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Geoderma

journal homepage: www.elsevier.com/locate/geoderma

Impact of microbial activity on the mobility of metallic elements (Fe, Al and Hg) in tropical soils

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ARTICLE INFO

Handling Editor: Yvan Capowiez

Keywords:

Tropical soils

Low molecular mass organic acids

DOC

DGT

Metals

Microbial activity

ABSTRACT

Dissolved organic carbon (DOC), especially low molecular mass organic acids (LMMOAs) derives principally from biota degradation process in which soil microorganisms are the main actors and from roots exudates. The presence of LMMOAs led to an increase of availability and mobility of metallic elements through the formation of organo-metallic complex. In tropical soils, very few information about LMMOAs quantification and their role in the biogeochemical process related to trace metals cycling was available. Quantification of LMMOAs is limited due to their low concentration and rapid degradation. Until now, the role of microbial activity as well as LMMOAs in the biogeochemical cycle of metallic elements in tropical soils has not been investigated. The present study was conducted to evaluate the effect of microbial activity and biomass on the availability and mobility of metallic elements (Fe, Al and Hg) in two tropical soils, Ferralsol and Acrisol. We also quantified LMMOAs contents in soil solutions and addressed to their role in the mobilization of metals.

Utilization of Diffuse Gradient in Thin film (DGT) method permits to analyze bioavailable metal in both fractions: organically complexed and free metals. The results show that the quantity of Fe, Al and Hg labile were higher in Ferralsol than Acrisol soils. This was more accentuated for the 50 cm-depth of soils where the microbial activities and the organic carbon content were important. Concentration of LMMOAs of Ferralsol and Acrisol were lower in compare to coniferous and deciduous forest soils. Proportions of LMMOAs in DOC were very small at 10.5% and 6.85% in the Ferralsol and Acrisol soils, respectively. The mobilization of Fe, Al and Hg in Ferralsol and Acrisol soils appeared to vary depending on the soil physico-chemical characteristics (sorption capacities and metals content) and also on the microbial biomass and activity. Soil pH influences the acidity of the functional groups in organic molecules and consequently their speciation. In addition, low pH increase proton competition within acidic functional groups involved in coordinate bond. The content of CEC in Ferralsol is higher than Acrisol that is related to the high contents of clay and organic carbon. Low CEC content can result in a decrease of retain of the cationic trace metals. Low CEC content led to a decrease of the capacity of retaining of metallic elements in tropical soils in compare to temperate soils.

1. Introduction

Tropical soils are usually deep soils because the process of weathering have been considerable long and intense. The continental weathering is also involved in the biogeochemical cycles of many elements beside carbon. At minor timescale, continental weathering is also a major source of nutrients for the continental biosphere. In these soils,

the exchange of cations and anions between the solid and liquid phases in the oxic horizons and overlying topsoils is mainly conditioned by the type and amount of mineral clays, oxides and organic matter (Legros, 2007). Tropical soils are rich in organic matter. However, the organic matter is degraded so fast that the formation of stable complex with the metals does not occur in these soils. Therefore, under these conditions, geochemical processes dominate mineral weathering in soil. These

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<https://doi.org/10.1016/j.geoderma.2018.07.044>

Received 10 October 2017; Received in revised form 26 July 2018; Accepted 27 July 2018

0016-7061/ © 2018 Published by Elsevier B.V.

geochemical processes are a neutral or slightly acid hydrolysis, which leads to a concentration of oxides in soils. Tropical soils derived from these geochemical processes are well drained allowing solution circulation through soil layers. In organic matter rich soils, rapid solubilization of organic matter through microbial activities leads to production of more amount of DOC. So that solutions percolating through soil layers become trace metal-enriched in colloidal forms as metal-DOC complexes from the soil surface to mineral layers (e.g. Antoniadis and Alloway, 2002; Pédrot et al., 2008; Sherene, 2009; Pontoni et al., 2016). Dissolved organic carbon (DOC), derived from biota degradation as well as from exudates produced by roots (van Hees et al., 2005), plays therefore a major role in the availability and mobility of metals in soil. DOC can be divided into high molecular mass (HMM) compounds such as humic acids and low molecular mass (LMM) compounds such as organic acids, peptides and siderophores (Lundström, 1993; Lundström et al., 2000a; van Hees et al., 2005). The LMMOAs such as acetate, oxalate, citrate, formate, lactate, malate and shikimate are formed via metabolic pathways (e.g. protein synthesis and tricarboxylic acid cycle) of plant and microbial cells. They are then mineralized in soil from few hours to a few days (van Hees et al., 2003). LMMOA compounds act as sink and source of nutrients and mediate key processes in the biogeochemical nutrient cycle. The associations between organic matter and metallic elements play a key role in the development of podzols (Lundström et al., 2000b; McBride, 1994; Sauer et al., 2007). Many works showed that vertical migration of organometallic compounds is an important factor in the formation of the spodic horizon (Lundström et al., 2000b; Sauer et al., 2007; van Breemen and Burman, 2002).

In tropical soils, very few information about LMMOAs quantification and their role in the biogeochemical process related to trace metals cycling was available. Quantification of LMMOAs is limited due to their low concentration and rapid degradation. Several works (van Breemen et al., 1983; Fujii et al., 2010; Fujii, 2014) reported that soil acidification results both of minerals weathering and dissociation of organic acids. As a consequent, soil acidification led to an increase of toxicity of Al in this ecosystem (Kochian et al., 2004). In Bornean tropical forests, the production of organic acids by plants and microorganisms (bacteria and fungi) promoted solubilization trapped in Al and Fe oxides (Johnson and Loeppert, 2006; Fujii, 2014). Nevertheless, quantifications of LMMOAs especially in tropical soils are limited due to their low concentration (few μM in tropical soil compared to several mM in boreal soil) and their rapid degradation (one to few days) depending the balance between production and consumption actors (Van Hees et al., 2008; Fujii et al., 2010). Until now, the importance role of LMMOAs in tropical soil as well as microbial activity and biomass on the biogeochemical cycle of metallic elements has not been investigated. The present study was conducted to evaluate the effect of microbial activity and biomass on the availability and mobility of metallic elements (Fe, Al and Hg) in two tropical soils, Ferralsol and Acrisol. We also quantified LMMOAs contents in soil solutions and addressed to their role in the mobilization of metals. The soil physico-chemical properties were also determinate.

2. Materials and methods

2.1. Site description and soil sampling

The study site is located in French Guiana on the Combat Creek watershed (52°23' W, 4°35'N), a small catchment of $\sim 1\text{km}^2$ covered by tropical rain forest. The climate is tropical humid, with an annual average rainfall of ~ 4000 mm and an annual average temperature of 26 °C.

The soil samples are collected along a toposequence with 3 types of soils. Soil distribution within the Combat Creek watershed is related to soil position along the slopes (Grimaldi et al., 2004; Guedron et al., 2006). Details of soil profile and the description of the toposequence have been reported by Grimaldi et al. (2004). Ferralsols are

predominant on the upslope, having typically a high clay ($< 2\ \mu\text{m}$ size fraction) content, a micro-aggregated structure and deep over 1 m depth, which allows a good vertical water drainage. Halfway down the slopes, Ferralsols steadily evolves to Acrisols, a massive lateritic horizon with a high content of fine silts at shallow depth ($< 1\text{ m}$). Downslope, the soils become hydromorphic, with dominant sands. A permanent aquifer is present and slowly drains by the river, thus imposing reducing conditions. Only the upper part of the studied watershed (Ferralsols and Acrisols) is sampled. These soils are considered to be pristine based on the soil structure and texture (Guedron et al., 2009).

For this study, the soil samplings were taken in June 2013 with a rainfall of ~ 300 mm and a temperature of 27 °C corresponding to the wet season. After removing of litter (OF) layer and using an auger, soil samples are systematically collected every 10 cm until 120 cm depth for Ferralsol and every 10 cm for Acrisol until 100 cm. Then, two additional 100–120 cm and 120–150 cm samples have been collected of Acrisol. All soil samples are stored in sterile polyethylene bags for further treatment and analyses.

2.2. Soil analyses

2.2.1. Physico-chemical analyses

The soil was air-dried and sieved using a 2 mm sieve prior to the experiment. Granulometric analysis was then determined according to the ISO NF X 31-107 standard protocol.

Cation exchange capacity (CEC) was measured with the soil kept at the same pH at which it was sampled using a buffered 0.1 M ammonium acetate salt solution (1:10 w/v) (Mathieu and Pieltain 2003). The exchangeable cations (Ca, Mg, Na, K, Fe, Al ...) collected from the extracted solution were analyzed by inductively coupled plasma optical emission spectroscopy (ICP-OES Spectroblue). The soil pH ($\text{pH}_{\text{H}_2\text{O}}$) was measured in a 1:5 (w/v) soil/water ratio suspension after 2 h of equilibration.

For total cations concentration determination, we used and adapted rock and soil dissolution procedure described by Bolou-Bi et al. (2009). In brief, soil samples were dissolved in Teflon digestion tube (SCP Science) at 80 °C in a mixture of concentrated HNO_3 -HF (3:1 ml) overnight using a hot block (Digiprep MS, SCP Science). Samples were evaporated to dryness at 80 °C, and then redissolved in 2 ml of concentrated HCl at 80 °C overnight with boric acid grains. The corresponding solutions were evaporated to dryness. Samples were then dissolved in 5% HNO_3 before the analysis using inductively coupled plasma optical emission spectroscopy (ICP-OES Spectroblue). All chemicals used were of trace metal grade purity.

Total Hg concentrations were determined by thermal decomposition atomic absorption spectrometry after gold amalgamation using an Automatic Mercury Analyzer (AMA 254) with a detection limit of 0.01 ppb.

2.2.2. Metals labile fraction: diffuse gradient in thin film

Samples of soil horizons (100 g) were put in big Petri dishes (about 1 cm depth of soil) and wetted with milliQ water for 4 days at soil moisture content of 70% of WHC (water hold capacity) at 20 °C. DGT unit (Diffuse gradient in thin film) samplers were assembled based on previously described procedures (Zhang and Davison, 2000) with 0.45 μm pore-size cellulose acetate filters. Units were then placed on the surface of about 0.5 cm depth of soil at 70% of WHC and pushed carefully into the surface by putting the device in full contact with the soil solution and by avoiding the formation of air bubbles. The Petri dishes and the devices were covered with parafilm® to limit evaporation. Four units were placed by Petri dishes. After maintaining at room temperature (± 20 °C) for 24 h, the DGT units were taken from the soil and rinsed with Milli-Q water. The resin layer was retrieved and the iron (Fe) and aluminum (Al) were eluted from the resin after its immersion in 1 ml 2 N HNO_3 for 48 h. The concentration of Fe and Al in the eluent was measured with ICP-OES (Spectroblue). The mass of

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