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Highly accumulated sulfur constituents and their mineralogical relationships in Andisols from central Japan

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ABSTRACT

To understand sulfur (S)-accumulating systems of Andisols in Japanese forests, this study examined the contributions of inorganic sulfate and organic S to S accumulation. The profiles showed high total S concentrations of 540 to 2240 mg S kg^{-1}. These high concentrations resulted in large pools of total S, ranging from 3370 to 8520 kg S ha^{-1} to 1 m depth. The sulfate concentration determined using a method combining 0.1 M $Na_4P_2O_7$ and 0.2 M acid ammonium oxalate extraction was higher than that determined by the conventional solvent $Ca(H_2PO_4)_2$. The additional sulfate, likely dominated by the precipitate form in sulfate-bearing minerals and the occluded form in short-range ordered minerals, ranged in concentration from 0 to 850 mg S kg^{-1} and accounted for 11% of the total S concentration. Values for Melanic Andisols (Melanudands) were larger than previously reported values for other soil orders. A significant correlation was found between the additional sulfate and soil mineral properties. These results suggest that the type of parent soil and its weathering degree are important in retaining additional sulfate. In the studied soils, approximately half of the accumulated S was inorganic forms of sulfate, with a ratio of organic S to inorganic sulfate of 55:45. The other half was organic S, 40% of which was the Al-associated form. Andisols have a high ability to consume acids by retaining sulfates and stabilizing organic S in the process of S dynamics.

1. Introduction

Soils receive sulfate inputs from the atmosphere via processes such as adsorption onto mineral surfaces, precipitation as Al-hydroxy sulfate minerals, and immobilization of organic sulfur (S), all of which can diminish or delay net acidification of soil. To understand S-accumulating systems, many researchers have evaluated the contents of such S constituents in soils. Conventional procedures for extracting sulfate from soils have commonly involved phosphate or bicarbonate solutions (e.g., Tabatabai, 1996). However, Violante et al. (1996) and Prietzel and Hirsch (1998, 2000) showed that an acid oxalate solution, NH_4F solution, and alkaline reagents such as NaOH and LiOH were more efficient than the conventional procedure in extracting inorganic sulfate fractions, particularly the precipitated form of sulfate-bearing minerals or the occluded form of secondary short-range ordered minerals. Therefore, conventional methods can underestimate sulfate levels. This was noted by Prietzel and Hirsch (2000), who found that ester sulfate was underestimated when calculated by subtracting inorganic S from analytically determined hydriodic acid (HI)-reducible S. To understand acid-consuming systems in forest soils, we must reevaluate inorganic sulfate, including precipitated and occluded forms in soil minerals, as well as organic S.

Recent studies of Andosols from Masaya Volcano (Nicaragua) have shown that these soils retain large amounts of both precipitated and occluded sulfates (Delmelle et al., 2003; Delfosse et al., 2005a). The Andisols of Masaya Volcano receive continuous inputs of SO_2 gas (200–700 mg m^{-2} day^{-1}; Delmelle et al., 2001). Delfosse et al. (2005a) suggested that this SO_2 promotes Al-hydroxy sulfate precipitation as a result of enhanced weathering caused by strong acid loading and the large sulfate concentrations in soil solutions.

Andisols with thick humus horizons, Melanic and Fulvic epipedons, occur widely in mountainous areas of Japan. These two epipedons have formed through intermittent contributions of ash deposition (Shoji et al., 1993). A central characteristic of Andisols is their development from volcanic ejecta and/or volcaniclastic materials that have colloidal fractions dominated by short-range ordered minerals and/or Al-humus complexes (Takahashi and Shoji, 2002). Short-range ordered aluminosilicates developed from volcanic ash deposits may serve as reactive Al pools in Andisols (Yagasaki et al., 2006). The potential pool of quantifiable Al^{3+} with a secondary short-range ordered mineral would create suitable conditions for the precipitation of Al-hydroxy sulfates and the occlusion of sulfates. Therefore, the existence of pedogenic minerals might lead to the formation of precipitated and occluded sulfates in Andisols without continuous SO_2 exposure.

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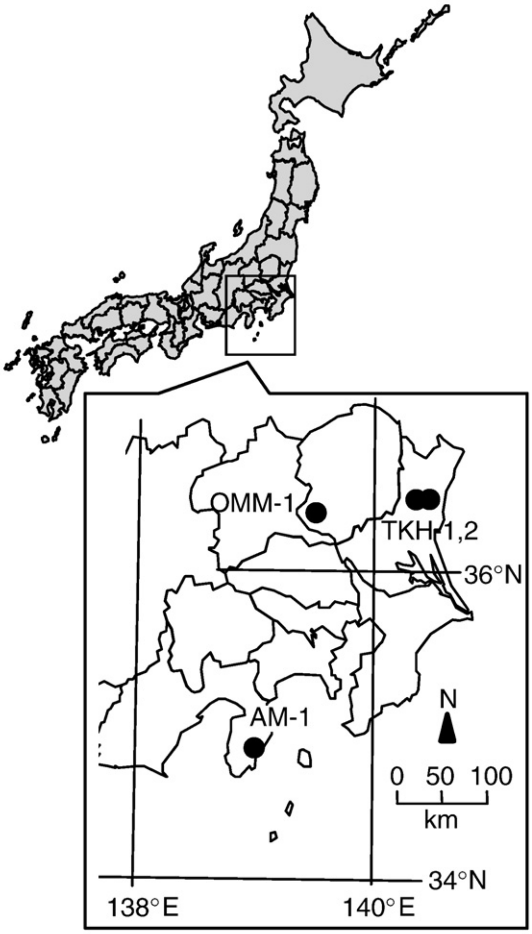

Fig. 1. Locations of the sampling sites in the Kanto region, Japan.

Andisols in Japan also show the highest accumulation of organic carbon among mineral soils (Nanzyo et al., 1993). The humic horizons of Andisols contain enormous quantities of Al/Fe-humus complexes. Yet we have little information on the abundance of the stabilized organic S fraction in Andisols. Because association with metals stabilizes organic substances, Andisols with thick humic horizons might contain stabilized organic S.

In this study, we sought to identify the major S-retention system and the soil properties that regulate S retention in Andisols without continuous SO_2 exposure (Melanudands and Fulvudands). These two soils have very similar properties; the fulvic surface horizon satisfies all the requirements for the melanic epipedon, except for the melanic color requirement and the melanic index (Shoji et al., 1993). We hypothesized that Andisols contain larger amounts of S constituents compared to other soil orders as a result of precipitated and occluded sulfate retention and metal-associated organic S retention. In addition, we expected that the reevaluated sulfate content would relate to the short-range ordered mineral content.

Among the newly proposed solvents for determining sulfates, oxalate and NH_4F do not have the risk of converting organic S into inorganic S (Prietzel and Hirsch, 2000; Delfosse et al., 2005a). Delfosse et al. (2005a) showed that compared to NH_4F, oxalate extracted more inorganic sulfates from Andosols. In Andosols, the oxalate solvent can apparently access a wider range of sulfates. Therefore, we used oxalate solution to extract the sum of sulfates and organic S associated with free oxides and minerals in Andisols.

To dissolve Al/Fe-humus complex portions of active Al and Fe, a 0.1 M $Na_4P_2O_7$ solution is preferred (McKeague, 1967; Wada, 1989). However, only a few studies have used this solvent to determine organically bound S. For example, Bettany et al. (1979, 1980) used pyrophosphate solution to separate organic S fractions, while Karltun and Gustafsson (1993) obtained organic S as the amount of S in pyrophosphate extract minus phosphate-extractable S. In this study, we determined organic S in Al/Fe-humus complexes using $Na_4P_2O_7$ solvent.

2. Materials and methods

2.1. Study area and soil sampling

We examined four soil profiles (from trenches 1 m wide and 2 m deep) of Andisols in forested areas of the Kanto district, Japan (Fig. 1). Table 1 presents information on the study sites, while Table 2 lists the soil properties. Imaya et al. (2005, 2007) provided further details on the basic soil properties. The annual S deposition in the Kanto district is 1.5 g S m^{-2} $year^{-1}$ (calculated after Fujita, 1996), which is equivalent to deposition in the eastern United States (Mitchell and Lindberg, 1992) and in European countries (Johnson and Mitchell, 1998). Melanudands with blackish and thick A horizons were predominantly derived from volcanic ash. Fulvudands with dark brown A horizons were derived from volcanic ash and influenced by underlying igneous rocks in deeper horizons (andesite at site AM-1 and quartz-porphyry at site OMM-1). Shoji et al. (1988) reported that Melanudands have high organic carbon concentrations that gradually decrease with increasing depth as compared to the lower organic carbon concentration and rapid decrease with depth in Fulvudands. Our soils showed the same tendencies (Table 2). We collected soil samples from each horizon of a representative profile at each study site. Field-moist samples passed through a 2-mm sieve were used to analyze soil pH (H_2O), phosphate-extractable, and water-soluble sulfate. Air-dried soil samples (<2 mm) were used to analyze other S fractions and soil properties described later. A portion of the air-dried soil samples was ground and passed through a 149-μm mesh sieve for later analysis of total S and HI-reducible S concentrations.

2.2. Determination of soil S fractions

Table 3 lists the methods used to assess the soil S fractions. Following the method of Tabatabai (1996), ground soil was oxidized to determine total S using HNO_3–$HClO_4$. The total S concentration in the digested materials was determined by inductively coupled plasma–atomic emission spectrometry (ICP-AES; Maxim; Fisons Inst., Switzerland). Hydriodic acid-reducible S, composed of organic and inorganic sulfates, was reduced directly with HI (Freney, 1961), as described by Tabatabai (1996). After reducing the sample to sulfide, the S concentration was colorimetrically determined using methylene blue (Johnson and Nishita, 1952).

Table 1
Altitude, climate, vegetation, and soil types and soil textures of the soil profiles studied.

Soil code	Soil taxonomy (Soil Survey Staff, 1998)	Texture	Altitude (m)	Mean annual temperature (°C)	Annual precipitation (mm)	Dominant tree species
TKH-1	Pachic Melanudand	Heavy clay	660	10.0	1760	*Cryptomeria japonica*
TKH-2	Acrudoxic Melanudand	Heavy clay	670	10.0	1760	*C. japonica*
AM-1	Eutric Pachic Fulvudand	Light clay	600	13.4	2910	*Zelkova serrata*
OMM-1	Acrudoxic Fulvudand	Light clay	1300	7.5	1890	*Quercus mongolica*