Effect of anthropogenic sulfur deposition on the sulfur dynamics in forest ecosystems

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Summary

Sulfur (S) is significant among the various elements present in forest ecosystems because it exists in several chemical forms and plays an important role in elemental cycle in forest ecosystems and physiological process in organisms. Since the Industrial Revolution, the combustion of fossil fuels such as oil and coal has added to atmospheric S in the form of anthropogenic gases, altering the natural S cycle. Despite the importance of the S cycle, studies of S dynamics in forest ecosystems have been limited. It is necessary to identify the effects of increased anthropogenic S deposition on the S cycle in forest ecosystems in order to make an accurate assessment and valid predictions of the impact of human activities.

Sulfur cycles with biotic and abiotic interactions in forest ecosystems. Atmospheric S is mainly deposited on soil in the form of sulfate and is gradually accumulated in soils. Sulfate in soils, a major form of inorganic S in aerobic forest soils, moves through water infiltration with repeating adsorption and desorption on soil materials. Finally, the sulfate ion is discharged from forest ecosystems. The effects of S deposition on forest soils depend on the sulfate adsorption capacity of the soils. Japanese forest soils have a higher sulfate

adsorption capacity (~47 mmol kg^{-1}) than those in soils in Europe and North America (largely less than 3 mmol kg^{-1}). As the majority of past investigations of S dynamics in forest ecosystems have been conducted in Europe and North America, it is now important to examine those in Japanese forest soils.

Atmospheric monitoring of S oxide has been conducted internationally in recent years. However, the available monitoring data is limited by regions and/or time periods. In Japan, for example, very little data is available from before the 1960s when monitoring began. The lack of S deposition data inhibits researchers from understanding its effects on ecosystems. In such areas where atmospheric S data is unavailable, tree rings could be used to evaluate S deposition. Although research on S in tree rings has been very limited, it is reported that chronological changes in S deposition are preserved in tree rings.

This study aims to reconstruct S deposition history and to evaluate the traces of past heavy anthropogenic S deposition in Japanese forests. Tree ring analysis and soil analysis have been conducted at two study sites in central Japan; Yokkaichi site (YOK) is considered to be a representative site where large amounts of S had deposited; Inabu site (INA) is considered to be less-affected by air pollution.

I investigated the S in the tree rings of Japanese cedar (*Cryptomeria japonica* D. Don). I demonstrated the validity using the disks from tree stumps for $\delta^{34}S$ analysis, based on the finding that the differences in $\delta^{34}S$ values between disks from stumps and living trees were not apparent. Using stump disks taken from the both sites, sulfur deposition history could be evaluated by $\delta^{34}S$ values in tree rings. The $\delta^{34}S$ values in rings of YOK in the late 1950s to 1970s (-7.0 to -1.3‰: mean) were lower than those of INA (-0.3 to +2.8‰) Since the $\delta^{34}S$ in anthropogenic S such as crude oil used in Japan is negative value (e.g. -0.6 to -4.0‰), larger amounts of anthropogenic S deposited at YOK in the 1950s to 1970s than at

INA. It is notable fact that the minimum value in tree rings of YOK was lower than the values in anthropogenic S any possible sources of S. The fact indicates that the $\delta^{34}S$ in tree rings are decreased by isotope effects through S cycle in forest ecosystems. In contrast, heartwood formation may not change the $\delta^{34}S$ in tree ring. I showed the long-term $\delta^{34}S$ profile in tree rings from the late 1830s, and the data showing the stability of $\delta^{34}S$ values before the 1940s demonstrates the background S level in Japan. In contrast, S concentration in tree rings was higher in sapwood than in heartwood in the disks taken from the stumps of both sites and, thus, cannot be a reliable indicator of S deposition. I attempt to restore quantitative S deposition by constructing a mixing model composed of isotope effects. The results of the model estimation are agreement with expected S deposition history in each area. The results suggested that the world's largest amount of S had deposited in the late 1960s to early 1970s at YOK (489 mmol m^{-2} yr^{-1}). In contrast, further small amounts of S deposition (less than 35 mmol m^{-2} yr^{-1}) were estimated at INA. I can propose the method of quantitative S deposition based on $\delta^{34}S$ in rings and the mixing model. In future, the estimation based on $\delta^{34}S$ values in tree rings will need to be verified by comparing S deposition estimated by the other methods and/or observed data.

I investigated the chemistry of soil, throughfall and stream water to assess the state of sulfate accumulation and to find the control factors of the accumulation. The distribution of adsorbed sulfate concentration did not differ between YOK (1.11 to 14.6 mmol kg^{-1}) and INA (0.40 to 11.0 mmol kg^{-1}), and the values were higher than published data for North America and Europe. Adsorbed sulfate concentration was significantly correlated with amounts of organic matter and Al oxide. These soil properties would primarily define the sulfate accumulation. The amounts of S deposition would be the secondary factor to define the adsorbed sulfate accumulation. The $\delta^{34}S$ value of adsorbed sulfate in soil is hardly indicator for anthropogenic S deposition, since the values did not differ between YOK (+2.9 to +6.9‰) and INA (+3.1 to +8.6‰). The mean sulfate ion concentration in stream water at YOK (40.7 ± 5.59 μmol L^{-1}) was significantly higher than that in throughfall at YOK (8.80 ± 0.83 μmol L^{-1}). The result may indicate that a delayed S outflow occur at YOK. A large amount of S deposition might saturate forest ecosystems at YOK with S.

The effects of S deposition on adsorbed sulfate concentration were unclear because of the primary effects of soil properties such as the organic matter and Al oxide on the adsorbed sulfate concentrations. Accordingly, I tried to find a trace of heavy S deposition in the equilibrium state of sulfate ions with soils. To achieve this, I determined the degree of sulfate saturation based on an adsorption isotherm equation. The degree of sulfate saturation in soils of YOK (1.00 ± 0.05) was higher than in soils of INA (0.74 ± 0.09). These results indicate that degree of sulfate saturation may reveal hidden effects of historical S deposition that cannot be identified by amount of adsorbed sulfate alone. The higher degree of saturation at YOK may be due to enhanced sulfate adsorption by soils resulting from substantial past S deposition.

In conclusion, I found that reconstruction of the S deposition history in forests ecosystem is possible based on the analysis of $\delta^{34}S$ values in tree rings of Japanese cedar. The traces of past heavy anthropogenic S deposition were found as $\delta^{34}S$ values in tree rings, the equilibrium state of sulfate ions with soils and S outflow from the ecosystem. These findings will strongly advance the elucidation of the S cycle and effect of human activity on the cycle. This study suggested that sulfate dynamics in forest soils have been changing even after the cease of serious air pollution in Japan. Furthermore, the overseas transportation of polluted air has not been neglected. Therefore, the successive investigation and monitoring about S deposition on forests should be important. The knowledge on the S dynamics and the evaluation method obtained in this study would be widely helpful for the understanding and prediction of the effects of S deposition on forest ecosystems in Asian developing countries.