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Characterization of allophanic Andisols by solid-state ^{13}C, ^{27}Al, and ^{29}Si NMR and by C stable isotopic ratio, δ^{13}C

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Abstract

Three representative allophanic Andisols in Japan were evaluated by solid-state ^{13}C, ^{27}Al, and ^{29}Si nuclear magnetic resonance (NMR) and stable isotopic ratio of carbon (δ^{13}C). The solid-state cross polarization magic angle spinning (CPMAS) ^{13}C NMR spectra were effective in characterizing crude soil C without any chemical treatment when soil C content was >100 g C kg^{-1}. Aliphatic, *O*-alkyl, and carbonyl C were relatively abundant in the uppermost horizons, whereas aromatic C was concentrated in the subsurface horizons, showing its persistence and tolerance to degradation in subsurface horizons. Contribution ratios of C4-plant-derived C (mainly from *Miscanthus sinensis*) on the total CR_{C4} which were evaluated from δ^{13}C value, were 35% to 42%, 59% to 62%, and 50% to 53% in subsurface horizons, and 12%, 23%, and 48% in uppermost horizons, for the three soils. The decline in CR_{C4} values in the uppermost horizons could be an effect of recent vegetation. Solid-state ^{27}Al and ^{29}Si NMR revealed that most part of the tetrahedral Al in volcanic glass had already weathered into octahedral Al and a large amount of allophanic constituents (allophane, imogolite, allophane-like constituents including protoimogolite) was formed in B horizon within the past 25,000 ^{14}C y. Allophanic constituents determined by ^{29}Si NMR were compared with those dissolved by acid-oxalate, and differences between them were discussed.

Keywords: Allophane; Andisols; Andosols; Allophanic constituents; Imogolite; Volcanic ash soils

1. Introduction

Many soil properties have been characterized by responses to the addition of chemicals. For example, the amounts of allophanic constituents (allophane, imogolite, and allophane-like constituents including protoimogolite), which are poorly crystalline aluminosilicates, have been estimated from acid-oxalate extractable Si (Si_o: Parfitt et al., 1983; Parfitt and Wilson, 1985; Wada, 1989; Parfitt, 1990; Dahlgren, 1994). However, if the acid-oxalate dissolves Si not only from allophanic constituents but also from other soil components, then content of allophanic constituents could be overestimated. On the other hand, it is possible that not all allophanic constituents are

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completely dissolved and content of allophanic constituents could be underestimated. Therefore, a non-destructive analysis that can characterize samples without any chemical treatment, would be helpful in characterizing soil properties, and in confirming analyses determined by chemical dissolution techniques.

Nuclear magnetic resonance (NMR) is one of the most powerful non-destructive analytical tools used in the characterization and speciation of atoms. To characterize soils without any chemical treatment, NMR instruments should be optimized for the solid-state measurement, although their resolution is much worse than that of liquid-state NMR (Hiradate, 2004). It would be, however, valuable to try to characterize soils using solid-state NMR, especially for ^{13}C, ^{27}Al, and ^{29}Si, because these atoms are abundant in soils. Whole soil NMR analysis for these atoms has been reviewed (Wilson, 1987; Hiradate, 2004), and the following applications and interpretations are possible: (1) ^{13}C NMR specifies aliphatic C, *O*-alkyl C, aromatic C, and carbonyl C; (2) ^{27}Al NMR differentiates tetrahedral Al (^{IV}Al) from octahedral Al (^{VI}Al); and (3) ^{29}Si NMR detects allophanic constituents, layer silicates, and silicon dioxides, separately. We have tested such applications by characterizing three representative allophanic Andisols in Japan using solid-state ^{13}C, ^{27}Al, and ^{29}Si NMR with high magnetic field.

Andisols develop from volcanic ash, tuff, pumice, and other volcanic ejecta with various compositions. The rapid weathering of these porous parent materials results in the accumulation of X-ray amorphous complexes and short-range-ordered minerals such as allophane and paracrystalline imogolite (Wada, 1989; Dahlgren, 1994; Lowe, 1995; ISSS Working Group RB, 1998). In Japan, there are two types of Andisols: allophanic and non-allophanic. Allophanic Andisols are typically younger than 10,000 y and have a high content of allophanic constituents, which contrasts with non-allophanic Andisols that are typically older than 10,000 y and have a low content of allophanic constituents (Shoji et al., 1993; Dahlgren et al., 2004). Generally, soil profiles of allophanic Andisols are well preserved and their parent materials (volcanic ejecta) have been well studied. Therefore, allophanic Andisols should provide excellent materials for studying the weathering products of volcanic ejecta using NMR.

Three representative soil profiles, classed as allophanic Andisols (Soil Survey Staff, 1999; FCSCN, 2003) were subjected to solid-state NMR analyses to characterize the chemical status of ^{13}C, ^{27}Al, and ^{29}Si. To characterize soil carbon (C), the relative isotopic ratio of ^{13}C to ^{12}C (δ^{13}C) was analyzed to clarify the contribution of C4-plant-derived C (mainly *Miscanthus sinensis* A., perennial grass) to the total C (CR_{C4}). Such data provide information regarding vegetation at the time when soil C was accumulating. The degree of weathering of volcanic glass is discussed on the basis of ^{27}Al NMR spectra obtained, and the amounts of allophanic constituents are estimated from the ^{29}Si NMR spectra and compared with those estimated from Si_o values.

2. Materials and methods

2.1. Soil samples

Samples from the horizons of three allophanic Andisol profiles were collected in Tochigi Prefecture, Japan: Funyu (FF) soil at a broad-leaved and red pine mixed forest in Funyu Experimental Forests of Utsunomiya University in Shioya town; Kiwadashima (KF) soil at a broad-leaved forest in Imaichi city; and Kawaraya-cho (KO) soil from reclaimed orchard land in an experimental field of Tochigi Prefectural Agricultural Experimental Station in Utsunomiya city. Descriptions of these soils are given in Table 1. Further data on KF soil are available in Wada (1986) and Thorson and Holmgren (1987).

2.2. Chemical analyses

Samples were air-dried and sieved (<2 mm). Soil pHs in H_2O, KCl, and NaF were measured using a standard pH meter: 1 g of soil was mixed with 2.5 mL of deionized water or 1 mol L^{-1} KCl for determining soil pH in H_2O and KCl, respectively. The mixture was allowed to stand for 1 day and the pH was measured in the suspension. For soil pH in NaF, 1 g of sample was mixed with 50 mL of saturated NaF and stirred continuously for 2 min, and then the pH of the suspension was measured. Total C content was determined with a C/N analyzer (dry combustion method, Vario-EL, Elementar, Hanau, Germany). The types of humic acids present were assessed using a melanic index value, the ratio of the absorbance at 450 nm to that at 520 nm (K_{450}/K_{520}, spectrophotometer: 330, Hitachi, Ltd., Tokyo, Japan) of the 0.5% NaOH extract, i.e., a melanic index <1.7 was termed A-type (highly humified-type). For measuring P adsorption capacity, 10 g of sample (oven-dry basis) and 20 mL of 2.5% $(NH_4)_2HPO_4$ solution (w/v, pH 7.0) were mixed, allowed to stand with occasional shaking at 20 °C for 1 day, and filtered through filter paper. The concentration of P in the filtrate was determined by the vanadomolybdophosphoric acid method (spectrophotometer: U 3000, Hitachi, Ltd.; Sparks, 1996; Soil Environmental Analysis Committee, 1997). For determining exchangeable acidity (*y*1), 10 g of