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Effects of sorption on biodegradation of low-molecular-weight organic acids in highly-weathered tropical soils

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ABSTRACT

Low molecular weight organic acids (LMWOAs) are key pools regulating carbon (C) stabilization and destabilization in tropical forest soils. The variation in clay contents and mineralogy between sites or within a profile might regulate magnitude of LMWOA sorption and biodegradation in tropical soils poor in short-range-order (SRO) Al/Fe oxides. We analyzed soil solution concentration, sorption isotherms, and mineralization kinetics of ^{14}C-radiolabeled acetate, oxalate, citrate, and glucose. The sorption capacities of LMWOAs increased with clay contents, but not with the abundance of SRO clay minerals. Sorption can reduce mineralization rates of multivalent LMWOAs (oxalate and citrate) and its effects could increase with increasing clay contents, especially in the clay-rich Bt horizon or in the clayey soil profile. The microbial respiration rates from LMWOAs and monosaccharides are primarily regulated by substrate availability and microbial biomass in the tropical soils, while mineralization of multivalent LMWOAs can be limited by sorption especially in the clayey soil horizon or profile. The smaller sorption capacities in the organic and sandier soil horizons could contribute to fast turnover of organic matters through LMWOA pools in tropical forest soils.

1. Introduction

Soil is the largest pool of organic carbon (C) in terrestrial ecosystems (Schlesinger and Andrews, 2000). Tropical forests exhibit massive aboveground biomass C stocks, while soil profiles are characterized by a thin organic horizon and low C concentrations in surface mineral soil horizons (Schlesinger, 1977; Fujii et al., 2009b). Despite this, tropical soil is also a major component of global soil organic C (SOC) pools because of the thickness of the highly-weathered and deep soil horizons (Jobbágy and Jackson, 2000).

The lower C concentrations and faster turnover of organic matter in the topsoil of tropical forests, when compared with those of temperate forests, can be explained by the high rates of organic matter decomposition by microorganisms and soil fauna (e.g., termites) (Fujii, 2014). However, soil mineralogy as well as climate has strong influences on SOC stabilization and destabilization. Sorption of organic matter on clays can retard microbial decomposition and increase SOC stabilization (Kramer et al., 2012). The combined effects of SOC-stabilizing and -destabilizing processes need to be studied to identify the dominant factors regulating SOC stocks and fluxes in tropical soils (Schimel et al., 1994).

Microbial mineralization and stabilization occur through the pool of low molecular weight organic acids (LMWOAs) and sugars in soil solution (Marschner and Kalbitz, 2003). Although the pool sizes of low molecular weight (LMW) organic compounds are typically small, the C fluxes of LMW organic compound mineralization contribute to the majority of soil microbial (heterotrophic) respiration (Van Hees et al., 2005; Boddy et al., 2008). The carbon dioxide (CO_2) fluxes from LMW organic compounds could be limited by substrate supply via root exudation and organic matter solubilization (Schneckenberger et al., 2008).

Because of the negatively-charged nature of LMWOAs, LMWOAs in soil solution can be removed by sorption onto the reactive surfaces of clays, especially short-range-ordered (SRO) clay minerals (Jones et al., 2003; Van Hees et al., 2003). The greater sorption in the soils rich in SRO clay minerals can reduce LMWOA availability and microbial mineralization (Van Hees et al., 2003; Fujii et al., 2010). These findings are based on the experiments using some temperate soils, while scarce knowledge is available for tropical soils with higher crystallinity of clay mineralogy.

Due to poorness of SRO clay minerals in tropical soils, we hypothesized that sorption will increase with clay contents (mainly

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crystalline clays) within the tropical soils (hypothesis 1). Further, sorption will reduce mineralization rates of LMWOAs to larger extent in clayey soil than in sandier soil when compared between tropical forest soils or within a soil profile (hypothesis 2).

2. Materials and methods

2.1. Site description

To analyze vertical variation and site variation, we compared two soil profiles and five topsoil samples with contrasting soil texture in tropical forests. Soil samples were collected from five tropical forest sites: Ban Rakpendin (RP) in Chiang Rai Province, Thailand, and Bukit Soeharto (BS) and Kuaro (KR1, KR2, and KR3) in East Kalimantan Province, Indonesia. All sites have a tropical climate, and the mean annual air temperature and annual precipitation range from 25.0 to 27.0 °C, and 1977 to 2427 mm yr^{-1}, respectively. The dominant vegetation is broad-leaved evergreen trees. The soils developed on sedimentary rocks and are classified as Ultisols at all sites, except for Oxisol in KR1 (Soil Survey Staff, 2006). We selected two profiles of RP (Thailand) and BS (Indonesia), where the C fluxes of litterfall and soil respiration are available (Fujii et al., 2009a), to analyze the vertical variation of sorption and mineralization kinetics of LMWOAs. To analyze the site variation caused by soil texture and mineralogy, we collected the surface mineral soil horizons (A horizon; 0–5 cm) from five sites (RP, BS, KR1, KR2 and KR3). The detailed features of these sites and soil properties are described in Fujii et al. (2009a, 2011).

2.2. Soil sampling

In May 2007, soil samples were collected from three pits at each site. The distance between each pit was 10 m. In sampling the soils for sorption and mineralization kinetic studies, the mineral horizons were taken in each pit using a spoon. The RP soil had only the Oi horizon, but the O horizon of the BS plot was composed of Oi and Oea horizons (Fujii et al., 2009b). The Oi horizon (fresh litter) was removed and the deeper Oea horizon was collected and immediately sealed in plastic bags and transported to the laboratory. The living organic matter (e.g., grass), large roots, and coarse woody debris in the O horizons were eliminated. When sampling the soils for soil solution extraction, the samples of the mineral soil horizons were taken in each pit by inserting three plastic cores (diameter 5 cm, length 7 cm) horizontally into the pit face. The samples of the O horizons were placed into the cores by hand to exclude large roots and coarse woody debris. These fresh field-moist, unsieved soils were used without eliminating fine roots for soil solution extraction and adsorption and mineralization kinetic studies. For physicochemical analysis of soils, the subsamples collected for adsorption and mineralization kinetic studies were air-dried and sieved (< 2 mm) to eliminate litter, roots and pebbles.

2.3. Soil physicochemical and microbiological properties

Soil pH was measured using a soil to solution (H_2O) ratio of 1:5 after shaking for 1 h. Total C and N concentrations in soils were determined using an NC analyzer (NC-800-13 N Sumigraph, Sumika Chem. Anal. Serv., Ltd., Tokyo). Particle size distribution was determined by the pipette method. Clay minerals in the clay fraction (< 0.002 mm) were identified by X-ray diffraction analysis with an X ray diffractometer (Rigaku, RAD-2RS; Cu-Kα radiation, 30 kV and 20 mA) after treatments: Mg saturation and glycerol salvation, and K saturation and heating at 350 °C and 550 °C). The exchangeable basic cation concentrations were determined using the ammonium acetate (1 M and pH 7.0) method. Exchangeable Ca and Mg were measured using atomic absorption spectroscopy (AA-640-01, Shimadzu), and exchangeable K were measured by flame photometry. The amounts of short-range-ordered (SRO) Fe and Al (hydr) oxides (Fe_o and Al_o) in soils were estimated by extraction in the dark with acidic (pH 3) 0.2 M ammonium oxalate (McKeague and Day, 1966). The amounts of well-crystalline and SRO Fe oxides (Fe_d) were estimated by extraction with a citrate-bicarbonate mixed solution buffered at pH 7.3 with the addition of sodium dithionite (DCB) at 80 °C (Mehra and Jackson, 1960). The Fe and Al concentrations in soil extracts were determined using an inductively coupled plasma atomic emission spectrometer (ICP-AES, SPS1500, Seiko Instruments Inc.).

The microbial biomass C was determined by the chloroform fumigation-extraction method (Vance et al., 1987). The soluble C of the fumigated and non-fumigated soil samples were extracted with 0.5 M K_2SO_4 (soil to solution ratio of 1:5) and were determined using a total organic carbon analyzer (TOC-V CSH, Shimadzu, Japan). Soil microbial biomass-C was calculated as the difference in soluble C between fumigated and unfumigated extracts divided by the extractable factor of microbial biomass C (k_{EC}). A k_{EC} factor of 0.45 was used (Wu et al., 1990).

Basal soil respiration rate was determined in the laboratory by measuring CO_2 evolution from field-moist-soils (equivalent to 10 g dry weight soil) that were incubated in the dark at 25 °C for 1 h in 100 mL Erlenmeyer flasks sealed with silicon rubber septa. The evolved CO_2 was collected in glass vials using a syringe, and measured with an infrared CO_2 controller (ZFP9, Fuji Electric Instruments Co., Ltd.).

2.4. Soil solution extraction and chemical analysis

Soil water was collected without addition of water, using the centrifugation-drainage technique described by Giesler and Lundström (1993). The fresh soil samples were centrifuged for 30 min at a speed of 8800 rpm (10,560 *g*; ~1.5 MPa; Kokusan centrifuge) within 36 h of sampling. The soil solution extracts were filtered through a 0.6 μm filter (GF/C, Whatman) and frozen at −24 °C prior to analysis. The concentrations of dissolved organic carbon (DOC) in soil solution were determined using a total organic carbon analyzer (TOC-V_{CSH}, Shimadzu, Japan). The concentrations of monosaccharides in soil solution were determined using periodate oxidation (Burney and Sieburth, 1977; Johnson and Sieburth, 1977) and glucose standards. The concentrations of LMWOAs in soil solution were determined by high performance liquid chromatography (HPLC, Shimadzu, Japan) using the method of Van Hees et al. (1999). Organic acids were separated on a Supelcogel C610-H ion exclusion column using 0.1% H_3PO_4 as the mobile phase at operating temperatures of 60 °C for citric acid and 30 °C for oxalic and acetic acids with UV detection at 210 nm.

2.5. Isotherms of organic acid sorption in soils

To estimate the equilibrium concentrations of organic acid in soil solution after the addition of the organic acid in the kinetic studies, sorption isotherms were measured based on Jones and Brassington (1998). In each of the plastic vials, 2.5 mL ^{14}C-radiolabelled organic acid solution (170 Bq mL^{-1}; pH 4.5) were added to 0.50 g of chloroform-fumigated (48 h) field-moist soil in 6 mL plastic vials (soil to solution ratio of 1:5 (w/v)). The initial concentrations of organic acids were 100, 500, and 1000 μM. Following the addition of organic acid solution, the samples were shaken for 10 min on a reciprocating shaker at a speed of 320 rpm. The samples were subsequently centrifuged (16,000*g* for 5 min) and the supernatant solution recovered. The equilibrium solution concentration of the organic acid was determined by liquid scintillation counting (Aloka liquid scintillation system, LSC-3050) using Optiphase HiSafe 2 scintillation fluid (Perkin Elmer, Japan).

The data of the sorption isotherm were then fitted to the Langmuir