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## Accumulation of sulfur compounds in Japanese volcanic soils

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Volcanic soils are found in Asian countries, particularly within the circum-Pacific volcanic belt. Their unique chemical properties are expected to contribute to sulfur (S) retention. Although S is an essential element for plants and microorganisms, there is little information about S dynamics in forest ecosystems of Asian countries. The aim of this study is to characterize S accumulating systems in Japanese volcanic soil from the following four aspects: i) S pool sizes; ii) spatial S distribution in a catchment; iii) organic S transformation processes; iv) upbuilding/topdown pedogenesis.

To achieve the purposes, we investigated i) S pools of forested volcanic soils from 0-2m depth in the Kanto district; ii) the spatial variations of S concentration in a small drainage basin covered by volcanic soil by a geostatistical analysis; iii) organic S transformation rates in incubation experiments; iv) the vertical distribution of S species using K-edge X-ray absorption near-edge structure (XANES) spectroscopy of S species in Melanudands developed above tephra Nt-S, dated at 14-15 cal. ka by upbuilding pedogenesis.

The above four studies showed unique S accumulating systems of volcanic soils in Japanese forests as follows: i) volcanic soils accumulate larger amounts of S than other soil orders previously studied in North America and Europe. Forty percent of organic S was composed of Al-associated forms. Significant correlation between S species and pedogenic minerals suggests that large amounts pedogenic minerals lead to the large S pools. ii) Geostatistical analysis revealed the strong similarity of the spatial patterns of total S concentration and those of the pedogenic minerals throughout the catchment area. More S accumulated in the residual soils (ash soils) on the upper slopes of the catchment than in the colluvial soils of the lower slopes. The most important factor that influenced the distribution of soil S in the catchment was the degree to which volcanic ash was retained in the soils, as reflected by the abundance of the pedogenic minerals derived from volcanic ash deposits. iii) During incubation, the concentration of ester sulfate-S increased in the soils with high concentrations of the pedogenic minerals, whereas the concentration of Carbon (C)-bonded S decreased in all soils. The decrease rate of ester sulfate-S concentrations was negatively correlated with the pedogenic mineral contents. Therefore, when C-bonded S was transformed into ester sulfate-S, complete mineralization to inorganic sulfate might be inhibited, because ester sulfate-S was probably stabilized due to organo-mineral association. iv) The striping distribution patterns of various S fractions were shown in the soil with upbuilding pedogenesis. The predominant S species was highly oxidized S in ester sulfates and inorganic sulfates (+6 oxidation state), nevertheless, proportions of S with reduced and intermediate oxidation states increased episodically. A close correlation was found between ester sulfate-S concentrations and Al-associated organic S concentrations; indeed, the concentrations themselves were roughly similar.

These results suggest that accumulation/transformation of S compounds in Japanese forests is controlled by the pedogenic minerals derived from volcanic ash. Episodic deposits of volcanic ash and eolian dust might trap detritus and humus beneath them during the buildup of the soil surface. The organic S compounds in this material might be decayed as topdown pedogenic processes in the soils. Therefore, the soils with upbuilding pedogenesis have high heterogeneity of S compounds. Volcanic soils might have high ability to retain ester sulfates as Al-associated organic S during transformation processes.

Keywords: Al and Fe hydrous oxides and short-range ordered minerals, forest soils, geostatistical analysis, K-edge X-ray absorption near-edge structure (XANES) spectros, pedogenic minerals, transformation of organic S