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Influence of parent material on the aluminium fractions in acidic soils under *Pinus pinaster* in Galicia (NW Spain)

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ABSTRACT

Study of the influence of the parent rock on Al fractionation in acidic soils that are rich in organic matter can provide useful information related to forest productivity in areas of high geological diversity. We studied how parent material affects several chemical parameters, mainly focusing on the total soluble aluminium and aluminium forms in solid fractions in different acidic soils in Galicia (NW Spain). The soils were developed over slate, biotitic schist, mica schist and granite and all were under *Pinus pinaster*. Six soil samples, three samples of rhizospheric and three samples of non-rhizospheric soil, were collected in each study plot. Aluminium was extracted from the solid phase with the following solutions: ammonium oxalate (Al_o), sodium pyrophosphate (Al_p), copper chloride (Al_{cu}), lanthanum chloride (Al_{la}) and ammonium chloride (Al_{NH4}). The total Al in the liquid phase (Al_t) was also determined. There was no significant difference in any parameter between rhizospheric and non-rhizospheric soils. In all soils, organo-aluminium complexes predominated over inorganic compounds of low crystallinity (Al_p always represented more than 96% of the Al_o). Overall, the parent material had a significant effect on chemical soil parameters. In the soil over biotitic schist, characterised by low acidity ($pH_{water} = 5.4$) and organic matter with relatively high evolution (C/N = 12.7), the concentrations of Al_o and Al_p were higher and tended to form highly stable organic–aluminium complexes, whereas the concentrations of exchangeable Al_{NH4} and Al_t were significantly lower than in the other soils. Nevertheless, in soils developed from slate, the higher acidity (pH = 4.7) and the organic matter with relatively low evolution (C/N = 20.7) favoured the formation of moderate and low stability organic–aluminium complexes (Al_{cu}, Al_{la}) and higher concentrations of exchangeable Al and Al in solution. The characteristics of the soils over granite and mica schist were intermediate. In more acidic conditions, the destabilisation of organo-aluminium complexes and the release of Al to the soil solution seem the most likely mechanisms of pH buffering.

1. Introduction

Parent material has a marked influence on forest soil properties (Hartmann and Moosdorf, 2012), even in surface horizons (Macías et al., 1982). The role of parent material as an explanatory factor for vegetation cover and tree growth has long been recognised and recently highlighted (Cocco et al., 2013; Hahm et al., 2014; Eimil-Fraga et al., 2014). Among the most abundant materials in Galicia (NW Spain), different types of schist (biotitic schist and mica schist) and slate of low to moderate grade metamorphism constitute about 46% of the total area, and rocks of more or less deformed granitic composition occupy about 45% of the area (Macías et al., 1982). In regions such as Galicia, characterised by long periods where rainfall is much higher than evapotranspiration, acidification is one of the main processes involved in soil evolution (Chesworth, 1992). These conditions cause a decrease in the acid neutralising capacity of the soil and a more or less rapid decrease in soil pH. The resulting geochemical conditions in turn lead to the gradual elimination of exchangeable bases and occupation of the exchangeable sites by acidic cations, mainly Al, which can thus enter the soil solution. Acidic soils are created and may become problematical as the Al chemistry becomes dominant. Thus, in such soils, the exchange complex is largely saturated with Al, solid forms of reactive Al appear (more or less crystalline hydroxides, Al islets in a clay 2:1 interlayer and organo-Al complexes), the 2:1 clay minerals are destabilised and different forms of Al appear in solution (Macías et al., 2005). Differences in rock weathering also influence the release of Al to soil, and the formation and stability of organo-Al complexes and Al concentrations in exchange sites and in soil solution.

Different geochemical processes lead to the formation of highly reactive Al compounds and Al-silicates (including organo-Al compounds), mainly in weathering systems in the pH range 4–5.5 (García-Rodeja et al., 1985). Galician soils are also characterised by high contents of organic matter, which exhibits a high complexing ability, particularly

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towards Al. The formation of Al–humus complexes leads to stabilisation of both organic matter and non-crystalline Al compounds (Carballas et al., 1978; Grand and Lavkulich, 2011). The chemistry of Al–humus complexes also plays a major role in soil pH buffering and in the regulation of Al activity in soil solution (Mulder and Stein, 1994; Takahashi et al., 1995). The Al bound to organic complexes is of low toxicity (Adams et al., 2000; Matús et al., 2006), and this may explain the lack of negative effects of Al on the growth of tree species on acid soils.

Given the importance of the Al fractions, different extractants such as acid ammonium oxalate and sodium pyrophosphate at pH 10 are commonly used in the quantification of Al fractions in soil (Paterson et al., 1993). Acid oxalate extraction is commonly considered to represent a good estimate of the entire Al reactive pool (Blakemore, 1978) as this extractant dissolves the Al in poorly ordered soil components, including Al bound to organic matter. The Al extracted with sodium pyrophosphate at pH 10 (Bascomb, 1968) is considered as the total Al bound to organic matter. Extractions with unbuffered salts, such as $CuCl_2$ (Juo and Kamprath, 1979), has also been proposed for estimation of the organic fraction of soil Al via ligand exchange reactions (Hargrove and Thomas, 1981). Copper has high affinity for the carboxylate sites and can readily replace the Al bound to organic matter. Although $CuCl_2$ does not remove large amounts of Al from Al-silicate minerals, it can extract some poorly ordered Al associated with the mineral soil (Oates and Kamprath, 1983). Use of this extractant in Galician soils provides an estimate of the Al in moderately stable organo-Al complexes (inner-sphere complexes, excluding chelates) (Urrutia et al., 1995).

The usefulness of these methods is limited by the existence of a continuum from a very short range ordered to crystalline components and by the weaker tendency of Al (relative to Fe) to form oxyhydroxides. However, these methods have been verified and used for many years (Urrutia et al., 1995; Fernández-Sanjurjo et al., 2001; Álvarez et al., 1992, 2002, 2010; Drabek et al., 2003; García-Rodeja et al., 2004, 2007; Matús, 2007; Frankowski et al., 2013; Ferro-Vázquez et al., 2014).

The presence of different forms of Al in the solid phase may be influenced by different factors related to soil formation. Vegetation plays an important role in determining the chemical properties and biological fertility of soils (Muys and Lust, 1992). Certain species, mainly conifers, are known to acidify the soil and have therefore been associated with degradation processes, particularly in cold regions (Augusto et al., 1998). However, vegetation may be of secondary importance for soil formation in other areas, relative to climate and parent material. The effect of the parent material is particularly clear when other soil-forming factors (i.e. climate, biota, topography and age) are very similar across the landscape. In such cases, the parent material becomes the main cause of variation in soil types, which may in turn determine soil processes and soil nutrient dynamics (Binkley et al., 1995).

In this study, we analysed the influence of parent material on different Al forms present in soils developed on slate, biotitic schist, mica schist and granite, all under *Pinus pinaster*. This species of pine has been considered as non-site-demanding and it has largely been planted for timber production and for restoration and landscaping purposes in northern Spain. Its widespread use in the Galicia, where it covers 0.53 Mha of land in pure and mixed stands, is due to its extraordinary adaptation to poor, acidic, shallow and sandy soils (Eimil-Fraga et al., 2014).

The specific objectives of this study were as follows: i) to investigate the influence of the parent material on the chemical properties of acidic soils under *P. pinaster*, especially in Al fractions in the soil solid phase and the total concentration of Al in solution; and ii) to determine soil chemical parameters that affect the presence of different Al forms.

2. Material and methods

Experimental plots of *P. pinaster* were chosen to represent different types of parent material (slate, biotitic schist, mica schist and granite) in Galicia (NW Spain). Soils developed from slate, mica schist or non-tectonised granite are often thin because the rock is very resistant to weathering (Macías et al., 1982). Slates usually alternate with quartzites and are formed by muscovite, chlorite, biotite and a variable amount of quartz. The mineralogical composition of mica schist mainly comprises variable amounts of quartz, as well as mica (muscovite and biotite) and some garnet, andalusite, sillimanite and staurolite. The granites comprise quartz, K-feldspar, muscovite, biotite and plagioclase (IGME, 1981). Soils developed from biotitic schist, which has similar characteristics to basic rocks, are usually deep as a result of the intense weathering that has occurred. Basic rocks comprise calcium plagioclase, quartz, biotite, muscovite, garnet and chlorite, and the corresponding soils are richer in nutrients. All studied soils are classified as Haplic Umbrisol (WRB, 2006).

The stands' dimensions were 20 × 30 m and the age ranged between 11 and 13 years. The sites are located at elevations between 325 and 773 m. The mean air temperature ranges between 10.4 and 12.9 °C in the area, and the mean annual rainfall is higher than 1000 mm. Site index (SI) has been defined as the dominant height of the stand, in metres, at a reference age of 20 years and considering two different ecoregions (Álvarez-Gónzalez et al., 2005) (Table 1). Other characteristics such as basal area and soil depth of the plots are included in Table 1.

Six soil samples, i.e. three samples of rhizospheric (RS) and three samples of non-rhizospheric soil (NRS), were collected in each plot. The RS and NRS samples were separated following the modified method of Chung and Zasoski (1994). In the field, the soil at a distance of about 20 cm from each stem was loosened to a depth of 20 cm depth to enable collection of roots and rhizosphere samples. The root segments were dissected and immediately after being cut they were gently separated from the soil and vigorously shaken. The soil detached during shaking was considered as NRS, while the soil remaining adhered to roots was considered as RS. In the laboratory, the roots were placed in a jar, which was mechanically shaken to remove the soil still adhering to the roots; the roots were then brushed to collect the total rhizospheric fraction (Courchesne and Gobran, 1997; Fernández-Sanjurjo et al., 2003).

The RS and NRS samples were dried at 40 °C and sieved through a 2 mm sieve. The following parameters were determined in the solid fraction: pH in water and in 0.1 M KCl; total C and N (in a LECO CNS-2000 autoanalyser); effective cation exchange capacity (eCEC), considered as the sum of Ca, Mg, Na, K, and Al (Kamprath, 1970) displaced by 1 M NH_4Cl (Peech et al., 1947) and measured by atomic absorption (Ca, Mg, and Al) and atomic emission (Na and K) spectroscopy (Perkin Elmer AAnalyst 200, USA), and Al saturation. The concentration of P was measured by the Olsen method (Olsen and Sommers, 1982).

Different forms of Al were extracted from the solid fraction by non-sequential extraction with different reagents. The Al extracted with acid ammonium oxalate (Al_o) (ratio soil:extractant 1:100, with 4 h shaking

Table 1
Summary of climatic, pedological and dendrometric characteristics of *Pinus pinaster* stands.

	Slate	Biotitic schist	Mica schist	Granite
Mean annual air temperature (°C)	11.6	12.4	10.4	12.9
Mean annual rainfall (mm)	1303	1395	1388	1024
Elevation (m)	655	325	773	340
Slope (%)	45	0	15	10
Aspect	Plain	Southwest	Southwest	East
Soil depth (cm)	25	40	30	60
Soil texture	Silty	Silty loam	Sandy clay loam	Sandy loam
Stoniness (%)	0	0	18	6
Drainage	Moderate	–	Good	Good
Age of plantation (years)	12	12	13	11
Basal area (m^2 ha^{-1})	11.3	30.5	6.7	21.0
Site index (m)	13	18	8.5	15