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Sorption reduces the biodegradation rates of multivalent organic acids in volcanic soils rich in short-range order minerals

Kazumichi Fujii[a,*], Chie Hayakawa[b], Yoshiyuki Inagaki[a], Kenji Ono[a]

[a] Forestry and Forest Products Research Institute, Tsukuba 305-8687, Japan
[b] Graduate School of Agricultural and Life Sciences, The University of Tokyo, Tokyo 113-8657, Japan

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ABSTRACT

Sorption can limit biodegradation of low-molecular-weight organic acids (LMWOAs), while this validity needs to be accessed in volcanic soils rich in short range order (SRO) Al/Fe minerals and organic matter. We tested whether both sorption and microbial mineralization of LMWOAs are controlled by the amounts of SRO minerals and organo-Al/Fe complex in volcanic soils. We analyzed the soil solution concentrations, sorption isotherms, and mineralization kinetics of ^{14}C-radiolabeled acetate, oxalate, malate, citrate, and glucose. The sorption of LMWOAs increased with increasing amount of SRO minerals and organo-Al/Fe complex, irrespective of indigenously adsorbed organic matter levels. Mineralization of multivalent LMWOAs (oxalate, malate, and citrate) displays a contrary pattern to sorption and decreased with increasing amount of SRO minerals and organo-Al/Fe complex. Sorption consistently reduces microbial mineralization rates through removal of LMWOAs from soil solution, but it can also suppress microbial activity of multivalent LMWOA mineralization. Both sorption and microbial mineralization of multivalent LMWOAs are more strongly controlled by the amounts of SRO minerals and organo-Al/Fe complex than acetate. Sorption-induced retardation of multivalent LMWOA mineralization contributes to preservation of organic matter in volcanic soils.

1. Introduction

Andisols or ando soils represent a large stock of soil organic matter (SOM) in Japan (Dahlgren et al., 2004). Andisols are rich in organo-Al/Fe complex and/or short-range order (SRO) Al/Fe minerals derived from volcanic deposition that contribute to sorption of OM (Hiradate et al., 2004; Imaya et al., 2010). It still remains unclear whether SOM stabilized is a relic of pedogenesis over tens of thousands of years or is being produced from newly added substrates (Ugolini and Dahlgren, 2002).

The cumulative carbon (C) balance between substrates input and mineralization can ultimately determine soil C storage (Hayakawa et al., 2013). Among dissolved organic matter (DOM), low-molecular-weight organic acids (LMWOAs) and monosaccharides are major substrates for microbial (heterotrophic) soil respiration (Boddy et al., 2008; Fujii et al., 2010). Substrates removal from soil solution by sorption onto the solid phase generally protects LMWOAs from microbial mineralization (Jones and Edwards, 1998), especially in soils rich in SRO minerals (e.g., spodic B horizon) (Van Hees et al., 2003; Fujii et al., 2010). In Andisols, however, sorption of LMWOAs might be hindered by indigenous SOM that is adsorbed, when the sorption sites in the OM-rich A horizons have already been occupied (Guggenberger and Kaiser, 2003) or when competition for sorption sites occurs between LMWOAs and indigenous SOM (Kalbitz et al., 2005). This questions whether sorption of LMWOAs can increase with amount of SRO minerals in soils including OM-rich volcanic soil.

Effects of sorption on LMWOA mineralization also could differ between substrate charges (Fischer et al., 2010; Keiluweit et al., 2015). Weak competition between microbial mineralization and sorption has been reported for acetate due to its weak sorption and low microbial respiratory demand (Fischer et al., 2010; Gunina et al., 2014), while stronger sorption of multivalent LMWOAs (citrate, malate, and oxalate) can compete with greater microbial respiratory demand. In addition, microbial community grown in absence of LMWOAs tends to decrease transporter activity and dependency of LMWOAs for microbial respiration (Jones et al., 1996). If this is the case in Andisols, LMWOA mineralization activity of microbial community exposed to low substrate concentrations might indirectly be suppressed as a result of substrate removal by sorption from soil solution. We hypothesized that both sorption microbial mineralization of multivalent LMWOAs can be more strongly controlled by the amount of SRO minerals compared to less-charged substrates (acetate or glucose).

* Corresponding author at: Forestry and Forest Products Research Institute, 1 Matsunosato, Tsukuba, Ibaraki 305-8687, Japan.
E-mail address: fjkazumichi@gmail.com (K. Fujii).

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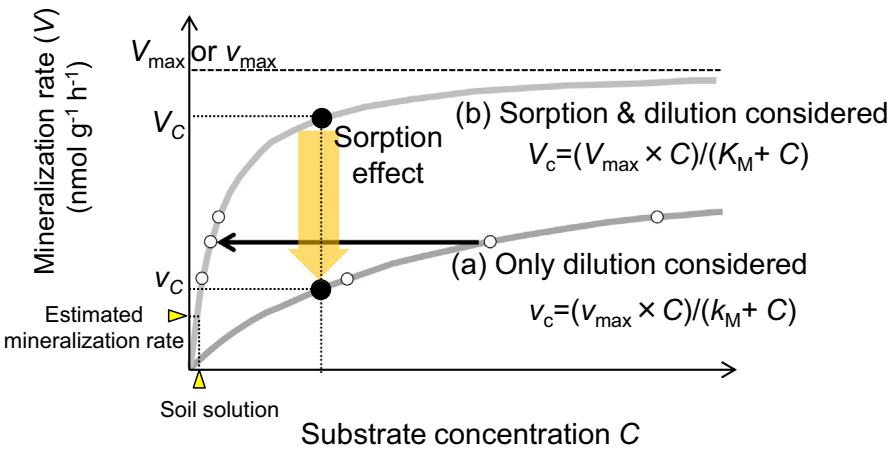

Fig. 1. Concept to estimate reduction of mineralization rates attributed to sorption. The substrate concentration (x-axis) of the first Michaelis-Menten plots (a) was reduced by sorption to the substrate concentration of the second Michaelis-Menten plots (b). The substrate concentration of the first Michaelis-Menten plots are calculated by taking into account only dilution after substrate addition, while substrate concentration of the second Michaelis-Menten plots are calculated by taking into account both dilution and sorption. Mineralization rates at actual substrate concentration in soil solution were estimated using the second Michaelis-Menten fitting curves.

To solve the technical challenge of distinguishing two fates of LMWOAs between sorptive stabilization onto solid phase and microbial mineralization to CO_2, we compared ^{14}C-labeled LMWOA mineralization rates fitted to two Michaelis-Menten models that neglect and consider sorption effects in substrate concentration calculation (Fig. 1). In the first Michaelis-Menten model, concentration dependency of microbial mineralization is described on substrate concentrations that only substrate dilution by intrinsic soil water is considered (the first Michaelis-Menten model in Fig. 1). In fact, sorption reduces substrate concentrations to equilibrium concentration calculated assuming complete mixing of the organic acid with the intrinsic soil water and the sorption reaction (the second Michaelis-Menten model in Fig. 1). The mineralization rate estimated using the first Michaelis-Menten model (v_C in Fig. 1) can underestimate the actual concentration dependency of microbial mineralization described by the second Michaelis-Menten model (V_C in Fig. 1) at a same concentration level (C). The ratios of mineralization rates (v_C and V_C) in two Michaelis-Menten models that neglect or consider sorption effects can be used to assess the direct effect of sorption-induced substrate removal on microbial LMWOA mineralization. In addition, the microbial mineralization potentials (V_{max} in the second Michaelis-Menten model; Fig. 1) of LMWOAs relative to those of non-charged glucose can be used as an indicator to assess indirect effects of SRO minerals on LMWOA mineralization.

In this paper, we address whether both sorption and microbial mineralization of LMWOAs are controlled by the amount of SRO minerals in the volcanic soils by comparing different soil horizons and substrate with different charges. Then, we further estimate LMWOA-derived C flux at actual substrate levels in soil solution to analyze effects of sorption on heterotrophic (basal) respiration and C storage in volcanic soils.

2. Materials and methods

2.1. Site description

To include samples with wide variations in SRO minerals, we selected four temperate forest sites and one cropland site as a reference in Japan. Two of the forest sites, in Appi (AP) and Morioka (MR), Iwate Prefecture, were dominated by beech (*Fagus crenata*); two, in Katsura (KTR) and Tsukuba (TKB) in Ibaraki Prefecture, were dominated by Japanese cedar (*Cryptomeria japonica*) plantations; and the cropland site was located in a green onion field in Ushiku (USK) in Ibaraki Prefecture. All soils were influenced by volcanic ash deposition but classified as Andisols (AP, MR, and USK) or Inceptisols (KTR and TKB) based on the abundance of oxalate-extractable Al and Fe minerals ($Al_o + 1/2Fe_o$) (Soil Survey Staff, 2006). The two Inceptisol soils were also influenced by other parent materials (i.e., sedimentary rocks in KTR and biotite gneiss in TKB). We selected the soil profiles of AP and MR, which share similar climates and vegetation, to analyze the vertical variation in the sorption and mineralization kinetics of LMWOAs. To analyze the site variation caused by the abundance of SRO minerals, the surface mineral soil horizons (A horizon; 0–5 cm) from all five sites (AP, MR, KTR, TKB, and USK) were compared. All sites have a temperate humid climate, and the mean annual air temperature and annual precipitation range from 6.1 to 14.3 °C and 1207 to 1449 mm yr^{-1}, respectively.

2.2. Soil sampling

In July 2011, soil samples were collected from three pits spaced 10 m apart at each site. When sampling the soils for the adsorption and mineralization kinetic studies, we collected the mineral horizons from each pit using a spoon (~200 mL) after removing the thin (< 2 cm) organic horizons or plant residues. When sampling the soils for soil solution extraction, we sampled the mineral soil horizons from each pit by inserting three plastic cores (diameter: 5 cm, length: 7 cm) horizontally into the pit face. "Fresh" unsieved field-moist soils were used for the soil solution extraction, microbiological analyses, and sorption and mineralization kinetic studies. For the soil physicochemical analyses, subsamples collected for the 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 analyses

The physicochemical properties of air-dried soil samples were examined using the following methods. Soil pH was measured using a soil-to-solution (H_2O) ratio of 1:5 after shaking for 1 h. Total C and nitrogen concentrations in soil were determined using an NC analyzer (NC-22F SUMIGRAPH; Sumika Chemical Analysis Services, Ltd.). The clay content (< 2 μm) was estimated using the pipette method after pre-treatment for OM removal and dispersion (Gee and Or, 2002). The amounts of the SRO Fe and Al minerals and organo-Al/Fe complex (Fe_o, Al_o, and Si_o) in soils were estimated by extraction in the dark with acidic (pH 3) 0.2 M ammonium oxalate for 4 h (McKeague and Day, 1966). The Fe, Al, and Si concentrations in soil extracts were determined using inductively coupled plasma atomic emission spectrometry (SPS1500; Seiko Instruments Inc.). The pyrophosphate-extractable C concentrations in soils were determined by extraction with 0.1 M pyrophosphate at pH 10 for 16 h (Schuppli et al., 1983). The available phosphorus (P) concentrations were estimated using the Bray 2 extraction method (Blakemore et al., 1987).

The microbiological properties of the field-moist soils were examined using the following methods. Microbial biomass C was determined using the chloroform fumigation-extraction method (Vance