Geoderma 145 (2008) 222–230

Contents lists available at ScienceDirect

Geoderma

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

Micromorphology and spectroscopic characteristics of organic matter in waterlogged podzols of the upper Amazon basin

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ARTICLE INFO

Article history:
Received 17 July 2007
Received in revised form 19 December 2007
Accepted 26 March 2008
Available online 5 May 2008

Keywords:
Amazon basin
Podzols
Soil organic matter
Micromorphology
FTIR
Solid-state 13C NMR

ABSTRACT

In waterlogged environments of the upper Amazon basin, organic matter is a major driver in the podzolisation of clay-depleted laterites, especially through its ability to weather clay minerals and chelate metals. Its structure in eight organic-rich samples collected at the margin and in the centre of the podzolic area of a soil sequence was investigated. The samples illustrate the main steps in the development of waterlogged podzols and belong either to eluviated topsoil A horizons or to illuviated subsoil Bhs, Bh and 2BCs horizons. Organic matter micromorphology was described, and the overall molecular structure of their clay size fractions was assessed using Fourier transform infrared (FTIR) spectroscopy and cross polarization/magic angle spinning (CP/MAS) ^{13}C nuclear magnetic resonance (NMR). Organic features of the horizons strongly vary both vertically and laterally in the sequence. Topsoil A horizons are dominated by organic residues juxtaposed to clean sands with a major aliphatic contribution. In the subsoil, numerous coatings, characteristic of illuviation processes, are observed in the following horizons: (i) At the margin and bottom parts of the podzolic area, dark brown organic compounds of low aromacity with abundant oxygen-containing groups accumulate in Bhs and 2BCs horizons. Their spectroscopic features agree with the observation of cracked coatings in 2BCs and the presence of organometallic complexes, whose abundance decreases towards low lying positions. (ii) By contrast, black organic compounds of high aromacity with few chelating functions accumulate as coatings and infills in the overlying sandy Bh horizon of well-expressed waterlogged podzols.

1. Introduction

Organic matter (OM) is a major soil component, consisting of a great diversity of more or less decomposed plant, animal and microbial residues. If organic compounds are major agents in soil fertility, for example in highly weathered tropical soils, where they provide most of the cationic and anionic exchange capacities (Zech et al., 1997), they can also play an important part in soil evolution processes such as podzolisation (Lundström et al., 2000). In this process, acidic organic compounds enhance mineral weathering and form mobile organometallic complexes with the Al^{3+} and Fe^{3+} ions. These complexes are then redistributed within podzolic profiles and accumulate at depth in spodic horizons or are exported towards drainage networks. These mechanisms are referred to as cheluviation (Swindale and Jackson, 1956).

In boreal, temperate and, to a lesser extent, tropical podzols, OM structures have been investigated at different scales. First, microscopic observation of thin sections provides a description of the OM morphology and its relationship with other soil constituents (e.g. De Coninck et al., 1974; Righi, 1977; Bravard and Righi, 1989). OM micromorphology can indicate the occurrence of mechanisms such as illuviation and accumulation of organometallic complexes in spodic horizons (e.g. De Coninck, 1980). Buurman and Jongmans (2005) revealed the influence of drainage conditions on the morphology of B horizons: organic pellets derived from root decay predominate in well drained podzols, while in their poorly drained counterparts, the presence of thick and cracked coatings indicates the accumulation of OM derived from dissolved organic carbon, possibly complexed with Al^{3+} and Fe^{3+}. Chemical characteristics of OM have been assessed for bulk samples, or following either chemical extraction of humic and fulvic acids (e.g. Bravard and Righi, 1991) or physical particle size fractionation (e.g. Schmidt et al., 2000). OM elemental composition provides information on the extent of decomposition processes through C/N values. Most authors show that C/N values in podzols are greater than in agricultural soils, for example (e.g. Petersen, 1976;

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doi:10.1016/j.geoderma.2008.03.008

Bravard and Righi, 1990; Skjemstad et al., 1992), probably due to reduced microbial activity associated with lower pH. In addition to bulk chemical data, spectroscopic techniques such as Fourier transform-infrared (FTIR) spectroscopy or solid state ^{13}C nuclear magnetic resonance (NMR) spectroscopy give insight into the main functional groups of OM in different podzolic horizons. For example, they have been used to show that organic compounds resistant to microbial degradation, mainly aliphatics, accumulate in surface horizons of podzols (e.g. Baldock et al., 1997; Rumpel et al., 2002). On the contrary, organic compounds in B horizons have contrasting characteristics. In particular, a high aromaticity is observed (e.g. Skjemstad et al., 1992; Schmidt et al., 2000), or not (e.g. Wilcken et al., 1997). At last, more recently, molecular characterization of OM in podzols has been achieved using pyrolysis and mass spectrometry (e.g. Beyer, 1996; Buurman et al., 2005). This shows that, in well drained podzol B horizons, a large part of the OM is derived from roots instead of dissolved organic carbon (Buurman et al., 2005), which can explain some of the micromorphological differences observed between well drained and poorly drained B horizons (Buurman and Jongmans, 2005).

In the upper Amazon basin, podzols develop at the expense of highly weathered lateritic formations (Dubroeucq et al., 1999) through localized lateral weathering fronts. They were first found to occur in footslope positions (e.g. Lucas et al., 1987; Righi et al., 1990), where they develop upwards at the expense of lateritic cover. More recently, Nascimento et al. (2004) studied waterlogged podzols lying in depressions of low plateaux and showed that they are formed at the expense of higher elevated and well drained, clay-depleted laterites. The authors link these soil dynamics to the development of reducing and acidic conditions in seasonally perched groundwater seated at shallow depth on a weakly permeable layer, and connected to the permanent rivers. The morphological, geochemical and mineralogical study of a representative soil sequence at the transition between laterite and podzol enabled the authors to highlight the main mechanisms involved in the podzolisation of these clay-depleted soils. Those are: (i) production of organic acids and mineral weathering, (ii) formation of organometallic complexes (mainly with Al), (iii) vertical and lateral transfer of these complexes, their accumulation first in a poorly-differentiated podzol with a Bhs horizon, and then in well differentiated Bh and 2BCs horizons and, (iv) desorption of metals from OM in downslope waterlogged podzols.

These first investigations by Nascimento et al. (2004) enabled selection of key samples representing the different steps in both vertical and lateral development of podzols. Bardy et al. (2007) further investigated Al speciation in this soil sequence. They showed that Al is present either in well crystallised minerals, namely kaolinite and gibbsite, or as organo-Al complexes. Moreover, the abundance of the complexes varies widely in clay size fractions of the horizons. In particular, the authors highlighted the idea that cheluviation processes lead to the virtually complete weathering of kaolinite in surface horizons. They showed that, in the first step, organo-Al complexes accumulate in the poorly differentiated Bhs horizon of the weakly expressed podzol, and that they then migrate down to well differentiated 2BCs horizons at the margin of the transformation front. With further podzol development, they become less abundant, probably as a result of desorption of Al^{3+} ions from OM and their lateral exportation.

In addition to previous studies, a detailed determination of the OM nature is required to specify a relevant model of soil evolution grading from clay depleted laterites to waterlogged podzols. This corresponds to a natural process of soil change (Fanning and Fanning, 1989) which is widespread in the upper Amazon basin. The present study focuses on the aforementioned soil sequence. It aims at investigating OM evolution in contrasting and well characterized horizons representative of podzol development in low plateaux of the upper Amazon basin. OM was studied on two different scales, which, to the best of our knowledge, have never been combined, especially for tropical podzols. Thin sections were observed in order to describe OM micromorphology, while its main functional groups were inferred from spectroscopic measurements (FTIR and solid state ^{13}C NMR). Taken together, the results are discussed in terms of OM decomposition, humification, complexation and illuviation mechanisms.

2. Materials and methods

2.1. Samples

A precise description of the site can be found in Nascimento et al. (2004). Briefly, it is located on the low plateaux of the Jau national park (upper Amazon basin, Fig. 1a). It is preserved from human activity and has a hot humid tropical climate with mean annual temperature and precipitation of respectively 26 °C and 2000 mm. The samples belong to a 200 m long and 2–3 m deep soil sequence along which podzolic soils develop at the expense of yellow clay-depleted laterites (Fig. 1b). Podzols are located in a depression while laterites remain in higher positions.

Clay size fractions (<2 μm) of eight organic-rich samples from the podzol area of the sequence were selected (Fig. 1b). They belong either to subsurface organo-mineral horizons (A) or deep illuviated horizons (B, 2BC) with accumulations of OM (suffix h) and/or metals (Fe and Al, suffix s). Three (II A11, II A13, II Bhs) come from the upper part of pit II and belong to horizons of weakly expressed podzols at the margin of the depression. The other five (II Bh, II 2BCs, III A11, III Bh, and III 2BCs) are specific to horizons of well expressed podzols sampled at the bottom part of pit II and towards the centre of the depression on the whole profile of pit III. Samples were collected from the freshly cleaned faces of pits. They were air-dried, sieved through a 2 mm screen and stored in the dark in sealed glass jars prior to analysis.

2.2. Micromorphology

Undisturbed samples from the main horizons were collected in cardboard boxes. They were impregnated with resin, cut and ground according to Fitzpatrick (1970). They were observed with a microscope, under unpolarized and polarized light. Thin sections were described according to De Coninck et al. (1974) and Righi (1977).

2.3. Physical and chemical treatment

Clay fractions were isolated by sieving of sand fractions and clay pipetting following dispersion with Na resin (Bartoli et al., 1991) without previous destruction of OM. Elemental analysis was performed at the Service Central de Microanalyse du CNRS, Vernaison, France. C, H and N contents were determined using infrared or catharometric detection of gases produced upon combustion at 1050 °C. Fe content was measured using Inductively Coupled Plasma–Atomic Emission Spectroscopy (ICP–AES) after HF treatment. Aliquots of clay size fractions were treated with dithionite-citrate-bicarbonate (DCB) to remove metals from Fe-oxides and poorly crystalline Fe and Al phases (Mehra and Jackson, 1960), and treated with H_2O_2 to destroy OM. The H_2O_2 treatment was adapted from Pansu and Gautheyrou (2003). Solid residues were stirred at room temperature with 30% H_2O_2 until bubbling ceased. The suspension was then progressively heated at 80 °C for several hours. The treatment was repeated after cooling. Suspensions were finally washed with deionised water by centrifugation.

2.4. FTIR spectroscopy

FTIR spectroscopy was performed in the transmission mode using a Nicolet Magna 560 IR Spectrometer. One mg of oven dried sample was mixed with 300 mg KBr and pressed at 10 tonnes cm^{-2} to form a