Sulfur accumulation rates in volcanic soils of eastern Japan over the last millennium based on tephrochronology

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ABSTRACT

Soils have an important role as a reservoir of essential elements for forest ecosystems. Although previous chronosequence studies have determined accumulation rates of several elements in soils, they have not focused on sulfur (S), a secondary macronutrient. We investigated S accumulation rates in five volcanic soils, dated by the use of tephras from the following volcanoes: Mt. Komagatake (tephra Ko-a, 1929 CE), Mt. Tarumae (tephra Ta-a, 1739 CE), Mt. Fuji (tephra F-Ho, 1707 CE), Towada caldera (tephra To-a, 915 CE), and Mt. Haruna (tephra Hr-FP520, 520 CE). The soils were sampled from A horizons formed above the tephra layer, and total S and pedogenic minerals (Al_d, Fe_d, Al_o, and Fe_o) were analyzed to determine the relationships between their estimated pools and soil age. The fractionation of S by oxidation state was determined by S K-edge XANES analysis in constituents of soils from Mt. Komagatake and Mt. Haruna. Our results showed that the S accumulation rate was almost constant over the last millennium. To extend our analysis to longer soil formation times, we extrapolated the S accumulation–age relationship to 10 cal. ka and compared the resulting values with previously reported S data from horizons that likely developed during that time period in soils from Mt. Nantai dated by tephra Nt-S (14–15 cal. ka). The similarity of the extrapolated values to the Nantai soil values suggests that the S accumulation rate may have been constant since 10 cal. ka. In addition, the growth of the S pool with soil age was linearly proportional to the growth of pedogenic mineral pools. Sulfur isotope composition of soil total S depended not on soil age, but rather on the soil origin as indicated by location. The predominant oxidation state of the S fraction changed from reduced to oxidized with soil age during the Holocene. These results suggest that the constant S accumulation rate may reflect the variable influence of exogenous S sources as well as the association of S compounds with pedogenic minerals. Sulfur compounds may accumulate at a constant rate in Japanese volcanic soils as the result of biological transformation followed by retention of S in association with the pedogenic minerals.

1. Introduction

Soils accumulate many elements with long residence times, giving soils an important role in storing nutrients and maintaining environmental quality of forests and their downstream ecosystems. Sequestration of the macronutrient carbon (C) in soil is particularly important in ecosystem services that include offsetting carbon dioxide emissions to mitigate climate change, maintaining freshwater resources, and promoting biodiversity and field productivity (Halldorsson et al., 2015; Lal et al., 2015; Stout et al., 2016). Studies have shown that the accumulation rate of soil C depends on soil age. In unperturbed conditions, soils achieve steady-state C pools over periods ranging from centuries to a few millennia as plant inputs come into balance with microbially mediated metabolic losses as carbon dioxide (Amundson et al., 2015). For example, Sollins et al. (1983) and Lilienfein et al. (2003) reported that C accumulation rates in an andesitic chronosequence averaged 13.9 g C m^{-2} year^{-1} over the first 600 years, then decreased after 600 years at Mt. Shasta, USA. Accumulation rates of two

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Abbreviations: XANES, X-ray absorption near-edge structure

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other primary macronutrient elements, phosphorus (P) and nitrogen (N), have also been investigated (e.g., Eger et al., 2011; Egli et al., 2012; Lilienfein et al., 2003; Walker and Syers, 1976). In the absence of exogenous sources P tends to become a limiting factor for plant growth, because the soil P mass decreases as the soil formation period lengthens (Eger et al., 2011; Walker and Syers, 1976). The accumulation pattern of N is similar to that of C; that is, N mass decreases as soil age increases (e.g., Lilienfein et al., 2003). In contrast, accumulation rates of sulfur (S), an essential secondary macronutrient for microorganisms, plants, and animals (Prietzel et al., 2013), have rarely been reported.

In volcanic regions, widely distributed soils with distinctive chemical properties form in volcaniclastic deposits. Their parent materials, which consist of volcanic ejecta and other volcaniclastic materials, have significant colloidal fractions (Takahashi and Shoji, 2002). We previously showed that volcanic soils in Japan have larger S concentrations than non-volcanic soils derived from other parent materials in Japan, North America, and European countries when soils of the same or similar depths are compared (Tanikawa et al., 2003, 2009). The reason for the higher S concentrations, which sometimes reach > 2000 mg S kg^{-1} (e.g., Tanikawa et al., 2009), and the resulting higher S pools is inferred to be the presence of large amounts of short-range ordered or nanocrystalline (as defined by Churchman and Lowe, 2012) minerals such as aluminum (Al) and iron (Fe) oxides, allophane, and imogolite. These minerals can adsorb or occlude inorganic sulfate-S (Delfosse et al., 2005; Kimsey et al., 2011; Strahm and Harrison, 2007; Tanikawa et al., 2003, 2009, 2013). Moreover, mineral-associated organic S is also resistant to mineralization (Eriksen et al., 1998; Prietzel et al., 2007; Solomon et al., 2003; Tanikawa et al., 2014b; Zhao et al., 1996). Traditionally, soil organic S has been categorized as carbon-bonded S (C-bonded S) and ester sulfates (Freney, 1986). Most S present in plant litter is C-bonded S (Schroth et al., 2007), and plant roots also exude C-bonded S in the form of amino acids, aliphatic acids, and proteins (Badri et al., 2009). In the soil, the plant-derived C-bonded S is first converted into ester sulfates, followed by hydrolysis ester sulfates (McGill and Cole, 1981; Ghani et al., 1991, 1992; Norman et al., 2002; Solomon et al., 2003, 2011; Churka Blum et al., 2013). Tanikawa et al. (2014b) showed that the second step of organic S degradation, hydrolysis of ester sulfate, was inhibited in Japanese volcanic soils, because ester sulfate-S is stabilized by organo-mineral associations. Because the accumulation of soil organic matter is largely governed by the cycling of mineral-stabilized C on timescales of centuries to millennia (Torn et al., 1997), we hypothesized that the growth of S pools with time is synchronized with that of pedogenic mineral pools produced by weathering of volcanic ejecta in volcanic soils. In this study, we defined the pool of a substance in a soil as the accumulated amount of that substance per unit area of a field, and the accumulation rate of a substance in a soil as increments of the pool relative to soil age increments.

Volcanic soils are also distinctive in that they develop by upbuilding pedogenesis, in which significant surface additions occur contemporaneously with topdown pedogenesis (Almond and Tonkin, 1999). Volcanic soils developed by upbuilding pedogenesis are reported in countries of the circum-Pacific volcanic belt (e.g., Inoue et al., 2011a, 2011b; Lowe and Tonkin, 2010; Sase and Hosono, 1996; Sase et al., 1993, 1996; Yoshinaga, 1995a, 1995b, 1996a, 1998). These soils sometimes retain layers of datable tephra, which serve as excellent chronostratigraphic markers (Miyairi et al., 2004). Thus, we can constrain soil ages and the timing of soil formation from these tephra layers. We previously reported (Tanikawa et al., 2014a) episodic increases of S with reduced and intermediate oxidation states (C-bonded S) in volcanic soils in eastern Japan that formed by upbuilding pedogenesis above tephra layer Nt-S, dated at 14–15 cal. ka, from Mt. Nantai (Fig. 1). That study used the variation of S oxidation states, determined by K-edge X-ray absorption near-edge structure (XANES) spectroscopy, as an indicator of the degree of degradation of organic S in soils. We found that the predominant S species in Nantai soils is oxidized S (S^{+6}), typically in ester sulfates and inorganic sulfates (Tanikawa et al.,

2014a), which correspond to later products of the organic S degradation process (Tanikawa et al., 2014b) described above. Here, we hypothesize that the episodic increases in relatively reduced S are the result of superposition of younger soils, carrying more of the initial forms of organic S in the degradation process. Thus, knowledge of the accumulation rates of S and how its dominant species shift with soil age promises to give us insights into plant availability, soil residence time, and accumulation mechanisms of S in the soil. However, there are few published studies of S speciation in volcanic soils of known ages, and no study to our knowledge has documented S accumulation rates in volcanic soils.

The aims of the present study were to (1) determine S accumulation rates, (2) confirm whether S accumulation rates were synchronized with those of the pedogenic minerals, and (3) identify S oxidation states in soils by S K-edge XANES spectroscopy in young volcanic soils in eastern Japan. We collected five soils, each containing one of the following dated tephra layers: Ko-a (Mt. Komagatake, erupted 1929 CE; Machida, 1976), Ta-a (Mt. Tarumae, erupted 1739 CE; Machida and Arai, 2003), F-Ho (Mt. Fuji, erupted 1707 CE; Machida and Arai, 2003), To-a (Towada caldera, erupted 915 CE; Machida and Arai, 2003), and Hr-FP520 (Mt. Haruna, erupted 520 CE; Machida and Arai, 2003). These soils are younger than the Nantai soils studied by Tanikawa et al. (2014a), allowing us to more closely constrain the S accumulation rate in volcanic soils. Soils were sampled from the A horizon formed within the parent tephra deposit in each soil profile, because stabilization of soil organic matter has been observed in A horizons of volcanic soils (Egli et al., 2008).

2. Materials and methods

2.1. Soils

We acquired multiple soil samples from horizons overlying dated tephra layers near each of five Holocene volcanoes in eastern Japan (Table 1, Fig. 1). The sites were covered by forest vegetation. In these soil profiles, the tephra layers lay at depths between 2.5 and 20 cm (Fig. 2), and their deposition is an example of retardant upbuilding (as defined by Lowe and Tonkin, 2010), because the tephra buried the antecedent soil and isolated it from surface processes. At each soil sampling site, developmental upbuilding has been ongoing since the deposition of the dated tephra, during which thin accessions of tephra and other materials have been incorporated into the soil profile without interrupting soil development. Although the relative contribution of different sources to the thin accessions depends on the site, it can be roughly estimated that tropospheric dust transported from the Asian continent by the northwest winter monsoon accounts for about 10–20% of the thin accessions, and the remaining 80–90% are volcanic materials (Yoshinaga, 1996b). During developmental upbuilding, the sampled soils did not receive tephras from distant volcanoes, although some regional tephras were deposited as a result of cataclysmic volcanic eruptions. Soils nearest to the volcanoes were classified as Regosols, whereas soils farthest from the volcanoes were classified as Andosols in the WRB system of classification (FAO-UNESCO, 1990). In the relatively older soils associated with Towada caldera and Mt. Haruna, the A horizon was divisible into A1 and A2 horizons (Fig. 2). Sampled soil ages were calculated by subtracting the sampling date from the tephra date. As a result, we obtained the following ages: Komagatake soils, 61 years; Tarumae soils, 251 years; Fuji soils, 282 years; Towada soils, 1070 years; and Haruna soils, 1466–1482 years. Air-dried soil samples (grain size < 2 mm) were used for wet chemical analysis of pedogenic minerals. A portion of each sample was ground and passed through a 147-μm-mesh sieve for wet chemical analysis of total S, for determination of S isotope composition (δ^{34}S), and for S speciation by S K-edge XANES spectroscopy.