ARTICLE IN PRESS

Journal of Inorganic Biochemistry xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Journal of Inorganic Biochemistry

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

Short communication

Behaviour of aluminium in forest soils with different lithology and herb vegetation cover

Petra Hubová[a,*], Václav Tejnecký[a], Michaela Češková[b], Luboš Borůvka[a], Karel Němeček[a], Ondřej Drábek[a]

[a] Department of Soil Science and Soil Protection, Faculty of Agrobiology, Food and Natural Resources, Czech University of Life Sciences Prague, Kamýcká 129, 165 00 Prague - Suchdol, Czech Republic
[b] Department of Forest Ecology, Faculty of Forestry and Wood Sciences, Czech University of Life Sciences Prague, Kamýcká 129, 165 00 Prague - Suchdol, Czech Republic

ARTICLE INFO

Keywords:
Aluminium
Low molecular mass organic acids
Vegetation cover
Forest soils
Lithology

ABSTRACT

The aim of this study was to determine the content, distribution and behaviour of Al in soils under beech forest with different parent rock, and to assess the role of herbaceous vegetation on soil Al behaviour. We hypothesize that the contents of elements in the soil sorption complex (Al etc.) are strongly influenced by vegetation cover. Also, low molecular mass organic acids (LMMOA) can be considered as an indicator of soil organic matter (SOM) decomposition and vegetation litter turnover. Speciation of LMMOA, nutrition content (PO_4^{3-}, Ca^{2+}, K^+) and element composition in aqueous extracts were determined by means of ion chromatography and inductively coupled plasma - optical emission spectrometry (ICP-OES) respectively. Active and exchangeable pH, sorption characteristics and exchangeable Al (Al_{ex}) were determined in $BaCl_2$ extracts by ICP-OES. Elemental composition of parent rocks was assessed by means of X-ray fluorescence spectroscopy. Herb-poor localities showed lower pH, less nutrients (PO_4^{3-}, Ca^{2+}, K^+), less LMMOA, a larger stock of SOM and greater cation exchange capacity. There was also lower mobilisation of Al in organic horizons, which explains the larger pools of Al. Generally, we can conclude that LMMOA, and thus soil vegetation cover, play an important role in the Al soil cycle.

1. Introduction

Aluminium is an element commonly present in soil in many different forms (e.g. available - exchangeable, organically bound, (oxo) hydroxide, and in silicate minerals) [1]. However, high levels of available Al (Al^{3+}) in soil can be potentially toxic toward plants, particularly at low soil pH, or can be mobile where there is a high content of soil organic matter (SOM), which acts as an Al chelating agent [2]. Increasing mobility of aluminium in connection with anthropogenic acidification has already been investigated by many authors [3,4]. This situation has improved since the 1990s [5]. In previously published works, the main effects on available Al contents in forest soils were attributed to the age of a spruce forest [6], season and/or vegetation cover [7–9]. However, a detailed study on Al soil pools with respect to the stand ground flora and soil bedrock under the same forest types (European beech) is missing.

We hypothesize that the total element contents in the sorption complex is strongly influenced by vegetation cover and that low molecular mass organic acids (LMMOA) can be considered as an indicator of SOM decomposition and vegetation litter turnover.

Four sites were selected in the Lužické Mountains (Czech Republic). The altitude of all studied plots ranges from 650 (bottom edge) to 749 (upper edge) m a.s.l. Annual precipitation is approximately 800–1000 mm and the annual mean temperature 5–7 °C [10,11]. Locality Lužické 1 – herb-rich floral beech forest of alliance *Fagion sylvaticeae* with high coverage of a herb layer (dominated by *Galium odoratum*, *Mercurialis perennis*, *Calamagrostis villosa*, *Melica uniflora*, *Dentaria bulbifera*, *Hordelymus europaeus* etc.). The herb layer covers > 50%, with young *Fagus sylvatica* trees in the shrub layer. Locality Lužické 2 – herb-poor beech forest *Fagetum nudum* with sporadic occurrence of the species of floral beech forests (e.g. *Dentaria bulbifera*, *Mycelis muralis* and *Milium effusum*). Locality Lužické 3 – acidophilous *Fagetum nudum* with herbal vegetation < 5% (*Vaccinium myrtillus*, *Avenella flexuosa*, *Oxalis acetosella* etc.). Locality Lužické 4 – medium

* Corresponding author.
E-mail address: hubova@af.czu.cz (P. Hubová).

http://dx.doi.org/10.1016/j.jinorgbio.2017.09.017
Received 30 June 2017; Received in revised form 15 September 2017; Accepted 19 September 2017

Table 1
Localities characteristics.

Locality	Geology	Vegetation	Site name	Soil type	Humus forms
Lužické	Sandstone	Herb-poor beech forests	Lužické 3	Arenic Cambisols	Mor
Mountains	Phonolite	Herb-rich beech forests	Lužické 1	Haplic Cambisols	Mullmoder
Czech Republic		Medium herb-rich beech forests	Lužické 4	Skeletic Cambisols	Moder
		Herb-poor beech forests	Lužické 2	Haplic Cambisols	Mormoder

Table 2
Basic soil properties of L and B horizons with different herb vegetation cover.

	1 herb-rich beech forest on phonolite		2 medium herb-rich beech forest on phonolite		3 herb-poor beech forest on phonolite		4 herb-poor beech forest on sandstone	
Horizon	L	B	L	B	L	B	L	B
pH_{H2O}	5.15	4.28	4.34	3.51	4.59	3.37	4.63	3.69
pH_{KCl}	5.20	3.77	4.55	3.78	4.25	3.31	4.38	3.82
CEC (mekv kg^{-1})	418	62.61	364.03	49.09	324.92	39.96	296.02	57.71
BS (%)	95.82	33.79	90.67	13.96	94.2	12.83	88.3	10.17
C tot (%)	40.31	1.76	43.82	2.69	44.7	3.12	45.18	8.97

herb-poor acidophilous beech forest with a 50% cover of vegetation, dominated by grasses (*Calamagrostis villosa*, *Calamagrostis arundinacea* and *Avenella flexuosa*).

The distance between the 4 localities did not exceed 3 km (the same slope). The soil types (Table 1) were classified using the World Reference Base for Soil Resources [12]. The dominated forms of soil humus were moder and mor [13].

On all 4 localities, 3 pits were excavated (12 pits in total – 60 samples). The soil pits were excavated in areas at a sufficient distance from the trees. In all cases, samples were collected from the surface - litter horizon (L), fermentation (F) and humified (H) organic horizons and subsurface A (humic) and B horizons (cambic).

The aqueous extracts of fresh samples were prepared according to [14]. Speciation of LMMOA, and content of PO_4^{3-} were determined by means of ion chromatography in aqueous extracts, according to a method by Mercl et al. [15]. Aluminium (Al_{H2O}) contents were determined in aqueous extracts by means of ICP-OES. Dissolved organic carbon (DOC) was measured according to [16]. Exchangeable elements (H^+, Mn, Fe, Al, Na, K, Mg, Ca) were determined in 0.1 M $BaCl_2$ extracts and cation exchange capacity (CEC) was calculated as the sum of exchangeable elements [17]. Active and exchangeable pH were also determined [14]. Forms of Al – Al_{H2O} (H_2O extractable) and Al_{ex} ($BaCl_2$ exchangeable) were determined by means of ICP-OES. The total content of C was determined by an Elementary Analyzer. Elemental composition of parent rocks was assessed by means of X-ray fluorescence spectroscopy (XRF) after agate ball mill grinding. For a detailed description of chemical analysis see Appendix 3.

For the calculation of elements pools, samples from organic horizons (L, F, H) were collected using a steel frame 25 × 25 cm. Approximate weight of each horizon per unit area (mg m^{-2}) was calculated from the thickness and bulk density of the horizons. The quantities of C in LMMOA (C_{LMMOA}) on different localities were also calculated. Statistical evaluation of obtained results was calculated in MS Excel or Statgraphics Centurion XVI.I. Multi-factorial analysis of variance was used to analyze the relationship between observed variables – influence of the environment – vegetation cover, parent rock and horizon. Multi range PCA diagrams of vegetation composition were created using the software CANOCO.

2. Influence of parent rock on soil composition

We compared the differences in geochemical reactivity based on carbonate content and the coefficient of alkalinity and susceptibility to weathering [18,19]. Phonolite was rated as parent rock with high reactivity, and sandstone as a low reactivity parent rock [20]. In phonolite parent rock, total contents of Al and Ca were 9% (Al), 1.5% (Ca), and in sandstone 2.6% (Al), 0.2% (Ca). It was confirmed, that parent rock has an effect on Al_{ex} and Al_{H2O} contents in B horizons. (There is also a statistically significant correlation between Al_{ex} and Al_{H2O} $r = 0.435$, $p < 0.001$). On sandstone in the B horizon, a lower content of Al_{ex} in comparison with the B horizon on phonolite was found (Fig. 2). In the A horizon, a stronger influence of vegetation was evident. Therefore, we did not find any statistically significant differences in the amount of Al_{ex} nor between different types of parent rocks. In the case of water extractable Al, we did not find significant differences between types of parent rocks either. An important impact on Al_{H2O} was found for the type of soil horizon, which has been already confirmed by various authors [6,9].

3. Influence of parent rock on vegetation

We compared 2 localities (Lužické 2 and Lužické 3) with herb poor vegetation cover. On locality Lužické 3 with sandstone parent rock we found acidophilous herb vegetation and mor type humus. Additionally, locality 3 had a lower pH value than on the other localities (Table 2). Locality Lužické 2 on phonolite with a similar cover has higher vegetation richness. Decocq [21] also evaluated the influence of parent rock on vegetation and concluded that in a managed forest, vegetation can reflect the parent rock diversity.

4. The influence of vegetation on soil composition

The importance of understory species on nutrient cycling processes in forests is related to their patterns of distribution in forest soils, as the distribution of most herbal species is strongly influenced by nutrients availability [22,23]. We hypothesized that the different vegetation cover (understory species) in beech forests would affect the