Current and historical patterns of heavy metals pollution in Estonia as reflected in natural media of different ages: ICP Vegetation, ICP Forests and ICP Integrated Monitoring data

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ABSTRACT

In order to characterise current and historical pattern of heavy metal (HM) pollution in Estonia, this article will compare the concentrations and stocks of Cd, Cr, Cu, Ni, Pb and Zn represented in current deposition (data from 18 local precipitation stations) with natural media of three different ages: 1–3-year-old moss carpet (ICP Vegetation moss survey data from 99 open area plots), 3–5-year-old litter layer, and several-decades-old organic layer (mor humus) of coniferous forest, in mostly podzolic soils (ICP Forest soil survey data, 75 stands).

Objectives of this study are (1) to assess differences in HM retention and accumulation in various aged media of coniferous stands (2) to estimate territorial differences in current HM distribution and previously accumulated concentrations and stores of HM (3) to compare territorial distribution of HM concentration in Estonia between five different regions: N-W; N-E; S-W; S-E and Western insular region, whereas the local oil shale industry in N-E part of Estonia has been the main source of HM pollution over a long period of time and therefore may have an effect on HM regional distribution.

Comparing the studied media, three types of HM retention patterns were detected: (1) for Cu, Ni, Cr (2) for Cd, Pb, (3) for Zn. The mean current level of HM deposition in Estonia is low comparison to previous decades, especially the 1980s. The effect of the previously significantly higher exposure of HM emissions and deposition is preserved in older part of soil organics (OF), where the highest stocks and concentrations of HMs (with the exception of Zn) are currently found. The HM proportions in fly ash of oil shale and in OF layer of soil were very similar with regards to Ni and Cr—indicating their origin from the oil shale industry in the N-E region. According to spatial distribution analysis, the greatest accumulated storages of Ni and Cr in OF layer of coniferous forest soils are characteristic to S-W Estonia.

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1. Introduction

Emissions of heavy metals (HM) have decreased in the European Union during 1990–2012 by: 89% for lead (Pb), 66% for cadmium (Cd), 74% for chromium (Cr), 67% for nickel (Ni), 42% for zinc (Zn) and 1% for copper (Cu) (European Environment Agency, 2014).

According to the official data main local sources of HM pollution in Estonia were and are point sources—oil shale-based power plants, oil and cement production and chemical industries located in the north-eastern part of the country (Kohv et al., 2001). Since the 1960s Estonia has been the greatest oil shale producer and consumer in the world (Raukas, 2010). The mineral part of Estonian oil shale is rich in metals especially Cr, Fe, Ni, Pb and Zn (Liiv and Kaasik, 2004). Over the decades the metals were spread to the local ecosystems with emissions of fly ash and solid particles. Local and trans-boundary environmental effects of industrial pollution related to oil shale-usage were the greatest at the end of 1980s (Raukas, 2010), when the total emission of fly ash and solid particles amounted to 280 thousand tons per year (Liblik and Pensa, 2001). Economic changes in the 1990s resulting from decrease in
industrial and electricity productions as well reconstruction of the plants and cement factories significantly reduced emissions of solid particles during 1990–2005 (Treier et al., 2008). According to the official data fly ash and solid particle emission was only 37 thousand tons in 2010 (Statistics Estonia, 2012). Over the same period emissions of HMs in Estonia have diminished significantly: by 81–99% for Pb, 85% for Cd, 44% for Cr, 52% for Cu, 77% for Ni, 47% for Zn (Kohv et al., 2009b). Thus, the emissions of Cd, Cu, Ni and Zn have decreased by more than the average in the European Union.

That metals can accumulate in soils over a long time period, especially in organic layers of forest soils is a widely published finding (Äyräs et al., 1997; Alriksson and Eriksson, 2001; Ukonmaanaho et al., 2001; Brumelis et al., 2002; Pajak and Jasik, 2011; Bringmark et al., 2013).

In order to find out the historical pattern of metal pollution in Estonia, the present article will compare the concentrations of HMs (Cd, Cr, Cu, Ni Pb and Zn) in natural media of three different ages: moss carpet (M) (ICP Vegetation moss survey data), litter layer (OL), and organic layer (OF) of coniferous forests (in mostly podzolic soils) with main tree species of Norway spruce (Picea abies) or Scots pine (Pinus sylvestris) (ICP Forest soil survey data). In order to see which layers have the greatest stores of HMs, the stocks were calculated for OL and OF layers as there layers had highest HM concentrations. Different media layers of coniferous forests consist of material with varying age and, therefore, reflect different periods of past air pollution levels. Green moss samples represent atmospheric input over last 3 years (Äyräs et al., 1997). The OL layer consists of mainly non-decomposed organic compounds like needles, leaves, and pieces of bark, twigs, cones and buds. The estimated age of soil litter layer could reach up to several years (Staaf and Berg, 1982). According to results of coniferous needle litterbag decomposition experiments (Bringmark et al., 2013), and assuming that non-needle litter decomposition would be slower, the age of OL would be 3–5 years. OL layer in coniferous forest soils is represented by mor type of humus and it is defined as slowly decomposing, therefore, thick organic layer of soil, which maintains a structure of decomposing plant residues. According to previous studies, the age of OF layer is estimated to be several decades (Äyräs et al., 1997; Ukonmaanaho et al., 2001; Pajuste and Frey, 2003). Based on results of measurements of carbon residence time in the humus layer in Scandinavian coniferous stands, the average age of humus layer varied between 36 and 41 years (Fröberg et al., 2011).

In addition to the above, litterfall (ICP Integrated Monitoring and ICP Forests) and bulk deposition (local precipitation monitoring) data were used to estimate recent annual average input of HM in stands. The comparison of different aged and composed natural media reflects the allocation of maximum concentrations and stocks of HMs and enables to estimate territorial distribution of HMs over a long time span.

The objectives of this study are (1) to assess differences of HM retention in various aged media of coniferous stands (2) to estimate territorial differences of current HM distribution and previously accumulated concentrations and stores of HM (3) to compare the territorial distribution of HM concentrations and storages in Estonia between five different regions: N-W; N-E; S-W; S-E and Western insular region. The local oil shale industry in the NE part of Estonia has been the main source of HM pollution over a long period of time.

2. Material and methods

2.1. Used datasets

The current study used data on heavy metals from International Co-operative Programmes (within the framework of the Convention on Long-Range Trans-boundary Air Pollution of the United Nations Economic Commission for Europe) ICP Forests, ICP Vegetation, and ICP Integrated Monitoring (ICP IM). For estimating HM’s bulk deposition, data of Estonian local precipitation network were used. All the datasets were acquired from Estonian National Monitoring Program databases. In total 450 samples from 195 plots were analysed.

2.2. Sampling

2.2.1. Moss samples

Moss (M) samples (Hylocomium splendens or Pleurozium schreberi) were collected from 99 open area sites (Fig. 1) according to the ICP Vegetation methods. One composite sample was formed from five to ten subsamples spread around each sampling site. Only green fully developed shoots, representing mainly two or three year’s growth, were separated and chemically analysed afterwards (Rühling et al., 1992; Rühling, 1994; ICP Vegetation Coordination Centre, 2005).

The absence of roots and cuticles enables these mosses to obtain nutrients and pollutants directly from precipitation and dry deposition. Furthermore, it has been found that H. splendens and P. schreberi accumulate heavy metals proportionally with current air pollution levels and are not affected by the heavy metals/nutrients concentrations present in soil layers (ICP Vegetation Coordination Centre, 2005).

Sampling years of 1995 and 2005/2006 of ICP Vegetation datasets were chosen because the age of used soil organics consists of material since 2006 and backwards. Comparison of these two moss sampling periods gives an overview of the changes in time.

2.2.2. Soil organics samples

Litter layer (OL) and organic layer (OF) samples were collected according to ICP Forests Manual of Soil Sampling and Analyses (2004) from 75 ICP Forests coniferous sites (level I network) with mostly podzolic soils in the framework of BioSoil project in 2006–2008 (Fig. 1). The OL and OF layers were sampled with a 40 × 25 × 6 cm frame placed on forest floor. Green plants and mosses were separated and thickness of each soil organic layer was measured. Thereafter the OL and OF layers were removed and placed separately into plastic bags. For each layer one composite sample from five subsamples was prepared for chemical analysis. (Most recent methodology available at ICP Forests website: http://icp-forests.net/. Programme Coordination Centre of ICP Forest and the Task Force of ICP Forests, 2010).

In addition, the OH layer was sampled, if present. The OH layer samples are not included in this study because the number of samples was too small to carry out the comparative tests with the other layers sampled.

2.2.3. Litterfall samples

Litterfall samples were collected using funnel-shaped traps at four sites: Saarejärve and Vilsandi ICP IM plots (in two mature pine stands and in one old spruce stand) and at Tõravere mature spruce stand of ICP Forest level II network (Table 1). In this paper we use annual litterfall input data of the above-mentioned four stands for 2010–2011. For chemical analysis yearly composite samples were formed from monthly sorted samples (shed brown needles and the remaining fine litter) and winter season samples (from Dec. to Apr.) (ICP IM Programme Centre, 2004; Programme Coordination Centre of ICP Forests and the Task Force of ICP Forests, 2010).

2.2.4. Bulk deposition

Annual loads of HMs (Cd, Cu, Pb and Zn) in bulk deposition from 18 stations of local precipitation network were used for calculating
The annual average input by deposition during 2002–2011. The sampling process was carried out according to the sampling protocol of EMEP Manual for Sampling and Chemical Analysis (1996).

2.2.5. Territorial distribution of sampling sites

All 195 sample collection plots (n = 450 samples) are shown on Fig. 1. In order to compare territorial distribution of HM concentrations in Estonia, the area was divided into five different regions: 1. N-W; 2. N-E; 3. S-W; 4. S-E and 5. Western insular region.

2.3. Chemical analysis

Chemical analyses of ICP Vegetation moss samples were performed by Finnish Forest Research Institute (METLA) laboratory. Analyses of samples gathered under ICP IM, ICP Forests and Estonian local precipitation network programmes were performed by Estonian Environmental Research Centre laboratory. Both of the laboratories used hold a certificate for chemical analysis for ICP Programmes. The laboratory of Estonian Environmental Research Centre is accredited by Estonian Accreditation Centre (www.eak.ee). The laboratory of Finnish Forest Research Institute (METLA) is accredited by Finnish Accreditation Service FINAS (www.finas.fi). The parameters of heavy metal analysis of precipitation, soil and plant material can be found in the accreditation documents available at the accreditation centres web pages.

Both of the laboratories are quality-assured as they regularly take part in international cross-calibration courses for laboratories, organised by ICP Programmes. The ring test results and participation info of ICP Forests Programme intercalibration courses are available online at Austrian Federal Research Centre for Forests (http://bfw.ac.at) and at Belgium Research Institute for Nature and Forest (http://www.inbo.be).

Cd, Cr, Cu, Ni, Pb, and Zn concentrations in M layer were determined using ICP-ES (Inductively coupled plasma emission spectrometry), and in litterfall, OL and OF layers using ICP MS (inductively coupled plasma mass spectrometry, according to ISO 11885, STJnr.M/U91 for Cu, Zn; STJnr.M/U94 for Cd, Cr, Ni, Pb, SFS 5074, certifications verified by Eesti Akrediteerimiskeskus, 2013).

<table>
<thead>
<tr>
<th>Natural media</th>
<th>Mosses (M) 99 plots</th>
<th>Litter layer of soil (OL) 75 plots</th>
<th>Organic layer of soil (OF) 75 plots</th>
<th>OF/M</th>
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<tbody>
<tr>
<td></td>
<td>AVG</td>
<td>MD</td>
<td>STDEV</td>
<td>AVG</td>
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<tr>
<td>Group 1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>3.5</td>
<td>3.4</td>
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<td>4.9</td>
</tr>
<tr>
<td>Cr</td>
<td>0.7</td>
<td>0.6</td>
<td>0.2</td>
<td>5.7</td>
</tr>
<tr>
<td>Ni</td>
<td>0.8</td>
<td>0.7</td>
<td>0.2</td>
<td>3.1</td>
</tr>
<tr>
<td>Group 2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cd</td>
<td>0.2</td>
<td>0.2</td>
<td>0.04</td>
<td>0.2</td>
</tr>
<tr>
<td>Pb</td>
<td>2.8</td>
<td>2.6</td>
<td>0.8</td>
<td>3.2</td>
</tr>
<tr>
<td>Group 3</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zn</td>
<td>29.0</td>
<td>27.5</td>
<td>5.8</td>
<td>64.2</td>
</tr>
</tbody>
</table>
Pre-treatment was done using microwave oven with HNO₃ and HClO₄ mixture. Bulk deposition was analysed according to EVS-EN ISO 11885.

2.4. Statistical analyses

Statistical analyses were performed using CANOCO (Version 4.5) (Ter Braak and Šmilauer, 1998) and STATISTICA 7.0 software.

Redundancy analysis (RDA) of logarithmically transposed data was used to detect and illustrate connections between HMs and the regions. The significance of each variable selected and of the ordination axes was verified by permutation tests available in Canoco.

Evident variance between HMs in the five different regions was proved by logarithmically transformed data with the ANOVA test \( (p < 0.05) \), available at STATISTICA 7.0 software.

The nonparametric Spearman’s rank correlation \( (r_s) \) analysis was used to describe the possible atmospheric origin of different HMs in OL and OF layers in correlation with HM concentrations in the moss layer. The same methodology has been previously used by Tamminen et al. (2004) and Pajak and Jasik (2011).

The map with sampling plots was drawn using MapInfo Professional software.

3. Results

3.1. HM concentrations and distribution in different natural media

In general the studied samples of various natural media had low HM (Cd, Cr, Cu, Zn, Pb and Ni) contents, within the range of concentration for non-polluted area (Table 1).

The comparison of HM concentrations in M, OL and OF layer samples revealed three groups of individual retention patterns.

The first group (Table 1) consists of the metals (Cu, Cr, Ni), the concentrations of which increase as follows: M layer < OL layer < OF layer. In comparison to M layer, the concentrations of these metal increased in OF layer as follows: Cr (18 times), Ni (8 times) Cu (2 times) (Table 1). The OF/M ratio was calculated for each HM following a method described by Tamminen et al. (2004), whereby high OF/M ratio shows strong retention in the organic layer of soil. Based on the calculation given in Table 1, Ni and Cr are highly accumulative, whereas Ni has the highest OF/M ratio of all studied HMs.

The second group is formed by Cd and Pb (Table 1) with maximum median and mean concentrations also obtained in the organic layer of soil. A difference from the previous pattern is the almost equal concentration of Pb and Cd in OL and M layer in comparison to the substantial difference, e.g. as was the case with Ni and Cr for the first group. For the second group OF/M ratio is especially high for Pb — the concentration in OF is 19 times higher in comparison to the respective concentrations in M layer.

The third type of retention pattern is characteristic to Zn and could be described in the increasing order of OF layer < M layer < OL layer, where the concentrations in M layer are a half and in OF layer three times lower than Zn concentrations determined in OL layer (Table 1, Fig. 2d). The OF/M ratio for Zn is extremely low in comparison with other previously described HMs.

The first two retention patterns show remarkable differences in HM concentrations in M and OF layers, especially in regard to Ni, Cr and Pb (Fig. 2a–c). The significantly higher values are present particularly in older part of soil organics, which is contrary to the division of Zn concentrations in the different layers studied (Fig. 2d).

Despite the extraordinary retention pattern of Zn, the largest supplies of all HMs were still found to be embedded in OF layer (on average of Pb 538 g/ha; Zn 1607 g/ha; Ni 26 g/ha; Cu 198 g/ha; Cr 729 g/ha; Cd 11 g/ha–Table 3). In summary, various correlation analyses repeatedly highlighted statistically significant correlations between HMs like Ni, Cr, Cu, Zn and Pb (Table 2).

3.2. Correlations analysis

In order to find correlations of HMs in different media and their relation to spatial distribution within Estonia, different types of correlation analysis were tested:

3.2.1. Correlations between HMs in distinct media

Correlations between HMs were studied in the different layers in order to identify possible common origins of HMs and their similar movement in the forest ecosystem (Spearman’s rank correlation \( r_s \) at \( p < 0.05 \)). The analysis revealed a high correlation between Ni and Cr inside all the studied media, especially strongly in OL \( (r_s 0.96) \) and OF \( (r_s 0.93) \) layers. Somewhat weaker correlations were found between Cu and Zn \( (r_s 0.24–0.40) \) in OL, OF and M layers (Table 2).

3.2.2. Correlations between HMs in distinct media layers in different regions

In-depth data analysis was carried out to detect correlations between HMs inside different regions and media. A significant correlation between Ni and Cr (Table 2) was found in all layers and in most of the regions (with the exception of M layer in S-W and OF layer in the western insular area), but the correlation was highest in OL \( (r_s 0.87–0.98) \) and OF \( (r_s 0.88–0.97) \) layers. An unanticipated finding was a correlation between Ni and Pb \( (r_s 0.46–0.78) \) in the M layer at four regions out of five (Table 2). Single statistically significant correlations were found for some other heavy metals, but no common pattern between the different media layers occurred.

In summary, various correlation analyses repeatedly highlighted statistically significant correlations between HMs like Ni, Cr, Cu, Zn and Pb (Table 2).

3.3. Spatial distribution of HMs in Estonia

RDA (redundancy analysis) and permutation test (to verify the significance of RDA test) of Canoco programme were chosen to illustrate and give an overall picture of the distribution of HMs between five different regions and in different media (Fig. 3).

Regional distribution of HMs based on earlier (1995) moss data reflects clearly the significant convergence of HMs in the N-E industrial region 2 (Fig. 3a). In the later years (2005/06), however, the N-E region could not be distinguished, and for some HMs, especially for Ni, a new tendency to concentrate near the capital area in N-W
More precise analyses (by ANOVA test, significant at \( p \leq 0.05 \)) of regional differences in OL database showed statistically significant higher concentrations (mg/kg) of Cu (\( p = 0.03 \)), Zn (\( p = 0.05 \)) and Pb (\( p = 0.01 \)) in S-W Estonia and the western insular area (regions 3 and 5). The same analysis of stocks (g/ha) show the highest supplies of Cu (\( p = 0.01 \)) and Zn (\( p = 0.02 \)) only in S-W, but of Pb (\( p = 0.01 \)) and also Cd (\( p = 0.05 \)) in the western insular area.

With regards to Ni and Cr, the statistically significant proof of higher concentrations and supplies in S-E Estonia was not found in OL database, but in older and deeper layers of soil organics (in OF) both average concentrations as well as stocks of Ni and Cr were statistically significantly higher in S-E Estonia in comparison with others regions (\( p = 0.01–0.02 \)).

4. Discussion

Over 90% of HM emissions in Estonia are found to originate from stationary sources, particularly from N-E Estonia's oil-shale-related industries (Kohv et al., 2009a). Currently, (2006–2012), average emissions from Estonia's stationary sources are 44,818 kg/y of Zn, 2236 kg/y of Cu, 32,806 kg/y of Pb, 5635 kg/y of Ni, 8811 kg/y of Cr and 561 kg/y of Cd (Estonian Environment Agency, 2013). According to Table 3, estimated annual average input of metals is higher by bulk deposition than by litterfall for Pb, Cu and Zn (10%, 62% and 72%, respectively) indicating that the impact of airborne emissions in Estonia is still higher in comparison to ecosystem's inner cycling. Considering the results of previous studies at 14 European forested catchments, the annual bulk deposition load of Zn and Cu is on average higher at Estonian sites—approximately 30% for Zn and 50% for Cu (Huang et al., 2011; Bringmark et al., 2013).

In our study, additional enrichment by canopy due to dry deposition does not become clear as the moss data used from ICP Vegetation programme's database is based on analyses of open area mosses only and, therefore, reflects only open field deposition. According to official data, the significance of dry deposition has historically been the greatest in the N-E and Eastern part of Estonia where oil shale-fired power plants and Kunda cement factory emitted enormous amounts of alkaline dust containing HMs. Significant decrease in electricity and cement production in the beginning of 1990s, and simultaneous installation of modernised flue gas purification systems for oil shale-burning thermal power plants in 1997, have resulted in tremendous reduction of solid particles emission (Talve and Riipulk, 2001). Despite the continuous retention process in the ecosystem, the decreasing trend of HM concentrations was noticeable especially for mosses. According to the ICP Vegetation programme the concentrations have dropped for all the HMs over the ten
years between 1995 and 2005/06 (Keskonnaministeeriumi Info-
ja Tehnokeskus, 2008). The change in concentrations is less
remarkable for Cu and Zn in mosses (Kaasik and Liiv, 2007;
Ukonmaanaho et al., 2008). Nevertheless, bryomonitoring results
indicate that the HM concentrations still remain higher in the
mosses of the NE region (Liv and Kaasik, 2004; Kaasik and Liiv,
2007).

The main factors that determine accumulation of HMs in the
organics of soil are initial input, plant’s capacity to bind HMs and
transport of HMs via plant uptake from lower parts of soil, and

<table>
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<tr>
<th>Metal</th>
<th>Annual input (g/ha/y)</th>
<th>Accumulated stocks (g/ha)</th>
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<tr>
<td></td>
<td>Bulk deposition CV %</td>
<td>Litterfall CV %</td>
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<tr>
<td>Cd</td>
<td>0.5</td>
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</tr>
<tr>
<td>Pb</td>
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<tr>
<td>Zn</td>
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<tr>
<td>Cu</td>
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<td>147</td>
</tr>
<tr>
<td>Cr</td>
<td>–</td>
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<tr>
<td>Ni</td>
<td>–</td>
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**Table 3**

Annual average input (g/ha/y) of HM by bulk deposition (2002–2011) (Estonian local precipitation network), and by litterfall (2010–2011) (Estonian data of ICP Forests and ICP IM). Stocks of HMs (g/ha) in different organic layers of coniferous forest soils (Estonian data of ICP Forests and ICP IM). Variation coefficient (CV %) is given to illustrate the high variability of HMs in natural ecosystems.
Bulk deposition of Zn is on average higher in the area of oil-shale burning industries in NE Estonia (according to local precipitation stations network), giving higher peaks in the immediate vicinity of oil-shale fired power plants. Higher bulk deposition in NE region is well correlated with the spatial distribution of the higher concentrations Zn in OL and OF layers (Fig. 2) in N-E of Estonia. Zn is a HM very prone to long-range trans-boundary transport and therefore it is very likely that the Zn emissions from local power plants have been carried with westerly winds to the East and will be deposited further away. High Zn, Ni, Cr and Cu concentrations have been found in the sediments of Narva River in N-E region (Roots and Nõmmsalu, 2011)—a fact supporting the argument that the industrial pollution from the oil-shale burning thermal power plants is carried to the Eastern direction as mentioned before.

The overall level of HM emissions in Estonia is currently low (European Environment Agency, 2013), the effect of previous significantly higher exposure of HM emissions is preserved in OF layer, where the average accumulated stocks of highly accumulative HMs reach the levels of 728.8 g/ha for Cr, 538.5 g/ha for Pb and 372.5 g/ha for Ni (Table 3). The finding that concentrations of Ni and Cr were significantly higher in OF layer than in moss layer, is once again an indication of the influence of previous high HM emissions.

Elevated Ni concentrations in mosses have been found in the surroundings of Tallinn (the capital area in N-W) and in N-E of Estonia (Kaasik and Liiv, 2007). According to 2013 ICP Vegetation moss analysis, in N-W area there has been a decrease in Ni concentration in comparison to an analysis from 2003 (increase of Ni was up to 2.2 times) (Liiv and Kösta, 2014). The concentrations of Ni and Cr in mosses show that Ni and Cr are mainly connected to oil shale usage-related emissions (Liiv and Kaasik, 2004). Over the long time span (1989–2011), it can be seen that the average content of Ni, Cr and also Pb in N-E Estonia’s mosses has been higher in comparison to the mean value for the country, however, nowadays the levels have become equal with other sample sites in Estonia (Kösta and Liiv, 2011). High ratio of Pb median concentration between OF/M layers, seen in Table 1, shows the high accumulation of Pb in organic part of soil and reflects the previously higher deposition levels and continuous HM retention process over a longer time span. The same applies to Ni and Cr as their OF/M ratio was several times higher in comparison to other studied HMs (Table 1). Common origin of Ni, Cr and Pb is revealed by statistically significant correlations between the concentrations of Ni–Cr and Ni–Pb, and that in different parts of Estonia as well as in different studied media.

Based on the assumption that the HM content in Estonian forest soils has to be related to emissions originating from the oil shale industry, the chemical composition of oil shale fly ash was observed and compared with HM emissions and HM content in OF layer. Table 4 shows that the proportions (%) between the HMs in OF layer are very similar to the proportions between

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<tbody>
<tr>
<td>Pb</td>
<td>48.8</td>
<td>20.3</td>
<td>11.1</td>
<td>60.0</td>
</tr>
<tr>
<td>Ni</td>
<td>15.8</td>
<td>11.3</td>
<td>13.4</td>
<td>11.0</td>
</tr>
<tr>
<td>Cu</td>
<td>9.8</td>
<td>7.3</td>
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<tr>
<td>Cr</td>
<td>25.6</td>
<td>23.8</td>
<td>26.0</td>
<td>18.0</td>
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Zn and Cd are not presented, as all the data for those HMs were not available.
the discussed HM's datasets of officially reported emissions (Estonian Environment Agency, 2013), as well as between the HM’s proportion in the chemical composition of oil shale fly ash (Talve and Riipulk, 2001)—especially for Ni and Cr. Therefore there is a reason to believe that these HMs are related to air pollution driven by oil shale usage. Ni and Cr clearly stood out in S-E of Estonia, where the highest concentrations (mg/kg) and largest stocks (g/ha) of these HMs were found in OF layer. The accumulated Ni and Cr stocks in S-E therefore originate from the industrial N-E from the period of high activity in the oil shale industry and the higher HM emissions that accompanied it—now accumulated in the organic layer of forest soil in south-eastern part of Estonia. Local heritage of Ni and Cr pollution has also been shown by other authors (Brumelis et al., 2002; Steiness and Friedland, 2006).

5. Conclusions

The main conclusions:

1. Current level of HM deposition in Estonia is modest, but HMs deposited during previous decades have accumulated in the organics of forest soils—especially the HMs that are unnecessary for the functioning of plants (e.g., Pb, Ni and Cr).

2. The greatest historical stationary emission source of HMs in Estonia—the oil shale industry has left its mark on soil organics of coniferous stands, where the large stocks have HM ratios that are similar to those characteristic to fly ash emissions of the oil shale industry.

3. Ni and Cr, originating from the oil shale industry, exhibit the highest stores in S-E Estonia indicating mostly local deposition and a high ability to accumulate in soil organics.

4. Zn is one of the most reused HMs at the ecosystem level. Despite that Zn has accumulated in soil organics equally in all the studied regions, although the highest and most variable deposition still occurred in the N-E oil shale region.

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