Metal and organic matter immobilization in temperate podzols: A high resolution study

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ABSTRACT

Aluminium and Fe fractions were obtained in samples from two temperate podzols by selective extraction with NaOH (Al_n, Fe_n), Na-dithionite-citrate (Al_d, Fe_d), acid NH4-oxalate (Al_o, Fe_o) and Na-pyrophosphate (Al_p, Fe_p) following the traditional fractionation procedures, and also by the use of the chlorides of K (Al_K), La (Al_{La}) and Cu (Al_{Cu}) as non-buffered extractants for Al. Carbon content was also determined in the Na-pyrophosphate extract (C_p). Soil sampling was done at high-resolution to allow a more detailed characterization of the vertical processes than the traditional sampling by whole soil horizons. Results showed that Al_p and Fe_p make a large proportion of the Al_o and Fe_o meaning that organoaluminic complexes dominated in the "active" metal pool instead of inorganic compounds. The degree of metal saturation of soil organic matter (estimated by the (Al_p Fe_p)/C_p molar ratios) increases with depth, especially in the uppermost samples of spodic horizons (Bhs1) where it increases up to 0.1. Aluminium dominates in the adsorption positions of the organic matter in the spodic horizon (Fe_p/Al_p ratios < 0.5), except in the Bhs1 horizon (ratios > 1), indicating that the immobilization of Fe containing complexes occurs 10–15 cm above that of Al. The highly stable Al–OM complexes accounted on average for 60% of the organoaluminic associations (> 70% in the Bhs horizons). The moderately stable complexes predominate in A horizons (57–77% in ACB1 and 37–48% in ACB2) and the largest proportions of low stability complexes were found in the uppermost samples of the spodic horizons (Bhs1) of both soils (9–21%), together with the highest Fe_p contents and a decrease in pH values. From a stepwise multiple regression model it is suggested that pH is the main variable accounting for the stability of Al–OM compounds together with C and organically bound Fe contents. It is suggested that the illuviation of unsaturated organic acids lower the pH in upper spodic horizons, leading to the complexation of metals from formerly precipitated organometallic complexes and/or leading to their redissolution, enabling their migration to deeper soil layers. Iron complexes would be less soluble at soil pH, resulting in a differentiation of an upper Fe-rich Bhs1 horizon and a lower Bhs2 Al-rich horizon. The depth variation in C accumulation was found to be related to the proportion of highly stable Al–OM fraction.

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1. Introduction

It is widely accepted that the organometallic associations play a key role in the development of podzols (Lundström et al., 2000a, 2000b; McBride, 1994; Sauer et al., 2007). Many authors propose that their vertical migration is an important mechanism in the formation of the spodic horizon (Lundström, 1993; Lundström et al., 1995; Sauer et al., 2007; Van Breemen and Buurman, 2002). Although, there is still controversy about the precise mechanisms (e.g., Buurman and Jongmans, 2005; Farmer and Lumsdon, 2001; Gustafsson et al., 2001; Lundström et al., 2000b; Mossin et al., 2002). The precipitation of organometallic complexes in spodic horizons by saturation of the adsorption sites of the organic ligands is a recurrent and well documented explanation

for the metal and organic matter accumulation in spodic horizons (Buurman, 1985; Jansen et al., 2003; McKeague et al., 1978; Nierop et al., 2002; Petersen, 1976), even though other mechanisms may be involved in organic matter (OM) accumulation such as the in situ decay of roots (Buurman et al., 2005a, 2007a, 2007b; Nierop and Buurman, 1999) and the adsorption of OM to inorganic surfaces (Anderson et al., 1982; Farmer and Lumsdon, 2001). Still, other theories postulate a non-active role of the OM complexes (Anderson et al., 1982; Farmer and Lumsdon, 2001) based in the formation in the upper B horizons and downwards migration of (proto)imogolite sols and other dissolved inorganic species, OM being immobilized by adsorption onto solid Al- and Fe-phases. One important reason for this controversy is the complex nature of podzols in which different mechanisms can operate simultaneously. Their relative importance depends on the local environmental conditions, soil composition and soil chemistry (Jansen et al., 2004, 2005). Some work suggests that the dominant

podzolization mechanisms are different depending on climate and parent materials (e.g. Kodama and Wang, 1989; Mossin et al, 2002).

The complexation of metals by organic compounds is directly involved in the preservation of soil organic matter (Grand and Lavkulich, 2011). In this sense, Schwesig et al. (2003) found that the complexation of Al can increase the half-life of the slowly degradable C pool as much as 50% and an Al/C ratio higher than 0.1 increases its resistance to biodegradation up to 4-fold. So the accumulation of these complexes may render soils that are effective C sinks. Moreover, Al–OM associations play an important role on the regulation of Al activity in soil solution (Bloom et al., 1979; Cronan et al., 1986; Dahlgren and Walker, 1993; Driscoll et al., 1985; Mulder and Stein, 1994; Nóvoa-Muñoz et al., 2002; Takahashi et al., 1995) being, together with the inorganic non-crystalline Al, one of the most contributing Al fractions for the neutralization of acid loads in podzolic soils (Berggren and Mulder, 1995; Berggren et al., 1998; Mulder et al., 1989; van der Salm et al., 2000; Zysset and Blaser, 1999). Still, Al–humus complexes are key components for controlling the risk of Al toxicity (Adams and Moore, 1983; Adams et al., 2000; Álvarez et al., 2005; Foy, 1984).

For the characterization of the podzolization process, the chemical operative fractionation scheme suggested by McKeague et al. (1971) has been extensively used. It is based on procedures of selective extraction by sodium dithionite-citrate, ammonium oxalate, and sodium pyrophosphate (Mokma and Buurman, 1982; Parfitt and Childs, 1988; Paterson et al., 1993). This approach allows a semiquantitative division of secondary Al and Fe into crystalline, non-crystalline and organically bound fractions that have been used to quantify the extent of podzolization and in the identification of podzols (McKeague et al., 1983). However, this general scheme defines a single organometallic fraction (Na-pyrophosphate extractable) that includes a wide range of different organometallic associations. Aiming to further characterize this fraction we addressed the extended Al fractionation using unbuffered chloride salts (KCl, LaCl$_3$ and CuCl$_2$) as non-sequential extractants. This procedure has shown to be a useful approach to estimate the stability of Al–OM bindings (Álvarez et al., 2002; García-Rodeja et al., 2004, 2007; Urrutia et al., 1995), and has been successfully applied in Andisols, Ultisols, Alfisols, Umbrisols (García-Rodeja et al., 2004, 2007; Matus et al., 2008) and Atlantic Rankers (i.e. stratified and colluvial soils; Kaal et al., 2008). For podzols, it has been applied only in tropical hydromorphic environments (Coelho et al., 2010a, 2010b) but, to the extent of our knowledge, it has not been applied to temperate podzols.

In this study, the assessment of the distribution of the different fractions of Al and Fe was carried out at much higher vertical resolution (5 cm) than previous studies that traditionally use a single soil sample, or a few, per horizon identified in the field, providing a much more detailed view of the depth variation of the soil properties and allowing the observation of intra-horizon variations. Our objectives are: i) to determine with high resolution the variations of Al and Fe fractions, aiming to get insights into the vertical expression of the podzolization mechanisms and ii) to get further information about the stability of Al–OM associations and their role in the pedogenetic process and long term carbon storage.

2. Material and methods

2.1. Site description and soil sampling

The two soils were sampled in the northern slope of Monte Acibro hill, at 450 m above sea level and 10 km south of the north Atlantic coast of Galicia (NW Spain, Fig. 1). The parent material is a Quaternary quartzitic colluvium. Present climate conditions are mild and humid, with an average annual temperature of 11 °C (6 °C in winter, 16 °C in summer) and a total annual precipitation about 1250 mm with low rainfall seasonality and frequent fogs throughout the year (Martínez-Cortizas and Pérez-Alberti, 1999). Current forest vegetation is composed of a eucalyptus stand (*Eucalyptus globulus*) and shrubs (mainly
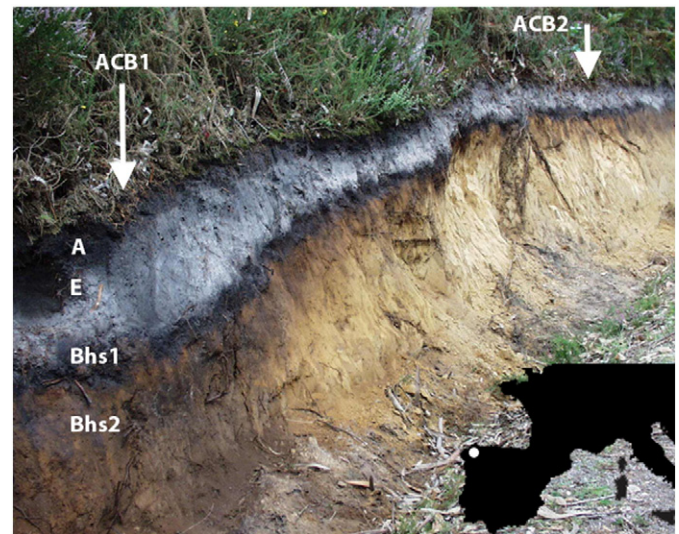

Fig. 1. An Umbric Albic Rustic Podzol (ACB1) and an Albic Rustic Podzol (ACB2) (IUSS-WRB, 2007) were sampled in Monte Acibro hill (Serra do Xistral, NW Spain). Identified horizons are indicated.

Ulex europaeus, *Daboecia cantabrica* and *Calluna vulgaris*). The soils are acidic, well-drained podzols, both with an Ah horizon, an albic E horizon and a well-defined B horizon that can be split up into a dark, organic rich Bhs1, and a brownish and more inorganic Bhs2. Two monoliths (ACB1 and ACB2) were sampled only 20 m apart, aiming to take into account the differences in vertical development observed within the soil column. The monoliths were sliced into continuous, 5 cm thick slices, down to the C horizon: 140 in ACB1 and 100 cm in ACB2.

2.2. Sample pretreatment and general physico-chemical analyses

The samples were air dried and sieved (mesh size 2 mm). In the resulting fine earth fraction pH in water (1:2.5, pH$_w$) (Guitián and Carballas, 1968), exchangeable base cations (NaNH$_4$, KNH$_4$, MgNH$_4$ and CaNH$_4$) after extraction with 1 M NH4Cl (Peech et al., 1947) and exchangeable acidic cations (Fe$_K$, Al$_K$ and Mn$_K$) using 1 M KCl solution (Lin and Coleman, 1960) were determined. The sum of basic and acidic cations was considered as an estimation of the effective cation exchange capacity (eCEC) of the soil. Total C and N contents were measured in finely milled samples (<50 μm) using a LECO Truspec CHN analyzer. Total C (C$_T$) is considered equivalent to organic C due to the lack of carbonates. Soil bulk density (Ds) of dry samples (at 105 °C until constant weight) was determined in undisturbed soil cylinders of known volume and was used to calculate the accumulation of total C, Al, Fe and Si.

2.3. Total Al, Fe and Si and selective dissolution techniques

Total Al, Fe and Si contents (Al$_T$, Fe$_T$ and Si$_T$) were measured by -XRF (XRF Energy-dispersive Miniprobe Multielement Analyzer) at the RIAIDT facility of the University of Santiago de Compostela. EMMA and its applications to elemental analysis are described in detail elsewhere (Cheburkin and Shotyk, 1996; Cheburkin et al., 1997; Weiss et al., 1998).

Selective dissolution techniques were applied on fine earth subsamples to assess the Al, Fe and Si in different fractions. These procedures comprised extractions with NaOH (Borggaard, 1985), Na-dithionite-citrate (Holmgren, 1967), NH$_4$ oxalate-oxalic acid (Blakemore, 1985) and Na-pyrophosphate (Bascomb, 1968). Aluminium, Fe and Si concentrations in the extracts were measured by atomic absorption spectrometry (Perkin Elmer 1100B) after the addition of Superfloc, centrifugation for 20 min at 3000 rpm, and filtration under vacuum using a 0.45 μm filter, aiming to remove suspended materials (Buurman et al., 1996;