

## Transition of soil organic carbon in a volcanic ash soil derived from Towada volcano, Japan

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Soil organic carbon (SOC) is generated from organic components by receiving biological and chemical transformations in soils. In volcanic ash soils, mean resident time of SOC is generally long, so the mechanisms of the long lives are of interest for the development of techniques for carbon sequestration in soils. In the present study, we aim to elucidate the transformation process of SOC by fractionating SOC representing the transition stage of the original organic components and characterized the SOC fractions by isotopic and nuclear magnetic resonance spectroscopic analyses.

In this study, we analyzed SOC from a buried soil layer formed between 6,200 and 9,400 cal yBP, because the SOC can be well conserved without the influence of serious human activity. In addition, the age of those buried SOC can be determined by <sup>14</sup>C analysis with high accuracy. The soil samples were collected from a buried soil horizon (six samples collected from the depth between 152 and 182 cm at 5 cm intervals) close to Towada volcano, Japan. From each of the soil sample, SOC were extracted and fractionated by precipitation with controlling pH of the extracted solution (Hiradate *et al.*, 2007), resulting in humin, humic acid, and four fulvic acid fractions (two hydrophilic fulvic acid fractions: FA<sub>1</sub> and FA<sub>2</sub>, and two hydrophobic fulvic acid fractions: FA<sub>3</sub>, and FA<sub>IHSS</sub>). The SOC fractions were freeze-dried and analyzed for determining  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  values by using isotope ratio mass spectrometer and for <sup>14</sup>C dating by using accelerator mass spectrometer. Solid-state <sup>13</sup>C CPMAS NMR analysis was also conducted to investigate the structural characteristics and quantify the carbon species of the SOC fractions.

The  $\delta^{13}\text{C}$  values of humic acid, FA<sub>1</sub>, FA<sub>2</sub>, FA<sub>3</sub>, and FA<sub>IHSS</sub> fractions were  $-23.85 \pm 0.36$ ,  $-20.75 \pm 0.32$ ,  $-21.10 \pm 0.38$ ,  $-22.81 \pm 0.41$ , and  $-23.22 \pm 0.33\%$ , respectively, while  $\delta^{15}\text{N}$  values were  $3.00 \pm 0.37$ ,  $8.16 \pm 1.73$ ,  $9.66 \pm 0.54$ ,  $4.73 \pm 0.83$ , and  $5.20 \pm 0.54\%$ , respectively. The <sup>14</sup>C age of humic acid, FA<sub>1</sub>, FA<sub>2</sub>, FA<sub>3</sub>, and FA<sub>IHSS</sub> fractions was  $6130 \pm 300$ ,  $5630 \pm 240$ ,  $5400 \pm 200$ ,  $5410 \pm 230$ , and  $5680 \pm 260$  cal yBP, respectively. Decomposition and recycling of plant residues during the transformation of SOC result in enrichment of heavier carbon and nitrogen isotopes due to preferential stabilization (Wada *et al.*, 2013). Therefore, the increase of  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  values in SOC fractions corresponds to successive transformation of SOC. The slope of the relationship between  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  values was 1.69, and the results were similar to the result of Wada *et al.* (2013), indicating successive transformation of SOC from plant organic matter to hydrophilic fulvic acid fraction. The hydrophilic fulvic acid fraction would be more microbially processed than hydrophobic fulvic acid and humic acid fractions. Because the humic acid fractions were rich in aromatic structure, they would be formed in the early stage of the formation right after C fixation by plants and chemically stabilized in the soil horizon by fire event etc. The hydrophobic fulvic acid horizons, which are less rich in aromatic C but relatively rich in aliphatic C, would be formed by microbial transformation

and stabilized by chemical and physical factor. The hydrophilic fulvic acid fractions, which are rich in *O*-alkyl C, would be microbially metabolized many times and stabilized physically in the soil horizons.

The validity of the chemical fractionation of SOC on the soil dynamics study has been discussed and sometimes regarded as questionable, but at least in our study on a buried volcanic ash soil, the chemical fractionation procedure successfully separated SOC receiving different metabolisms and having different genesis and chemical structural features.

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