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Tree species affect cation exchange capacity (CEC) and cation binding properties of organic matter in acid forest soils

Piotr Gruba [a,*], Jan Mulder [b]

[a] Department of Forest Soil Science, University of Agriculture, Al. 29 Listopada 46, 31-425 Krakow, Poland
[b] Department of Plant and Environmental Sciences, Norwegian University of Life Sciences, P.O. Box 5003, N-1432 Aas, Norway

HIGHLIGHTS

- We investigated cation bonding to SOM in stands of several European tree species.
- The CEC_t to C_t ratio increased in the order hornbeam ≈ oak < beech < spruce ≈ pine.
- The apparent dissociation constant (pK_{app}) values were largest under oak.
- Maximum Al saturation occurred at higher pH under pine and spruce than under oak.
- At similar pH pine soil had less Al complexed and more adsorbed H than soils from oak.

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ABSTRACT

Soil organic matter (SOM) in forest soil is of major importance for cation binding and acid buffering, but its characteristics may differ among soils under different tree species. We investigated acidity, cation exchange properties and Al bonding to SOM in stands of Scots pine, pedunculate oak, Norway spruce, European beech and common hornbeam in southern Poland. The content of total carbon (C_t) was by far the major contributor to total cation exchange capacity (CEC_t) even in loamy soils and a strong relationship between C_t and CEC_t was found. The slope of the regression of CEC_t to C_t increased in the order hornbeam ≈ oak < beech < spruce ≈ pine, suggesting that the number of negatively charged sites of SOM at any value in the acid pH range was smallest for hornbeam and oak, and largest for spruce and pine soils. This was supported by the apparent dissociation constant (pK_{app}) values of SOM, which were largest in soils under oak. The maximum values of Al saturation were similar between the stands. However, maximum Al bonding to SOM occurred at higher pH values in soils under pine and spruce than under oak. Therefore, at any value in the acid pH range, the SOM in pine soil has less Al complexed and more adsorbed H^+ than SOM from oak soils. Such differences in Al and H bonding are not only important for pH buffering and metal solubility controls, but also for stabilization of SOM via saturation of functional groups by Al and H.

1. Introduction

Forest management, including changing species composition, can be considered ecological engineering in practice, and may lead to significant modifications of soil properties. These include changes in soil organic carbon (SOC) stocks, pH, cation exchange capacity (CEC), exchangeable cations, base saturation and bonding of metals like aluminium (Al) (e.g. Nihlgård, 1971; Augusto et al., 1998; Brandtberg and Simonsson, 2003; Berger et al., 2004, 2006; Hobbie et al., 2007; Paluch and Gruba, 2012; Galka et al., 2014). Generally, coniferous forests have a more acidifying effect on the soil than deciduous or mixed forest (Nihlgård, 1971; Ranger and Nys, 1994; Augusto et al., 1998; Gruba and Mulder, 2008; Mueller et al., 2012). According to Augusto et al. (2002) the acidifying effect of common European tree species decreases in the order: *Picea abies*, *Pinus sylvestris* > *Abies alba* > *Betula pendula*, *Fagus sylvatica*, *Quercus petraea*, *Quercus robur* > *Acer platanoides*, *Carpinus betulus*, *Fraxinus excelsior*, *Tilia cordata*. A similar order for congeners was reported by Finzi et al. (1998).

Soil acidity and complexation of metals to soil organic matter (SOM) may affect the stability of SOM in soils and consequently the biogeochemical cycling of carbon (C) in forest ecosystems (Mulder et al., 2001). Also Hobbie et al. (2007) confirmed that the increasing saturation of CEC with Al and iron (Fe) had a positive impact on the stabilization of SOM via cation bridging between SOM and minerals, enhancing flocculation. Also inhibitory effects of Al or low pH on decomposers may cause the storage of organic C in forest soils to increase. Recently, Mueller et al. (2012) proposed a conceptual model of SOM stabilization in forest soil, accounting for effects of soil acidification, dissolution of Al and Fe-containing minerals and metal complexation to SOM. Thus, tree species are likely to contribute to SOM dynamics through their effect on

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* Corresponding author.
E-mail address: rlgruba@cyf-kr.edu.pl (P. Gruba).

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the intrinsic characteristics of soil organic matter, soil acidification and availability of hydrolyzing cations like Al and Fe.

Binkley et al. (1989) attributed the impact of forest stands on soil acidity to the acid input in the soil and to the apparent acid dissociation constant (K_{app}) of soil organic acids.

Comparing soils under different tree species Binkley and Valentine (1991) and Valentine and Binkley (1992) presented the differences in K_{app} of acid groups of SOM based on observed shifts of the titration curves. Values of K_{app} differ due to differences in functional groups of SOM derived from different forest tree species (Strobel et al., 1999).

However, some studies suggest that the relationships between pH_{H_2O} and the fraction of exchangeable cations (H, Al, Ca, Mg, K, Na) in soil are irrespective of the type of forest tree species. For example, Gruba and Mulder (2008) found that Al binding in soil of spruce and of mixed stands (dominated by European beech) could be described by the same relationship even though soil pH values were significantly different.

In acid forest soil the pH is related to specific acid buffering mechanisms. Below pH 5.5 Al mobilization becomes increasingly important, involving two major mechanisms, namely organic complexation of Al and precipitation or dissolution of $Al(OH)_3$ (gibbsite) (Berggren and Mulder, 1995; Wesselink et al., 1996; Gruba et al., 2013). In previous studies we showed that acid neutralization through these two mechanisms operates in different pH ranges. On theoretical grounds we have defined $pH_{threshold}$, which is the soil pH below which $Al(OH)_3$ is unstable and pH is controlled by chemisorption of Al to soil organic matter (Mulder et al., 1989; Gruba and Mulder, 2008). By contrast, at $pH > pH_{threshold}$, the $Al(OH)_3$ solubility model applies (Berggren and Mulder, 1995). According to Gruba et al. (2013), $pH_{threshold}$ can be estimated for any acid soil by the following equation:

$$pH_{threshold} = 6.06–0.47pH_{KCl}. \tag{1}$$

In acid, organic matter-rich forest soils, the value of the solution pH can be explained by the Henderson–Hasselbalch (H–H) equation, describing the dissociation of weak acids. Originally, the H–H equation was applied to explain pH of the solution of weak organic acids (McBride, 1994):

$$pH = pK_{app} + n\mathrm{Log}\frac{(A^-)}{(HA)} \tag{2}$$

where pK_{app} is the negative logarithm of the apparent dissociation constant, n is an empirical stoichiometry constant of the reaction, indicating the number of moles of H^+ reacting with one mole of charged sites associated with soil organic matter, A^- is the fraction of dissociated groups, and HA is the fraction of non-dissociated groups. The latter equation was modified by Bloom and Grigal (1985):

$$pH = pK_{app} + n\mathrm{Log}\left(\frac{BS_e}{1-BS_e}\right) \tag{3}$$

where BS_e is the effective base saturation, i.e. the fraction of the effective cation exchange capacity (CEC_e) neutralized by base cations. Thus, $1 - BS_e$ refers to the fraction of exchangeable acidity. So far, modelling the relationship between soil pH and exchangeable base cations was often successfully performed using effective cation exchange capacity CEC_e, estimated as the content of extractable cations (H, Al, Ca, Mg, K, Na) by un-buffered salts, e.g. KCl, $BaCl_2$ or NH_4NO_3 (see, for example: Reuss, 1983; Reuss et al., 1990; Prenzel and Schulte-Bisping, 1995).

Others (e.g. Skyllberg, 1999; Lofts et al., 2001) have modelled soil pH as a function of the amount of organically complexed H and Al, determined as total acidity and Al extractable in 0.5 M $CuCl_2$, respectively. This fraction includes both the exchangeable and organically bound fraction of Al (Hargrove and Thomas, 1981).

The pH of extraction is of great importance for the CEC. Extraction at pH values higher than soil pH (e.g. at pH 8.2) gives higher CEC values (so called CEC_t), due to increased deprotonation and hydrolysis of organically-bound Al. By contrast, base cations extracted by unbuffered NH_4Cl solution were used for calculation of CEC irrespectively of the method of acidity measurement applied. This approach is justified by statement that the amount of base cations extracted from acid soil is little affected by pH (Borge, 1997).

The aim of the present work was to investigate the exchange properties of SOM derived from different tree species by assessing relationships between SOM-derived CEC and the content of organic C. In addition, we tested the concept of $pH_{threshold}$, where its values represent the transition between two Al buffer ranges. This is done by comparing the Al-binding characteristics to soil organic matter of a large number of samples taken from the upper 10 cm of mineral soils over a wide pH range. The investigations were carried out using soil samples from forest stands in the Polish lowlands, which are now dominated by Scots pine (*P. sylvestris* L.) (Brus et al., 2011). The dominance of pine monocultures even on nutrient-rich soils (Brożek and Zwydak, 2003) is due to large scale planting, a common forest management practices at the end of the 19th century and at the beginning of the 20th century. Samples were taken from the upper 10 cm of the mineral soil of pairs of adjacent stands of Scots pine (*P. sylvestris* L.) and one of the following: pedunculate oak (*Q. robur* L.), Norway spruce (*P. abies* (Karst.)), European beech (*F. sylvatica* L.) and common hornbeam (*C. betulus* L.). For each pair the parent material is similar.

2. Material and methods

Investigations were carried out in forested areas of Southern Poland. Six paired plots, each 12 m × 12 m, were established in homogeneous, mature (40–80 years) pine (*P. sylvestris*) (six plots), oak (*Q. robur*) (three plots), spruce (*P. abies*), beech (*F. sylvatica*) and hornbeam (*C. betulus*) (all one plot) forests. The plots were set up such that the paired plots (one of them always pine) were adjacent and had the same parent material (Table 1). Differences in soil units shown in Table 1 resulted from the diagnostic properties of deeper horizons (B). The A or AE horizons of the paired sites were assessed to be similar, especially in terms of their texture and dominating soil forming process.

The influence of pine on soil pH and exchange characteristics was compared pairwise with that of the other four tree species. The oak, beech and hornbeam stands originated from seed recruitment, whereas pine and spruce forests were planted in shallow furrows. Species composition on the plots has changed little during the last decades. The history of the stands, including forest management and tree species composition, is well documented by the local forest administration offices. We assumed that in all cases SOM is derived from the current vegetation, due to the relatively short turnover time of SOM reported for topsoil horizons of forest soils (e.g. Chabbi et al., 2009), especially in sandy soils.

The pairs pine 1–oak 1 and pine 2–oak 2 were located in the forest inspectorate Dabrowa Tarnowska, about 50 km east of city of Krakow. Soils, classified as Arenosol and Podzol (Table 1), were derived from sandy glacial deposits. Forest stands were classified as coniferous-mixed.

The pairs pine 3–oak 3 and pine 4–spruce were located in the Niepolomice forest, 40 km east of Krakow. The soils (Podzols), parent material and forest stands were similar to those of pairs 1 and 2, described above. In the 1960s the sites located in the Niepolomice Forest were drained, thus decreasing the groundwater table (Socha, 2012).

Pairs pine 5–beech and pine 6–hornbeam were located 20 km west of Krakow, on relatively rich Luvisols derived from aeolian deposits (decalcified loess). These sites were originally covered by deciduous forest, with pine planted at the beginning of the 20th century.

Soil samples were taken from the top 10 cm of the mineral soil directly below the O horizon in a regular 4 m × 4 m grid, i.e. we obtained 16 samples per plot. Additionally, at each plot one deep (up to 1.5 m)