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## Accumulation of metallic elements into the superficial peat layer of mires and wet mineral soils of Estonian forest land

Akumulacja metali w powierzchniowej warstwie gleb torfowych i wilgotnych glebach mineralnych ekosystemów leśnych Estonii

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**Keywords:** accumulation coefficient, metallic elements, peat, peaty epipedon, forest land  
**Słowa kluczowe:** współczynnik akumulacji, metale, torf, torfowy epipedon, gleby leśne

### Abstract

This article studied the extent of accumulation of *aqua regia* extractable metallic elements (Al, Mg, Pb, Zn, Hg, Cd) into peaty (histic) epipedon (EP) of fen soils, transitional bog soils, peaty gley soils and peaty podzols. The accumulation coefficients (Kac) of the elements in EP were estimated in relation of forest floor (FF, as an input) as a comparison to deeper levels (SS, as a past background). The study revealed that the extent of accumulation and its order depend on soil (peat) type or pedo-ecological conditions of peatification. In the forming of EP from FF, the concentrations of Al and Pb were increased on an average 2.5–5.0 times, but that of Hg increased significantly only in peaty soils (on an average 1.5–1.6 times). The contents of Zn were significantly decreased (Kac 0.1–0.5) in all soil groups. The comparison of EP peats concentrations with SS data demonstrated a considerable accumulation of Pb, Cd, Zn and Hg into thin (~20 cm) superficial peat layer.

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## 1. INTRODUCTION

The peat-topped soils form 45.3% of the total Estonian forest lands area. These soils include the mire soils (36.9%) distributed on peatlands and the peaty soils (8.4%) on wet paludified mineral lands [Reintam et al. 2005]. The formation and chemistry of superficial peat horizons of mires and wet mineral soils are widely variegated depending on local geological, pedo-ecological, hydrological and anthropogenic conditions [Brożek, Zwydka 2003; Arold 2005; Oleszczuk et al. 2008]. The great impact on peaty topsoil may be expressed as well by atmospheric sediments [Görres, Frenzel 1997; Orru, Orru 2006]. Consequently, the elements content in the peaty topsoil may be influenced by variegated factors such as (i) the bioaccumulation in plant cover and its falling debris element content, (ii) feeding seepage and ground water, (iii) atmospheric sediments and (iv) underlying peat mineral sediments.

This article studied the extent of accumulation of *aqua regia* extractable Al, Mg, Pb, Zn, Hg and Cd into superficial peat layer in the process of peat forming from the forest floor (FF). The main

### Streszczenie

Z wykorzystaniem wody królewskiej badano stopień akumulacji metali (Al, Mg, Pb, Zn, Hg, Cd) w epiedonie torfów wysokich (EP), torfów przejściowych, oglejonych glebach torfowych oraz zabagnionych glebach bielcowych. Współczynnik akumulacji metali (Kac) w EP oszacowano w zależności od runa leśnego (FF, jako wkład) i w porównaniu do głębszych poziomów (SS, jako tło przeszłości). Stwierdzono, że stopień akumulacji metali jest uzależniony od typu gleby (torfu) oraz jej właściwości. W powstałym EP z FF stężenia Al i Pb zwiększyły się średnio 2.5–5.0 razy, natomiast Hg istotnie jedynie w glebach torfowych (średnio 1.5–1.6 razy). Istotnie zmniejszyły się (Kac 0.1–0.5 razy) zawartości Zn we wszystkich glebach. Porównując zawartości metali w EP z SS stwierdzono znaczącą akumulację Pb, Cd, Zn i Hg w (~20 cm) powierzchniowej warstwie torfowej.

objectives of this research are (i) the comparative analysis of metallic elements content in the epipedon (EP) of peatlands and paludified wet mineral soils and (ii) the evaluation of the extent of accumulation of elements in EP's peat.

## 2. RESEARCH AREAS

The researches were conducted in forest soils of fens (group I, 5 research areas), transitional bogs (II, 8), peaty gley soils (III, 6) and peaty podzols (IV, 7), and their pedo-ecological characterisation is shown in Table 1. The peats of I and II soil groups are thick (>100 cm), whereas those of III and IV groups are thin (10–30 cm). The superficial layer of I and III soil groups peats are slightly or moderately acid, but those of II and IV groups very strongly acid.

The character of peaty soil cover feeding is different by soil groups. The soils of group I are fed with minerotrophic ground and surface water, but the soils of group II mostly are fed with

Table 1. Pedo-ecological characterisation of soil groups

Soil group		EP acidity, pH <sub>CaCl<sub>2</sub></sub>	Type of epipedon	Composition of tree layer <sup>1)</sup> and quality class	Forest site type
No	name				
I	Fen soils	Moderately acid 4.6–5.5	Eutrophic peat	Bt6–7Pn2Al1Pc1 III–IV	Oxalis drained, Alder-birch fen
II	Transitional bog soils	Very strongly acid 2.6–3.5	Mesotrophic peat	Pn7–8Bt2(Pc) IV–V	Myrtillus drained bog
III	Peaty gley soils	Slightly to strongly acid 3.5–6.4	Peaty mull and peaty moder	Bt5–6Pc1–4Pn1–3 II–IV	Dryopteris, Filipendula, Polytrichum-Myrtillus, Carex
IV	Peaty podzols	Very strongly acid 2.6–3.5	Peaty mor	Pn10(Bt) III–V	<i>Vaccinium uliginosum</i> , Polytrichum-Myrtillus

1) Tree species: Bt – Betula, Pn – Pinus, Al – Alnus and Pc – Picea (number following the tree – share of 10).

rainfall and mesotrophic seepage surface water. Located on depressions and transitional areas (between mineral and organic soils), soils of groups III and IV are fed by minerotrophic surface water with different acidity.

### 3. METHODS

#### 3.1. Sampling

The soil sampling was carried out in 2006–2007 by the methods of the project “Long-Range Transboundary Air Pollution” [Forest Focus...2006]. The FF and its sub-horizons (OL, OF, OH) and peat layers of peaty soils were sampled with metallic frame (25 cm x 40 cm). The sampling of top layers' peats were carried out by the fixed depth. For zero line in sampling of peat soils, the boundary between FF and peat layers was taken, whereas in case of peaty soils, the boundary was between peat and mineral layers. Both soils were sampled from zero line by 0–10, 10–20, 20–40, 40–80 cm layers. The samples were taken from five soil pits, to form one composite sample for every layer. The living macroscopic roots and all particles with a diameter of >2 mm were removed from the samples by dry sieving. Organic layer samples were milled.

#### 3.2. Chemical analyses

The analyses of peat and mineral soil samples were done according to abovementioned projects' manual [Forest Focus...2006]. Soil pH<sub>CaCl<sub>2</sub></sub> was measured using soil:liquid mixture 1:5. The content of *aqua regia* extractable Al, Mg, Pb, Zn, Hg and Cd were assayed using inductively coupled plasma optical emission spectrometry (ICP-OES) method. All analyses were run in triplicate, and the results were averaged.

#### 3.3. Statistical analysis and calculations

For the statistical analysis, the MS Excel and a free software R version 3.2.0 [R Core Team 2015] were used. The level of

statistical significance was set at  $p < 0.05$  by Tukey. The extent of accumulation of elements into the peat of EP (as benchmark) was estimated by means of accumulation coefficients (Kac) calculated in relation to FF (EP/FF, as an input) and subsoil (EP/SS, as a past background) (Table 2).

### 4. RESULTS

The concentration of metallic elements in EP peats varies by soil types (Fig. 1). The content of the most studied metallic elements (Al, Pb, Hg and Cd) is higher in EP as compared with that of FF. In the forming of EP from FF, the concentration of Al and Pb was increased on an average 2.4–4.9 times, but that of Hg increased significantly only in peaty soils (on an average 1.5–1.7 times). The concentration of Zn were significantly decreased (Kac 0.1–0.5) in all soil groups, whereas that of Mg decreased only in more acid peats (groups II and IV). As regards the EP formation, the changes in the concentration of Cd in all soil groups, Hg in soil groups I and II and Mg in soil group I and III were not statistically proved or they remain approximately at the same level as compared with FF. The generalized decreasing order of elements' accumulation (>1 accumulated, <1 eliminated) is as follows: Al(2.9–4.9) > Pb(2.4–4.4) > Hg(1.1–1.7) > Cd(0.9–1.4) > Mg(0.5–1.0) > Zn(0.1–0.5).

The comparison of EP peats concentrations with SS data demonstrates a considerable accumulation of Pb, Cd, Zn and Hg into thin (~20 cm) superficial peat layer. Very high Kac in the case of peaty podzols shows their poorness in relation to the studied metallic elements. Mg content was significantly higher only in mires' SS peats; however, the differences in Al contents were not statistically proved. The richness of EP peats in relation to SS is characterised in mire soils (soil groups I and II) by the order Pb(2.9–5.8) > Cd(2.9–3.9) > Zn(2.3–3.3) > Hg(2.1–2.7) > Al(0.6–1.3) > Mg(0.8–0.9), and in peaty soils (III and IV) - Hg(2.0–16.8) > Pb(3.9–13.7) > Zn(2.7–10.6) > Cd(6.5–7.5) > Mg(1.0–2.7) > Al(0.7–1.4).

Table 2. Accumulation coefficients (Kac) of metallic elements into peaty epipedons (EP) of different soil groups

Kac <sup>1)</sup>	Soil group <sup>2)</sup>	Al	Mg	Pb	Zn	Hg	Cd
EP/FF	I	3.8* <sup>3)</sup>	1.03	2.4*	0.10*	1.25	0.88
	II	2.9*	0.54*	3.2*	0.25*	1.08	1.03
	III	4.9*	0.87	3.5*	0.47*	1.55*	1.44
	IV	4.8*	0.46*	4.4*	0.32*	1.74*	1.14
EP/SS	I	1.28	0.84*	5.8*	2.3*	2.1*	3.9*
	II	0.66	0.87*	2.9*	3.3*	2.7*	2.9*
	III	0.73	0.96	3.9*	2.7*	2.0*	6.5*
	IV	1.38	2.7*	13.7*	10.6*	16.8*	7.5*

1) FF – forest floor, SS – subsoil; 2) see Table 1; 3) \* indicates significant difference at the  $p < 0.05$  level

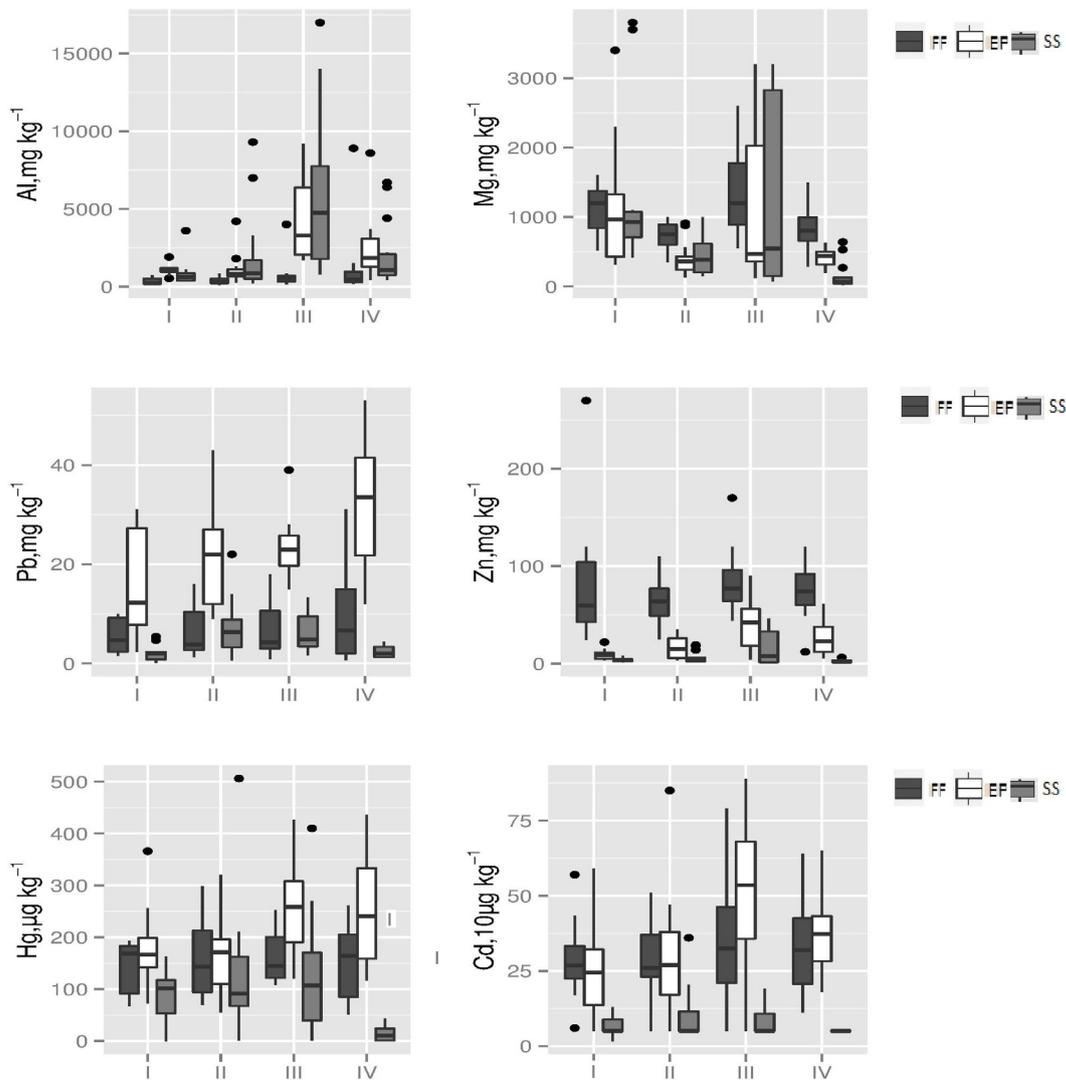


Fig. 1. Concentrations of metallic elements in the forest floor (FF), peaty epipedon (EP) and subsoil (SS) of fen soils (I), transitional bog soils (II), peaty gley soils (III) and peaty podzols (IV).

## 5. DISCUSSION AND CONCLUSIONS

The EP data (as benchmark level) reflect the properties of relatively young peat, which was formed under the influence of the past centuries' atmospheric–hydrologic, pedo-ecologic and anthropogenic conditions. The average EP age of peat soils is approximately 400–500 years [Valk 1988; Kõlli *et al.* 2009]. The age of peaty EP of wet mineral soils is more variable.

The concentration of elements in peaty EP is the function of annual forest debris composition and amount, peat-forming character, atmospheric sediments input rate, mineral dissolution from feeding water and forest fires [Görres, Frenzel 1997; Bendell-Young 2003; Malawska *et al.* 2006]. The significant influence of feeding water composition (among this laterally penetrating water) on the peat geochemistry and ecology was mentioned in numerous works [Valk 1988; Vitt, Chee 1990]. Most

of the studied soils were also influenced by drainage, which raises the decomposition rate of peat and causes the subsidizing of peat surface [Okruszko 1993].

The study revealed that the peat formation and chemistry depend on soil type. In very strongly acid meso- and oligotrophic peats of transitional bogs, the smallest values of most elements' contents were recorded. Owing to the low position of wet mineral soils on the landscape, they are to a great extent influenced by SS mineral sediments. The decomposition of FF and EP is accompanied with an increase in concentration of insoluble compounds in peat.

## ACKNOWLEDGEMENTS

*We thank Estonian Centre of Forest Protection and Silviculture for the project "BioSoil" data, collected under the framework of EC regulation Forest Focus.*

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