# Chemical properties of surface peat on forest land in Estonia

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## SUMMARY

The chemical properties of surface peat cover (SPC) were studied in the context of Estonian pedoecological conditions. SPC comprises the superficial layers of fens (Group 1) and transitional bogs (Group 2), together with slightly acid peaty mull / strongly acid peaty moder (Group 3) and very strongly acid peaty mor (Group 4) layers overlying mineral soils. Thus, it spans organic soils, namely Histosols (Groups 1 and 2); together with Histic Gleysols (Group 3) and Histic Podzols (Group 4), which are developmentally intermediate between organic and mineral soils. Moderately acid eutrophic (Group 1) and very strongly acid mesotrophic (Group 2) peats (forest litter layers excluded) were uniformly characterised up to 40 cm depth; whereas for Groups 3 and 4 we examined the full thickness of available peat layers, which ranged from 10 to 30 cm. The results show that Al, K and heavy metal contents are significantly higher and organic carbon content is lower in Histic Soils (3, 4) than in Histosols (1, 2). The amounts of Ca, Mg, Mn and Fe are significantly higher and C:N ratio, exchangeable acidity and content of free $H^+$ lower in less acidic (1, 3) than in more acidic (2, 4) soil types. The total concentration of elements (excluding heavy metals) extracted by nitro-hydrochloric acid (*aqua regia*) is considerably higher in less acidic soils, at 28–45 g $kg^{-1}$ (1, 3) *versus* 10–12 g $kg^{-1}$ (2, 4); and mean contents of individual elements decrease in the order Ca(51%) > Fe(20%) > S(10%) ≥ Al(10%) > Mg(3%) ≥ P(3%) > K(2%) > Mn(1%) > Na(<1%). The most abundant heavy metals are Pb (12–33 mg $kg^{-1}$), Zn (7–41 mg $kg^{-1}$), Cu (3–12 mg $kg^{-1}$), Cr (2–23 mg $kg^{-1}$) and Ni (2–8 mg $kg^{-1}$); Cd and Hg contents are very low, ranging from 0.2 to 0.5 mg $kg^{-1}$. The dominant exchangeable basic cations are $Ca^{2+}$ (78–93%) and $Mg^{2+}$ (7–15%), and the peat contains much smaller amounts of $K^+$ (1–6%) and $Na^+$ (<2%). The total exchangeable acidic cations (1–14 cmol $kg^{-1}$) are dominated by $H^+$ (51–83%) and $Al^{3+}$ (15–47%), whereas Mn and Fe (2–4%) cations are modestly represented.

**KEY WORDS:** exchangeable cations, heavy metals, Histic Gleysols, Histic Podzols, Histosols.

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## INTRODUCTION

Large parts of the Nordic countries are covered by peat soil layers (ESBN EC 2005, Montanarella *et al.* 2006, Oleszczuk *et al.* 2008), for which we use the integrated conventional term “surface peat cover” (SPC). Those SPCs which are >40 cm thick are classified as different types of Histosols (HS), and form superficial biologically active layers within peatlands or overlying peat deposits (IUSS Working Group WRB 2006, Kõlli *et al.* 2009). Thinner SPCs are classified as Histic (mineral) soils in which a superficial peat layer (10–30 cm thick according to the Estonian soil classification) directly overlies mineral soil layers (Kokk 1985). Histosols are the classical mire soils, and form 23.5% of Estonia’s soil cover. Histic Soils (6.3% Estonia’s of soil cover), which were formed by paludification of mineral soils, occur on transitional areas between waterlogged mineral and organic (peat) soils; these are most extensive on flat lowland areas and within closed shallow depressions (Kokk 1995).

As only the surface layers of peatlands belong to the soil cover, most of the published data on chemical properties of Estonian peat characterise peat deposits rather than peaty soils (Truu *et al.* 1964, Valk 1988, Veber *et al.* 1989, Orru 1992). The chemical properties of peaty soils have been less thoroughly investigated than those of mineral soils, and our research seeks to fill this gap. To this end we have investigated Histosols located on forested fens and transitional bogs, Histic Gleysols on moderately acidic paludified areas, and Histic Podzols on very strongly acidic mineral areas. The main objectives of this paper are: (i) to characterise the chemical properties of SPC (i.e. of peat belonging to the soil cover); (ii) to analyse the relationships between peat properties and chemical element contents; and (iii) to elucidate the existing ranges and geographical distributions of element contents in the SPCs of Estonia.

## METHODS

### Research areas

The distribution of research areas (RAs) across the Estonian counties is shown in Figure 1. For analysis of SPC properties the RAs were classified, on the basis of their soils, into four groups. The RAs are arranged according to soil group, county and location (village) in Table 1, and a general ecological characterisation for each soil group is given in Table 2. The peat layers of Groups 1 and 2 are thick whereas those of Groups 3 and 4 are thin; the peats of Groups 1 and 3 are slightly or moderately acidic, and those of Groups 2 and 4 are very strongly acidic. Masing (1975) distinguished two types of mire vegetation in Estonia, namely minerotrophic and oligotrophic; a third type, mixotrophic, was added later (Kõlli *et al.* 2009). According to this classification the SPC of Groups 1 and 3 is minerotrophic and that of Groups 2 and 4 is mixotrophic.

### Sampling

Sampling was carried out in 2006–7 using methods developed for the project "Long-Range Transboundary Air Pollution" (Forest Focus 2006). The shallow organic sub-horizons of the forest floor OL (unaltered litter), OF (fragmented, partly decomposed litter) and OH (well-decomposed organic matter) were sampled separately from the underlying peat layers, but the OH horizons of Histic Soils were subsequently combined with the peat layer. The organic top layers (litter for all soils, plus the peat layer for Histic Soils) were collected from areas of 1000 cm$^2$, as defined by a quadrat frame laid on the ground surface. The thickness of each organic top layer and sub-horizon was measured individually. Soil samples were collected from fixed depth layers (horizons) in the faces of five soil pits and bulked to form a composite sample for each layer per RA. The layers were 0–10, 10–20, 20–40 and 40–80 cm below the datum level, which was set for Histosols at the interface of forest litter

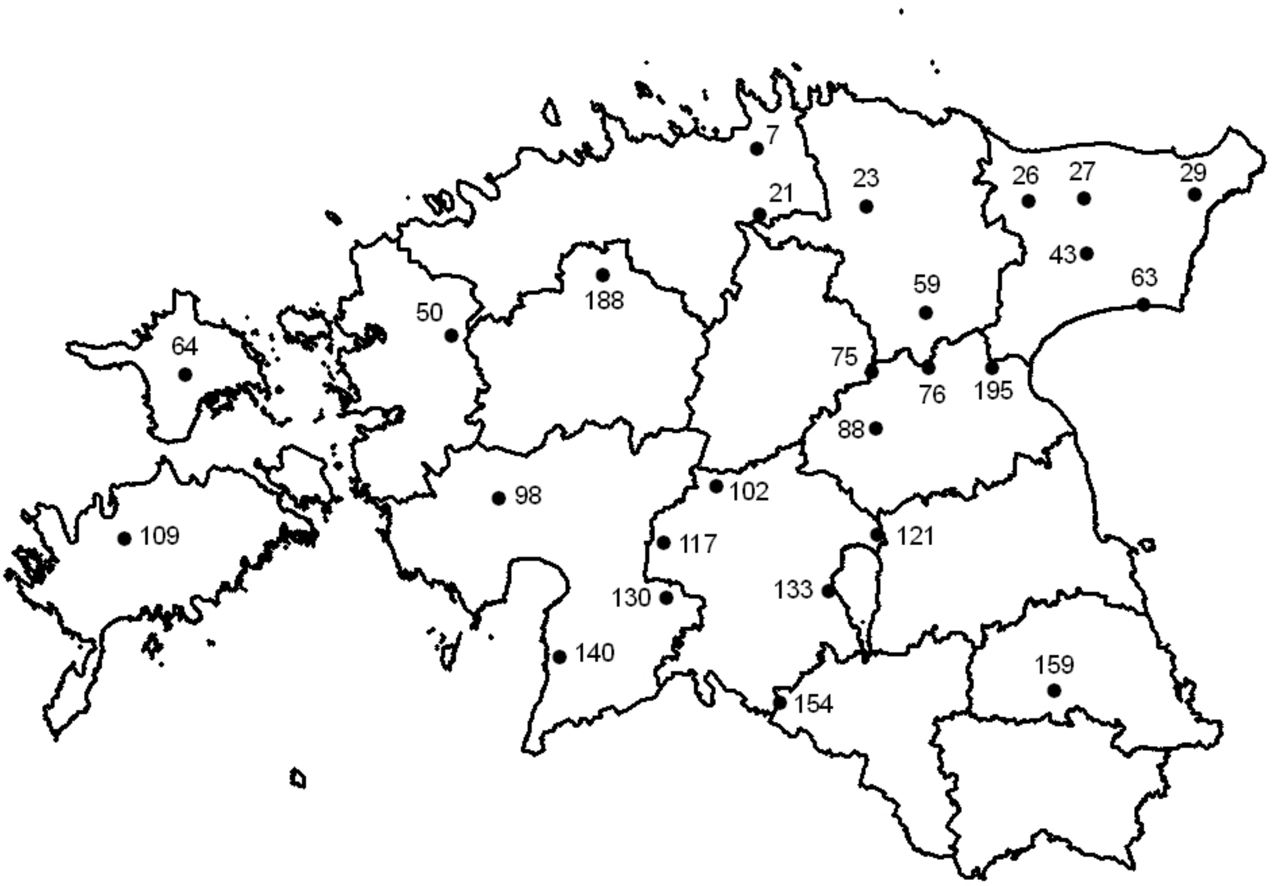

Figure 1. Map of Estonia showing county boundaries and the locations (filled black circles) of the research areas (RAs). See Table 1 for classification and characteristics of the RAs.

Table 1. Listing of research areas (RAs) according to soil group and county, and general characteristics of soil groups.

| Soil group | | RA no. | Site name | County | Number of samples[1)] Ff-Pt-Sm-Sb | Landscape position, trophic status and principal origin(s) of water supply | Composition of tree layer; forest quality class[2)] |
|---|---|---|---|---|---|---|---|
| No. | Name | | | | | | |
| 1 | Histosols on fens | 21<br>59<br>76<br>98<br>133 | Mustjõe<br>Käru<br>Reastvere<br>Kuhu<br>Kalbuse | Harju<br>Lääne-Viru<br>Jõgeva<br>Pärnu<br>Viljandi | 8-15-0-5 | Minerotrophic rich fen plains; terrestrialised lakes and depressions enclosed by uplands; groundwater and surface water supplies. | Bt (6–7)<br>Pn (2)<br>Al (1)<br>Pc (1);<br>III–IV |
| 2 | Histosols on transitional bogs | 23<br>43<br>50<br>75<br>88<br>117<br>121<br>140 | Neeruti<br>Mäetaguse<br>Jaakna<br>Tooma<br>Kaavere<br>Sandra<br>Meleski<br>Võidu | Lääne-Viru<br>Ida-Viru<br>Lääne<br>Jõgeva<br>Jõgeva<br>Viljandi<br>Viljandi<br>Pärnu | 13-25-0-8 | Mixotrophic bog plains at edges and in central parts of fens; fed mostly by rainfall and mesotrophic surface seepage water. | Pn (7–8)<br>Bt (2)<br>Pc (<1);<br>IV–V |
| 3 | Histic Gleysols | 29<br>64<br>195 | Mustanina<br>Käina<br>Rassiku | Ida-Viru<br>Hiiu<br>Jõgeva | 4-3-9-6 | Floors of depressions in the landscape and on transitional areas between mineral ground and peatland; receive minerotrophic surface water. | Bt (5–6)<br>Pc (1–4)<br>Pn (1–3);<br>II–IV |
| | | 27<br>102<br>188 | Kalina<br>Rääka<br>Loone | Ida-Viru<br>Viljandi<br>Rapla | 4-5-9-6 | | |
| 4 | Histic Podzols | 7<br>26<br>63<br>109<br>130<br>154<br>159 | Vahastu<br>Aruvälja<br>Remniku<br>Aula-Vintri<br>Kanaküla<br>Taagepera<br>Mustjõe | Harju<br>Ida-Viru<br>Ida-Viru<br>Saare<br>Pärnu<br>Valga<br>Põlva | 11-17-28-7 | Depressions in nutrient-poor sandy wet areas and between (beach) dune ridges; receive minerotrophic and acid surface water. | Pn (10)<br>Bt (<1);<br>III–V |

1) Numbers of samples taken from:- Ff: forest floor (OL and OF horizons); Pt: SPC peat; Sm: mineral subsoil; Sb: substrate.

2) Tree genera:- Bt: *Betula*; Pn: *Pinus*; Al: *Alnus*; Pc: *Picea* (number in parentheses indicates genus share of ten trees); for further detail on forest quality classes, see Table 2.

with peat (i.e. between layers O and H1 in Figure 2), and for Histic Soils at the interface of peat (Hf-s) with the uppermost mineral layer (M1). In Figure 2, the layers from which soil samples were taken in Histosols are labelled H1–H4 and those for mineral soil layers of Histic Soils are labelled M1–M4. The soil samples were prepared for analysis according to ISO 11464. After air drying, living macroscopic roots and all mineral and organic particles of diameter >2 mm were removed from the samples by dry sieving; and samples taken from organic layers were milled.

## Explanation of terminology

SPC includes all organic horizons, but here the OL and OF layers of forest floor soils are not included in the composition and properties of SPC. Therefore, the mean characteristics of SPC presented here are for Histosol peat samples H1–H3 and for Histic Soil epipedon H horizons (Hf, Hf-s, Hs) (which varied greatly between RAs), with the OH sub-horizon added (Figure 2). Considering SPC in this way underlines the fact that the superficial layer of a peatland differs fundamentally from the underlying peat, which is regarded as a peat deposit but not as peat soil.

## Chemical analyses

Peat and mineral soil samples were analysed in the Environmental Research Laboratory (Tartu), following the quality standard EVS-EN-/ISO/IEC 17025:2000. Data for peat samples only are

Table 2. Pedo-ecological characterisation of Soil Groups 1–4.

| Group | Soil Group (complex) name[1)] | | SPC acidity; $pH_{CaCl2}$ | Degree of decomposition; type of SPC | Type of epipedon[2)] | Forest site type and quality class of pristine areas[3)] | Thickness of O+H horizons (cm)[4)] |
|---|---|---|---|---|---|---|---|
| 1 | Sapri-hemic & 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) |
| 2 | Sapri-hemic, Fibri-hemic & Hemic **Histosols** (dystric, ombric, drainic, abruptic) | | very strongly acid; 2.6–3.5 | moderate; hemic, fibrihemic, saprihemic | mesotrophic peat | mesotrophic transitional bog, *Myrtillus* drained bog; IV–V | >100 (40–100) |
| 3 | a) | Sapri-histic **Gleysols** (endocalcaric, calcic, drainic, clayic, luvic) | slightly acid; 5.5–6.4 | strong; sapric | peaty mull | rich paludified *Dryopteris* & *Filipendula* mixed forest; II–III | 12–18 |
| | b) | Spodic & Sapri-histic **Gleysols** (dystric, arenic, drainic) | strongly acid; 3.5–4.5 | strong; saprihemic | peaty moder | paludified *Polytrichum-Myrtillus* & *Carex* forests; III–IV | 17–30 |
| 4 | 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* & *Polytrichum-Myrtillus* forests; III–V | 17–27 |

1) according to IUSS Working Group WRB (2006); 2) according to Kõlli (1992); 3) according to Lõhmus (2006), where, on a five-class scale, 'I' has the highest and 'V' the lowest quality; 4) total thickness of organic (forest floor litter and peat) layers used in characterisation of SPC.

presented here. Moisture content was measured gravimetrically (drying temperature 105°C, ISO 11465) and soil pH (in $CaCl_2$ and $H_2O$) was determined by electrochemical methods using a 1:5 soil:liquid mixture and a Jenway pH meter 3320 (ISO 10390). Organic carbon ($C_{org}$) content was determined spectrometrically after combustion at 1100°C, using a Primacs-sc TOC Analyser/Skalar (EN 13137), and total nitrogen ($N_{tot}$) was measured by the modified Kjeldahl method using the titrimetric Kjeldec system (ISO 10048). The exchangeable (xch) and free $H^+$ acidity were determined electrochemically after barium chloride extraction (titrated up to pH 7.8); free $H^+$ acidity was determined using sodium fluoride (ISO 11260 and 14254). Inductively Coupled Plasma spectroscopy (ICP-AES Varian/USA, EN ISO 11885 and ISO 11466) was used to assay:

- Ca, Mg, K, P, S, Na, Mn, Al, Fe, Pb, Cd, Cu, Zn, Cr, Ni and Hg extractable (xtr) with nitro-hydrochloric acid (*aqua regia*);
- the exchangeable (xch) cations (using barium chloride extraction) $Ca^{2+}$, $Mg^{2+}$, $K^+$, $Na^+$, $Mn^{2+}$, $Al^{3+}$ and $Fe^{3+}$; and
- acid ammonium oxalate extractable (rct) Fe and Al.

All the analyses were carried out in triplicate, and the results were averaged and expressed on an oven-dry mass basis. All chemicals used were of analytical grade. A detailed description of the laboratory analyses is given by Forest Focus (2006).

### Statistical analyses

Two-way analysis of variance, followed by the Student t-test of homogenous groups, was carried out using the Statistica 7 program (©StatSoft, Tulsa, OK). The level of statistical significance was set at $P < 0.05$.

## RESULTS

### Chemical elements

Mean values (n = 65) for the 33 SPC characteristics determined are shown, together with statistical parameters, in Table 3. In many cases the coefficient of variation (CV) of peat characteristics is high (>100%) and differences between minimum and maximum values are large. The dominant characteristics (80% of samples) are situated between the lower (D0.1) and upper (D0.9) deciles. Comparison of median values with arithmetical

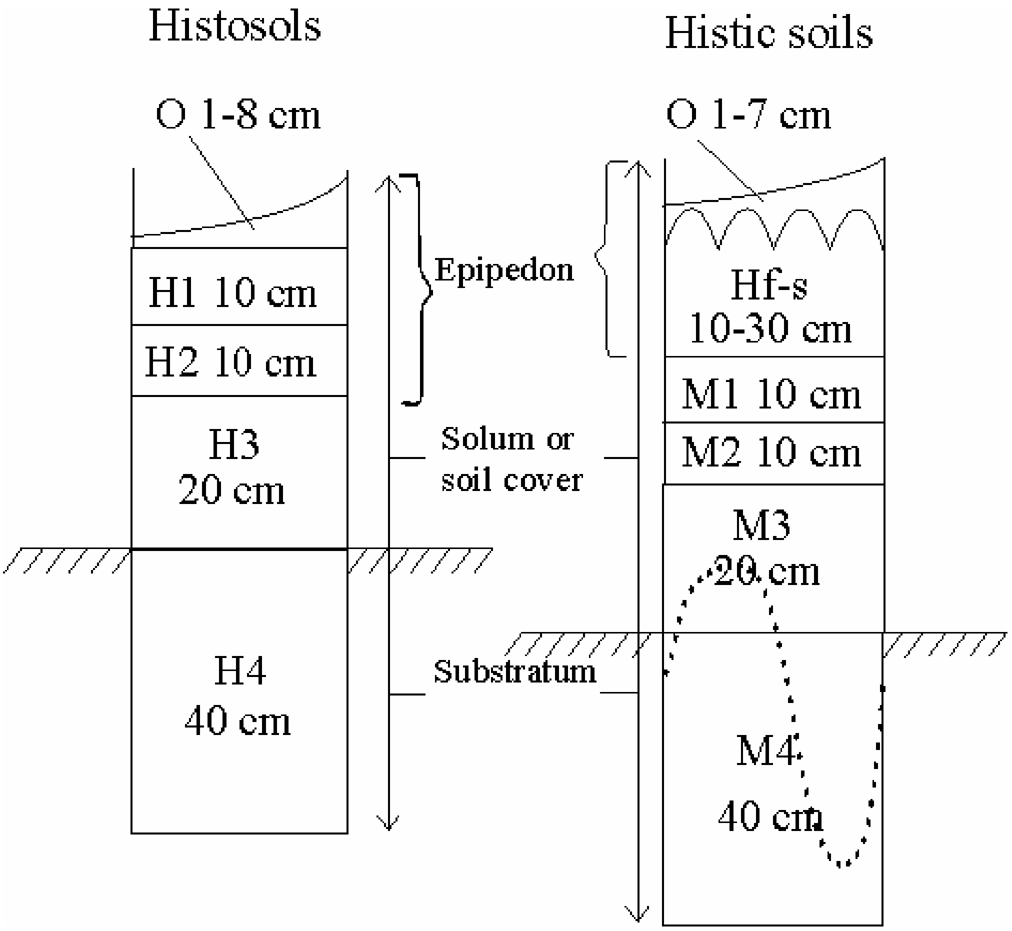

Figure 2. Conceptual schema of sampling and characterisation of SPC for Histosols and Histic Soils. Sampled materials are: O: forest floor; H1–H4 and Hf-s: peat; M1–M4: mineral soil. The dotted curve indicates the variability of solum thickness (or the boundary between solum and substratum) for Histic Soils.

means indicates that, for many of the characteristics, the distribution of values exhibits positive excess in comparison with the normal distribution because atypically high values were recorded for some of the samples. These large deviations from the mean and median values have specific causes, and our work attempts to elucidate pedo-ecological and environmental causes. Some variation of properties can be attributed to soil peculiarities, which are reflected by statistically significant differences amongst the four soil groups (Tables 4 and 5). Part of the variability of characteristics is caused by deposition of airborne emissions, which can be elucidated by geographical analysis (Roots & Talkop 1997). Activities directed towards the regulation of ecosystem productivity are also relevant (Chertov 1981).

The comparison of element contents (Tables 4 and 5) reveals that the quantity of Al (including reactive Al), K and heavy metals is significantly higher and the content of organic carbon lower in Histic Soils (Groups 3 and 4) than in Histosols (Groups 1 and 2). Significant differences in element contents and general properties are also observed between very strongly acid and moderately–slightly acid peat. The contents of Ca, Mg, Mn and Fe (including reactive Fe) and pH are significantly higher, and C:N ratio, exchangeable acidity and content of free $H^+$ lower in Groups 1 and 3 (less acid) than in Groups 2 and 4 (more acid). Therefore, the C:N ratio clearly depends on total N content ($r = -0.77$) rather than on organic carbon content ($r = 0.19$). Clear dependence of S and Na contents on soil type was not observed.

The sum of the measured element contents (without heavy metals) is considerably higher in the less acid soils (Groups 1 and 3: 28–45 g per kg of air-dry peat) than in the more acid soils (Groups 2 and 4: 10–12g per kg of air-dry peat). The ash content of Histic Soils (151–256 g per kg of air-dry peat) is higher than that of Histosols (40–104 g per kg of air-dry peat). High correlation is observed between soil pH (determined in $CaCl_2$ or $H_2O$) and exchangeable and free acidity ($r = -0.66 – -0.87$). High correlation ($r = 0.6 – 0.7$) is shown for acidity indicators as well for total N content, which is

Table 3. Statistical analysis of the characteristics of all SPC peat samples (n=65). Abbreviations: SD: standard deviation; CV: coefficient of variation; org: organic; tot: total; xch: exchangeable; xtr: extractable; rct: reactive; Ac-xch: exchangeable acidity.

| Characteristics | Units | Mean | SD | CV | Limits | | Median | Deciles | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | min | max | | D0.1 | D0.9 |
| Ash | g kg$^{-1}$ | 110 | 115 | 104 | 7 | 513 | 71 | 26 | 307 |
| $C_{org}$ | g kg$^{-1}$ | 453 | 75 | 16 | 202 | 570 | 477 | 360 | 520 |
| $N_{tot}$ | g kg$^{-1}$ | 18.2 | 7.0 | 38 | 9.0 | 35.4 | 16.4 | 11.1 | 30.4 |
| C:N | ratio | 27.6 | 9.1 | 33 | 11.4 | 48.8 | 27.1 | 15.5 | 39.5 |
| $pH_{CaCl2}$ | | 3.7 | 1.1 | 29 | 2.5 | 6.4 | 3.2 | 2.6 | 5.6 |
| $pH_{H2O}$ | | 4.4 | 1.0 | 22 | 3.2 | 6.6 | 4.0 | 3.5 | 6.1 |
| Ac-xch | mmol kg$^{-1}$ | 103 | 74 | 72 | 0 | 250 | 110 | 0 | 210 |
| Free $H^+$ | mmol kg$^{-1}$ | 78 | 62 | 79 | 0 | 220 | 87 | 0 | 170 |
| Ca-xtr | g kg$^{-1}$ | 10.4 | 12.2 | 117 | 0.6 | 53.0 | 5.2 | 1.2 | 28.0 |
| Mg-xtr | mg kg$^{-1}$ | 691 | 767 | 111 | 120 | 3700 | 420 | 190 | 1400 |
| K-xtr | mg kg$^{-1}$ | 334 | 286 | 86 | 28 | 1000 | 240 | 49 | 830 |
| Na-xtr | mg kg$^{-1}$ | 62 | 30 | 49 | 23 | 200 | 52 | 31 | 110 |
| P-xtr | mg kg$^{-1}$ | 583 | 314 | 54 | 150 | 1900 | 530 | 260 | 980 |
| S-xtr | g kg$^{-1}$ | 2.1 | 0.9 | 40 | 0.8 | 4.7 | 1.9 | 1.2 | 3.4 |
| Mn-xtr | mg kg$^{-1}$ | 147 | 407 | 276 | 2 | 2300 | 13 | 4 | 340 |
| Al-xtr | g kg$^{-1}$ | 2.0 | 2.2 | 108 | 0.2 | 9.2 | 1.1 | 0.5 | 4.2 |
| Fe-xtr | g kg$^{-1}$ | 4.1 | 7.7 | 187 | 0.4 | 49.0 | 1.7 | 0.8 | 8.4 |
| Ca-xch | mmol kg$^{-1}$ | 403 | 434 | 107 | 26 | 1500 | 220 | 50 | 1200 |
| Mg-xch | mmol kg$^{-1}$ | 41 | 40 | 97 | 6 | 200 | 26 | 12 | 79 |
| K-xch | mmol kg$^{-1}$ | 5.1 | 4.7 | 93 | 0.1 | 18.0 | 4.0 | 0.3 | 13.0 |
| Na-xch | mmol kg$^{-1}$ | 2.5 | 2.1 | 83 | 0.5 | 7.7 | 1.8 | 1.0 | 5.1 |
| Mn-xch | mmol kg$^{-1}$ | 0.7 | 1.2 | 161 | 0.1 | 5.7 | 0.2 | 0.1 | 2.6 |
| Al-xch | mmol kg$^{-1}$ | 24 | 28 | 117 | 0 | 120 | 13 | 0 | 76 |
| Fe-xch | mmol kg$^{-1}$ | 2.5 | 2.3 | 93 | 0.1 | 9.5 | 2.1 | 0.1 | 6.4 |
| Al-rct | 10mg kg$^{-1}$ | 115 | 126 | 110 | 9 | 660 | 65 | 22 | 300 |
| Fe-rct | 10mg kg$^{-1}$ | 274 | 435 | 159 | 20 | 2500 | 130 | 40 | 620 |
| Cd-xtr | 10µg kg$^{-1}$ | 29.6 | 21.0 | 71 | 4.3 | 89.0 | 27.0 | 5.0 | 60.0 |
| Pb-xtr | mg kg$^{-1}$ | 20.8 | 13.1 | 63 | 1.7 | 53.0 | 21.0 | 4.7 | 39.0 |
| Hg-xtr | µg kg$^{-1}$ | 192 | 96 | 50 | 0 | 436 | 171 | 89 | 331 |
| Cr-xtr | mg kg$^{-1}$ | 8.7 | 19.6 | 224 | 0.5 | 110.0 | 2.5 | 1.0 | 21.0 |
| Ni-xtr | mg kg$^{-1}$ | 3.8 | 6.0 | 159 | 0.3 | 32.0 | 2.1 | 0.8 | 8.1 |
| Cu-xtr | mg kg$^{-1}$ | 4.7 | 4.9 | 106 | 1.2 | 37.0 | 3.3 | 1.8 | 7.9 |
| Zn-xtr | mg kg$^{-1}$ | 18.8 | 18.3 | 97 | 1.8 | 90.0 | 13.0 | 2.9 | 46.0 |

significantly higher in fen Histosols (Group 1) than in the other three soil groups. Mean element contents decrease in the following order: Ca(51%) > Fe(20%) > S(10%) ≥ Al(10%) > Mg(3%) ≥ P(3%) > K(2%) > Mn(1%) > Na(<1%). The exceptionally high contents of Ca, Fe and S in Sapric Histosol peat and relatively high contents of Al, Mn and P in Histic Soil peat are also noteworthy. The correlation analysis of *aqua regia* extractable elements (excluding heavy metals) indicates close and significant correlation between Ca and Mg ($r = 0.7$) with which S and Mn are also associated. In addition, Fe and Mn ($r = 0.7$) as well as P, K and Al ($r > 0.5$) are relatively highly correlated.

**Heavy metals**

Heavy metals account for very modest fractions of the total *aqua regia* extractable elements for all soil groups (0.06%, 0.39%, 0.34% and 0.82% for Groups 1 to 4 respectively, calculated from the data in Table 5). The mean percentage contents of heavy metals in peat, in descending order, are as follows: Pb(36%) > Zn(33%) > Cr(15%) > Cu(8%) > Ni(7%) > Cd(1%) > Hg(<1%). This order is similar for the peat of all four soil groups, with rare exceptions (e.g. high Zn content in Group 3 peat). However, in all cases, the heavy metal content of peat is higher in Histic Soils than in Histosols. The dominant heavy metals in SPC peat are Pb (12–33 mg kg$^{-1}$), Zn (7–

Table 4. Characterisation of SPC peat by soil groups. SD: standard deviation. Letters following the data indicate significant differences at the $P < 0.05$ level.

| Characteristic | Units | Histosols | | | | Histic Soils | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | Group 1 (n=15) | | Group 2 (n=25) | | Group 3 (n=8) | | Group 4 (n=17) | |
| | | mean | SD | mean | SD | mean | SD | mean | SD |
| General characteristics of SPC peat | | | | | | | | | |
| Ash | g kg $^{-1}$ | 104b | 46 | 40a | 35 | 256c | 175 | 151b | 127 |
| $C_{org}$ | g kg $^{-1}$ | 483c | 33 | 493c | 33 | 351a | 120 | 414b | 57 |
| $N_{tot}$ | g kg $^{-1}$ | 28.6b | 5.4 | 15.8a | 3.9 | 15.4a | 4.0 | 14.1a | 2.9 |
| C:N | ratio | 17.7a | 4.7 | 33.2b | 8.4 | 23.6a | 8.0 | 30.0b | 4.9 |
| $pH_{CaCl2}$ | | 5.0c | 0.6 | 3.0a | 0.4 | 4.4b | 1.5 | 3.1a | 0.4 |
| $pH_{H2O}$ | | 5.6c | 0.5 | 3.9a | 0.4 | 5.0b | 1.4 | 3.8a | 0.4 |
| Ac-xch | mmol$^+$ kg$^{-1}$ | 9.2a | 8.6 | 140.1c | 58.2 | 93.1b | 97.1 | 135.8bc | 33.4 |
| Free $H^+$ | mmol$^+$ kg$^{-1}$ | 4.7a | 9.1 | 115.9c | 53.5 | 61.4b | 67.1 | 96.2bc | 37.1 |
| Content of *aqua regia* extractable elements in peat | | | | | | | | | |
| Ca | g kg$^{-1}$ | 28.20c | 11.84 | 4.34a | 3.29 | 11.29b | 9.82 | 3.29a | 1.91 |
| Mg | mg kg$^{-1}$ | 1221a | 1080 | 404a | 224 | 1170b | 1224 | 420a | 122 |
| K | mg kg$^{-1}$ | 116a | 68 | 199a | 182 | 604b | 320 | 598b | 216 |
| Na | mg kg$^{-1}$ | 56.6a | 44.1 | 55.0a | 19.1 | 74.6a | 30.0 | 69.3a | 27.0 |
| P | mg kg$^{-1}$ | 554bc | 313 | 408a | 176 | 965c | 472 | 687b | 178 |
| S | 10g kg$^{-1}$ | 3.21b | 0.76 | 1.82b | 0.51 | 2.00a | 0.83 | 1.76b | 0.64 |
| Mn | mg kg$^{-1}$ | 236a | 401 | 8a | 8 | 652b | 883 | 36a | 32 |
| Al | 10g kg$^{-1}$ | 1.01a | 0.45 | 1.20a | 1.43 | 4.45b | 2.98 | 2.87b | 2.43 |
| Fe | g kg$^{-1}$ | 10.17b | 13.58 | 1.29a | 0.81 | 6.59ab | 7.03 | 1.82a | 0.80 |

Table 5. Content of exchangeable cations and *aqua regia* extractable heavy metals in peat. SD: standard deviation. Letters following the data indicate significant differences at the $p < 0.05$ level.

| Cations, heavy metals | Units | Histosols | | | | Histic Soils | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | Group 1 (n=15) | | Group 2 (n=25) | | Group 3 (n=8) | | Group 4 (n=17) | |
| | | mean | SD | mean | SD | mean | SD | mean | SD |
| Content of exchangeable (xch) cations and reactive (rct) Al and Fe (III)) | | | | | | | | | |
| Ca-xch | mmol$^+$ kg$^{-1}$ | 1056c | 325 | 176a | 131 | 461b | 398 | 135a | 81 |
| Mg-xch | mmol$^+$ kg$^{-1}$ | 75.8b | 59.4 | 27.6a | 16.7 | 52.1ab | 48.4 | 25.3a | 9.5 |
| K-xch | mmol$^+$ kg$^{-1}$ | 2.0a | 1.5 | 3.4ab | 4.3 | 6.0b | 2.9 | 10.1c | 4.0 |
| Na-xch | mmol$^+$ kg$^{-1}$ | 2.3ab | 2.3 | 2.0a | 1.1 | 1.9ab | 1.3 | 2.9ab | 2.0 |
| Mn-xch | mmol$^+$ kg$^{-1}$ | 1.1b | 1.6 | 0.2a | 0.3 | 1.3b | 1.6 | 0.9b | 1.2 |
| Al-xch | mmol$^+$ kg$^{-1}$ | 4.3a | 4.6 | 21.6b | 26.2 | 23.2abc | 28.8 | 44.2c | 29.5 |
| Fe-xch | mmol$^+$ kg$^{-1}$ | 0.5a | 0.5 | 3.0bc | 2.0 | 1.5ab | 1.7 | 4.1c | 2.7 |
| Al-rct | 10mg kg$^{-1}$ | 45a | 23 | 83a | 114 | 192b | 95 | 186b | 158 |
| Fe-rct | 10mg kg$^{-1}$ | 697b | 731 | 108a | 84 | 336a | 287 | 115a | 62 |
| Content of *aqua regia* extractable heavy metals | | | | | | | | | |
| Cd | 10µg kg$^{-1}$ | 19.4a | 16.4 | 23.3a | 19.1 | 51.3b | 28.6 | 37.6b | 13.0 |
| Pb | mg kg$^{-1}$ | 11.8a | 10.9 | 16.9ab | 10.4 | 24.0bc | 7.3 | 32.8c | 12.0 |
| Hg | µg kg$^{-1}$ | 152a | 85 | 154a | 73 | 255b | 102 | 253b | 93 |
| Cr | mg kg$^{-1}$ | 1.9a | 1.3 | 2.3a | 2.2 | 12.0ab | 7.0 | 22.6b | 34.4 |
| Ni | mg kg$^{-1}$ | 1.9a | 0.9 | 1.5a | 1.0 | 5.0ab | 3.1 | 8.2b | 10.3 |
| Cu | mg kg$^{-1}$ | 3.3a | 1.0 | 2.9a | 1.9 | 11.5b | 11.6 | 5.2a | 1.6 |
| Zn | mg kg$^{-1}$ | 7.3a | 5.5 | 14.2a | 11.0 | 40.8c | 29.4 | 25.5b | 17.4 |

41 mg kg$^{-1}$), Cu (3–12 mg kg$^{-1}$), Cr (2–23 mg kg$^{-1}$) and Ni (2–8 mg kg$^{-1}$). Apart from Pb, the environmentally hazardous heavy metals are Cd and Hg, and these are present mostly at concentrations within the range 0.2–0.5 mg kg$^{-1}$. The concentrations of the hazardous heavy metals (Pb, Cd, Hg) are significantly correlated with one another and with Zn and Cu levels. Cr and Ni form a separate group of very strongly correlated (r = 0.95) elements; in some work, Ni is treated as environmentally hazardous (Orru & Orru 2003, 2004, 2006).

## Exchangeable cations

The contents of exchangeable Ca and Mg are higher in less-acidic peat, whilst those of Fe and Al are higher in more-acidic peat. The content of exchangeable K is higher in Histic Soils or in peat lying directly on mineral horizons, whereas a clear dependence on soil type is absent in the case of Mn and Na (Table 5).

The quantity of each species of exchangeable cations correlates highly with the total (*aqua regia* extractable) content of the same element. The highest correlation coefficient was observed for Ca and the lowest for Fe, with the other elements determined falling between these extremes in the following order (r values in parentheses): Ca (0.98) ≥ Mg (0.95) > K (0.75) ≥ Na (0.70) > Al (0.55) ≥ Mn (0.53) > Fe (0.22). The correlation coefficients between the contents of different exchangeable cations are low (r = <0.5), the only exception being between exchangeable Ca and Mg (r = 0.64).

The exchangeable cation content as a percentage of *aqua regia* extractable element content depends on soil type (Table 6); it is higher in more-acidic peat than in less-acidic peat, and the greatest differences are observed for Fe, Al and Mn contents. The same tendency is observed for oxalate extractable (reactive) Al and Fe.

Total cation exchange capacity (sum of exchangeable basic and acidic cations) is lowest in acidic peat and varies amongst the soil groups from 31 to 115 cmol kg$^{-1}$ of peat (Table 7). The roles of basic (Ca, Mg, K and Na) and acidic (H, Al, Mn and Fe) exchangeable cations per soil group are shown in Table 5, and their weighted means in Table 3. The dominant basic cations are the bivalent $Ca^{2+}$ (78–93%) and $Mg^{2+}$ (7–15%), as also observed by Malawska *et al*. (2006); whereas the monovalent cations $K^+$ (1–6%) and $Na^+$ (<2%) have only a modest roles. The ratio Ca-xch:Mg-xch is, therefore, in the range 5–14 (Table 7). The sum of acidic cations (1–14 cmol kg$^{-1}$) is dominated by $H^+$ (51–

Table 6. Mean contents of exchangeable cations and reactive Al and Fe per soil group and group combinations, expressed as percentages of the *aqua regia* extractable quantities of the same elements.

| Soil group | n | Exchangeable cations | | | | | | | Reactive | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | Ca | Mg | K | Na | Mn | Al | Fe | Al | Fe |
| 1 | 15 | 75 | 76 | 67 | 93 | 13 | 3.9 | 0.1 | 44 | 68 |
| 2 | 25 | 81 | 83 | 67 | 84 | 69 | 16.2 | 4.3 | 69 | 84 |
| 3 | 8 | 82 | 54 | 39 | 59 | 6 | 4.7 | 0.4 | 43 | 51 |
| 4 | 17 | 82 | 73 | 66 | 96 | 69 | 13.8 | 4.2 | 63 | 63 |
| 1+3 | 23 | 77 | 68 | 57 | 81 | 11 | 4.2 | 0.2 | 44 | 62 |
| 2+4 | 42 | 81 | 79 | 67 | 89 | 69 | 15.2 | 4.3 | 67 | 76 |
| Total | 65 | 78 | 72 | 60 | 93 | 14 | 10.8 | 1.1 | 58 | 67 |

Table 7. Contents of basic and acidic exchangeable cations for SPC peats according to soil groups.

| Character of Exchangeable (xch) cations | Histosols | | | | Histic Soils | | | | Total | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Group 1 (n=15) | | Group 2 (n=25) | | Group 3 (n=8) | | Group 4 (n=17) | | Groups 1–4 (n=65) | |
| | mmol kg$^{-1}$ | % | mmol kg$^{-1}$ | % | mmol kg$^{-1}$ | % | mmol kg$^{-1}$ | % | mmol kg$^{-1}$ | % |
| Basic cations | 1137 | 99 | 209 | 60 | 521 | 85 | 173 | 56 | 451 | 81 |
| Acidic cations | 9 | 1 | 140 | 40 | 93 | 15 | 136 | 44 | 103 | 19 |
| Sum of cations | 1146 | 100 | 349 | 100 | 614 | 100 | 309 | 100 | 554 | 100 |
| Ca-xch:Mg-xch[1)] | 13.9 | - | 6.4 | - | 8.8 | - | 5.3 | - | 9.8 | - |

1) xch: exchangeable

83%) and $Al^{3+}$ (15–47%) with only modest contributions from $Mn^{2+}$ and $Fe^{3+}$ (mostly 2–4%). An exception is the peat of Group 1, for which the relative role of $Mn^{2+}$ in providing cation exchange capacity is *ca*. 12%. The degree of base saturation depends primarily on peat soil acidity or calcium status; in more acid peat (Groups 2 and 4) it is below 60% and in less acid peat (Groups 1 and 3) it exceeds 85%.

## DISCUSSION

### Comparison and critical analysis of general characteristics

In peatland research, benchmarks are usually based on the middle layers of peat deposits (Orru 1992, Orru & Orru 2003, 2004, 2006). In our work, we took the superficial peat layer (40 cm thick in Histosols and 10–30 cm thick in Histic Soils, excluding forest litter sub-layers) as the benchmark for comparative analyses of peat chemical composition. Because we investigated only the soil layers of Histosols and the epipedon of Histic Soils, our data reflect the properties of younger peat which formed under the atmospheric-hydrological influences of recent centuries or millennia. The smallest values recorded for most elements originate from Histosols that are partly precipitation-fed (Group 2); and the highest values from Histosols that are fed by groundwater or which developed under the influence of laterally penetrating water (Group 1). The trophic conditions of Histosol and Histic Soil peat are controlled by position in the landscape and the character of geological sediments, although these influences are modest in the case of Group 2 soils.

Our data on pH and ash, N, Ca and P contents for fen and transitional bog Histosols agree well with the results of previous research in Estonia (Niine 1964, Truu *et al.* 1964, Veber *et al.* 1989, Orru 1992, Kask 1996) and neighbouring countries (Lupinovitch & Golub 1958, Pjavchenko 1973, Tsareva 1976, Jefimov 1980, Ilnicki 2002, Brožek & Zwydak 2003, Klavins *et al*. 2008). A partial exception is Ca content, which in some cases is higher in our fen and Histic Gleysol peats than reported by authors working in neighbouring countries (Lupinovitch & Golub 1958, Jefimov 1980, Klavins *et al.* 2008). However, classification of peat by its Ca content, as proposed by Pjavchenko (1972) for Russian peats, is also appropriate for Estonia.

It is interesting to note that most of the peat in Poland differs from Estonian peat in that Na predominates over K and it is only in raised bogs that K is more abundant than Na because Na is eliminated rapidly by lateral seepage through the poorly decomposed surface layer (Malawska *et al.* 2006).

The composition of epipedon peat in our Histic Podzols coincides well with Estonian Soil Survey data for Histic Podzols occurring in unpolluted areas (Kokk 1985). On the other hand, in peats near Kuremäe and Narva which are influenced by fly-ash, the contents of K, P and Ca are 2–3 times the background levels. Contamination of peat with fly-ash also raised pH (by 0.8–2.1 units) and ash content, and reduced exchangeable acidity and C:N ratio (Kokk 1985, Rajaleid & Tuuga 1989). There are practically no data characterising Estonian Histic Gleysol peats.

The approximate peat age for Histosol SPC is approximately 1100 years (Valk 1988, Kõlli *et al.* 2009), but peat age for Histic Soils is likely to be highly variable due to periodical fluctuations in the relative intensities of peat accumulation and mineralisation contributing to peat formation. When the peat is relatively dry, oxidation increases, the rate of peat accumulation decreases, and more highly decomposed layers are formed (Ikonen 1993). The presence of surface water causes high-amplitude temporal fluctuations in peat soil wetness, oxygen and nutrient levels, which enhance microbiological processes and promote the mineralisation of forest floor and superficial peat layers (Malawska *et al.* 2006). The decomposition of forest floor and superficial peat layers is accompanied by an increase in concentration of sparingly soluble compounds.

Ash content and peat composition are functions of the forest litter composition, peat accumulation character, dust input rate (including inputs from snow), mineral dissolution from the water supply and forest fires (Dugmore *et al.* 1992, Frey 1998, Malawska *et al.* 2006). Most of the soils in our RAs are also influenced by drainage, the only exceptions (drainage absent) being RAs 59 and 109. Okruszko (1993) pointed out that drainage of peatland raises the N and ash contents, as well as the decomposition rate of peat; and as a result of drainage the peat surface subsides rapidly (Minkkinen *et al.* 2008). Highly decomposed peat may otherwise develop under the influence of laterally penetrating water (Valk 1988, Lõhmus 2006).

### Extremes

Certain extreme element contents are related to soil type. For example, very high Ca content (Ca-xtr >30 mg $kg^{-1}$, Ca-xch >1100 mmol $kg^{-1}$ for RAs 76 and 133) indicates calcic (or hypereutrophic) conditions, whereas very low Ca content (Ca-xtr <1 mg kg$^{-1}$ and Ca-xch <100 mmol kg$^{-1}$) signifies oligotrophic conditions. Although Mg correlates highly with Ca, its concentration in peat reaches a relatively high level due to peculiarities of the water supply, as in the case of the transitional bog in RA Sandra (117) where the Mg content reaches a level (~900 mg kg$^{-1}$) which is usually characteristic of Soil Goups 1 and 3.

Mn content is exceptional on account of its high variability between sites and soils, but causes are difficult to find. Very high (>1500 mg kg$^{-1}$) Mn content relative to background (2–100 mg kg$^{-1}$) was determined in Sapric Histosol peat at RA 76 (Reastvere) and Histic Gleysol peat at RAs 27 and 195 (Kalina and Rassiku). High Fe-xtr content in fen peats at Mustjõe (21) and Reastvere (76), as well as in the peat layers of Histic Soil at Rassiku (195), may be due to the formation of bog iron (primarily iron oxyhydroxides) in these soils.

The K, Na, N, S and P contents lie within expected ranges and noticeable extreme values are absent. Nonetheless, in most of the fens and some of the peaty soils (Histic Podzols in Ida-Viru County and Histic Gleysols in Hiiu County), the mean S content is higher than the maximum permissible limit (MPL) (3.0 mg kg$^{-1}$) established for Nordic countries (Orru & Orru 2003).

### Hazardous elements

The breakdown of organic matter releases organic molecules that are capable of chelating with metals, whose mobility within the soil profile is thus increased. The important influence of organic matter on the reactions of heavy metals in soil, and hence on their availability to plants, requires that special attention be given to metal-organic matter complexes, their formation and their role in plant nutrition (Stevenson 1986). Low concentrations of heavy metals and/or micronutrients are required for the normal life activities of ecosystems and have, therefore, been studied at both global (Sillanpää 1982, 1990) and country levels (Petersell *et al.* 1997, Buivydaite 2005). In Estonia the ecology, mean content and MPL of hazardous elements have been researched most thoroughly for the soils of mineral arable areas (Kärblane *et al.* 2000). Because organic colloids (e.g. humic acids) are major players in the retention of heavy metals (Stevenson 1986), the percentage of heavy metals associated with organic matter will be particularly high in soils that are rich in organic matter (e.g. Histosols and Mollisols according to Soil Survey Staff (1999)) and will be influenced by pH; however, available data about peat soils are sparse (Petersell *et al.* 1997, Orru & Orru 2003). In the SPC that we investigated, the content of hazardous heavy metals does not, in general, exceed the MPL. An exception is Pb content, which exceeds MPL (50 mg kg$^{-1}$) in Histic Podzols near the south-western border between Estonia and Latvia. Relatively high (but below MPL) Cd content was also recorded in this area. The MPL (100 mg kg$^{-1}$) of Cr was exceeded in Histic Podzol peat at some sites near Tallinn, in Ida-Viru County and in Estonia's industrial regions; where the contents of Hg, Ni, Cu, Mn and Zn were also elevated but below MPL.

Our Pb, Hg, Mn, Cd, Cr and Zn levels were 2–3 times higher than, and our Cu and Ni levels similar to, background levels (or overall means) for Estonian peats (Orru & Orru 2003, 2004, 2006). This may arise from the more superficial origin of our samples, or because the origin of Histic Soils is intermediate between organic and mineral soils. Our data for Cr, Ni, Mn and Zn were 2–4 times lower, for Cd approximately the same, and for Hg and Pb considerably higher than the background level (or total mean) for the A horizons of Estonian mineral soils (Petersell *et al.* 1997). As hazardous elements that are bound to the peat of Histosols and Histic Soils are not readily released, the surface peat cover may be preserved as an environment-purifying medium for the area; and most SPC (even if the concentration of hazardous elements exceeds the MPL) may be used successfully for forestry (Chertov 1981, Valk 1988, Minkkinen *et al.* 2008).

## CONCLUSIONS

1. In Histic Soils the content of Al, K and heavy metals is statistically significantly higher than in Histosols.
2. In slightly and moderately acid peats the contents of Ca, Mg, Mn and Fe are significantly higher, but the C:N ratio, exchangeable acidity and content of free $H^+$ are lower than in strongly acid peat soils.
3. The sum of *aqua regia* (nitro-hydrochloric acid) extractable elements is considerably higher in slightly and moderately acid peat soils (28–45 g kg$^{-1}$ without heavy metals) than in strongly acid peat (10–12 g kg$^{-1}$).
4. Mean total content of *aqua regia* extractable elements decreases in the order: Ca(51%) > Fe(20%) > S(10%) ≥ Al(10%) > Mg(3%) ≥ P(3%) > K(2%) > Mn(1 %) > Na(<1%).
5. The dominant heavy metals in SPC peat are Pb (12–33 mg kg$^{-1}$) and Zn (7–41 mg kg$^{-1}$), followed by Cu (3–12 mg kg$^{-1}$), Cr (2–23 mg kg$^{-1}$) and Ni (2–8 mg kg$^{-1}$); Cd and Hg contents are in the range 0.2–0.5 mg kg$^{-1}$.

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