delta^{34}S$ analysis.

The profiles of $\delta^{34}S$ in the disks from the stumps and living trees are shown in Fig. 4. The $\delta^{34}S$ values in disk samples from the stumps showed a drastic change from the range between the outermost samples (+2.5 to +2.8‰) and the innermost samples (+5.0 to +6.1‰) with a minimum value of −1.6 to +1.1‰ occurring around 35 to 39 years before harvest (Fig. 4a). The minimum values in stump samples were detected in the rings corresponding to the period of 1968 to 1972 for three sampling points on the slope. The $\delta^{34}S$ values in the disks from living trees showed a decreasing trend from the present to the past, except for the data at the innermost sample, which corresponds to ring formation in 1974 to 1977 (Fig. 4b). Consistent patterns between $\delta^{34}S$ profile and slope position were not observed for either forest stand type.

Figure 5 shows the profiles of the mean $\delta^{34}S$ values by forest stand type along with plots of the $\delta^{34}S$ values for throughfall. There were no significant differences between older forest stand (stump) and younger forest stand (living tree) samples for mean $\delta^{34}S$ values taken from rings of the same age ($p > 0.05$). The mean $\delta^{34}S$ value in the innermost samples from living trees was 1.2‰ higher than those from the same period (1973–1977) in stumps, although the differences were not significant. The $\delta^{34}S$ values in throughfall obtained in April and August 2010 were almost the same (+3.5‰) and slightly higher than values from living trees in the period from 2008 to 2013 (Fig. 5).

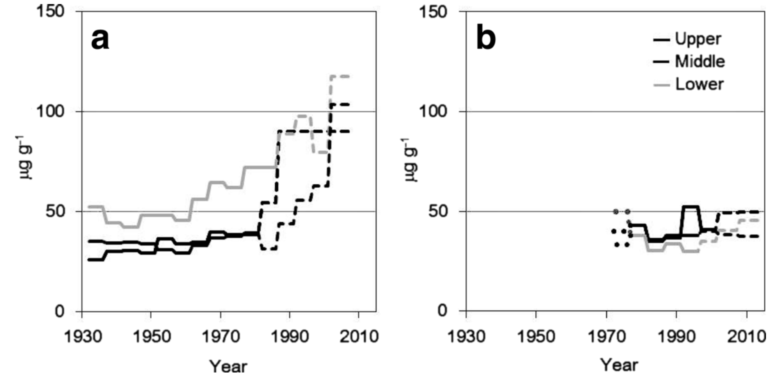

Fig. 2 Sulfur concentration profiles in the older forest stand (**a**) and the younger forest stand (**b**). *Line color* indicates the slope position, and *dotted*, *solid*, and *dashed lines* represent the zone including pith, heartwood, and sapwood zones of the ring, respectively. Samples from 1988 to 2007 for stumps at the upper slope position were combined

Long-term trends in sulfur concentration and δ^{34}S values over the period of industrialization

The profile of sulfur concentration over the period of industrialization for the disk from stump at the lower position on the slope is shown in Fig. 6a. Sulfur concentration was high in sapwood, declined with progression through the heartwood, and then increased again in the center part of tree ring. The long-term trend of δ^{34}S values is shown in Fig. 6b along with anthropogenic SO_2 emissions in Japan, as estimated by Okita et al. (1997). The change in δ^{34}S values was negatively correlated with estimated SO_2 emissions ($r = -0.76$, $p < 0.05$). The δ^{34}S values from 1838 to 1887 were highly stable (+5.4 to +6.1‰), and then, the values decreased gradually to +4.2‰ by 1947.

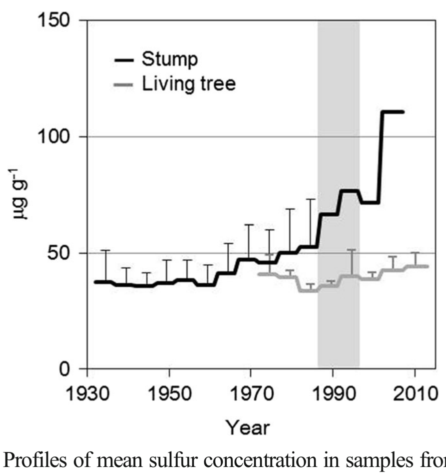

Fig. 3 Profiles of mean sulfur concentration in samples from older and younger forest stands ($n = 2$–3). *Error bars* are standard deviation of the mean for three samples. Data from the stumps (older forest stand) from the upper slope for the years 1988 to 2007 were not included in the calculation of the mean sulfur concentration. *Gray shading* indicates the period during which all samples from stumps (older forest stand) were from heartwood and all samples from living trees (younger forest stand) belonged to sapwood

Discussion

Availability of stumps for long-term analysis of environmental sulfur levels

One aim of our study was to evaluate the use of tree stumps for the analysis of long-term sulfur deposition history. Stumps are considered to be affected by various depositions onto the surface through environmental and/or by biological activities. Precipitation is a possible source of addition to the stumps. However, it has been reported that drying of fallen Japanese cedar proceeds even under natural conditions in forests (Iwata et al. 1981). Worm holes in stumps should allow for easier infiltration of water, but sulfur concentrations did not differ from those of samples without worm holes (Fig. 2a). These facts indicate that infiltration of precipitation water into stumps is limited. In addition, decomposition of coarse woody debris like stumps is known to be very slow (Sakai et al. 2013), and little visible decay was found on the cut surfaces of the stumps. Thus, sulfur contamination after stump cutting can be neglected. This is supported by the finding that there were no significant differences in δ^{34}S values between disks collected from living trees and those from stumps that left after cutting 5 years earlier (Fig. 5). Differences in sulfur concentration patterns between the disks from stumps (increased sapwood) and living tree (remained stable) would be affected by physiological process rather than contamination. Higher sulfur concentration in sapwood was reported in the disks of other species (Visser 1992; Fairchild et al. 2009). Our results indicate

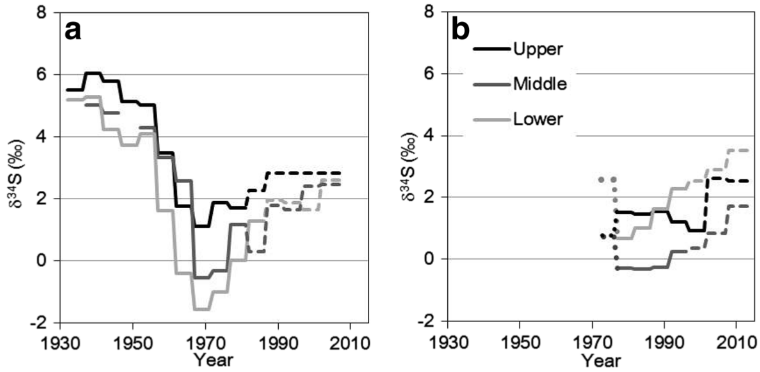

Fig. 4 The $\delta^{34}S$ profiles in disks from older (**a**) and younger (**b**) forest stands. *Line color* indicates the slope position, and *dotted*, *solid*, and *dashed lines* represent the zone including pith, heartwood, and sapwood zones of the ring, respectively. Samples from 1988 to 2007 for stumps at the upper slope position were combined

that Japanese cedar stumps can be utilized as sampling resources in Japan for trees that had been harvested within the past 5 years.

Sulfur concentrations in rings

Sulfur concentration was higher in sapwood than in heartwood in the disks taken from stumps (Fig. 2a) and, thus, cannot be a reliable indicator of sulfur deposition. The same trend of sulfur concentration was previously reported in the rings of oak (*Quercus robur* L., Visser 1992) and silver fir (*Abies alba* Miller, Fairchild et al. 2009). In addition, phosphate and nitrogen in tree rings have also been shown to have similar distribution patterns across many tree species (Meerts 2002). Sapwood is composed of both dead and living cells. On the other hand, heartwood is made up entirely of dead cells, and this difference in distribution may account for the sulfur concentration pattern shown in Fig. 2a. These results indicate that sulfur in rings is translocated during heartwood formation, rendering the methodology unsuitable for use as an archival record of environmental conditions. This theme is in greater detail in section “Effects of heartwood formation and age on $\delta^{34}S$” below. In contrast, sulfur concentrations in the rings of living trees showed no differences between sapwood and heartwood (Fig. 2b). Although the metabolism of S and heartwood formation in woody plants are not fully understood (Rennenberg et al. 2007; Imai 2012), these different profiles in sulfur concentration were also reported in Norway spruce (*Picea abies* L. Krast, Barrelet et al. 2008). The differences in sulfur concentration patterns in tree rings suggest that the distribution of sulfur may be affected by various factors including structural and physiological characteristics that depend on tree age.

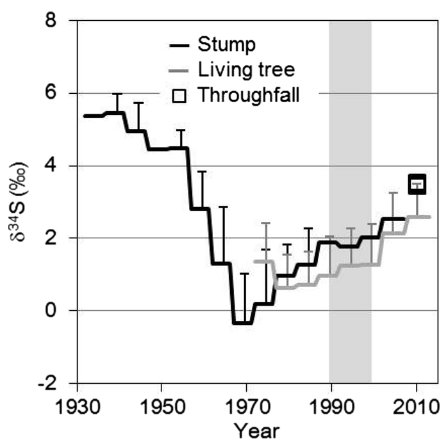

Fig. 5 Mean $\delta^{34}S$ values in older forest stand (stump) and younger forest stand (living tree) samples (n = 2–3) and $\delta^{34}S$ values in throughfall. *Error bars* are standard deviation of the mean for three samples. Data from the stumps (older forest stand) from the upper slope for the years 1988 to 2007 were not included in the calculation of the mean $\delta^{34}S$ value. *Gray shading* indicates the period during which all samples from stumps (older forest stand) were heartwood and all samples from living trees (younger forest stand) belonged to sapwood

Effects of heartwood formation and age on $\delta^{34}S$

Clarification of the factors affecting $\delta^{34}S$ in tree rings is important for evaluating the validity of using these samples as environmental archives. Here, we examined the effects of heartwood formation and tree age by comparing $\delta^{34}S$ values in disks from stumps with those in disks from living trees.

Sulfur translocation during heartwood formation was suggested based on sulfur concentration patterns in tree rings from stumps (Fig. 2a). The radial translocation of elements such as sulfur, nitrogen, phosphate from older rings to younger rings was suggested by previous research (e.g., Penninckx et al. 2001; Tomlinson et al. 2014). Tomlinson et al. (2014) used ^{15}N data to suggest that nitrogen in tree rings was translocated mainly to newer tree rings and partly to older tree rings, but not beyond the sapwood-heartwood boundary. Besides mobile sulfur, sulfur was suggested to be mainly fixed in the primary cell walls of tree rings (Fairchild et al. 2009). Therefore, sulfur in heartwood, which would be exclusively of the fixed form, should record the chronological changes in environmental sulfur, if sulfur shows the same movement in tree rings as nitrogen. In contrast, sulfur in sapwood would be composed of fixed and mobile forms. Therefore, δ^{34}S in sapwood should be interpreted carefully. In this study, the effect of heartwood formation on δ^{34}S in rings was not observed. The δ^{34}S values in the disks from both forest stands did not show differences across the sapwood-heartwood boundary (Fig. 4). In addition, the δ^{34}S values did not differ significantly between forest stands, despite that the sapwood-heartwood boundary in the disks occurred at different ages (Fig. 5). These results indicate that heartwood formation does not affect δ^{34}S values in the rings of Japanese cedar. Further research on the metabolism and translocation of sulfur is needed in order to interpret δ^{34}S values in tree rings.

The age effect (juvenile effect) has been reported for the other isotope ratios such as δ^{13}C (Jansen 1962; Freyer 1979), δ^{18}O (Treydte et al. 2006), δ^{2}H (Gray and Song 1984; Lipp et al. 1993), and δ^{15}N (Hietz et al. 2010). To avoid any possible effect, some researchers have omitted the first several decades from analysis (e.g., Wynn et al. 2014). In this study, we conducted δ^{34}S analysis for all rings of the living trees. The δ^{34}S values in the annual rings set between 1974 and 1977 corresponded to the first 4 years and had a different trend, being 1.2‰ higher than the values from the corresponding period in stumps (Fig. 5). Therefore, the first 4 years of annual rings should be omitted from δ^{34}S analysis. Nonetheless, this age effect is not enough to affect the evaluation of the long-term trend in δ^{34}S in the stump disk (Fig. 6b).

Evaluation of sulfur deposition history over the period of industrialization in Japan

Our study revealed the δ^{34}S profile in tree rings from the late 1830s, which predates the start of industrialization in Japan (Fig. 6b), which is longer than the profile of δ^{34}S in tree rings extending back to the late 1920s in Japan (Kawamura et al. 2006) and to the 1880s in Italy (Wynn et al. 2014). The profile of δ^{34}S in tree rings of the stump remained stable to the early 1940s, then abruptly decreased in the 1960s to 1970s, and gradually increased thereafter (Fig. 6b). The profile can be explained by history of anthropogenic sulfur deposition and its associated δ^{34}S value. Anthropogenic SO_2 emissions in Japan estimated by Okita et al. (1997) was significantly correlated with the δ^{34}S values in tree rings ($r = -0.76$, $p < 0.05$). The mean δ^{34}S value of SO_2 collected in industrial areas of Japan from 1971 to 1977 was −4.0‰ (Nakai et al. 1991). Anthropogenic sulfur emitted in Japan had low δ^{34}S attributable to the lower value for imported oil, ranging from −8.2 to +7.2‰ (average value of −3.3‰, Ohizumi et al. 1991) or from −6.8 to +9.1‰ (average value of −0.6‰, Maruyama et al. 2000). It should be noted that δ^{34}S values in recent throughfall were consistent with the values in the

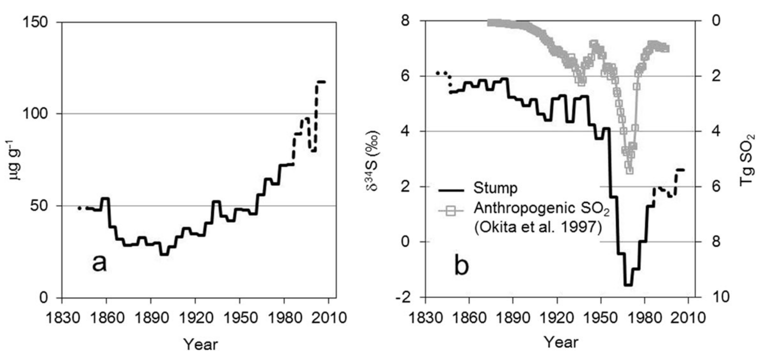

Fig. 6 Sulfur concentration (**a**) and δ^{34}S (**b**) profiles of the older forest stand (stump) sample over the past 170 years. The δ^{34}S value profile of the disk from the stump at the lower position on the slope (*left axis*) and anthropogenic SO_2 emissions in Japan (*right axis*) were estimated by Okita et al. (1997). The right axis was inverted to match the direction of change in the δ^{34}S values. *Dotted*, *solid*, and *dashed lines* represent samples taken from the zone including pith, heartwood, and sapwood zones of the disk, respectively

outermost rings (Fig. 5). Therefore, the $\delta^{34}S$ values in the rings of Japanese cedar trees reflect the characteristics of sulfur being deposited. A similar profile of $\delta^{34}S$ values was reported by Kawamura et al. (2006) using the rings of Japanese cedar covering the range of the 1920s to the 1990s taken from the industrial area in Kyusyu, Japan. Our study demonstrated that the trees grown in a rural area, 60 km away from the nearest urban area and the source of pollution, also produced a record of air pollution.

In Japan, the $\delta^{34}S$ values before the late 19th century should represent background $\delta^{34}S$ values, and values in rings set down before 1887 showed highly stable values in the range of +5.4 to +6.1‰. These values were lower than the much higher value reported for the late 1920s at Fukuoka, Japan (10.9‰, Kawamura et al. 2006), which may have been caused by the contribution of sea salt. Since our investigation area was located in a mountainous area, deposition of sea salt should be lower than that at Fukuoka, which faces the sea. In addition, the $\delta^{34}S$ values showed little variation from the 1830s to the 1940s. Kawamura et al. (2006) also reported that $\delta^{34}S$ values in tree rings were stable from the late 1920s to the late 1940s. These results indicate that human activities up to the 1940s had little effect on the $\delta^{34}S$ values in deposited sulfur; anthropogenic sulfur emissions were low (Okita et al. 1997). Therefore, the $\delta^{34}S$ values previous to the 1940s can be considered to be background levels, suitable for evaluating the effects of human activity on sulfur deposition in Japan. Thus, tree ring samples collected from this period can be used to determine the $\delta^{34}S$ value.

In this study, stumps remaining from the harvest of Japanese cedar contained tree rings formed in the 1830s and provided the materials for the analysis of natural $\delta^{34}S$ values. This access to samples from before industrialization in Japan affords useful information for biogeochemical study and for the assessment of the impact of human activities.

Conclusion

We demonstrated the validity using the disks from tree stumps for $\delta^{34}S$ analysis, based on the finding that differences in $\delta^{34}S$ values between disks from stumps and living trees were not apparent. Expanding the availability of dated organic material for $\delta^{34}S$ analysis to tree stumps allows the characterization of the sulfur deposition history over the period of industrialization for the first time. The obtained profile was consistent with sulfur deposition history and $\delta^{34}S$ in emitted anthropogenic sulfur. Thus, the disk from the stump of Japanese cedar serves as a good environmental archive for sulfur deposition. Data showing the stability of $\delta^{34}S$ values before the 1940s demonstrates the background sulfur level in Japan. Tree disks containing annual rings, particularly those pre-dating the 1940s, provide valuable information on natural environmental sulfur for biogeochemical studies or the assessment of the impact of human activities.

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