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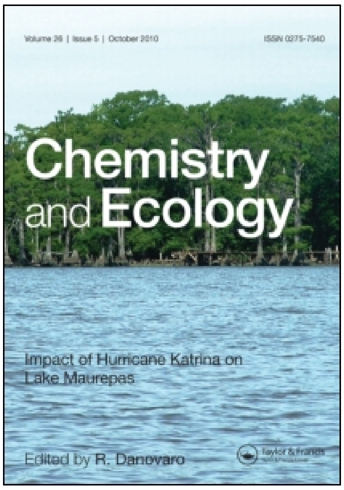

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Formation of the chemical composition of Histosols and histic soils in the forest lands of Estonia

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The formation and vertical distribution of the chemical properties of fen (group I, five research areas) and transitional bog (group II, eight research areas) Histosols, and situated depressions of mineral landscape Histic Gleysols (group III, six research areas) and Histic Podzols (group IV, seven research areas) soil covers were studied. As a benchmark in the comparative analysis of Histosols, we used the 20 cm epipedon peat layers of eutrophic moderately acid (I) and mesotrophic very strongly acid (II) types. The thickness of histic soil epipedon peat varied from 10 to 30 cm and was classified as slightly acid peaty mull (IIIa) or strongly acid peaty moder (IIIb), and as very strongly acid peaty mor (IV). In forming the epipedon of the forest floor, aqua regia (mixture of hydrochloridic and nitric acids, 3:1)-extractable Fe, Cr, Al, Pb and Ni accumulated to a great extent (accumulation coefficient >2.5), and S, Na and Hg accumulated to a medium extent (accumulation coefficient 1.2–2.0); the amounts of Zn, K and Mn decreased to a great extent (accumulation coefficient <0.5), and those of Mg and P to a medium extent (accumulation coefficient 0.6–0.8); levels of Ca, Cu and Cd remained practically unchanged. Comparison of Histosol subsoil and substratum peats with a Histosol epipedon demonstrates considerable accumulation of Mn, Pb, Cd, Zn, Hg and Na in the thin (20 cm) superficial peat layer of mires.

Keywords: peat soil; histic soil; heavy metals; fen; transitional bog; peat chemistry; forest floor; vertical peat chemistry profile

1. Introduction

Peatlands with Histosols (HS) and wet paludified mineral landscapes with histic Gleysol and histic Podzol soil cover are widely distributed in Nordic areas [1–3]. The formation, thickness, age and chemistry of superficial peat horizons of organic and mineral soils are widely variegated depending on local geological, pedoecological, hydrological and anthropogenic conditions [4–9]. The impact on peaty soil cover may be expressed by atmospheric sediments [10–13]. Noteworthy are processes connected with climate change [14,15].

Different aspects of peat chemistry (including the chemistry of superficial layers or peaty soil cover) have been studied, including general agrochemical characterisation and the levels of macro elements [16–20] and trace and/or hazardous elements [13,21–24], as well as biochemical aspects [25]. Research on the chemistry of peaty soils in Estonia has included studies of general

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(agrochemical) characteristics [16,26–29] and of the concentrations of different micro- and hazardous elements [23,24,30,31].

In Estonia, HS form 23.7% and histic soils (hS) 6.3% of the total area covered by soils [32,33]. Therefore, a peaty epipedon (EP) layer may be found on 30% of the land area. On forested peatlands, the EP is covered by a thin (1–10 cm) layer of forest floor (FF), which is not stabilised to the same extent as the peat layers of EP, subsoil and substratum. In a previous study [20], we analysed the general characteristics and chemical properties of different types of HS and hS soil cover peats. Our current study focuses on analysing the vertical distribution of the chemical properties of peat layers (from the forest floor to the substratum). Therefore, we pay special attention to comparative studies of peat formation from the forest floor and the vertical distribution of chemical properties. Fragments of similar treatments have also been found in some previous studies [10,25,34,35]. Detailed (layer-by-layer) analysis of the vertical distribution of the properties explains the processes of peat formation and elucidates the peculiarities of mire peat contamination.

The main objectives of our study were to: (1) characterise and compare the chemical composition and properties of the forest floor and peat of the EP; (2) evaluate the chemical properties and composition of subsoil in comparison with EP, i.e. the vertical distribution of the chemical properties within the peat soil profile; and (3) give a comparative characterisation of the chemical properties of the substratum (not belonging to soil cover). Our studies were conducted in HS on forested fens and transitional bogs, in histic Gleysols in paludified moderately acid mineral areas, and histic Podzols in very strongly acid mineral areas.

2. Research areas and objects

The distribution of research areas (RA) by Estonian counties is shown in Figure 1. Grouping of RAs by soils and location site, and other general information are given in Table 1. For analysis of peat

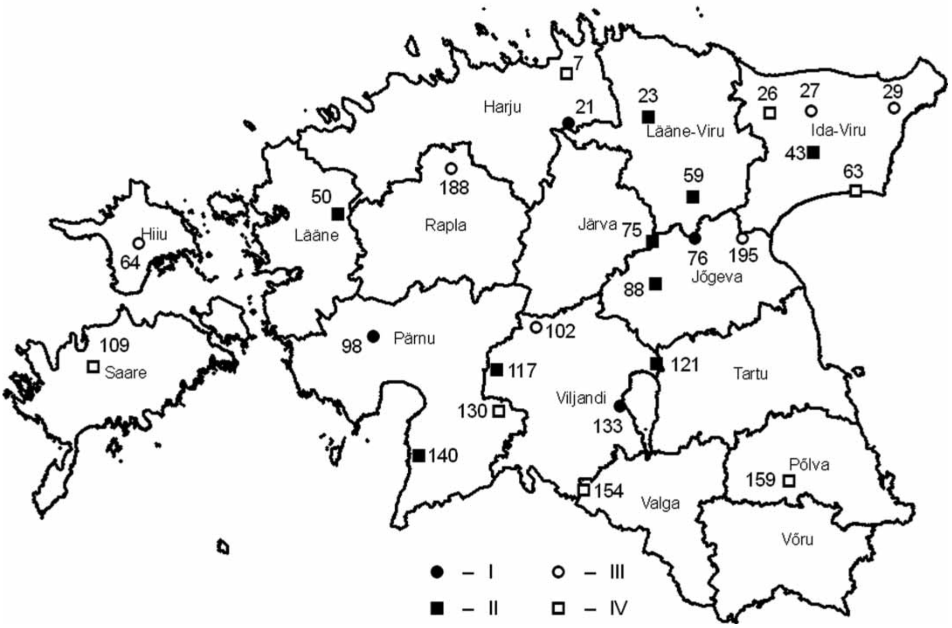

Figure 1. Location of research areas (RA) on a county map of Estonia. RA divisions and characterisations by soil groups (I–IV) are given in Table 1.

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Table 1. Distribution of research areas (RA) by soil groups and their general characterisation.

Soil group					
No.	Name	Site and RA number	Number of samples FF/EP/SS/SB[a]	Position on landscape and type of water feeding	Composition of tree layer[b], quality class
I	Histosols on fens	Mustjõe (21), Käru (59), Reastvere (76), Kuhu (98), Kalbuse (133)	8/10/5/5	Fed with ground and surface water minerotrophic-rich fen plains, closed depression of uplands and terrestrialised lakes	Bt6–7 Pn2 Al 1 Pc 1; III–IV
II	Histosols on transitional bogs	Neeruti (23), Mäetaguse (43), Jaakna (50), Tooma (75), Kaavere (88), Sandra (117), Meleski (121), Võidu (140)	13/17/8/8	Fed mostly on rainfall and mesotrophic seepage surface water mixotrophic bog plains edges and middle areas of fens	Pn7–8 Bt 2(Pc); IV–V
III	Histic Gleysols	Subgroup IIIa: Mustanina (29), Käina (64), Rassiku (195)	4/3/9/6	Depression bottoms (lowest parts) on landscape and transitional areas between mineral and organic soil covers; fed by minerotrophic surface water	Bt 5–6 Pc 1–4 Pn 1–3; II–IV
		Subgroup IIIb: Kalina (27), Rääka (102), Loone (188)	4/5/9/6		
IV	Histic Podzols	Vahastu (7), Aruvälja (26), Remniku (63), Aula-Vintri (109), Kanaküla (130), Taagepera (154), Mustjõe (159)	11/17/28/7	Depressions on poor sandy wet areas and between beach ridges; fed by minerotrophic and acid surface water	Pn 10 (Bt); III–V

Notes: [a]Samples taken from RA: FF, forest floor or litter (OL and OF); EP, peat of epipedon; SS, subsoil; SB, substrate. [b]Tree species: Bt, *Betula*; Pn, *Pinus*; Al, *Alnus*; Pc, *Picea* (numeral following the tree in formula – number of tenths).

properties, the soils in the RAs are divided into four groups; general ecological characterisations are given in Table 2. The peats of soil groups I and II are thick, those of groups III and IV are thin; the peats of groups I and III are slightly or moderately acid, and those of groups II and IV are very strongly acid.

The epipedon peat layer or EP is taken as the benchmark (baseline) when studying peat soil properties (Figure 2); in comparative analysis, EP is taken as H1 and H2 in HS and Hf, Hfs and Hs in hS. The properties of the benchmark EP layer are compared with: (1) forest floor (litter [OL] and fermented and partially decomposed subhorizons [OF]); and (2) subsoil and substrate layers.

3. Methods

3.1. *Sampling*

Soil sampling was carried out in 2006–2007 using methods elaborated for the 'Long-Range Transboundary Air Pollution' project [38]. The forest floor and its subhorizons (OL, OF) at the soil surface were sampled separately from the underlying peat layers. To sample the organic top layers (litter for all of soils and the peat layer of hS) a frame with a total surface area of 1000 cm^2 was used. The thickness of each organic top layer was measured separately. Soil sampling was carried out by fixed depth. For the zero line, in-depth measurements and HS sampling are taken from the boundary between the forest floor and the peat layers, and for hS, from between the peat and mineral layers. Both soils were sampled from the zero line using 0–10, 10–20, 20–40, 40–80 cm layers; in Figure 2, peat samples for HS are labelled H1–H4 and mineral soil samples are labelled M1–M4. Samples were taken from the wall of five soil pits, to form one composite sample for each layer in every RA. Soil sample preparation was based on the ISO 11464 method. Samples were air dried and living macroscopic roots and all particles, mineral and organic, with a diameter >2 mm were removed by dry sieving as a preparation for analysis. Organic layer samples were milled.

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3.2. *Chemical analyses*

Peat and mineral soil samples were analysed in the Environmental Research Laboratory (Tartu); the quality system follows the requirements of EVS-EN-/ISO/IEC 17025:2000. Moisture content was measured by gravimetric methods (105 °C, ISO 11465) and soil pH in $CaCl_2$ and H_2O by electrochemical methods using a soil/liquid mixture of 1 : 5 and a Jenway 3320 pH meter (ISO 10390). Total nitrogen (N_{total}) was determined by infrared (combustion at 1100 °C) using a Primacs-sc TOC Analyzer/Skalar (EN 13137). Organic carbon (C_{org}) was assayed spectrometrically by a modified Kjeldahl method using the titrimetric Kjeldec system (ISO 10048). Exchangeable (xch) and free H^+ (acidity) were analysed electrochemically by barium chloride extraction (titrated to pH 7.8); free H^+ acidity was determined using sodium fluoride (ISO 11260 and ISO 14254).

The levels of aqua regia (mixture of hydrochloridic and nitric acids, 3:1 [AR])-extractable (xtr) elements Ca, Mg, K, P, S, Na, Mn, Al, Fe, Pb, Cd, Cu, Zn, Cr, Ni and Hg, exchangeable (from barium chloride extraction) cations (xch) Ca, Mg, K, Na, Mn, Al and Fe, and acid ammonium oxalate extractable (rct) Fe and Al were assayed spectrometrically using inductively coupled plasma spectroscopy (ICP-AES Varian/USA, EN ISO 11885 and ISO 11466). A detailed description of the laboratory analyses is given in the abovementioned project manual [38]. All results are expressed as oven dry mass. Experiments were run in triplicate and the results averaged. All the chemicals used in this study were of analytical grade.

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Table 2. Pedo-ecological characterisation of investigated soil groups.

Group	Soil complex name[a]	EP acidity, pH_{CaCl_2}	Decomposition degree and type of EP	Type of epipedon[b]	Forest site type and quality class of pristine areas[c]	OL thickness[d] (cm)
I	Sapri-hemic and sapric Histosols [rheic, (endo)eutric, drainic, abruptic]	Moderately acid, 4.6–5.5	Very strong to moderate; sapric, saprihemic	Eutrophic peat	Minero-eutrophic fen, Oxalis drained fen, Alder–birch fen; III–IV	>100 (80–100)
II	Sapri-hemic, fibri-hemic and hemic Histosols (dystric, ombric, drainic, abruptic)	Very strongly acid, 2.6–3.5	Moderate; hemic, fibrihemic, saprihemic	Meso-trophic peat	Mesotrophic transitional bog, Myrtillus drained bog; IV–V	>100 (40–100)
III	(i) Sapri-histic Gleysols (endocalcaric, calcic, drainic, clayic, luvic)	Slightly acid, 5.5–6.4	Strong; sapric	Peaty mull	Rich paludified *Dryoptris* and *Filipendula* mixed forest; II–III	12–18
	(ii) Spodic sapri-histic Gleysols (dystric, arenic, drainic)	Strongly acid, 3.5–4.5	Strong; saprihemic	Peaty moder	Paludified *Polytrichum–Myrtillus* and *Carex* forests; III–IV	17–31
IV	Carbic histic Podzols (drainic, albic, ortsteinic, entic)	Very strongly acid, 2.6–3.5	Low to strong; hemic, fibrihemic	Peaty mor	Poor paludified *Vaccinium ulginosum* and *Polytrichum–Myrtillus* forests; III–V	17–27

Notes: [a]FAO [2]. [b]Kõlli [36]. [c]Lõhmus [37]. [d]Total thickness of organic layers (OL) used in characterisation of peaty soil cover. EP, peat of epipedon.

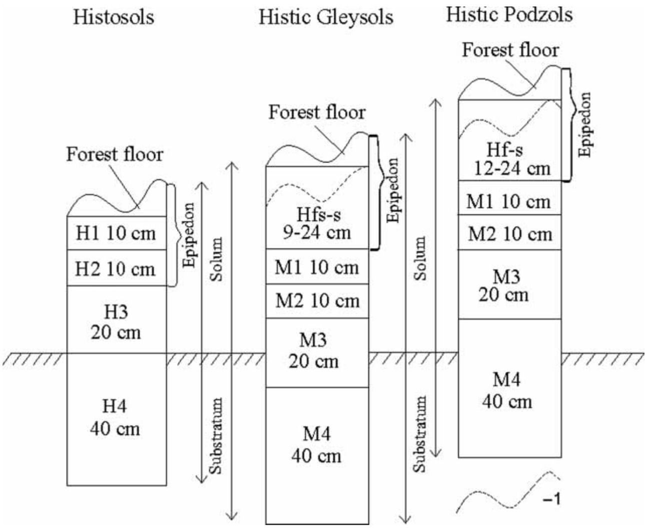

Figure 2. Conceptual schema of sampling and characterisation of Histosols, histic Gleysols and histic Podzols.

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3.3. *Statistical analysis*

The Statistica 7 program was used for statistical analysis. Two-way analysis of variance, followed by the Student's test of homogenous groups, was used to process the collected data. The level of statistical significance of differences between vertical layers was set at $p < 0.05$.

4. Results

4.1. *Comparative analysis of FF and EP chemistry*

The treated characteristics (33) of FF and EP (as the benchmark) and their statistical parameters are given in Table 3. In most cases, the coefficient of variation (CV) of FF characteristics is lower than that of EP characteristics. The exceptions are the CV values for exchangeable Fe (Fe-xch) and AR-extractable Pb (Pb-xtr) content. The CV value was approximately the same for C : N, Al-xtr and reactive Al (Al-rct). The large differences between the minimum and maximum limits of characteristics may be caused by soil peculiarities, which may be elucidated by comparing them at a more detailed (soil group) level. Some variability may also be caused by external influences (hydrological conditions, atmospheric emissions and anthropogenic stress).

Comparison of the arithmetical means of FF characteristics with means for EP show remarkably higher levels of xtr, rct and xch Al and Fe, as well of Pb, Hg, Cr, Cd, Ni, S and ash, in EP. The levels of Mg, K, Mn, P, Zn and Cu are generally higher in FF than in EP. Indices of acidity (pH, Ac-xch and free H^+) demonstrate higher acidity in EP than in FF.

Comparison of the properties and contents of FF and EP by soil group (Tables 4 and 5) generally supports the above differences, but also shows that in one or another soil group these differences are not significant. For example, the increase in Al-xch and Fe-xch in EP compared with FF is statistically significant only in histic Podzols (group IV) and for Fe-xch in transitional bog soils (group II).

With rare exceptions, it may be concluded that during peat formation from FF, levels of Fe, Al, Pb, Ni and ash increase significantly (accumulated), but levels of K and Zn decrease in all soil groups. The amount of S increased and that of Cu decreased in HS (groups I and II) peats; Mn,

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Table 3. Statistical analysis of forest floor and epipedon peats' characteristics.

		Forest floor					Peat of epipedon ($n = 52$)			
					Limits				Limits	
Characteristics	Units	n	Mean	CV	Min.	Max.	Mean	CV	Min.	Max.
Ash	$g \cdot kg^{-1}$	40	44	60	17	138	122	102	8	513
C_{org}	$g \cdot kg^{-1}$	40	479	7	414	568	442	17	202	543
N_{tot}	$g \cdot kg^{-1}$	40	15.2	24	7.3	22.0	17.9	38	9.0	35.4
C : N	ratio	40	34.1	34	19.9	69.2	27.3	32	11.4	48.8
pH_{CaCl_2}		40	4.2	16	3.0	5.8	3.6	30	2.5	6.4
pH_{H_2O}		16	4.6	16	3.7	6.2	4.3	22	3.2	6.6
Ac-xch	$mmol \cdot kg^{-1}$	16	70	52	5	145	110	65	1	250
Free H^+	$mmol \cdot kg^{-1}$	16	66	51	1	128	83	72	1	220
Ca-xtr	$g \cdot kg^{-1}$	40	9.7	58	3.2	25.0	9.6	125	0.6	53.0
Mg-xtr	$mg \cdot kg^{-1}$	40	984	46	350	2600	672	109	120	3400
K-xtr	$mg\ kg^{-1}$	40	1035	38	490	1900	398	71	64	1000
Na-xtr	$mg \cdot kg^{-1}$	40	44	41	16	93	64	50	23	200
P-xtr	$mg\ kg^{-1}$	40	758	27	340	1200	649	48	180	1900
S-xtr	$g \cdot kg^{-1}$	40	1.4	32	0.6	2.5	2.1	40	0.8	4.7
Mn-xtr	$mg\ kg^{-1}$	40	374	74	78	1400	176	256	2	2300
Al-xtr	$g \cdot kg^{-1}$	40	0.5	120	0.1	4.0	2.2	101	0.2	9.2
Fe-xtr	$g\ kg^{-1}$	40	0.7	126	0.1	4.5	4.5	191	0.4	49.0
Ca-xch	$mmol \cdot kg^{-1}$	16	306	73	130	990	368	114	26	1500
Mg-xch	$mmol \cdot kg^{-1}$	16	55	67	22	170	39	95	6	200
K-xch	$mmol \cdot kg^{-1}$	16	16.0	35	9.0	29.0	6.1	78	0.1	18.0
Na-xch	$mmol \cdot kg^{-1}$	16	2.3	50	1.0	5.5	2.3	71	0.5	7.7
Mn-xch	$mmol \cdot kg^{-1}$	16	6.4	90	2.1	24.0	0.9	151	0.0	5.7
Al-xch	$mmol \cdot kg^{-1}$	16	6	68	0	19	26	105	0	100
Fe-xch	$mmol \cdot kg^{-1}$	16	0.8	172	0.1	5.4	2.7	85	0.0	9.5
Al-rct	$10\,mg \cdot kg^{-1}$	16	42	104	15	190	124	99	9	660
Fe-rct	$10\,mg \cdot kg^{-1}$	16	59	89	20	230	282	167	20	2500
Cd-xtr	$10\,\mu g \cdot kg^{-1}$	40	31.0	52	5.0	79.0	34.8	58	5.0	89.0
Pb-xtr	$mg \cdot kg^{-1}$	40	6.6	82	0.7	19.0	24.3	50	2.4	53.0
Hg-xtr	$\mu g \cdot kg^{-1}$	40	153	41	51	299	213	44	55	436
Cr-xtr	$mg \cdot kg^{-1}$	40	2.3	96	0.4	13.0	10.4	207	0.5	110.0
Ni-xtr	$mg \cdot kg^{-1}$	40	1.7	74	0.1	6.6	4.4	149	0.6	32.0
Cu-xtr	$mg \cdot kg^{-1}$	40	5.4	38	1.5	14.0	5.0	107	1.2	37.0
Zn-xtr	$mg \cdot kg^{-1}$	40	78.2	55	24.0	270.0	21.9	87	3.0	90.0

Notes: org, organic; tot, total; xch, exchangeable; xtr, extractable; rct, reactive; Ac-xch, exchangeable acidity; CV, coefficient of variation.

Ca, Mg and P content and pH decreased. However, exchangeable acidity is increased in strongly acid soils (groups II, IV), and the amounts of Hg and Cr increased and C_{org} decreased in hS EP (groups III, IV). The amounts of Na and Cd and the C : N ratio do not differ significantly between FF and EP. Some peculiarities may be noted when comparing FF and EP characteristics in group I soils: namely, a considerable increase in N_{tot}, Ca (xtr, xch), Fe (xtr, rct) and pH, but decreased exchangeable acidity and free H^+ on peat formation.

The mean decrease in levels of AR extracted elements (percentages are given in parentheses) are: Ca(63) $>$ S(9) $>$ K(7) $>$ Mg(6) $>$ P(5) $>$ Fe(4) $>$ Al(3) $>$ Mn(2) $>$ Na($<$1) in FF, and Ca(47) $>$ Fe(22) $>$ Al(11) $>$ S(10) $>$ Mg(3) $\geq$ P(3) $>$ K(2) $>$ Mn(1) $>$ Na($<$1) in EP.

Comparison of the mean element content for FF and EP demonstrates the accumulation (increase) of Fe, Al, S and Na, and the elimination (decrease) of K, Mn, Mg and P during peat-forming processes. The accumulation coefficients (the element content ratio EP/FF is given in parentheses) decrease in the following order: Fe(6.4) $>$ Al(4.4) $>$ S(1.5) $>$ Na(1.4) $>$ Ca(1.0) $>$ P(0.8) $>$ Mg(0.7) $>$ Mn(0.5) $>$ K(0.4).

The heavy metal content decreases in the following order: Zn(82.6) $>$ Pb(7.0) $>$ Cu(5.7) $>$ Cr(2.4) $>$ Ni(1.8) $>$ Cd(0.3) $>$ Hg(0.2), in FF, and Pb(36.5) $>$ Zn(32.9) $>$ Cr(15.5) $>$

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Table 4. Comparison of general characteristics and the contents of aqua regia extractable elements in forest floor (FF) and in epipedons' peat (EP) by soil groups.

		Histosols				Histic soils			
		Group I		Group II		Group III		Group IV	
Characteristic	Unit	FF $n = 8$	EP $n = 10$	FF $n = 13$	EP $n = 17$	FF $n = 8$	EP $n = 8$	FF $n = 11$	EP $n = 17$
General characteristics									
Ash	g·kg $^{-1}$	40^{a}	114^{b}	29^{a}	34^{a}	78^{a}	256^{b}	38^{a}	151^{b}
C_{org}	g·kg $^{-1}$	478^{a}	470^{a}	483^{a}	495^{a}	454^{b}	351^{a}	493^{b}	415^{a}
N_{tot}	g·kg $^{-1}$	16.3^{a}	29.8^{b}	14.4^{a}	15.7^{a}	16.0^{a}	15.4^{a}	14.6^{a}	14.1^{a}
C : N	ratio	31.8^{a}	16.2^{a}	36.2^{a}	32.9^{a}	29.7^{a}	23.6^{a}	36.4^{a}	30.0^{a}
pH_{CaCl_2}		4.4^{a}	4.9^{a}	3.8^{b}	2.9^{a}	5.0^{a}	4.4^{a}	4.0^{b}	3.1^{a}
pH_{H_2O}		4.7^{a}	5.5^{b}	4.0^{a}	3.8^{a}	6.2^{a}	5.0^{a}	4.5^{b}	3.8^{a}
Ac-ch	mmol^{+}·kg^{-1}	43.0^{b}	11.8^{a}	93.7^{a}	149.1^{b}	37.0^{a}	93.1^{a}	69.8^{a}	135.8^{b}
Free H^{+}	mmol^{+}·kg^{-1}	42.3^{b}	6.8^{a}	87.5^{a}	125.8^{a}	34.8^{a}	61.4^{a}	68.2^{a}	96.2^{a}
Aqua regia-extractable elements									
Ca	g·kg^{-1}	13.4^{a}	28.8^{b}	5.9^{b}	3.7^{a}	15.8^{a}	11.3^{a}	7.1^{b}	3.3^{a}
Mg	mg·kg^{-1}	1136^{a}	1168^{a}	733^{b}	397^{a}	1351^{a}	1169^{a}	902^{b}	420^{a}
K	mg·kg^{-1}	886^{b}	150^{a}	857^{b}	248^{a}	1278^{b}	604^{a}	1176^{b}	598^{a}
Na	mg·kg^{-1}	38.0^{a}	58.5^{a}	45.9^{a}	57.0^{a}	50.4^{a}	74.6^{a}	41.5^{a}	69.3^{b}
P	mg·kg^{-1}	699^{a}	659^{a}	656^{b}	455^{a}	880^{a}	965^{a}	831^{b}	687^{a}
S	g·kg^{-1}	1.47^{a}	3.25^{b}	1.33^{a}	1.79^{b}	1.63^{a}	2.00^{a}	1.38^{a}	1.76^{a}
Mn	mg·kg^{-1}	640^{a}	315^{a}	287^{b}	10^{a}	334^{a}	652^{a}	313^{b}	36^{a}
Al	g·kg^{-1}	0.34^{a}	1.16^{b}	0.40^{a}	1.07^{b}	0.92^{a}	4.45^{b}	0.58^{a}	2.87^{b}
Fe	g·kg^{-1}	0.48^{a}	12.80^{b}	0.47^{a}	1.21^{b}	1.30^{a}	6.59^{b}	0.63^{a}	1.82^{b}

Note: Letters following the data indicate significant difference between FF and EP at the $p < 0.05$ level.

Table 5. Comparison of exchangeable cations, reactive Al and Fe and aqua regia-extractable heavy metals in forest floor (FF) and in epipedons' peat (EP) by soil groups.

		Histosols				Histic soils			
		Group I		Group II		Group III		Group IV	
Elements	Units	FF $n = 8$	EP $n = 10$	FF $n = 13$	EP $n = 17$	FF $n = 8$	EP $n = 8$	FF $n = 11$	EP $n = 17$
Exchangeable (xch) cations and reactive (rct) Al and Fe									
Ca-xch	mmol^{+}·kg^{-1}	457^{a}	1062^{b}	183^{a}	150^{a}	610^{a}	461^{a}	240^{b}	135^{a}
Mg-xch	mmol^{+} · kg^{-1}	65.3^{a}	72.7^{a}	39.8^{a}	27.0^{a}	102.0^{a}	52.1^{a}	47.2^{b}	25.3^{a}
K-xch	mmol^{+}·kg^{-1}	14.7^{b}	2.3^{a}	14.7^{b}	4.4^{a}	12.5^{b}	6.0^{a}	19.8^{b}	10.1^{a}
Na-xch	mmol^{+}·kg^{-1}	2.8^{a}	2.3^{a}	2.4^{a}	1.8^{a}	1.4^{a}	1.9^{a}	2.3^{a}	2.9^{a}
Mn-xch	mmol^{+}·kg^{-1}	11.4^{b}	1.4^{a}	5.3^{b}	0.2^{a}	2.5^{a}	1.3^{a}	6.3^{b}	0.9^{a}
Al-xch	mmol^{+}·kg^{-1}	5.7^{a}	4.6^{a}	7.5^{a}	20.2^{a}	3.4^{a}	23.2^{a}	6.8^{a}	44.2^{b}
Fe-xch	mmol^{+}·kg^{-1}	0.2^{a}	0.6^{a}	1.3^{a}	3.2^{b}	0.3^{a}	1.5^{a}	0.7^{a}	4.1^{b}
Al-rct	10 mg·kg^{-1}	17^{a}	50^{b}	28^{a}	73^{a}	112^{a}	193^{a}	46^{a}	187^{b}
Fe-rct	10 mg·kg^{-1}	48^{a}	835^{b}	45^{a}	99^{b}	139^{a}	337^{a}	52^{a}	115^{b}
Aqua regia-extractable heavy metals									
Cd	10 μg·kg^{-1}	28.9^{a}	25.4^{a}	28.0^{a}	29.6^{a}	35.5^{a}	51.3^{a}	33.0^{a}	37.6^{a}
Pb	mg·kg^{-1}	5.5^{a}	16.1^{b}	6.3^{a}	20.8^{b}	6.9^{a}	24.0^{b}	7.5^{a}	32.8^{b}
Hg	μg·kg^{-1}	142^{a}	178^{a}	159^{a}	174^{a}	164^{a}	255^{b}	145^{a}	252^{b}
Cr	mg·kg^{-1}	1.6^{a}	2.2^{a}	1.7^{a}	2.3^{a}	2.6^{a}	12.0^{b}	3.5^{a}	22.7^{b}
Ni	mg·kg^{-1}	1.0^{a}	2.1^{b}	1.5^{a}	1.7^{a}	1.9^{a}	5.0^{b}	2.4^{a}	8.2^{b}
Cu	mg·kg^{-1}	4.8^{b}	3.4^{a}	4.6^{b}	2.7^{a}	7.2^{a}	11.5^{a}	5.4^{a}	5.2^{a}
Zn	mg·kg^{-1}	88.6^{b}	9.1^{a}	65.7^{b}	17.1^{a}	87.4^{b}	40.8^{a}	78.7^{b}	25.5^{a}

Note: Letters following the data indicate significant difference between FF and EP at the $p < 0.05$ level.

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Cu(7.5) > Ni(6.6) > Cd(0.5) > Hg(0.3), in EP. However, heavy element accumulation (where > 1 = accumulated, < 1 = eliminated) decreases in the order: Cr(4.5) > Pb(3.7) > Ni(2.6) > Hg(1.4) > Cd(1.1) > Cu(0.9) > Zn(0.3).

In the EP composition, the majority of exchangeable basic cations are Ca and Mg, but a modest role is played by K and Na. From the sum of exchangeable acid cations, the biggest share belongs to H^+ and Al^{3+}, and a modest part is played by Mn and Fe. However, the order of accumulation of exchangeable cations in the EP-forming process decreases as: Al(4.3) > Fe(3.4) > Ca(1.2) > H(1.2) > Na(1.0) > Mg(0.7) > K(0.4) > Mn(0.1).

4.2. *Vertical distribution of chemical characteristics in the profiles of Histosols and histic soils*

In the profile (from EP to substratum peat) of both group I and II HS, a statistically significant decrease is observed for exchangeable and free acidity, AR-extractable K, P, Cd, Pb, Hg and Zn level, and in exchangeable K content (Tables 6 and 7). In both HSs, only pH and Cu content increase significantly with depth. Neither significant decreases nor increases were observed in the vertical distribution of N, Na, S, Al and Mg content; their levels remain approximately the same (with some small changes) in all horizons. In addition, levels of ash, Ca, Cr and Ni decreased significantly at much deeper peat layers in transitional bog soils. In sapric Histosols, in which Mn and Fe levels are relatively high in the superficial layers, a significant decrease is observed in the deeper layers, along with an increase in organic C and Mg content and C : N ratio.

The chemical characterisation of subsoil (H3) and substratum (H4) peat of HS by soil groups (I, II) and mean HS is given in Tables 6 and 7. Comparison of these data with peat benchmark layers (H1 + H2) in percentage terms enables elucidation of the relative increase or decrease in peat characteristics over the vertical distribution. Analysis reveals that Mn, Pb, Cd, Zn and K(xch) decrease to a greater extent (by ∼70% or approximately to <30%) in subsoil and substratum.

Table 6. Vertical distribution of general characteristics and contents of aqua regia-extractable elements in peat of Histosols.

		Group I			Group II			Histosols		
Characteristic	Units	H1 + H2 $n = 10$	H3 $n = 5$	H4 $n = 5$	H1 + H2 $n = 17$	H3 $n = 8$	H4 $n = 8$	H1 + H2 $n = 27$	H3 $n = 13$	H4 $n = 13$
General characteristics										
Ash	$g \cdot kg^{-1}$	114^a	85^a	101^a	34^a	54^{ab}	97^b	63^a	66^a	98^{ab}
C_{org}	$g \cdot kg^{-1}$	470^a	511^b	496^{ab}	495^a	492^a	486^a	485^a	499^a	490^a
N_{tot}	$g \cdot kg^{-1}$	29.8^a	26.1^a	24.0^a	15.7^a	15.8^a	16.1^a	20.9^{ab}	19.8^a	19.1^a
C : N	ratio	16.2^a	20.8^{ab}	22.3^b	32.9^a	34.0^a	34.4^a	26.7^a	28.9^a	29.7^a
pH_{CaCl_2}		4.9^a	5.2^a	5.3^a	2.9^a	3.2^{ab}	3.7^b	3.7^a	4.0^{ab}	4.3^b
pH_{H_2O}		5.5^a	5.9^a	6.0^a	3.8^a	4.1^{ab}	4.6^b	4.5^a	4.8^{ab}	5.1^b
Exch. acid	$mmol^+ \cdot kg^{-1}$	12^b	4^{ab}	0^a	149^b	121^{ab}	85^a	98^b	76^{ab}	53^a
Free H^+	$mmol^+ \cdot kg^{-1}$	7^b	0^a	0^a	126^b	95^{ab}	63^a	82^b	58^{ab}	39^a
Aqua regia-extractable elements										
Ca	$g \cdot kg^{-1}$	28.8^{ab}	27.0^a	25.8^a	3.7^a	5.7^{ab}	8.7^b	13.0^a	13.9^a	15.3^{ab}
Mg	$mg \cdot kg^{-1}$	1168^a	1326^a	1452^{ab}	398^a	416^a	491^{ab}	683^a	766^a	861^a
K	$mg \cdot kg^{-1}$	145^b	50^a	153^b	248^{ab}	93^a	90^a	212^b	76^a	114^a
Na	$mg \cdot kg^{-1}$	58^a	53^a	55^a	57^a	51^a	46^a	58^a	52^a	50^a
P	$mg \cdot kg^{-1}$	659^b	344^{ab}	268^a	455^{ab}	310^a	321^a	530^b	323^a	301^a
S	$g \cdot kg^{-1}$	3.2^a	3.1^a	3.9^{ab}	1.8^a	1.9^a	2.0^a	2.3^a	2.4^a	2.7^{ab}
Mn	$mg \cdot kg^{-1}$	315^b	78^{ab}	53^a	10^a	5^a	12^a	123^a	33^a	28^a
Al	$g \cdot kg^{-1}$	1.2^a	0.7^a	1.1^a	1.1^a	1.5^a	2.3^a	1.1^a	1.2^a	1.8^a
Fe	$g \cdot kg^{-1}$	12.8^b	4.9^{ab}	4.2^a	1.2^a	1.5^a	2.1^a	5.5^a	2.8^a	2.9^a

Note: Letters following the data indicate significant difference in vertical distribution at the $p < 0.05$ level.

Table 7. Vertical distribution of exchangeable cations, reactive Al and Fe and aqua regia-extractable heavy metals in peat of Histosols.

		Group I			Group II			Histosols		
Elements	Units	H1 + H2 $n = 10$	H3 $n = 5$	H4 $n = 5$	H1 + H2 $n = 17$	H3 $n = 8$	H4 $n = 8$	H1 + H2 $n = 27$	H3 $n = 13$	H4 $n = 13$
Exchangeable (xch) cations and reactive (rct) Al and Fe										
Ca-xch	mmol$^{+}\cdot$kg^{-1}	1062^{a}	1044^{a}	1024^{a}	150^{a}	232^{ab}	364^{b}	488^{a}	544^{a}	618^{ab}
Mg-xch	mmol$^{+}\cdot$kg^{-1}	73^{a}	82^{a}	97^{ab}	27^{a}	29^{a}	34^{ab}	44^{a}	49^{a}	58a^{b}
K-xch	mmol$^{+}\cdot$kg^{-1}	2.3^{b}	1.3^{ab}	0.5^{a}	4.4^{b}	1.2^{ab}	0.8^{a}	3.6^{b}	1.2^{a}	0.7^{a}
Na-xch	mmol$^{+}\cdot$kg^{-1}	2.3^{a}	2.3^{a}	3.1^{a}	1.8^{a}	1.9^{a}	2.1^{a}	2.0^{a}	2.0^{a}	2.5^{a}
Mn-xch	mmol$^{+}\cdot$kg^{-1}	1.4^{b}	0.4^{a}	0.4^{a}	0.2^{a}	0.1^{a}	0.2^{a}	0.7^{a}	0.2^{a}	0.3^{a}
Al-xch	mmol$^{+}\cdot$kg^{-1}	4.6^{a}	3.7^{a}	3.7^{a}	20.2^{a}	21.3^{a}	24.7^{a}	14.4^{a}	16.6^{a}	14.5^{a}
Fe-xch	mmol$^{+}\cdot$kg^{-1}	0.6^{a}	0.3^{a}	0.2^{a}	3.2^{a}	2.7^{a}	2.1^{a}	2.2^{a}	1. 8^{a}	1.4^{a}
Al-rct	10 mg$\cdot$ kg^{-1}	50^{a}	35^{a}	44^{a}	73^{a}	105^{a}	165^{a}	64^{a}	78^{a}	118^{a}
Fe-rct	10 mg$\cdot$ kg^{-1}	835^{b}	422^{ab}	343^{a}	99^{a}	130^{a}	198^{a}	371^{a}	242^{a}	254^{a}
Aqua regia-extractable heavy metals										
Cd	10 μg$\cdot$ kg^{-1}	25.4^{b}	7.5^{a}	5.4^{a}	29.6^{b}	9.8^{a}	10.2^{a}	28.1^{b}	8.9^{a}	8.4^{a}
Pb	mg$\cdot$ kg^{-1}	16.1^{b}	3.2^{a}	1.0^{a}	20.8^{b}	8.5^{a}	5.8^{a}	19.1^{b}	6.5^{a}	4.0^{a}
Hg	μg$\cdot$ kg^{-1}	178^{b}	100^{ab}	72^{a}	174^{ab}	114^{a}	138^{a}	175^{b}	108^{a}	113^{a}
Cr	mg$\cdot$ kg^{-1}	2.2^{a}	1.2^{a}	2.7^{a}	2.3^{a}	2.4^{ab}	11.3^{b}	2.3^{a}	1.9^{a}	8.0^{b}
Ni	mg$\cdot$ kg^{-1}	2.1^{a}	1.4^{a}	2.3^{a}	1.7^{ab}	1.2^{a}	4.1^{b}	1.8^{a}	1.3^{a}	3.4^{ab}
Cu	mg$\cdot$ kg^{-1}	3.4^{a}	3.0^{a}	4.2^{ab}	2.7^{a}	3.4^{ab}	6.6^{b}	3.0^{a}	3.3^{a}	5.7^{b}
Zn	mg$\cdot$ kg^{-1}	9.1^{b}	3.8^{a}	4.0^{ab}	17.1^{b}	8.0^{ab}	3.8^{a}	14.1^{b}	6.4^{a}	3.9^{a}

Note: Letters following the data indicate significant difference in vertical distribution at the $p < 0.05$ level.

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Exchangeable and free acidity, and the concentration of Fe(xtr, xch), P and K(xtr) are decreased to approximately half. Concentrations of Hg, Fe(rct) and Na(xtr) are decreased to a remarkable level (10–40%) also. C_{org}, N_{tot} and Al(xch) remained at approximately the same level (±10%). A considerable increase (10–50%) was observed for ash, Ca, Mg, S and Na(xch) content, as well as peat pH and the C : N ratio. Statistically proven are prompt increases in Cr, Ni and Cu in substratum peat, although their levels were decreased in subsoil peat. The considerable increase (>160%) in Al(xtr, rct) was not statistically significant.

In hS, where EP is underlain by mineral horizons (M1 and M2), the amounts of most of the studied elements decreased significantly (Table 8). An exception was the decrease in AR-extractable Mg, K, Al and Fe in mineral soil compared with peat horizons of hS, which was not proved statistically. Moreover, acidity indices show a significant decrease along the vertical profile from EP to the substratum. It should also be mentioned that in the mineral part of hS, levels of Ca, Mg, K, P, Mn and Fe(rct) and pH increased with depth, but exchangeable Al and acidity, and the free acidity of C and N decreased. The amounts of exchangeable Ca, Mg, K, Na, Mn and Fe decreased slightly (nonsignificantly) or fluctuated at the same level.

Comparison of the superficial mineral layers (M1 + M2) with the peat benchmark layer (H) enables elucidation of a relative decrease or increase in peat characteristics from organic soil to mineral. C_{org}, N_{tot} and S, exchangeable Fe, K, Na and Mn, and free acidity decreased by <10%. Ca, P, Mn and Mg(xch) content, exchangeable acidity and most heavy metals (Pb, Cd, Cr, Ni, Hg and Zn) showed decreases of 10–30% from benchmark (H) levels. Considerable decreases (of 20–60%) from benchmark levels were seen for extractable K, Na and Cu, Al(xch, rct) and Fe(rct). Extractable Al, Fe and Mg are increased in group III soil, but decreased in group IV soil.

The chemical characterisation of subsoil (M1, M2, M3) and substratum (M4) mineral materials of hS by soil groups (III, IV) and hS mean is given in Table 9. These data enable us to follow vertical changes in the mineral part of the hS profile. Of course, in this aspect, characteristics connected with soil organic matter (C_{org}, N_{tot}, S) and some exchangeable cations (Ca, Mg) are considerably decreased. Clear changes are connected with soil acidity, which resulted in increased

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Table 8. Comparative analysis of histic soils' chemical characteristics in peat and underlying mineral soil.

		Histic Gleysols		Histic Podzols		All histic soils	
Characteristic	Unit	H $n = 8$	M1 + M2 $n = 18$	H $n = 17$	M1 + M2 $n = 21$	H $n = 25$	M1 + M2 $n = 39$
C_{org}	$\mathrm{g\cdot kg^{-1}}$	351^b	38^a	415^b	12^a	394^b	24^a
N_{tot}	$\mathrm{g\cdot kg^{-1}}$	15.4^b	2.1^a	14.1^b	0.5^a	14.5^b	1.2^a
C : N	ratio	23.6^a	18.7^a	30.0^a	26.3^a	28.0^a	22.8^a
pH_{CaCl_2}		4.4^a	5.2^b	3.1^a	3.6^b	3.5^a	4.4^b
pH_{H_2O}		5.0^a	5.7^b	3.8^a	4.5^{ab}	4.2^a	5.1^b
Ac-xch	$\mathrm{mmol^{+}\cdot kg^{-1}}$	93.1^b	13.7^a	135.8^b	24.9^a	122.1^b	19.7^a
Free H^+	$\mathrm{mmol^{+}\cdot kg^{-1}}$	61.4^b	3.3^a	96.2^b	6.8^a	85.1^b	5.2^a
Ca-xtr	$\mathrm{g\cdot kg^{-1}}$	11.3^b	4.0^a	3.3^b	0.2^a	5.8^b	1.9^a
Mg-xtr	$\mathrm{mg\cdot kg^{-1}}$	1169^a	1701^a	420^b	198^a	660^a	887^a
K-xtr	$\mathrm{mg\cdot kg^{-1}}$	604^a	647^a	598^b	300^a	600^a	460^a
Na-xtr	$\mathrm{mg\cdot kg^{-1}}$	75^a	53^a	69^b	29^a	71^b	40^a
P-xtr	$\mathrm{mg\cdot kg^{-1}}$	965^b	358^a	687^b	79^a	776^b	208^a
S-xtr	$\mathrm{g\cdot kg^{-1}}$	2.0^b	0.5^a	1.8^b	0.1^a	1.8^b	0.2^a
Mn-xtr	$\mathrm{mg\cdot kg^{-1}}$	652^b	130^a	36^b	19^a	233^b	70^a
Al-xtr	$\mathrm{g\cdot kg^{-1}}$	4.4^a	6.0^a	2.9^a	2.1^a	3.4^a	3.9^a
Fe-xtr	$\mathrm{g\ kg^{-1}}$	6.6^a	6.7^a	1.8^b	0.9^a	3.4^a	3.5^a
Ca-xch	$\mathrm{mmol^{+}\cdot kg^{-1}}$	461^b	113^a	135^b	2^a	239^b	53^a
Mg-xch	$\mathrm{mmol^{+}\cdot kg^{-1}}$	52^b	17^a	25^b	0^a	34^b	8^a
K-xch	$\mathrm{mmol^{+}\cdot kg^{-1}}$	6.0^b	1.0^a	10.1^b	0.2^a	8.7^b	0.5^a
Na-xch	$\mathrm{mmol^{+}\cdot kg^{-1}}$	1.9^b	0.3^a	2.9^b	0.1^a	2.6^b	0.2^a
Mn-xch	$\mathrm{mmol^{+}\cdot kg^{-1}}$	1.3^b	0.1^a	0.9^b	0^a	1.0^b	0.1^a
Al-xch	$\mathrm{mmol^{+}\cdot kg^{-1}}$	23.2^b	10.1^a	44.2^b	17.6^a	37.5^b	14.1^a
Fe-xch	$\mathrm{mmol^{+}\cdot kg^{-1}}$	1.5^b	0.2^a	4.1^b	0.1^a	3.3^b	0.1^a
Al-rct	$\mathrm{10\ mg\cdot kg^{-1}}$	193^a	148^a	187^b	96^a	189^b	120^a
Fe-rct	$\mathrm{10\ mg\cdot kg^{-1}}$	336^b	143^a	115^b	20^a	186^b	77^a
Cd-xtr	$\mathrm{10\ \mu g\cdot kg^{-1}}$	51.3^b	7.9^a	37.7^b	5.0^a	42.0^b	6.4^a
Pb-xtr	$\mathrm{mg\cdot kg^{-1}}$	24.0^b	6.2^a	32.8^b	2.4^a	30.0^b	4.1^a
Hg-xtr	$\mathrm{\mu g\cdot kg^{-1}}$	255^b	128^a	252^b	15^a	253^b	68^a
Cr-xtr	$\mathrm{mg\cdot kg^{-1}}$	12.0^a	7.6^a	22.7^b	1.8^a	19.2^b	4.5^a
Ni-xtr	$\mathrm{mg\cdot kg^{-1}}$	5.0^a	3.4^a	8.2^b	0.2^a	7.2^b	1.7^a
Cu-xtr	$\mathrm{mg\cdot kg^{-1}}$	11.5^b	5.6^a	5.2^b	1.0^a	7.2^b	3.2^a
Zn-xtr	$\mathrm{mg\cdot kg^{-1}}$	40.8^b	15.3^a	25.5^b	2.4^a	30.4^b	8.4^a

Notes: Letters following the data indicate significant difference at the $p < 0.05$ level. org, organic; tot, total; xch, exchangeable; xtr, extractable; rct, reactive; Ac-xch, exchangeable acidity.

pH and decreased exchangeable and free acidity. Levels of extractable Ca, Mg and K increased to a large extent (3–5 times), and levels of P, Mn(xtr), Fe(rct) and Al(rct) increased to a lesser extent. The vertical distribution of heavy metals in the lower part of the hS mineral profile (M3, M4) was not studied.

5. Discussion and conclusions

5.1. *Pedo-ecological analysis and comparison of received results*

In characterising peat soil chemical properties, EP is taken as the benchmark, i.e. the superficial peat layer situated 10–30 cm below FF in hS and 20 cm below FF in HS. This differs from the usual peatland scientific practice, in which layers situated at a medium depth in peat deposits are taken as the benchmark [23]. Therefore, our EP data reflect the properties of relatively young peat, which was formed under the atmospheric–hydrologic, pedo-ecologic and anthropogenic conditions of recent centuries. The average EP age of our HS is ~ 400–500 years [27,33]. The age of EP in hS is more variable and greater, because its formation was probably initiated thousands of years

Table 9. Vertical distribution of chemical characteristics in mineral part of histic soils.

		Histic Gleysols				Histic Podzols			
Characteristic	Unit	M1 $n = 12$	M2 $n = 6$	M3 $n = 6$	M4 $n = 6$	M1 $n = 14$	M2 $n = 7$	M3 $n = 7$	M4 $n = 7$
C_{org}	$g\cdot kg^{-1}$	49.2^{b}	15.1^{a}	7.0^{a}	3.3^{a}	12.0^{ab}	11.9^{ab}	13.2^{b}	6.8^{a}
N_{tot}	$g\cdot kg^{-1}$	2.9^{b}	0.5^{a}	0.3^{a}	0.3^{a}	0.5^{b}	0.4^{ab}	0.5^{b}	0.2^{a}
C : N	ratio	17.0^{a}	22.3^{a}	15.8^{a}	17.6^{a}	23.3^{a}	32.3^{a}	26.7^{a}	53.0^{a}
pH_{CaCl_2}		5.1^{a}	5.5^{a}	5.8^{a}	6.2^{a}	3.5^{a}	3.8^{ab}	4.1^{bc}	4.4^{c}
pH_{H_2O}		5.6^{a}	6.0^{a}	6.5^{a}	6.7^{a}	4.5^{a}	4.5^{a}	4.7^{ab}	5.1^{b}
Ac-xch	$mmol^{+}\cdot kg^{-1}$	14.5^{a}	12.0^{a}	7.5^{a}	3.0^{a}	24.1^{b}	26.4^{b}	23.8^{ab}	13.5^{a}
Free H^{+}	$mmol^{+}\cdot kg^{-1}$	4.0^{ab}	1.9^{a}	1.1^{a}	0.7^{a}	7.7^{c}	4.9^{b}	3.1^{ab}	2.0^{a}
Ca-xtr	$g\cdot kg^{-1}$	4.0^{a}	4.0^{a}	8.1^{ab}	19.0^{b}	0.1^{a}	0.2^{ab}	0.4^{b}	0.7^{c}
Mg-xtr	$g\cdot kg^{-1}$	1.2^{a}	2.7^{ab}	4.5^{ab}	7.1^{b}	0.2^{a}	0.3^{ab}	0.5^{bc}	0.9^{c}
K-xtr	$mg\cdot kg^{-1}$	600^{a}	735^{a}	1438^{ab}	2837^{b}	291^{a}	320^{a}	391^{a}	645^{a}
P-xtr	$mg\cdot kg^{-1}$	373^{a}	327^{a}	298^{a}	407^{a}	74^{a}	89^{a}	163^{b}	249^{c}
S-xtr	$mg\cdot kg^{-1}$	470^{b}	–	–	70^{a}	60^{a}	–	60^{a}	60^{a}
Mn-xtr	$mg\cdot kg^{-1}$	158^{a}	73^{a}	152^{a}	194^{a}	18^{a}	20^{a}	32^{a}	57b
Ca-xch	$mmol^{+}\cdot kg^{-1}$	149^{b}	40^{a}	38^{a}	48^{a}	2.3^{a}	1.9^{a}	2.7^{a}	4.1^{a}
Mg-xch	$mmol^{+}\cdot kg^{-1}$	20^{a}	11^{a}	12^{a}	13^{a}	0.4^{a}	0.4^{a}	0.5^{a}	1.4^{a}
K-xch	$mmol^{+}\cdot kg^{-1}$	0.9^{a}	0.8^{a}	1.0^{a}	1.8^{a}	0.3^{a}	0.2^{a}	0.2^{a}	0.2^{a}
Na-xch	$mmol^{+}\cdot kg^{-1}$	0.3^{a}	0.3^{a}	0.2^{a}	0.4^{a}	0.1^{a}	0.1^{a}	0.1^{a}	0.1^{a}
Mn-xch	$mmol^{+}\cdot kg^{-1}$	0.1^{a}	0.1^{a}	$<0.05^{a}$	$<0.05^{a}$	$<0.05^{a}$	$<0.05^{a}$	$<0.05^{a}$	$<0.05^{a}$
Al-xch	$mmol^{+}\cdot kg^{-1}$	10.4^{a}	9.6^{a}	5.6^{a}	1.5^{a}	16.0^{a}	20.7^{a}	19.8^{a}	11.0^{a}
Fe-xch	$mmol^{+}\cdot kg^{-1}$	0.2^{a}	0.1^{a}	0.1^{a}	0.1^{a}	0.1^{ab}	0.2^{b}	0.1^{ab}	$<0.05^{a}$
Al-rct	$10\ mg\cdot kg^{-1}$	155^{a}	133^{a}	123^{a}	85^{a}	61^{a}	167^{b}	279^{c}	174^{bc}
Fe-rct	$10\ mg\cdot kg^{-1}$	141^{a}	147^{a}	153^{a}	139^{a}	13^{a}	34^{ab}	100^{bc}	108^{c}

Notes: Letters following the data indicate significant difference at the $p < 0.05$ level. org, organic; tot, total; xch, exchangeable; xtr, extractable; rct, reactive; Ac-xch, exchangeable acidity.

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ago, but there have apparently been major periodical fluctuations in the rate of peat formation or accumulation/mineralisation.

The ash composition and element concentration in EP are a function of annual forest debris composition and the content, peat-forming character, atmospheric sediments input rate and mineral dissolution from feeding water and forest fires [6,10,19,34]. The presence of surface water in hS leads to high-amplitude temporal fluctuations in EP wetness, oxygen and nutrient levels, which enhance microbiological processes and promote the mineralisation of FF and EP [19]. When peat is relatively dry, oxidation increases, the rate of peat accumulation decreases and more highly decomposed layers are formed [39]. Decomposition of FF and EP is accompanied by an increase in the concentrations of insoluble compounds in peat.

Most of our RA soils are influenced by drainage, exceptions (no drainage) are RA59 and RA109. Okruszko [5] pointed out that drainage of peatland increases the N and ash content, as well as the decomposition rate. As a result, the peat surface subsides rapidly [14]. Highly decomposed peat may also develop under the influence of laterally penetrating water [27,37].

The feed water composition significantly influences peat geochemistry and ecology [6,35,40]. Malawska et al. [19] postulated that the mineral status of a mire is the most important factor in explaining the vegetation patterns of peat soils, because there is no clear relationship between ash content and the botanical type of peat. The use of a solely botanical classification in explaining the trophic status of peatlands may lead to false conclusions about their genesis.

The breakdown of EP releases organic molecules that are capable of chelating with metals and increases their mobility within the soil profile. The percentage of metal–organic matter complexes is particularly high in eutrophic (weakly acid) EP, in which organic colloids (particularly humic acids) are major soil components involved in the retention of heavy metals [22]. Trivalent cations, notably Fe and Al, form stronger complexes with organic molecules than divalent cations. Therefore, special attention should be given to the formation of metal–organic matter complexes and their role in plant nutrition [22].

Hazardous elements from the environment which are bound into HS and hS peat are not readily released and the peaty soil cover may therefore be preserved as an environment-purifying medium for the area [23]. HS and hS may be successfully used for forest growing, even when the concentration of hazardous elements exceeds the maximum permissible limit (MPL) [14,27,41].

The EP composition of our histic Podzols coincides well with Estonian Soil Survey data about histic Podzol peat [26]. Our data on pH and ash, N, Ca and P content of fen and transitional bog HS show significant agreement with previous research in Estonia [16,28,29,42] and neighbouring countries [4,7,17,25,43–45]. An exception is the Ca content, which is higher in our fen and histic Gleysol peats than in previous studies [4,25,44]. By contrast to our results, in peat from fens in south Poland, Na predominates over K; low K concentrations are associated with a demand for this nutrient by rich and diverse vegetation [19].

Comparison of our data on heavy metals with the background level (or total mean) for Estonian peats [13,23,31] reveals an approximately similar level for Cu and Ni, but a level that is 2–3 times higher for Pb, Hg, Mn, Cd, Cr and Zn. This may be connected with the more superficial origin of our samples, or possibly with hS, which by origin are situated between organic and mineral soils. In comparison with the background level (or total mean) of Estonian mineral soil A horizon [24], our data for Cr, Ni, Mn, Zn are 2–4 times lower, Cd is approximately the same, and Hg and Pb levels are considerably higher.

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5.2. *About regional peculiarities*

Although Mg correlates highly with Ca [20], its level in peat may be relatively high ($\sim 900\,\mathrm{mg\,kg^{-1}}$) due to feed water peculiarities. One example of this is the transitional bog on RA Sandra (117). A very high Ca content (Ca-xtr $>30\,\mathrm{mg\,kg^{-1}}$, Ca-xch $>1100\,\mathrm{mmol\,kg^{-1}}$ on RA 76 and 133) demonstrates calcic (or hypereutrophic) properties.

The Mn content of peat is exceptional. The reason for its high variability among sites and soils is difficult to explain. A very high ($>1500\,\mathrm{mg\,kg^{-1}}$) Mn level compared with relatively low background levels (2–100 $\mathrm{mg\,kg^{-1}}$) in most of the other peats was determined in sapric HS peat from RA76 (Reastvere) and in peat from histic Gleysols RA27 and RA195 (Kalina and Rassiku). The high Fe-xtr content of Mustjõe (RA21) and Reastvere (RA76) fen peat and of hS peats from Rassiku (RA195) suggests the formation of fens iron ore in these soils. In most fens and histic Podzols in Ida-Viru and histic Gleysols in Hiiu EP, the mean S content is higher than the conventional MPL ($3.0\,\mathrm{mg\,kg^{-1}}$) established for Nordic countries [23].

Influenced by airborne ash, in histic Podzol EP, K, P and Ca levels near Kuremäe and Narva are 2–3 times higher in comparison with other RAs of the same soil type [26]. Contamination of EP with airborne ash also resulted in an increase in pH (by 0.8–2.1 units) and ash content, and a decrease in exchangeable acidity and the C : N ratio [12].

Heavy metal and/or micronutrient contents have been studied at the global [21,46] and country levels [9,24]. In the peats we investigated, the level of hazardous heavy metals does not generally exceed the MPL. An exception was Pb content, which exceeds MPL ($50\,\mathrm{mg\,kg^{-1}}$) in histic Podzols in southwestern Estonia at the Latvian border. Cd content is also relatively high (but below the MPL) in that region. The MPL ($100\,\mathrm{mg\,kg^{-1}}$) for Cr was surpassed in peat of histic Podzols for some sites near Tallinn and Ida-Viru County or in Estonia's industrial regions. Levels of Hg, Ni, Cu Mn and Zn were also higher (but below MPL) in those regions.

5.3. *Concluding remarks*

During the formation of EP from FF, AR extractable Fe, Cr, Al, Pb and Ni were accumulated to a great extent (accumulation coefficient >2.5), and S, Na and Hg to a medium extent (accumulation coefficient 1.2–2.0); Zn, K and Mn decreased to a great extent (accumulation coefficient <0.5), and Mg and P decreased to a medium extent (accumulation coefficient 0.6–0.8); Ca, Cu and Cd were practically unchanged (accumulation coefficient 1 ± 0.1).

Comparison of HS subsoil and substratum peats with EP of HS demonstrates considerable accumulation of Mn, Pb, Cd, Zn, Hg and Na into the mire thin (20 cm) superficial peat layer, whereas the subsoil and substratum are richer in ash, Ca, Mg and S.

Comparative analysis illustrated an existing certainty connected with soil-type peculiarities in peat chemistry, in its formation and the vertical distribution of peat chemical characteristics in peaty soil cover. For the moderately acid meso- and eutrophic peats of EP, the subsoil and substratum of fens (group I) exhibit the characteristically high levels of extractable Ca, S and Fe, total N, and exchangeable Ca, Mg and Mn. The lowest levels of most elements (some among them hazardous) were recorded in very strongly acid meso- and oligotrophic peats of transitional bog HS (group II); but these soils showed the highest values for exchangeable acidity and free H^+.

Due to their low position on the landscape, the EP of hS (groups III and IV) are minerotrophic (ash content $>150\,g{\cdot}kg^{-1}$) and are to a large extent influenced by subsoil and substratum mineral sediments. The EP of histic Gleysols (group III) may be divided into two types. The slightly acid peaty mull type EP (IIIa) (influenced by Ca carbonate-rich feed water) contains somewhat more extractable and exchangeable Ca and Mg in comparison with the strongly acid peaty moder (IIIb) type. In additiona, the EP of histic Gleysols contain the highest average levels of ash ($250\,g{\cdot}kg^{-1}$), Al, P, Mn, Zn and Cu.

The chemistry of the very strongly acid peaty mor type EP of histic Podzols reflects the presence of minerotrophic pedo-ecological conditions, because it is influenced by both mineral subsoil layers and water seepage from the surrounding area. Although these peats are the poorest in Ca and Mg, they are rich in Cr, Ni and Pb, as well as in exchangeable Al, Fe, K and Na.

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