DISSERTATIONES
GEOGRAPHICAE
UNIVERSITATIS
TARTUENSIS
65

ÜLLE NAPA

Heavy metals in Estonian coniferous forests

DISSERTATIONES GEOGRAPHICAE UNIVERSITATIS TARTUENSIS
65

DISSERTATIONES GEOGRAPHICAE UNIVERSITATIS TARTUENSIS
65

ÜLLE NAPA

Heavy metals in Estonian coniferous forests

UNIVERSITY OF TARTU
Press

Department of Geography, Institute of Ecology and Earth Sciences,
Faculty of Science and Technology, University of Tartu, Estonia

Dissertation was accepted for the commencement of the degree of *Doctor philosophiae* in physical geography at the University of Tartu on October 09, 2017 by the Scientific Council of the Institute of Ecology and Earth Sciences University of Tartu.

Supervisors: Jane Frey, University of Tartu, Estonia
Ivika Ostonen-Märtin, University of Tartu, Estonia

Opponent: Guntis Brūmelis, University of Latvia, Latvia

Commencement: J.G. Granö auditorium (room 327), 46 Vanemuise Street, Tartu, on 28 November 2017 at 10.15 a.m.

Publication of this thesis is granted by the Institute of Ecology and Earth Sciences, University of Tartu

ISSN 1406-1295
ISBN 978-9949-77-604-7 (print)
ISBN 978-9949-77-605-4 (pdf)

University of Tartu Press
www.tyk.ee

CONTENTS

ORIGINAL PUBLICATIONS

This thesis is based on the following publications referred to in the text by Roman numerals:

I. **Napa Ü,** Kabral N, Liiv S, Asi E, Timmusk T, Frey J (2015) 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. Ecological Indicators (2015) 52: 31–39.

II. **Napa Ü,** Ostonen I, Kabral N, Kriiska K, Frey J (2017) Biogenic and contaminant heavy metal pollution in Estonian coniferous forests. Regional Environmental Change (2017) 17: 2111–2120.

III. Ostonen I, Truu M, Helmisaari HS, Lukac M, Borken W, Vanguelova E, Godbold DL, Lõhmus K, Zang U, Tedersoo L, Preem JK, Rosenvald K, Aosaar J, Armolaitis K, Frey J, Kabral N, Kukumägi M, Leppälammi-Kujansuu J, Lindroos AJ, Merilä P, **Napa Ü**, Nöjd P, Parts K, Uri V, Varik M, Truu J (2017) Adaptive root foraging strategies along a boreal–temperate forest gradient. New Phythologist (2017) 215: 977–991.

IV. **Napa Ü,** Kabral N, Ostonen I, Kriiska K, Asi E, Apuhtin V, Timmusk T, Frey J (201X) Heavy metal fluxes at coniferous monitoring stands in Estonia. Manuscript will be submitted for publication to journal of Environmental Monitoring and Assessment.

Author's contribution:

	I	II	III	IV
Original idea	*	*		*
Study design	*	*		*
Data collection	*	*	*	*
Data analysis	*	*		*
Manuscript preparation	*	*	*	*

ABSTRACT

The aim of this thesis was to get an overview of heavy metal pollution in coniferous forests in Estonia based on the data of environmental monitoring programmes. The specific aims of this study were i) to assess differences in heavy metal concentrations and accumulation in variously aged media (forest mosses, soil organic layers, litterfall, fine roots, and living needles), ii) to estimate the extent of different input and uptake fluxes of heavy metals in comparison to storages in the soil organic layer, and iii) to estimate and compare territorial differences in current heavy metal deposition (data on bulk deposition and data from mosses) and previously accumulated concentrations and storages of heavy metals in forest soil organic horizons in Estonia.

In this thesis six different heavy metals (Zn, Cu, Cr, Ni, Cd, and Pb) in Estonian coniferous forests were investigated. Samples of bulk deposition, living needles, litterfall, mosses, upper soil organic layers, fine roots, and ecto-mycorrhizal mycelia collected as part of different international and local monitoring programmes were combined and analysed (ICP Forests, ICP IM, ICP Vegetation, and data from national precipitation network stations) to understand the differences in heavy metal concentrations and accumulation in different parts of the coniferous forests. In addition, the concentrations, accumulation, and fluxes of different heavy metals in coniferous forests, and regional differences in heavy metal depositions and accumulation were estimated.

The sharp decrease in heavy metal airborne depositions during the 1990s were followed by slower decreasing trends over 2003–2013, and heavy metal depositions levels are now considered modest. Nevertheless, deposition remains an important heavy metal input source, especially for biogenic heavy metals, such as Zn and Cu. This was not the case for contaminant heavy metals however. Cd and Pb had higher storage levels in short-living compartments of trees (fine roots and current-year living needles) in comparison to the input flux of deposition and litterfall.

The highest storages of heavy metals were found in the soil organic layers. High concentrations of heavy metals in fine roots correlated positively with heavy metal concentrations in soil organic horizons. This indicates to earlier heavy metals accumulation into soil organic layers, particularly during the peak oil-shale-usage period in Estonia. In some cases, these heavy metals might still be transported to the above-ground biomass of coniferous trees. High accumulation of heavy metals – especially Pb – into fine roots prolongs the heavy metals' stay in the ecosystem and delays the soil purification processes of upper soil organic layers.

Regional differences occur in current heavy metal deposition and previously accumulated concentrations and storages of heavy metals in Estonia. These differences were especially remarkable in the past, as the NE part of Estonia has been historically most affected by pollution from the oil shale and cement industries.

Combining the results of international monitoring programmes with local datasets gave a unique insight into distribution of heavy metals in coniferous forests in Estonia both currently and in the past. This kind of scientific analysis of environmental data helps to form an overview of the current environmental status of forests and predict the effects of previously accumulated pollutants under changing environmental conditions. Therefore, environmental monitoring and scientific analyses of collected datasets remains a priority.

1. INTRODUCTION

According to the European Environmental Agency (EEA), an overall decline in heavy metal emissions since the 1990s is characteristic of all European Union (EU) countries, especially for emissions of Pb, Cd, Cr, Ni, and to a lesser extent Zn (EEA, 2014). Emissions of the most toxic contaminant heavy metal – Pb – declined by up to 90% over the last two decades (EEA, 2015), demonstrating the success of regulations and protocols adopted to reduce heavy metal emissions in Europe and worldwide. Critical loads of heavy metals defined by the EEA represent the limit values that once exceeded are likely to have harmful effects on the natural environment (EEA, 2013). Today, critical loads of heavy metals of the most toxic contaminants Cd and Pb are in general not exceeded in the EU, including in Estonia (de Wit *et al.,* 2015).

1.1. The sources of heavy metals

The main sources of heavy metals could be divided in two: natural and anthropogenic sources. Natural sources include volcano eruptions, weathering, sea spray, soil dust, forest fires etc., but since the beginning of 20th century the anthropogenic heavy metal sources (mainly road transport, metallurgical industries, use of fossil fuels, fertilisers etc.) have been prevailing (Tyler, 1984; Bergkvist, 1986; Rühling & Tyler, 2001; Franco, 2005; Kabata-Pendias, 2011; Abraham *et al.,* 2017; Shahid *et al.,* 2017).

Heavy metals pose a potential threat to forest ecosystems functioning. Herein is important to acknowledge the accumulative nature of heavy metals which could lead to possible harmful effects on forests even in the case of modest or low heavy metal inputs over long time periods. High concentrations of heavy metals in trees and ambient environment affect various functions of forest ecosystems e.g. growth of trees, their photosynthetic capacity and uptake of necessary nutrients, functioning of fine roots, composition and functioning of soil bacterial communities, soil fauna etc. (Tyler, 1984; Bojarczuk & Kieliszewska-Rokicka, 2010; Kabata-Pendias, 2011; Shahid *et al.,* 2017). Despite that, one should not forget that in micro quantities heavy metals like Zn and Cu are necessary for plant's normal functioning (Tangahu *et al.,* 2011). This in turn is one of the factors affecting heavy metal cycling in the forest ecosystem. Therefore distinction between biogenic heavy metals and contaminant heavy metals (according to Bruno Franco, 2005) must be made.

The main local anthropogenic sources of heavy metal emissions in Estonia have been and still are the oil shale-based power plants, oil and cement industries, and chemical industries located in the NE part of the country (Kohv *et al.,* 2002). Oil shale is the most important mineral resource in Estonia and has been very intensively used – mainly in electricity production – since the 1960s, making Estonia the largest oil shale producer and consumer in the world

(Raukas, 2010). The mineral part of the oil shale is rather rich in heavy metals (e.g. Cr, Fe, Ni, Pb, and Zn), and therefore ecosystems have been subjected to long-term heavy metal exposure and accumulation (Liiv & Kaasik, 2004). The majority (90%) of Estonia's heavy metal emissions remain related to solid particle emissions from the oil shale power plants and industries located in the NE (Kohv *et al.,* 2009a). According to the Estonian Environmental Strategy 2030, there is a planned reduction in electricity production from oil shale which is to be replaced with alternative types of electricity production (Ministry of the Environment, 2007). However, oil shale based electricity will to some extent still be used in the long term, as renewable energy sources (e.g. wind energy, solar panels, biomass) are unlikely to entirely cover the needs of Estonia (Ministry of the Environment, 2007). During 2005–2015 the use of oil shale in Estonia increased by 21%, but solid particle emissions decreased by 38% over the same period (Statistics Estonia, 2017). For many decades heavy metals have spread to natural forest ecosystems via solid particle air pollution. Currently, 97% of particulate emissions and over 90% of airborne heavy metals originate from the energy sector, which means directly from oil shale-related electricity production (EEA, 2013; Kohv *et al.,* 2009a). Today, the main ambient air quality concern in Estonia is particulate air pollution, as even if emissions of solid particles have reduced over 1990–2012 by 90%, PM_{10} (particles with a diameter <10 μm) limit values are regularly exceeded, especially in the region of the capital city, Tallinn (EEA, 2015; SOER, 2015).

Estonian forest ecosystems are also affected by long-range transboundary pollution of heavy metals from highly industrialised and densely populated areas of Europe. That should be suspected especially for Zn, Cd and Pb (Kyllönen *et al.,* 2009; Huang *et al.,* 2011; Bringmark *et al.,* 2013; Ilyin *et al.*, 2016).

1.2. Data of heavy metals in National Environmental Monitoring Programme

To reduce heavy metal emissions locally, the Estonian government has ratified the Åarhus Protocol on Heavy Metals (1998) of the Convention on Long-Range Transboundary Air Pollution (CLTRAP), and is committed to fulfilling its requirements. The main legislative act at a national level regulating heavy metal emissions is the Atmospheric Air Protection Act and its regulations. Estonia has also joined international environmental monitoring programmes to obtain internationally comparable data to assess the state of its environment and these programmes are currently part of the National Environmental Monitoring Programme. Among other important air, precipitation, soil quality, and eco-system state parameters, heavy metals are monitored under the framework of international environmental monitoring programmes, e.g. the International Co-operative Programme on Assessment and Monitoring of Air Pollution Effects

on Forests (ICP Forests), the International Cooperative Programme on Integrated Monitoring of Air Pollution Effects on Ecosystems (ICP IM), and the International Cooperative Programme on Effects of Air Pollution on Natural Vegetation and Crops (ICP Vegetation).

The ICP Forest programme was launched in 1985 in response to the extensive destruction and damage of forests during the 1980s (ICP Forests, 2017). This programme aims at monitoring forest conditions in Europe. Currently there are 42 countries in Europe and outside taking part in the programme's activities. Monitoring is done at two different degrees of intensity: at level I plots data on forest canopy condition and soil parameters are collected. At level II plots intensive monitoring activities are carried out to detect and monitor stress factors, including from air pollution (ICP Forests, 2017). In Estonia, there are 98 ICP Forests level I plots and 6 level II plots (Apuhtin *et al.,* 2017).

Since 1987, the ICP Integrated Monitoring Programme has monitored forest ecosystems at a catchment level (ICP IM, 2017). The long-term monitoring activities and long time series of this programme are especially important to provide an overview of the effect of air pollutants and climate change on the ecosystems over time. Currently, there are 41 ICP IM plots in 17 different countries (Lundin & Forsius, 2016), including two active plots in Estonia (Kabral, 2017a).

The ICP Vegetation Programme started in 1987 due to the harmful effect of ozone on crops and (semi) natural habitats (ICP Vegetation, 2017). This programme focuses on air pollution-related problems, and includes various analyses, such as heavy metal concentrations in mosses, to address them. Currently 50 countries are taking part in the ICP Vegetation Programme (ICP Vegetation, 2017). In Estonia, regular monitoring of heavy metal concentrations in forest mosses is carried out at 99 ICP Vegetation monitoring sampling plots (Liiv & Kösta, 2017).

The first Estonian national precipitation network sites were established in 1994, and currently there are 18 stations covering the whole territory of Estonia (Kabral, 2017b). Precipitations are collected on a daily basis and among other ions heavy metal levels have also been recorded at all the stations since 1999.

Since the 1990s, heavy metal emissions in Estonia have diminished significantly: Pb by 81–99%, Cd by 85%, Cr by 44%, Cu by 52%, Ni by 77%, and Zn by 47% (Kohv *et al.,* 2009b). In total, heavy metal emissions in Estonia have dropped more than the European Union average (Hettelingh *et al.,* 2007). This was mainly due to rapid economic changes and a decrease in electricity production during the early 1990s in combination with the subsequent introduction of new industrial technologies, implementation of new environmental regulations, and higher investment in technologies for better air protection over 2005–2015 (Treier *et al.,* 2008; Statistics Estonia, 2017). The heavy metal emissions in Estonia have been declining since the 2000s onwards. The statistically significant decreasing trends of heavy metal depositions were recorded for the period 2003–2013 at the majority of national precipitation network stations for Cd and Cu and at a few stations for Pb and Zn depositions (publication IV).

Average heavy metal depositions for noted decade were 0.5 g ha^{-1} of Cd, 27 g ha^{-1} of Cu, 5.2 g ha^{-1} of Pb, and 387 g ha^{-1} of Zn (publication IV).

Despite the significant decrease in heavy metal emissions and the current relatively modest levels of heavy metal depositions, the accumulative nature of heavy metals and data of the environmental programmes have shown retention of previously deposited heavy metals in different parts of the forest ecosystems. On this basis, it remains important to participate in environmental monitoring programmes and continuously analyse the collected data. Therefore, this study concentrated on the analysis of the heavy metal databases measured in the framework of the previously mentioned international environmental programmes.

1.3. Heavy metals in coniferous forests

With the aim of understanding how the most typical coniferous forests – spruce and pine stands – were affected by different heavy metals (Zn, Cu, Cr, Ni, Cd, and Pb), data of the different international and local monitoring programmes were combined and analysed (ICP Forests, ICP IM, ICP Vegetation, data from national precipitation network stations). The concentrations of the heavy metals mentioned above were compared in terms of bulk deposition, living needles, litterfall, forest mosses, upper soil organic layers, fine roots, and ectomycorrhizal mycelia (publications I and II). The accumulation and fluxes of the studied heavy metals in the spruce and pine stands were also assessed (publication IV) and the territorial difference in heavy metal input and retention in the organic layers of forest soils was estimated (publication I). According to the methods of the ICP Programmes, large material (such as coarse roots, stones, branches) and living fine roots are removed before chemical analyses of soil samples, thus removing the heavy metals stored in e.g. fine roots. Nevertheless, publications that deal with heavy metals and environmental remediation have shown accumulation of different heavy metals in fine roots (Gordon & Jackson, 2000; Prapagdee *et al.,* 2014). The translocation of up taken heavy metals from roots to aboveground biomass is controlled by plants (Yoon *et al.,* 2006; Prapagdee *et al.,* 2014). Herein again the differences between biogenic and pollutant heavy metals must be taken into account (Yoon *et al.,* 2006; Shahid *et al.,* 2007).

From the literature, it is also known that the life-span of the fine roots of the most widespread conifers in Estonia (Scots pine and Norway spruce) is short and therefore the amount of carbon and nutrients returned to the soil from the turnover of fine roots might be in the same range or even higher that from leaf litter (Brunner *et al.,* 2013; Gordon & Jackson, 2000). As the root–soil complex affects both heavy metal concentrations in soil layers and roots (Jobbagy & Jackson, 2004), the special focus of this study was the role of fine roots and their associated ectomycorrhizal mycelia in connection with the uptake and retention of heavy metals in soil. Inspired by the fine root biomass dynamic along boreal–temperate forest gradient (publication III), additional samples of fine roots and ectomycorrhizal mycelia were collected and analysed to better

understand their role in terms of retention of heavy metals in forest topsoil organic layers (publications II and IV).

According to Schroder *et al.* (2017), northern forests still accumulate Pb, Cd, Cu, and Zn. Accumulation of heavy metals in older needles and bark and other older parts of conifers has been previously described by Alriksson & Eriksson, 2001; Ukonmaanaho *et al.,* 2001; Asi *et al.,* 2009. As plants accumulate heavy metals from the ambient environment they could therefore be considered as intermediate reservoirs of heavy metals before bond to forest soils (Abraham *et al.,* 2017). Once adsorbed to the upper most organic-rich top layers the heavy metals are stored there up to centuries (Klaminder *et al.,* 2008). The biological processes in the organic soil layer will be seriously affected if heavy metal concentrations exceed 2–3 μg g^{-1} for Cd, 300 μg g^{-1} for Zn, 20 μg g^{-1} for Cu, and 150 μg g^{-1} for Pb (Tyler, 1992). The desorption of heavy metals from the soil organic layer takes a very long time (Alumaa *et al.,* 2001) and thereafter the concentration in the upper part of the B horizon could be expected (Bergkvist, 1987; Kabata-Pendias, 2011). The high peaks of leach out from soil of (pollution originated) heavy metals to streams and groundwater is expected (e.g. for Pb) to occur about 200–800 years from now (Klaminder *et al.,* 2006).

1.4. Aims

My general aim with this thesis was to get an overview of heavy metals in Estonian coniferous forests through combining the databases of different monitoring programmes. More precisely, in order to study the concentrations, pools and fluxes of heavy metals in Estonian coniferous forests, special attention was paid to the role of fine roots and needles in the dynamics of heavy metals. Currently that kind of scientific analysis of heavy metals involving data from different environmental monitoring programmes is missing for Estonia.

The specific aims of this study were i) to assess differences in heavy metal concentrations and accumulation in variously aged media of forest ecosystem (forest mosses, soil organic layers, litterfall, fine roots, and living needles), ii) to estimate the extent of different input and uptake fluxes of heavy metals in comparison to storages in the soil organic layer, and iii) to estimate and compare territorial differences in current heavy metal deposition (data on bulk deposition and data from mosses) and previously accumulated concentrations and storages of heavy metals in forest soil organic horizons in Estonia.

The main hypotheses were: i) There are regional differences in heavy metal depositions, retention, and accumulation to coniferous forest stands. ii) Fine roots have an important role in taking up and storing heavy metals, thus prolonging their retention in stands and thereby preventing soil purification from heavy metals. iii) The highest concentrations of heavy metals are found in soil organic layers where are also located the highest storages of heavy metals from the studied media. iv) The importance of deposition as a heavy metal input source is currently minor.

2. MATERIALS AND METHODS

2.1. Study sites

Data used in this study were mainly collected under the framework of three International Co-operative Programmes (ICP Forests, ICP IM, and ICP Vegetation) (Fig. 1.). Datasets were acquired from the Estonian National Monitoring Programme database, available online at http://seire.keskkonnainfo.ee/

From the ICP Forests Programme heavy metal data from 75 ICP Forests level I plot coniferous stands' soils were used (publication I). The majority of these 75 coniferous stands had podzolic soils and the main tree species were Norway spruce (*Picea abies* (L.) Karst.) and Scots pine (*Pinus sylvestris* (L.)). From the ICP Forests level II plots datasets from the Tõravere (in publications I, II, III, IV), Sagadi (II, IV) and Vihula (II, IV) stands were used.

Datasets used from Saarejärve Scots pine and Norway spruce stands (in publications I, II, III, IV) along with Vilsandi Scots pine stand (I, II, III, IV) belong to ICP IM programme.

Data of heavy metal concentrations in moss (*Hylocomium splendens* or *Pleurozium schreberi*) from 99 open area sampling sites of the ICP Vegetation programme were used in publication I.

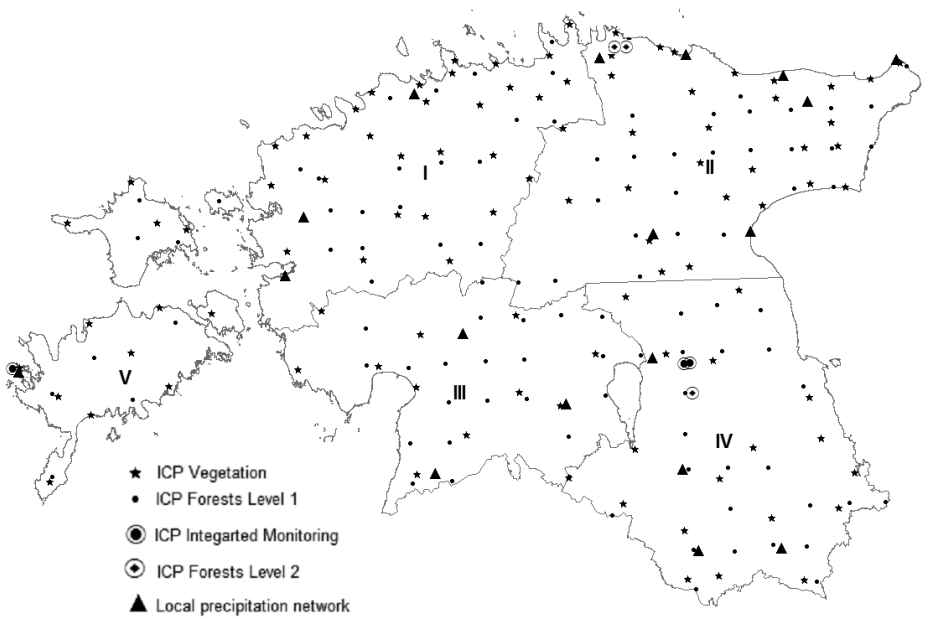

Figure 1. Sample collection plots. To compare the spatial distribution of heavy metals in forest soils, Estonia was divided into five different regions: (I) NW; (II) NE; (III) SW; (IV) SE, and (V) Western insular region (modified from publication I).

In addition, data of heavy metal depositions (2003–2013) from 18 national precipitation network sites covering all Estonia were used.

Outside the above-mentioned programmes, additional data on fine roots were collected from the 30 cm topsoil at both the Saarejärve stands and at the Vilsandi, Vihula, Sagadi, and Tõravere sites (publications II, III, IV), as fine root sampling is not part of the ICP Programmes. To better understand the role in heavy metal cycling and differences in heavy metals concentrations of fine roots and ectomycorrhizal mycelia, at the Saarejärve Scots pine test stands ectomycorrhizal mycelia samples were collected (publication II).

ICP Forest stands were managed and samples collected by the Estonian Environment Agency, ICP IM stands and national precipitation network sites were managed by the Estonian Environmental Research Centre, and IM Saare and ICP Vegetation stands by the Tallinn Botanic Garden.

2.2. Sampling

2.2.1. Moss samples

Unfortunately, deposition data on heavy metals for all 18 national precipitation network stations in Estonia is available only since 1999. Therefore additional heavy metal data of mosses were used instead. As mosses obtain heavy metals directly from dry and wet deposition, and are not affected by heavy metals in the soil layers, they present the current air pollution levels (ICP Vegetation Coordination Centre, 2005). Forest moss (*Hylocomium splendens* or *Pleurozium schreberi*) samples from the years 1995 and 2005–2006 were collected from 99 open area sites (publication I). Sampling was done in accordance with ICP Vegetation methods. One composite sample was formed from five to ten sub-samples spread across each sampling site. Only green fully developed shoots, representing mainly two to three years growth, were collected and chemically analysed afterwards (ICP Vegetation Coordination Centre, 2005).

2.2.2. Bulk deposition samples

Heavy metal bulk deposition samples (publications I and IV) were collected from 18 national precipitation network sites and the annual average deposition load of heavy metals (Cd, Cu, Pb, and Zn) calculated. Sampling was done in accordance with the European Monitoring and Evaluation Programme (EMEP) Manual for Sampling and Chemical Analysis (1996). Two NILU-type poly-ethylene precipitation and particulate fallout collectors (20 cm in diameter), which were placed in an open area at a height of 120 to 150 cm were used for precipitation collection. The annual deposition load for Estonia was calculated. If forest stand specific heavy metal input by deposition was needed, data from the nearest precipitation network station was used (publication IV), as in the

framework of the ICP Programmes heavy metal data were not analysed in terms of bulk deposition or throughfall.

2.2.3. Litterfall samples

Litterfall samples (publications I, II, IV) were collected in accordance with ICP Forests and ICP IM manuals (respectively http://icp-forests.net/ and http://www.syke.fi/nature/icpim), using four to ten funnel-shaped traps with a cumulative collection surface of 2.5 m^2 per site. Samples were collected monthly except during the winter period. Litterfall fractions were separated into litterfall needle fraction and litterfall miscellaneous fraction, and annual compound samples were made for parallel chemical analyses. Based on litterfall annual biomass and average heavy metals concentrations in litterfall (publication IV), the annual input flux of heavy metals by litterfall was calculated for different litterfall fractions.

2.2.4. Needle samples

Needle samples (publications II and IV) were collected and analysed per ICP Forests and ICP IM manuals (respectively http://icp-forests.net/ and http://www.syke.fi/nature/icpim). From the upper third of the crown of the main tree species (*Pinus sylvestris* or *Picea abies*), needles were sampled during the dormant period. Needles were sorted by age and chemical analyses were made separately from current-year living needles and older living needles. Annual heavy metals translocation to current-year needles was assessed in publication IV. As the biomass of current-year living needles per the stand was not known, the annual biomass data of the litterfall needle fraction were used instead, following the assumption that the biomass of annual needle growth in mature steady state coniferous forests equals the biomass of annually shed needles.

2.2.5. Fine roots samples

Fine roots (diameter < 2 mm) in publications II, III, and IV were collected according to the methods used in publication III from the upper 30 cm organic layer of soil using a soil core (∅ 40 mm). In publications II and IV, fine roots from the soil organic horizon (OL, OF, OH) were used or in case of its absence (depth < 1 cm), fine roots from the uppermost organic-rich A horizon were collected, as at the Tõravere and Vilsandi (publication IV).

Fine roots were separated from the soil and sorted into living and dead based on colour, elasticity, and toughness (Persson, 1983) under a microscope. Only living roots of the dominant tree species were used.

In publication IV, the storage of heavy metals in fine roots was calculated based on biomass and heavy metals concentrations.

An additional pilot study was conducted at the Saarejärve Norway spruce and Scots pine stands in 2015, with the aim of finding out how heavy metal concentrations in fine roots and soils change over the first three genetic layers of podzols (O horizon, E horizon, and B horizon).

To determine the vertical profile of heavy metals storage, fine root and soil samples were collected from the O horizon, E horizon, and B horizon using a soil corer (∅ 40 mm). A composite sample of each layer and sample type was made from three subsamples and heavy metal storages per each layer calculated.

2.2.6. Ectomycorrhizal mycelia samples

In publication II, samples of ectomycorrhizal mycelia were collected from root ingrowth nets installed in the soil at the Saarejärve Scots pine stand in autumn 2010. Sampling was carried out after a year – in 2011 – with root-associated mycelia (grown along and through the net) collected separately to roots and cleaned of soil particles before chemical analysis.

2.2.7. Soil samples

Samples of soil organic and mineral layers used in this study were collected from ICP Forests level I (publication I) and level II (publications II and IV) plots and ICP IM sites (publications II and IV). All samples were collected per the ICP Forests Manual of Soil Sampling and Analyses (2004) available at http://icp-forests.net/ and ICP IM Manual (2004) available at http://www.syke.fi/nature/icpim. Only soil organic layers were used in this study, as heavy metal concentrations were tens higher in these layers (especially Cd, Pb, Cu, and Zn) compared to the mineral soil layers, and it is also known from the literature that the topsoil retains received heavy metals very strongly (Alumaa *et al.,* 2001). In publication I, only OL and OF horizons were distinguished and included in the study. In publications II and IV, OL, OF, and OH were considered as one organic layer, and in the case of their absence, the organic rich A horizon was used instead. In publications I and IV, heavy metal storage in the soil organic layer was calculated, and therefore the heavy metal concentration and weights of the respective horizons (OL, OF, OH) or bulk density data (for A horizon) had to be taken into account.

2.3. Chemical analyses

Chemical analyses of samples were primarily done by the Estonian Environment Research Centre laboratory, which holds a certificate for chemical analyses of ICP Programmes in Estonia. The ICP Vegetation moss samples were analysed

by the laboratory of Finnish Forest Research Institute (METLA). Both laboratories were regularly taking part in international cross-calibration courses for laboratories and were accredited for ICP Programmes. The Estonian laboratory was accredited by the Estonian Accreditation Centre (www.eak.ee), and the Finnish laboratory by the Finnish Accreditation Service FINAS (www.finas.fi). All the parameters of the heavy metal analysis of the different samples used in this study can be found in the accreditation documents available at the accreditation centres' web pages.

Chemical analyses of Cd, Cr, Cu, Ni, Pb, and Zn concentrations in bulk precipitation, needles, litterfall, fine roots, and soil organic horizons were performed using the ICP-AES method (inductively via coupled plasma spectroscopy: ISO 11885 STJnr.M/U91 per Cu and Zn; STJnr.M/U94 per Cd, Ni, Pb; and SFS 5074 and EVS-EN ISO 17294-2 per precipitation; certification was verified by the Eesti Akrediteerimiskeskus 2013). Cd, Cr, Cu, Ni, Pb, and Zn concentrations in moss were determined using ICP-ES (inductively coupled plasma emission spectrometry). Pre-treatment was done using a microwave oven with *Aqua regia* per the soil organic horizon samples and with HNO_3 per the other plant material samples.

2.4. Statistical analyses

Statistical analyses were mainly performed using STATISTICA 7.0 software, MS Excel 2010, Canoco Version 4.5 (Ter Braak & Šmilauer, 1998), and MapInfo Professional software. All the used statistical methods had to be suitable for non-parametric data.

The redundancy analysis (RDA) of logarithmically transposed data used in publications I, II, and IV determined and illustrated connections between heavy metals and deposition loads of the national precipitation network stations (publication IV) and of the moss data (publication I), and illustrated the distribution of heavy metals in different aged media (publication I, II) in five different regions of Estonia NW, NE, SW, SE, and the Western insular region (publication I).

The Monte Carlo permutation test available in Canoco (publications I, II, IV) was used to test the significance of constrained ordination models, therefore it was used to verify the significance of each variable and ordination axes.

ANOVA (publication I) was performed with logarithmically transformed data ($p<0.05$) to further analyse the variance in heavy metals among the five different regions.

The non-parametric Mann-Kendall test (Salmi *et al.,* 2002) was used to test long-term trends in precipitation weighted annual mean concentrations and estimate if they were significant ($p<0.05$) (publication IV).

The nonparametric Spearman's rank order correlation test ($p<0.05$) was carried out to detect possible correlations between heavy metal storage in fine roots and soil organic layers (publication IV), and to describe the possible

atmospheric origin of heavy metals in OL and OF horizons by correlated them with concentrations in the moss layer (publication I).

Coefficient of variation (CV%) in publications I and IV was given to illustrate the variability of heavy metals in studied media. CV% represented in these studies the ratio of standard deviation to the mean, expressed in percentages.

2.5. Indexes

The Root Uptake Factor (RUF), Translocation Factor (TF), and Accumulation Index (AI) were used in publication II to calculate and characterise the movement and retention of heavy metals in the pine and spruce stands.

The root uptake factor was adapted from Prapagdee *et al.* (2014). In publication II, it represented the ratio of heavy metal concentration in fine roots (C_{FR}) to the soil organic horizon (or to A horizon) (C_{SO}).

$$RUF = C_{FR}/C_{SO}$$

The translocation factor has been used by Yoon *et al.* (2006) and Prapagdee *et al.* (2014), and it described the ratio of heavy metal concentrations in shoots to that in fine roots, thus describing heavy metal translocation inside trees. Using the data available from the ICP programmes, translocation factor in our study represents the ratio of heavy metal concentrations in current-year needles ($C_{N\_Current}$) to fine roots (C_{FR}).

$$TF = C_{N\_Current}/C_{FR}$$

The accumulation index represented the ratio of heavy metal concentrations in the litterfall needle fraction ($C_{LF\_Needles}$) compared to the current-year living needles ($C_{N\_current}$).

$$AI = C_{LF\_Needles}/C_{N\_current}$$

Some heavy metals (e.g. Zn and Cu) are essential for plants' functioning. Therefore distinction between biogenic heavy metals and contaminant heavy metals must be made. In this thesis the distinction between heavy metals was made according to Bruno Franco (2005): biogenic heavy metals (Cu, Zn) and non-biogenic (contaminant) heavy metals (Cd, Pb, Cr, Ni).

2.6. Territorial distribution of sampling sites

In publication I, Estonia was divided into five regions to allow a comparison of heavy metal distribution among different regions. The regions were: 1. NW; 2. NE; 3. SW; 4. SE, and 5. Western insular region (Fig. 1.).

3. RESULTS AND DISCUSSION

3.1. Local heavy metal sources and long-range transboundary heavy metal pollution

During the last decade, levels of heavy metal depositions in Estonia have been quite stable. Unfortunately, deposition data for heavy metals does not exist for previous decades, especially for the 1980s. According to Statistic Estonia (2017), the use of oil shale for electricity and heat production in Estonia rose from 13,510 thousand tons in 2007 to 15,429 thousand tons in 2015, causing a rise in emitted heavy metals from 122 tons in 2008 to 137 tonnes in 2013. A higher impact of dry deposition historically occurred mainly in the NE and Eastern part of Estonia, where oil shale-fired power plants and the Kunda cement factory emitted enormous amounts of alkaline dust, containing among other chemical compounds heavy metals. A decrease in electricity and cement production since the beginning of 1990s, and simultaneous installation of modernised flue gas purification systems at oil shale-burning thermal power plants in 1997 resulted in a tremendous reduction in solid particles emissions (Talve & Riipulk, 2001). Even though oil shale using point sources have remained the main heavy metal emitters (Kohv *et al.,* 2002), a decrease in the emissions of fly ash and solid particles has occurred. The emissions have dropped from 280,000 tons per annum in the 1980s (Liblik & Pensa, 2001) to 21,845 tons of particulate matter in 2014 (Statistics Estonia databases, 2017). The levels of emitted fly ash from the main oil shale user Eesti Energia dropped to 3,500 tons in 2015, whereas in 2011 the amount of emitted fly ash was 28,100 tons (Eesti Energia AS, 2016). The emitted amount of oil shale usage related fly ash is an important indicator of emitted heavy metals, as according to Reinik *et al.* (2013) the heavy metals are concentrated in fine particles and their concentration in fly ash could therefore reach higher values than their initial concentration was in the oil shale. In addition, the proportions of heavy metals in emitted fly ash and in soil organic layers in Estonia have been found to be connected (publication I), indicating the origin of the studied heavy metals is the oil shale industry.

The wet and dry deposition of heavy metals was reflected in the datasets of the heavy metal content of mosses. The extent of heavy metal enrichment via tree canopies was not clear in this study, due to the limitations of the available data. Forests are very effective at filtering heavy metals and the concentrations under canopies have been found to be higher due to leaching from the crowns (Meyer *et al.,* 2015). The tests in Estonian ICP Forests stands have shown that deposition loads of Fe, Al, Cu, Mn, and Zn were 53, 62, 24, 80, and 28% (respectively) higher in throughfall waters under canopies than in bulk precipitations (Asi *et al.,* 2009). Pb concentrations at Saarejärve have been found in moss (*Hylocomium splendens*) at 23% higher for samples collected under the canopy in comparison to open areas moss samples (Asi *et al.,* 2009). Thus, use

of bulk deposition data only and the moss data of the ICP Vegetation programme's database (collected from open areas) reflected only open field deposition and is therefore an underestimation of the actual deposition load. Dry depositions from canopies were partly reflected in the datasets of litterfall and needles, but the share of dry deposition of the total heavy metals deposited remains unknown.

Long-range transboundary pollution also has an effect on heavy metals deposited locally. For example, in Finland the impact of long-range transport of heavy metals from highly industrialised and densely populated areas of Europe, has been found to be considerable in terms of the deposition of Zn, Cd, and Pb (Kyllönen *et al.,* 2009). This is especially important with Cd, as the level of this heavy metal has been found to be in general low and with little variability in the forested ecosystems of Nordic countries (Huang *et al.,* 2011; Bringmark *et al.,* 2013). According to a recent publication by Ilyin *et al.* (2016), emissions of Cd and Pb in the Baltic region are higher than in Scandinavia, but are still lower than in Central Europe. Previous studies in Northern Europe also confirm the airborne history of Pb and Cd, whilst Cu and Zn were mainly considered to originate from forest ecosystems' inner cycling (root uptake, decomposition of organic material) (Lomander & Johansson, 2001). In Latvia, the contribution of long-range heavy metal deposition is estimated to be around 40% (Nikodemus *et al.,* 2004) and in Lithuania it is even higher at 70–90% (Kvietkus *et al.,* 2011). When comparing the average heavy metal deposition loads in Estonia (publications I and IV) to depositions in Lithuania (Kvietkus *et al.,* 2011) and the EUs average depositions at ICP IM stations (Bringmark *et al.,* 2013), average depositions in Estonia per some heavy metals (e.g. Cu and especially Zn) were rather high in an European context, but in the same range as at other sites in the Baltic region. However, the average annual deposition of Pb and Cd were at the lower end, when compared to data from Lithuania and the EU's average depositions (Kvietkus *et al.,* 2011; Bringmark *et al.,* 2013).

3.2. Heavy metal input to ecosystems in Estonia by bulk deposition

Ecosystems in Estonia have been affected by long-term heavy metal exposure due to extensive use of oil shale during the previous decades. All the heavy metals discussed herein are present in Estonian oil shale and have therefore been emitted during the oil shale combustion processes (Reinik *et al.,* 2013). According to data of the Estonian national precipitation network, the current average annual deposition loads of heavy metals in bulk precipitation were: 0.5 g ha^{-1} of Cd, 25.8 g ha^{-1} of Cu, 4.8 g ha^{-1} of Pb, and 224.9 g ha^{-1} of Zn (publication IV). Variability (CV%) of deposited heavy metal loads between stations was high: for all heavy metal depositions it was higher than 50%.

The statistically significant decreasing trends in heavy metal bulk deposition (presented in publication IV) reflect the overall decreasing trend in heavy

metals emissions over the last decade (2003–2013) in Estonia. When comparing the data presented in publications I (average depositions in 2002–2011) and IV (average depositions in 2003–2013), the average depositions of heavy metals in bulk precipitations seem to have slightly decreased.

3.3. Territorial differences in depositions

The comparison of different regions of Estonia presented in publication I (1. NW; 2. NE; 3. SW; 4. SE, and 5. Western insular region) and data from precipitation stations showed that overall, heavy metal decrease in bulk deposition has been most remarkable in the NE and E part of Estonia. Estonian national precipitation stations (in publication IV) were grouped in the redundancy analysis (RDA) in connection to deposition loads of different heavy metals (Fig. 2.). The obtained distribution of stations in publication IV is to some extent still in agreement with previously defined groups by Treier *et al.* (2008) of precipitation stations based on SO_4-S and solid particle deposition data from 1994–2005.

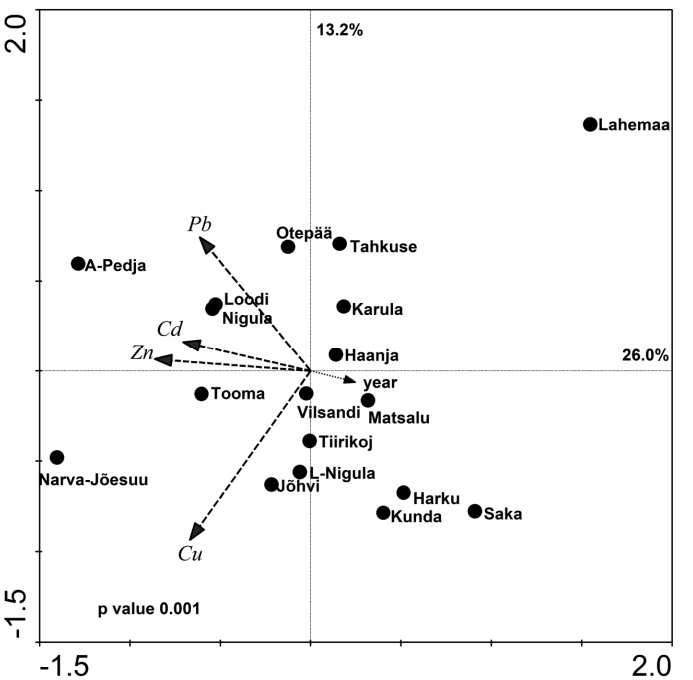

Figure 2. Ordination biplot of 18 national precipitation stations in terms of heavy metal annual deposition loads (2003–2013). Distribution of stations in connection to heavy metal loads by redundancy analysis (RDA). Stations and year account for 48.5% of total heavy metal annual deposition variability. Axis 1 describes 26% and axis 2 13.2% of the total annual deposition variability (p=0.001). Sampling year described 3.4% of the total deposition variability (publication IV).

Treier *et al.* (2008) suggested that the national precipitation stations could be divided as follows: i) Stations still affected by the oil shale industrial region (Kunda, Jõhvi, Saka, Harku); ii) NE industrial region background stations (Tiirikoja, Tooma, Lahemaa, Saarejärve); iii) Natural background stations (Vilsandi, Lääne-Nigula).

In publication IV, the NE station Narva-Jõesuu was clearly distinguishable from other stations and from the NE stations the Jõhvi station also showed higher depositions of Cu (Fig. 2.). In the case of the Narva-Jõesuu (and the Jõhvi) station, the effect of being closely located to oil shale burning power plants must certainly be taken into account regarding the high loads of deposited heavy metals. Especially as the prevailing winds in Estonia are westerly and therefore it could be assumed that the emitted heavy metals were largely heading in an easterly direction (Narva-Jõesuu is the only station located east of the power plants). A tendency for a decrease in Pb, Zn, and Cd depositions over time was also observed in the Narva-Jõesuu and Jõhvi stations, however statistically significant trends were not detected.

The Saka, Kunda, and Harku stations were previously stated as being highly affected by oil shale industrial pollution (Treier *et al.,* 2008) and human activity (Harku is located in the vicinity of the capital, Tallinn), still grouped together, but should now be seen more as background stations that are lightly affected by industrial pollution. However, since the 2000s, an increased impact from the capital region has been evident: according to moss data, especially per heavy metals such as Ni (Kaasik & Liiv, 2007).

The Nigula, Loodi, Tooma, and Alam-Pedja stations are not located in the NE industrial region, but were still differentiated from other background stations by the RDA analysis (publication IV). Tooma station was the only station that showed statistically significant increases in Cd, Pb, and Zn bulk depositions. For the same heavy metals, the Alam-Pedja station had very high deposition loads in comparison to other – especially background – stations. Therefore, the effect of some local pollution source should be considered. This is most likely to be an effect of the nearby peat industry, especially the higher precipitation of heavy metals at the Alam-Pedja station.

If the Alam-Pedja and Tooma stations are excluded – due to the effect of strong local pollution sources – from the RDA analysis of bulk deposition data of heavy metals (publication IV), then the Narva-Jõesuu and to lesser extent Jõhvi stations were opposed to other stations. As Jõhvi and Narva-Jõesuu stations were closest to the oil shale burning power plants, the direct influence from oil shale combustion should still be taken into account. From the RDA analysis in publication IV, it occurred that the sampling year was rather unimportant for deposition loads over 2003–2013, accounting for only 3.4% of the total variability.

3.4. Heavy metal depositions retrospectively reflected in different media

Concentrations of heavy metals in studied living needles, litterfall, mosses, soil organic layers, fine roots, and ectomycorrhizal mycelia differed considerably (publications I and II), but were still within the range of concentrations for non-polluted area. Concentrations of heavy metals were, with the exception of Zn and Cu, highest in the soil organic layer, i.e. 24 mg kg^{-1} of Pb, 6 mg kg^{-1} of Cr, 4 mg kg^{-1} of Ni, and 0.6 mg kg^{-1} of Cd, which reflects most the heavy metal depositions of previous decades. High concentrations were also recorded in fine roots (Fig. 3.) where biogenic heavy metals had the highest concentrations (109 mg kg^{-1} of Zn and 10 mg kg^{-1} of Cu). The pilot study at the Saarejärve Scots pine stand revealed even higher concentrations of Cu, Zn, Pb, Ni, and Cr in root-associated ectomycorrhizal mycelia (Cu = 20 mg kg^{-1}; Zn = 560 mg kg^{-1}; Pb = 37 mg kg^{-1}; Cd = 0.4 mg kg^{-1}; Cr = 14 mg kg^{-1}; and Ni = 9 mg kg^{-1}). That was likely due to the higher absorption area of mycelia in comparison to fine roots (Clarholm & Skyllberg, 2013). Given that current heavy metal depositions are low, the origin of heavy metals in soil organic layers is almost certainly to be from the previously high emissions.

The variability of heavy metal concentrations in different media and in different stands was high. The most variable were the current-year living needles samples, especially in terms of Pb (CV% = 102%) and Cr (CV% = 97%). The most stable heavy metal concentrations were characteristic to soil organic horizon samples, where CV% varied between 29–50% (publication II). Differences in the concentrations of studied media are presented using data from publication IV (Tõravere Norway spruce stand, Saarejärve Scots pine and Norway spruce stands, Vilsandi pine stand, and Vihula and Sagadi pine stands) (Fig. 3.).

It is known from the literature that heavy metals concentrate around fine roots and in the case of a low ambient soil pH, considerable amounts of heavy metals enter the fine root tissues (Tyler, 1984). Therefore, site specific root–soil complexes affect the concentrations of heavy metals in fine roots and soil (Jobbagy & Jackson, 2004; Klaminder *et al.,* 2005), and its related site-specific continuum impacts the concentrations and accumulation of heavy metals in the soil organic horizon (publication III). For example, according to publication III, a lower proportion of cellulose degrading soil bacteria indicates the slowdown of the decomposition of organic components in the soil, and therefore prolongs the stay of heavy metals – which are strongly bonded to soil organic material – in the ecosystems. However, the rise in concentrations and accumulation of heavy metals to the upper soil organic layers will gradually change the soil bacterial community, which might in turn further slow down the decomposition processes.

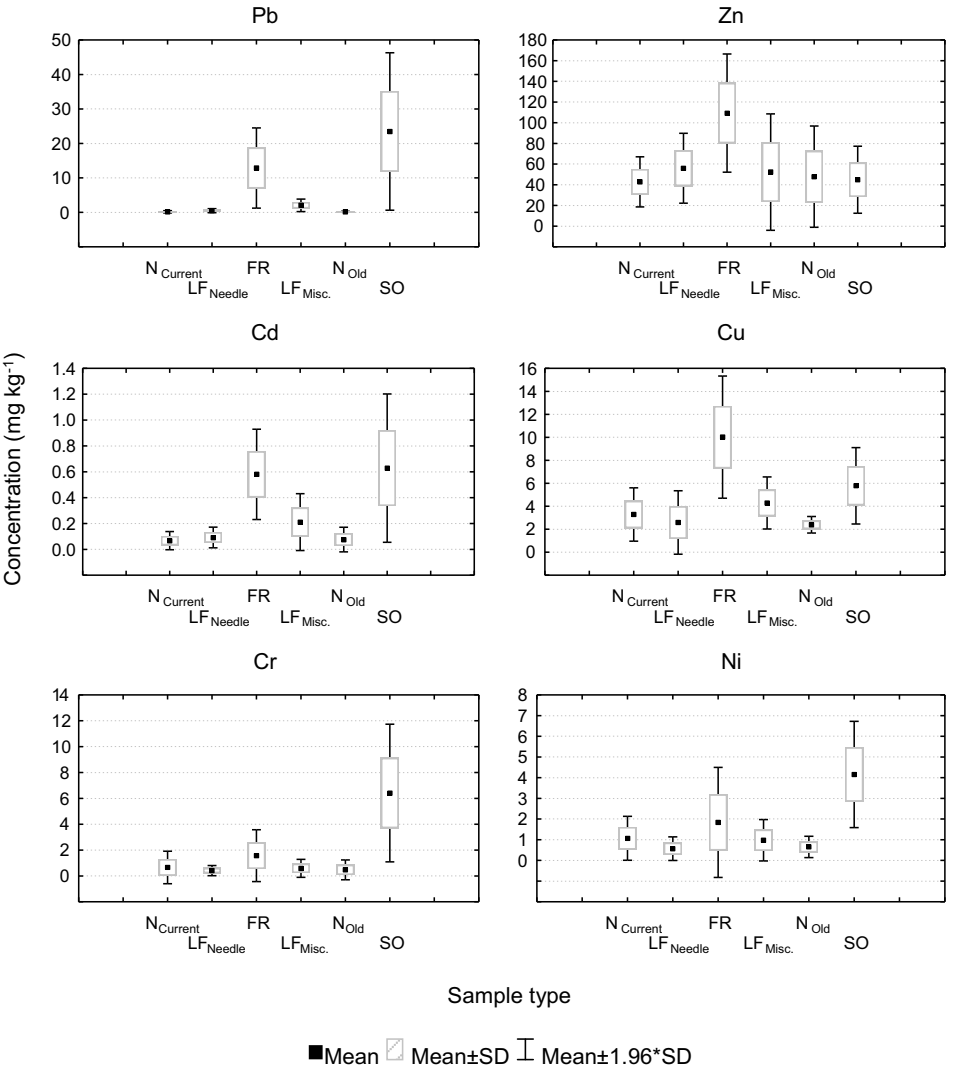

Figure 3. Mean concentration (mg kg^{-1}) of Zn, Cu, Cd, Cr, Pb, and Ni in: $N_{Current}$ = current-year living needles; LF_{Needle} = litterfall needle fraction; FR = fine roots; $LF_{Misc.}$ = litterfall miscellaneous fraction; N_{Old} = older living needles; SO = soil organic horizons at ICP Forests level II stands (Tõravere, Sagadi, Vihula) and ICP IM stands (Saarejärve stands, Vilsandi stand). Boxes indicate ± standard deviation; whiskers indicate mean ± 1.96* standard deviation (Publication II).

The moss data were especially important to characterise short-term heavy metal depositions over a certain time-period (up to 3 years), as the absence of roots and cuticles enables mosses to obtain nutrients and pollutants directly from precipitation and dry deposition (Äyräs *et al.,* 1997; ICP Vegetation Coordination Centre, 2005). The comparison of regional heavy metal distribution in different media using RDA analysis (in publication I) demonstrated (p=0.001) that based

on the heavy metal content of mosses in 1995, it could be confirmed that the NE region in the 1990s was clearly distinguishable from the other regions in terms of higher heavy metal content in the region (Fig. 4.). The same analysis of moss data from 2005/2006 reflected that the capital region (NW) played a more important role in terms of the heavy metal content in mosses than the NE region ($p=0.020$).

Previous studies (Kaasik & Liiv, 2007; Treier *et al.,* 2008) have also shown that closeness to the capital raised the average annual heavy metal deposition loads at NW Estonian stations, especially per Ni. The importance of cities as air pollution sources and the decrease in importance of industry related point sources is also evident in Latvia (Nikodemus *et al.,* 2004). A significant decrease in emission loads occurred in Latvia before 1992 (Nikodemus *et al.,* 2004), in Estonia this change occurred later. In Estonia, the amount of oil shale used has decreased gradually since the beginning of the 1990s, but with the introduction of new firing technologies and flue gas purification filters in electrical power plants in 1997, the emissions of different pollutants decreased remarkably (Talve & Riipulk, 2001). Therefore, it could be concluded that in terms of deposition loads, the closeness of the studied stands to the NE oil shale region has been especially important in the past and based on a comparison of bulk deposition data, it also stayed somewhat important during 2003–2013.

Mosses' responses to heavy metal air pollution changes is fast in comparison to heavy metal-induced changes in soil organic layers, which has been found to be delayed (Meyer *et al.,* 2015). The RDA analysis including soil organic layers data (publication I) showed that the SE part of Estonia differs from the other regions due to higher Ni and Cr concentrations. This was verified using ANOVA and it also applied for stocks of Ni and Cr in the SE of Estonia. Heavy metals overall convergence towards the NW and NE of Estonia is especially noticeable in the older soil organic layer (in the OF horizon, not the OL) (RDA analysis, publication I), as this layer contains heavy metals from decades ago, i.e. from the 1980s and earlier.

The critical loads of heavy metals set by the EEA, which when exceeded are harmful to the environment, have not lately been exceeded in the EU (EEA, 2013). That does not automatically reflect the state of soil organic layers, as the response to changes in heavy metal depositions is delayed in the soil (Meyer *et al.,* 2015). For example, Pb soil concentrations in some places in Europe might, according to ICP Forests data, still exceed the value that affects soil organisms (Schroder *et al.,* 2017). According to Tyler (1992), the biological processes in the organic soil layer will be seriously affected if heavy metal concentrations exceed 2–3 μg g^{-1} for Cd, 300 μg g^{-1} for Zn, 20 μg g^{-1} for Cu, and 150 μg g^{-1} for Pb. These limits were not exceeded in the studied soil organic layers and were significantly lower at all studied coniferous stands. However, it is particularly interesting that the concentrations in mycelia exceeded the secure concentration levels at the test site at the Saarejärve pine stand for Cu and Zn (respective concentrations in mycelia were 29 mg kg^{-1} and 560 mg kg^{-1})

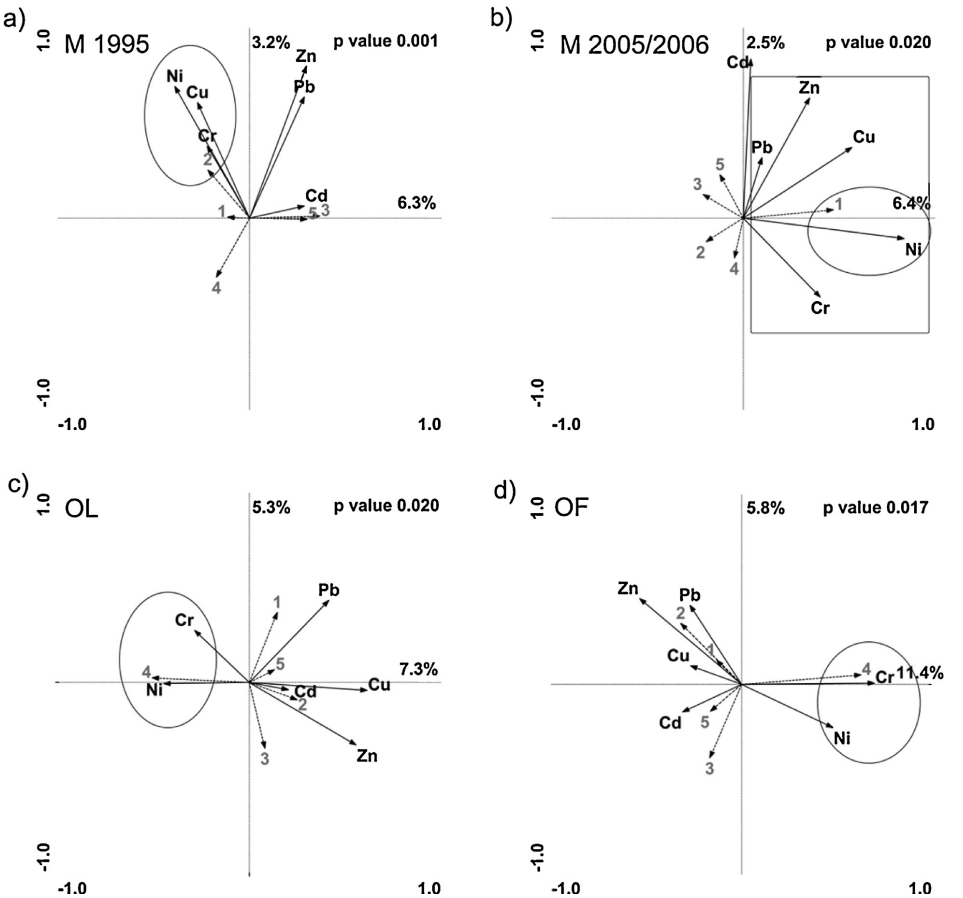

Figure 4. Ordination biplots of regional heavy metal concentration distribution from RDA analysis: a) in moss (1995), b) moss (2005/06); c) OL and d) OF horizon (2006–2008). Estonia was divided into five regions: 1. NW 2. NE; 3. SW; 4. SE; and 5. Western insular region. Heavy metal concentrations and regions account for 12.6% (moss 1995), 9.9% (moss 2005/06), 17.8% (OL), and 19.7% (OF) of the total variability. The graphs show how much of the total variation is described by axes 1 and axes 2 (%) (publication I).

Spearman's rank order correlations for non-parametric data were used to analyse the concentrations data to describe the atmospheric origin of heavy metals in the OL and OF horizons by correlating them with the concentrations in the moss layer (publication I). The results showed correlations between heavy metals such as Ni-Cr, Cu-Zn, and Ni-Pb in OL, OF, and moss layers. Statistically significant correlations between these heavy metals were also found in different regions. The strongest were the correlations between Ni-Cr in OL (r_s = 0.87–0.98) and OF (r_s = 0.88–0.97) horizons in the NE and especially the SW and SE regions. Therefore, one could assume a common heritage of Ni and Cr from the oil shale combustion industry.

3.5. The importance of litterfall as heavy metal input source

In publication I, the input of heavy metals by airborne deposition was higher for Pb, Cu, and Zn than input of these heavy metals by litterfall. Our more recent study (publication IV) showed that the decrease in heavy metal bulk depositions has occurred, but bulk deposition was still an important source of heavy metals entering ecosystems, forming one third to half, or for some heavy metals (Cu, Zn), even more of the heavy metal input. In addition, if we compare the results of these two studies the importance of litterfall as a heavy metal input source has been rising. According to the data of the ICP IM and ICP Forests Programmes, the maximum age of older needles varies from 3 to 4 years for Scots pine and 6 to 9 years for Norway spruce, and sets the average age of litterfall needle fraction at studied stands. The age of miscellaneous litterfall fractions is obviously older, as it also contains e.g. pieces of branches, bark. During the decomposition of litterfall, needles lose their outer layers, e.g. the epidermis and cuticle (Tyler, 1984), and thereafter the potential of obtaining heavy metals from the ambient increases, leading to an increase in heavy metal concentrations. One reason behind the rise in importance of litterfall as a heavy metal input source might be the slight rise in the use of oil shale for electricity production and the related rise in heavy metal emissions from 2007 onwards (Statistics Estonia, 2017). In addition, in publication IV litterfall data from additional stands (Vihula, Sagadi) closer to the NE region were used together with stands from publication I, therefore their effect on the average of added heavy metals by litterfall should be taken into account. The annual flux of litterfall was very stand specific and varied between 1190 kg ha^{-1} (Vilsandi pine stand) to 4200 kg ha^{-1} (Saarejärve old spruce stand) in 2013. In this study, the extent and effect of occasional events, e.g. huge storms, to annual amounts of litterfall and its related heavy metal input was not addressed. However, it can be assumed that storms or pest outbreaks in older coniferous forests also increase the heavy metal input by litterfall due to increased amounts of shed needles.

3.6. Cycling, uptake, and accumulation of biogenic and contaminant heavy metals

The nature and necessity for plants (e.g. biogenic or contaminant heavy metal) of studied heavy metals defined their cycling, uptake, and accumulation in the ecosystems. To better understand the heavy metals-related processes in the ecosystems, concentrations of heavy metals in different, but most dynamic, media were analysed via indexes, as the movement of biogenic (Zn, Cu) and contaminant (e.g. Pb) heavy metals in coniferous ecosystems is rather different. For example, Zn which is highly necessary for plants' functioning, had higher concentrations in litterfall and the OL horizon than in deeper soil organic layers

(publications I and IV), indicating a rapid reuse of this element by the ecosystem. Cu and Zn also showed correlations in moss (r_s 0.38), and OL (r_s 0.24) and OF (r_s 0.40) horizons (publication I) that suggests similar movement in the ecosystems and an origin from the same source of pollution. In addition, the root uptake factor (RUF) showed highest mobility of these two heavy metals (RUF_{Zn}=2.63 and RUF_{Cu}=1.58), in comparison to strong attachment of some other heavy metals (RUF_{Pb}=0.60, RUF_{Ni}=0.40, and RUF_{Cr}=0.23) (publication II). The higher mobility of Cu and Zn in the ecosystem is in good agreement with the findings of Bergkvist *et al.* (1989). According to the results in publications I and II, the Ni and Cr cycling patterns in the ecosystem were similar, as these heavy metals exhibited similar decreasing concentration patterns in the different studied media.

Translocation of heavy metals within the tree evaluated with the translocation factor (TF) also demonstrated highest values per Cu and Zn (TF_{Cu}=0.34 and TF_{Zn}=0.42), but also per Ni (TF_{Ni}=0.77), which is also a necessary plant nutrient in micro quantities (Tangahu *et al.,* 2011). In general, the concentrations of Pb, Cd, Cr, and Ni were many times higher in fine roots than in current-year living needles, indicating the passive uptake of heavy metals by fine roots. High accumulation in roots and older needles was especially characteristic of Pb, with a low translocation factor (TF_{Pb}=0.02) and a high accumulation index (AI) (AI_{Pb}=4.16) observed. The example of Pb demonstrated that even if concentrations of heavy metals were elevated in fine roots, they were very slowly transported to higher parts of the tree (low TF + low concentrations of Pb in current-year living needles), and Pb mainly tends to accumulate in soil (Alumaa *et al.,* 2002). Here the findings of Klaminder *et al.* (2008) are interesting, as 70–90% of Pb in Scandinavian conifers were found to originate from air pollution, mainly from direct input from the atmosphere or from uptake of previously retained pollution in upper soil organic layers. Some differences in accumulation of heavy metals could also occur between different tree species, as some differences were observed in the values of AI between Scots pine and Norway spruce dominated stands. In this case, the rate of degradation of needles may be significant, as spruce needles have been found to decompose more slowly (Kaila *et al.,* 2012). Soil type is also important in absorption of heavy metals to soils. Tests with Estonian soils have shown that Cd and Cu are most affected by soil type, and their concentrations tend to be for example lower in podzols than in rendzinas (Alumaa *et al.,* 2002).

The uptake of heavy metals is also affected by differences in heavy metal mobility within the plants and antagonistic or synergistic interactions between heavy metals. High mobility of Cu, Zn, and Ni within the plant (Charney & Giordano, 1977), especially in a case of low pH (Bergvist *et al.,* 1989), would explain the high TF of these heavy metals, and antagonism between Zn and Cd (Kabata-Pendias, 2011) could be the reason behind low TF in our study of the otherwise mobile and weakly adsorbed Cd (Alumaa *et al.,* 2002).

3.7. PH as one of the important factors regulating heavy metal cycling in Estonian coniferous forests

Historically the territory of Estonia has been under significant alkaline pollution due to intensive oil shale usage and production of cement in the NE part of the territory, with industrial production peaking in the 1980s (Raukas, 2010). The fly ash produced by oil-shale burning is very alkaline (pH of the oil shale ash leachate has been measured to reach up to pH 12 or more) and contains heavy metals condensated on its surface (Reinik *et al.,* 2014). As the oil shale-based industries have emitted fly ash for decades, the alkaline fly ash has been available to ecosystems for a long period (especially in NE part), and therefore upper soil organic layers have been affected by alkaline compounds for decades. Despite the decrease in alkaline deposition there are still coniferous stands where pH of the upper soil mineral layers is still artificially raised (especially in NE region), keeping the heavy metals from moving downward and slowing ecosystems' self-purification (Kabata-Pendias, 2011; Hale *et al.,* 2012). From the literature, it is known that in comparison to Scandinavian stands, the accumulation of some heavy metals, such as Pb and Cd, is rather higher in the Baltic region, as water discharge in the Baltic area is lower than in Scandinavia (Bringmark *et al.,* 2013). This, in combination with alkaline substances in Estonian soils enhances the accumulation of heavy metals further.

Despite the previous alkaline depositions, pH of the upper soil organic layer was at some of the studied stands very low, and statistically significant trends in decreasing pH values have been detected in soil water samples at the Saarejärve stands (Frey & Frey, 2015). This shows that the alkaline ions have been washed/leached out from the upper soil organic layers during the past 20 years at the studied stands. This result could not be applied to the whole of Estonia, as ICP Forests (level II) and ICP IM Programmes did not have stands in the NE of Estonia in close vicinity of the oil shale industry. The pH in soil organic layers varied from 2.8 at the Saarejärve Norway spruce stand to 4.6 at the Tõravere stand and 5.2 at the Vilsandi stand. At other stands the pH of the soil organic horizon was around 3.0. PH values less than 5.5–6.0 are known to enhance heavy metal leaching and availability, and a pH over 6 has the opposite effect (Kabata-Pendias, 2011; Hale *et al.,* 2012). Therefore, at some podzol stands a leach out of heavy metals from the upper organic horizons could be expected in the future. That, especially in the case of a further decrease in the pH of the soil organic layer due to natural decomposition processes in the coniferous forests, but in some of the stands in Estonia the pH will and has already decreased partially also because of the decreased levels of alkaline air pollution.

3.8. Heavy metal fluxes in the studied stands

In this study, the input flux of heavy metals to the ecosystem was calculated as the sum of the average annual bulk deposition and average annual flux of litterfall (needles + the miscellaneous fraction). According to the results of publication IV, currently the annual average input of heavy metals to the studied stands by bulk deposition and litterfall, varied between 22–55 g ha^{-1} y^{-1} for Cu, 259–550 g ha^{-1} y^{-1} for Zn, 8–13 g ha^{-1} y^{-1} for Pb, and 1–2 g ha^{-1} y^{-1} for Cd. Within the framework of the ICP Forests and ICP IM programmes, bulk and throughfall precipitations were collected, but unfortunately heavy metals were not analysed. Thus, it was decided to use data from the nearest national precipitation station, as further described in publication IV. Therefore, some uncertainties remain as to the exact deposition at the stands.

The biological above- and below-ground uptake in this study was represented by flux of heavy metals in fine roots (up to two years of age) in combination with heavy metal flux in current-year living needles. The biological above- and below-ground uptake was in the range of 24–37 g ha^{-1} y^{-1} of Cu, 252–478 g ha^{-1} y^{-1} of Zn, 13–52 g ha^{-1} y^{-1} of Pb, and 1–2 g ha^{-1} y^{-1} of Cd. It is important to note, that this does not represent the total uptake, and therefore it is likely that the total uptake was somewhat higher.

In general, the input of heavy metals (bulk deposition + litterfall) tended to be higher than uptake by fine roots and storage in current-year needles in terms of the biogenic heavy metals (Cu and Zn), and the uptake + storage in current-year needles was higher than the input in terms of the contaminant heavy metals (Cd and Pb). However, there were a few exceptions, for example at drier Scots pine stands (Sagadi, Vihula, Vilsandi) Zn uptake was higher than input via deposition and litterfall. Also, at the Vilsandi stand the summed input of Cd was greater than the uptake, therefore a strong influence from the long-distance heavy metal pollution at the remote Vilsandi island could be suspected. The variation between input and uptake fluxes was high between the stands, and therefore in future studies it would be wise to concentrate more on site specific indicators.

3.9. Accumulation and stocks of heavy metals in coniferous forests

Sometimes plants are regarded as intermediate reservoirs of heavy metals, as they accumulate heavy metals from the ambient air, soil, and water (Abraham *et al.,* 2017). Accumulation of heavy metals in older needles and bark and other older parts of conifers has been previously described by various authors (Alriksson & Eriksson, 2001; Ukonmaanaho *et al.,* 2001; Asi *et al.,* 2009). The highest accumulation index was found in this study for Pb ($AI_{Pb} = 4.16$), but an $AI > 1$ was also characteristic for Cd, Cr, and Zn. It clearly showed the accumulation of these heavy metals in older needles that thereafter formed litterfall. Accumulation in older parts of litterfall was important, especially in terms of

heavy metal input, as the miscellaneous part of the litterfall formed a significant share of the heavy metal input (39–79% for Cu, 26–56% for Zn, 71–88% for Pb, and 55–75% for Cd) compared to the litterfall needle fraction. According to recent studies, northern ecosystems still accumulate Pb, Cd, Cu, and Zn (Schroder *et al.,* 2017).

In the case of Estonia, the high spot of industrial pollution was at the end of the 20th century and therefore the upper soil layers have been affected by anthropogenic pollution. As the heavy metal concentrations were found to be high in the soil organic layer and fine roots, a pilot study was conducted at the Saarejärve stands to find out how heavy metal concentrations have changing via the soil profile. The heavy metal concentrations in fine roots in different upper soil horizons (O, E, B) were studied in 2015 at the Saarejärve (both at Norway spruce and Scots pine dominated stands) test site. Concentrations in fine roots were highest at both stands for Zn in the O horizon (pine stand 310 mg kg^{-1}, spruce stand 160 mg kg^{-1}), for Pb in the E horizon (pine stand 47 mg kg^{-1}, spruce stand 65 mg kg^{-1}), for Cd in the O horizon (pine stand 1.7 mg kg^{-1}) and in the E horizon (spruce stand 1.4 mg kg^{-1}), and for Ni (pine stand 15 mg kg^{-1}, spruce stand 5.4 mg kg^{-1}) and Cr (pine stand 3.9 mg kg^{-1}, spruce stand 2.1 mg kg^{-1}) in the B horizon. In the same stands the heavy metal concentrations throughout the soil profile decreased with depth, being highest in the soil organic horizons that have been the most affected by anthropogenic pollution. There were some exceptions, with Ni and Cr having almost equal concentrations in the B as in O horizon. This shows that high concentrations of heavy metals in the soil organic layer did not automatically mean highest concentrations and high storage in fine roots, as the highest storages of all the studied heavy metals were found in the lowest B horizon. Whereas Spearman's rank order correlation analysis showed the strongest correlations between the concentrations of fine roots and the soil organic horizon per Cu, Pb, Cd, Ni, and Cr (publication II), analysis of heavy metal storages did not give any statistically significant correlations.

Principally, once adsorbed to the upper most organic-rich top layers the heavy metals are stored there for very long time. For example, a study by Klaminder *et al.* (2008) found that Pb is retained in the mor layer in mature northern coniferous forests for up to 400 years. The desorption of heavy metals from the soil organic layer takes a very long time, causing an increase in the heavy metal concentrations of the upper soil organic layers (Alumaa *et al.,* 2001). In the case of heavy metal leaching from the soil organic layers, the heavy metals are therefore concentrated in the upper part of the B horizon (Bergkvist, 1987; Kabata-Pendias, 2011). Therefore, due to further leaching of heavy metals in the future, a rise of heavy metal concentrations in B horizons could be expected. The high peaks of leach out from soil of (pollution originated) heavy metals to streams and groundwater is still ahead, e.g. for Pb it is predicted to occur about 200–800 years from now (Klaminder *et al.,* 2006).

Heavy metal allocation to fine roots depends among other factors on site specific soil conditions and the presence of mycorrhizal fungi (Bojarczuk &

Kieliszewska-Rokicka, 2010). As the biomass of fine roots and ectomycorrhizal mycelia was small in comparison to the mass of e.g. the soil organic layer, the storage of heavy metals in these media remained very modest, especially in comparison to soil mineral layers. However, the effect of understorey vegetation and related roots were not addressed in this study. Therefore, the total heavy metal allocation to fine roots was somewhat underestimated, since the roots of the understorey vegetation were not taken into account.

Contrary to the highest concentrations of heavy metals in the upper organic layers, the storage of heavy metals were according to the monitoring programme's data highest in the lower mineral layers, due to the higher thickness and bulk density of the mineral layers. It is known from the literature that uplifted and deposited heavy metals are stored in very stable complexes in soil organics, especially Cu, Pb, Ni, and Zn (Lomander & Johansson, 2001; Kabata-Pendias, 2011), making these heavy metals largely unavailable to plants. Currently, the share of up taken heavy metals from lower mineral soil layers has been estimated to be small in the upper soil organic layer, and the heavy metals there originate mainly from anthropogenic pollution (Alumaa *et al.,* 2001; Klaminder *et al.,* 2005, 2006, 2008, 2011). The binding of heavy metals and soil organics to long-lasting stable complexes depends on various factors. Scientific experiments have shown that the addition of an organic substance to a substrate or simply having a higher organic matter content in the soil will reduce the bioavailability of heavy metals to plants, but this might not be the main or only factor determining the mobility of heavy metals in natural coniferous ecosystems (Kiikkilä *et al.,* 2014). Bioavailability is also affected by other factors, such as the concentration of other heavy metals, the amendment properties of heavy metals, climatic conditions, pH, redox conditions, the surrounding mineral composition, and microbial activity (Lomander & Johansson, 2001; Romkens *et al.,* 2009; Tangahu *et al.,* 2011; Prapagdee *et al.,* 2014; Venegas *et al.,* 2016). A high organic matter content and clay particles in soils have been found to be very important factors in terms of Pb and Cr bonding, whereas Cu and Cd are adsorbed more efficiently if calcites and dolomites are present in the soil (Alumaa *et al.,* 2001).

Based on the root uptake factor, it could be inferred that the ability to obtain heavy metals from the soil or for it to retain them differed among the heavy metals. Pb, Ni, and Cr (RUF_{Pb}=0.60, RUF_{Ni}=0.40, and RUF_{Cr}=0.23) had very low root uptake from soil organics; in this study soil organics mainly accumulated heavy metals, most likely due to strongly bonding, thus these heavy metals had low mobility from the stocks of soil organics. In contrast, Zn and Cu (RUF_{Zn}=2.63 and RUF_{Cu}=1.58), which are micronutrients, were more easily taken up from the soil organic layers.

Coarse roots (especially in the case of pine), reach the bedrock and are able to transport heavy metals from the deeper soil layers, from which the heavy metals are taken up and returned through different litter to the cycle (Jobbagy & Jackson, 2004). Therefore, the depth of roots might affect the composition/ quantity of heavy metals uplift, affecting the composition/quantity of the heavy

metals in the respective soil layers. However, the uptake of heavy metals from soil mineral layers has been shown to be low, e.g. Pb in mineral soils is largely not bioavailable (Klaminder *et al.,* 2004, 2011). If one includes the fine roots only, it is clear that depending on the soil type, their physical location in the O or A horizon has already impacted their heavy metal levels and the availability of heavy metals to plants. In these layers, the concentrations of heavy metals also differed and were not automatically reflected in the size of heavy metal storage. The bulk density in the A horizon at the Tõravere site was highest in comparison to the other stand's soil organic layers (publication IV). More active nutrient cycling, decomposition processes, and soil mixing was characteristic to this site's soil type (luvisol) in comparison to the others' podzol soils. Therefore, it could be assumed that in Tõravere there were many more sites available for heavy metals to form strong and long-lasting complexes. The mor type of humus characteristic to podzol soils has been found to be the most effective filter of heavy metals (Ferro-Vazquez *et al.,* 2014, Alumaa *et al.,* 2001), but at Tõravere the mor layer is missing.

Decomposition tests with coniferous needle litterbags have shown the age of the OL horizon to be around 3–5 years (Bringmark *et al.,* 2013). According to previous studies, the age of the OF layer has been estimated to be several decades, as this layer decomposes very slowly due to its components (e.g. twigs, fine roots, pieces of bark) and the acidic decomposition processes in the soil organic layers of coniferous forests (Äyräs *et al.,* 1997; Ukonmaanaho *et al.,* 2001; Pajuste & Frey, 2003; Froberg *et al.,* 2011). The retention of heavy metals in the soil organic layer could further slow the decomposition process, especially in areas with relatively low heavy metal deposition, e.g. Scandinavia or Estonia (Lomander & Johansson, 2001). That may simultaneously also cause a further accumulation of heavy metals in soil organics, wherein the heavy metals could be bound for decades (Froberg *et al.,* 2011). Therefore, even if fine roots have a relatively short life span (up to 2 years), they could slow down the decomposition process of the soil organic layer due to their high heavy metal content and slower decay in comparison to needle litter (McClaugherty *et al.,* 1984). This is especially characteristic in northern coniferous ecosystems, where the absorptive fine root tissue density and fine root biomass per basal area has been found to be higher than in temperate forests (publication III). That likely refers to higher heavy metal tolerance (Eldhuset *et al.,* 2006; Márquez-García *et al.,* 2012), but may also indicate a slower decomposition rate of fine roots in northern ecosystems. Therefore, the heavy metals in fine roots are retained longer in soil organic layers. However, plant uptake from deeper soil (mineral) layers does not significantly prolong the self-purification of the mor layer, as the amounts of up taken heavy metals are small (Klaminder *et al.,* 2005), and therefore do not significantly contribute to the anthropogenically originated pollution stored in soil organic layers.

Heavy metal storage of the soil organic layer (OL+OF+OH) or organic rich A horizon were calculated in publication IV per six ICP IM and ICP forests stands. The storages were highly variable and depended on the soil and site

type. Owing to dataset limitations, in the first publication only the OL and OF horizons of ICP Forests level I stands were used to calculate the average storages of heavy metals in the soil organic layer. It would explain the differences in heavy metal storages in the soil organic layer in publications I and IV, as in the latter one OF and A horizons were also used.

In publication IV, the six stands were divided into three groups according to their heavy metal storages in the soil organic layer or organic rich A horizon. The first group was comprised of Sagadi, Vihula, and Vilsandi stands, where storages varied from 124–303 g ha^{-1} of Cu, 1207–1561 g ha^{-1} of Zn, 367–742 g ha^{-1} of Pb, and 12–46 g ha^{-1} of Cd. The second group was comprised of the oldest stands (Saarejärve Norway spruce and Scots pine stands), where the storages were more variable: 977–1071 g ha^{-1} of Cu, 5450–6120 g ha^{-1} of Zn, 4142–5508 g ha^{-1} of Pb, and 109–153 g ha^{-1} of Cd. The storages were always higher at the Saarejärve Scots pine stand. The Tõravere Norway spruce stand was the sole member of the third group and the heavy metal storages in the organic rich A horizon were calculated to be 14,138 g ha^{-1} of Cu, 64,727 g ha^{-1} of Zn, 28,957 g ha^{-1} of Pb, and 1278 of Cd g ha^{-1}. The main reasons behind the Tõravere stand's higher storages were the different and soil and site types. The A horizon was thick (up to 18cm) and the bulk density was much higher due to mineral components, compared to the organic layers at the other stands used in this study.

The detection of heavy metals from samples (e.g. soil organic layer samples) treated with *aqua regia* could also have an effect on the results, as concentrations measured using *aqua regia* were not the same which were available for the trees. As the deposition of heavy metals is currently low, it is very likely that the heavy metals stored in Estonian ecosystems and especially in the soil organic layer are the result of previous high emissions.

The RDA ($p=0.017$) and ANOVA ($p < 0.05$) tests used in publication I showed differences in heavy metal distribution at a regional scale, with somewhat higher Ni and Cr concentrations and stocks principally in the OF horizon detected in SE Estonia. The origin of the Ni and Cr was likely to be local, as a local heritage of these heavy metals has been shown by several authors (Brumelis *et al.,* 2002; Steinnes & Friedland, 2006). The overall converging of heavy metals into soil organic layers (especially OF) was also noticeable for the NW and NE of Estonia (publication I). The trans-boundary nature of heavy metals supported the idea that due to the prevailing westerly winds, a remarkable share of heavy metals emitted in Estonia have been carried in an easterly direction and stored in over-border ecosystems in Russia. High concentrations of Ni, Cr, and Zn have for example been found in the Narva river (Roots & Nõmmsalu, 2011), which flows in an easterly direction from the main oil shale burning electrical power plants. Therefore, the location of stands in connection to stored heavy metals is important, in terms of heavy metals deposited decades ago and especially per storages in the soil organic layer. Location of a stand is less important than in the past, as depositions have decreased significantly.

4. CONCLUSIONS

This thesis provides scientific analysis of heavy metal data from different international programmes (ICP Forests; ICP Integrated Monitoring; the ICP Vegetation sub-programme Atmospheric Heavy Metal Deposition in Europe) and from national precipitation monitoring network. All the set aims were reached.

The concentrations of the heavy metals (Zn, Cu, Cr, Ni, Cd and Pb) in bulk deposition, mosses, living needles, litterfall, upper soil organic layers, fine roots, and ectomycorrhizal mycelia differed considerably, but were still within the range of concentrations of a non-polluted area. High concentrations of heavy metals in fine roots and forest soil organic layers, and significant correlations between them, indicated that heavy metals have accumulated in soil organic layers. In some cases, these heavy metals might still be transported to the above-ground living biomass of coniferous trees. However, a distinction must be made between biogenic heavy metals (Zn and Cu) and contaminant heavy metals (Pb, Cd, Cr, and Ni). Concentrations of both biogenic elements were higher than that of contaminant metals in plant material samples, indicating a biological demand of Zn and Cu for growth. High concentrations of Zn and Cu in fine roots and particularly in root-associated mycelia could indicate active root uptake, and an active translocation of these microelements from soil organic layers to growing trees. Rapid reuse of Zn at ecosystem level was also indicated by highest Zn concentrations in the OL (litter horizon, i.e. the topmost soil organic layer) according to the results of the analysis of the 75 ICP Forests coniferous sites (level I network).

Contrary to the biogenic heavy metals, contaminant heavy metals (Pb, Cr, and Ni) had a very low uptake from soil organic layers, which indicates high attachment of these heavy metals to the soil organic layers. An interesting exception was Ni, as once present in fine roots; this heavy metal was easily translocated to needles. This, along with the low accumulation index of Ni and Cu, indicates living needles' need of these heavy metals for growth. Cd was more easily mobile from the soil organic layers, but was (similarly to Pb) almost not translocated from fine roots to the upper parts of trees. Therefore, high retention of Cd and especially of Pb could be suspected in fine roots. High accumulation (Pb) and retention (Cr, Cd) of contaminants, and biogenic Zn in older needles was observed. This reflected that contaminant heavy metals were cycled from the soil organic layer via fine roots while needles were simultaneously obtaining contaminant heavy metals from the ambient air (as the translocation factor, e.g. of Pb, was very low).

The overall level of heavy metal bulk deposition in Estonia is currently low: 0.5 g ha^{-1} of Cd, 25.8 g ha^{-1} of Cu, 4.8 g ha^{-1} of Pb, and 224.9 g ha^{-1} of Zn. The comparative analysis of moss data from 1995 and 2005/2006 showed significant changes in the territorial distribution of heavy metal pollution. Nowadays, the NE of Estonia could not be distinguished from the other regions based on the heavy metal content of mosses. However, the effects of previous significantly

higher exposure to heavy metal emissions are preserved in the OF soil horizon of natural coniferous ecosystems (data of 75 ICP Forests coniferous sites), where the average stocks of highly accumulative heavy metals reach levels of up to 728.8 g ha^{-1} for Cr, 538.5 g ha^{-1} for Pb, and 372.5 g ha^{-1} for Ni. Significantly higher concentrations of Ni and Cr in the OF horizon than in moss layer indicate the influence of the previous high heavy metal emissions. An analysis of the organic layer of forest soils showed the highest storages of Ni and Cr are in SE Estonia. This mostly showed local deposition from oil shale-based industry and the high ability of these heavy metals to accumulate in soil organic layers. Therefore, it could be said that the greatest historical stationary emission source of heavy metals in Estonia – the oil shale industry – has left its mark on the soil organic layers of coniferous stands, where large stocks of heavy metals have ratios similar to those characteristic of fly ash emissions from the oil shale industry.

Based on the results of this thesis, the support was found for hypothesis that regional differences in heavy metal depositions and accumulation in Estonian coniferous ecosystems still occur. The important role of fine roots was confirmed in taking-up and storing heavy metals (especially Pb) in Estonian coniferous forests, thus prolonging their retention in stands and thereby preventing soil purification from heavy metals. However, some heavy metals (especially Cu, Zn, and Cd) were taken up more easily than others.

Heavy metal concentrations in the soil organic layers were highest for Pb, Cr, and Ni, but in fine roots even higher concentrations than those of the soil organic layers were found for Cu, Zn, and Cd. The heavy metal concentrations in root-associated ectomycorrhizal mycelia were unexpectedly high: concentrations (with the exception of Cd) were many times higher than in the fine roots or soil organic layers. Despite this, the highest storages of heavy metals in the studied media were still found in the soil organic layers.

Expectations regarding the minor importance of heavy metal depositions were not supported as despite the current modest heavy metal input by precipitation, deposition remained an important heavy metal input source at a stand level, especially for biogenic heavy metals, and in particular for Zn.

International monitoring programmes such as ICP Forests, ICP IM, and ICP Vegetation provide high quality databases of different environmental data. Different datasets are suitable for different purposes, e.g. long-term or short-term evaluations of environmental status. Combining the results of international monitoring programmes with local datasets gave a unique insight into occurrence of heavy metals in Estonian coniferous ecosystems both currently and in the past. This kind of scientific analysis of environmental data helps to form an overview of the current environmental status of forests and predict the effects of previously accumulated pollutants under changing environmental conditions, e.g. clear cuts, forest fires, decreased heavy metal emissions, and climate change. For example, climate change could possibly alter the accumulation and translocation processes of heavy metals in forest stands, which could result in increased heavy metal bioavailability (Mander *et al.,* 2017). Therefore, environmental monitoring and the scientific analysis of collected datasets should remain a priority.

REFERENCES

Abraham J, Dowling K, Florentine S (2017) The Unquantified Risk of Post-Fire Metal Concentration in Soil: a Review. Water, Air, and Soil Pollution 228: 175. doi: 10.1007/s11270-017-3338-0.

Alriksson A, Eriksson HM (2001) Distribution of Cd, Cu, Pb and Zn in Soil and Vegetation Compartments in Stands of Five Boreal Tree Species in N.E. Sweden. Water, Air, and Soil Pollution 1: 461–475. doi.org/10.1023/A:101758640

Apuhtin V, Asi E, Õunap H, Timmusk T (2017) Riiklik keskkonnaseire. Alamprogramm 7. Metsaseire. 2016.a. aruanne. Keskkonnaagentuur, Tartu.

Asi E, Napa Ü, Frey J (2009) Concentrations of trace metals in epigeic moss Hylocomium splendens and needles of Scots pine and Norway spruce on Estonian ICP Forests sites Finnish Forest Research Institute, 6th International Symposium on Ecosystem Behaviour BIOGEOMON 2009. Conference Programme & Abstracts. Vantaa.

Alumaa P, Kirso U, Petersell V, Steinnes E (2002) Sorption of toxic heavy metals to soil. International Journal of Hygiene and Environmental Health 204: 375–376 doi: 10.1078/1438-4639-00114

Alumaa P, Steinnes E, Kirso U, Petersell V (2001) Heavy metal sorption by different Estonian soil types at low equilibrium solution concentrations. Proceedings of the Estonian Academy of Sciences. Chemistry 50: 104–115.

Äyräs M, Pavlov V, Reimann C (1997) Comparison of sulphur and heavy metal contents and their regional distribution in humus and moss samples from the vicinity of Nikel and Zapoljarnij, Kola Peninsula, Russia. Water, Air, and Soil Pollution 98: 361–380. doi: 10.1023/a:1026420627519.

Bergkvist B (1986) Leaching of metals from a spruce forest soil as influenced by experimental acidification. Water, Air, and Soil Pollution 31: 901–916. doi: 10.1007/bf00284236.

Bergkvist B (1987) Soil solution chemistry and metal budgets of spruce forest ecosystems in S-Sweden. Water, Air, and Soil Pollution 33: 131–154. doi: 10.1007/bf00191383.

Bergkvist B, Folkeson L, Berggren D (1989) Fluxes of Cu, Zn, Pb, Cd, Cr, and Ni in Temperate Forest Ecosystems – A Literature-Review. Water, Air, and Soil Pollution 47: 217–286. doi: 10.1007/bf00279328.

Bojarczuk K, Kieliszewska-Rokicka B (2010) Effect of Ectomycorrhiza on Cu and Pb Accumulation in Leaves and Roots of Silver Birch (*Betula pendula* Roth.) Seedlings Grown in Metal-Contaminated Soil. Water, Air, and Soil Pollution 207: 227–240. doi: 10.1007/s11270-009-0131-8.

Bringmark L, Lundin L, Augustaitis A, Beudert B, Dieffenbach-Fries H, Dirnboeck T, Grabner M-T, Hutchins M, Kram P, Lyulko I, Ruoho-Airola T, Vana M (2013) Trace Metal Budgets for Forested Catchments in Europe-Pb, Cd, Hg, Cu and Zn. Water, Air, and Soil Pollution 224: 1502. doi: 10.1007/s11270-013-1502-8.

Brumelis G, Lapina L, Nikodemus O, Tabors G (2002) Use of the O horizon of forest soils in monitoring metal deposition in Latvia. Water, Air, and Soil Pollution 135: 291–309. doi.org/10.1023/A:101471411.

Brunner I, Bakker MR, Bjork RG, Hirano Y, Lukac M, Aranda X, Borja I, Eldhuset TD, Helmisaari HS, Jourdan C, Konopka B, Lopez BC, Perez CM, Persson H, Ostonen I (2013) Fine-root turnover rates of European forests revisited: an analysis of data

from sequential coring and ingrowth cores. Plant and Soil 362: 357–372. doi: 10.1007/s11104-012-1313-5.
Bruno Franco P (2005) Distribution of Biogenic and Non-biogenic Trace Metals in Roadside Soils. A study of Uppsala City, Sweden. Swedish University of Agricultural Sciences, Uppsala.
Charney RL, Giordano PM (1977) Microelements as related to plant deficiencies and toxicities, In: Elliot LF, Stevenson FJ (eds) Soils for management of organic wastes and waste waters. American Society of Agronomy, Soil Science Society of America, Madison.
Clarholm M, Skyllberg U (2013) Translocation of metals by trees and fungi regulates pH, soil organic matter turnover and nitrogen availability in acidic forest soils. Soil Biology & Biochemistry 63: 142–153. doi: 10.1016/j.soilbio.2013.03.019.
de Wit HA, Hettelingh JP, Harmens H (2015) Trends in ecosystem and health responses to long-range transported atmospheric pollutants. Report No. 6946–2015 ICP Waters report 125/2015. Norwegian Institute for Water Research, Oslo.
EEA (2013) European Union emission inventory report 1990–2011 under the UNECE Convention on Long-range Transboundary Air Pollution (LRTAP). European Environment Agency (EEA), Luxembourg.
EEA (2014) Air quality in Europe – 2014 report. European Environmental Agency (EEA), Copenhagen.
EEA (2015) Indicator Assessment. Data and Maps. Heavy metal emissions. European Environment Agency (EEA), Copenhagen.
Eesti Akrediteerimiskeskus (2013) Accreditation certificate No L008 of Estonian Environmental Research Centre. Eesti Akrediteerimiskeskus, Tallinn.
Eesti Energia AS (2016) Eesti Energia aastaaruanne 2015. Eesti Energia AS, Tallinn.
Eldhuset TD, Lange H, de Wit HA (2006) Fine root biomass, necromass and chemistry during seven years of elevated aluminium concentrations in the soil solution of a middle-aged *Picea abies* stand. Science of the Total Environment 369: 344–356. doi: 10.1016/j.scitotenv.2006.05.011.
EMEP (1996) European Monitoring and Evaluation Programme. Manual for Sampling and Chemical Analysis. Norwegian Institute of Air Research, Kjeller.
European Environment Agency (2013) Air pollutant emissions data viewer (LRTAP convention). EU emission inventory report 1990–2011 under the UNECE Convention on LRTAP. European Environment Agency, http://www.eea.europa.eu/data-and-maps/data/data-viewers/air-emissions-viewer-lrtap. Accessed 28.06.2013.
Ferro-Vazquez C, Novoa-Munoz JC, Costa-Casais M, Klaminder J, Martinez-Cortizas A (2014) Metal and organic matter immobilization in temperate podzols: A high resolution study. Geoderma 217: 225–234. doi: 10.1016/j.geoderma.2013.10.006.
Frey T, Frey J (2015) Kompleksseire saarejärvel. Aruanne 2014. TÜ IM Saare, Tartu.
Froberg M, Hansson K, Kleja DB, Alavi G (2011) Dissolved organic carbon and nitrogen leaching from Scots pine, Norway spruce and silver birch stands in southern Sweden. Forest Ecology and Management 262: 1742–1747. doi: 10.1016/j.foreco.2011.07.033.
Gordon WS, Jackson RB (2000) Nutrient concentrations in fine roots. Ecology 81: 275–280. doi: 10.1890/0012-9658(2000)081[0275:ncifr]2.0.co;2.
Hale B, Evans L, Lambert R (2012) Effects of cement or lime on Cd, Co, Cu, Ni, Pb, Sb and Zn mobility in field-contaminated and aged soils. Journal of Hazardous Materials 199: 119–127. doi: 10.1016/j.jhazmat.2011.10.065.

Hettelingh JP, Sliggers J, Bolcher Mvh, Denier van der Gon H, Groenenberg JE, Ilyin I, Reinds GJ, Slootweg J, Travnikov O, Visschedijk A, Vries Wd (2007) Heavy Metal Emissions, Depositions, Critical Loads and Exceedances in Europe. Directorate for Climate Change and Industry of the Netherlands Ministry of Housing, Spatial Planning and the Environment, The Hague.

Huang J-H, Ilgen G, Matzner E (2011) Fluxes and budgets of Cd, Zn, Cu, Cr and Ni in a remote forested catchment in Germany. Biogeochemistry 103: 59–70. doi: 10.1007/s10533-010-9447-0.

ICP Forests (2017) ICP Forests Programme's official web page – http://icp-forests.net/. Accessed on 24.09.2017.

ICP IM (2017) ICP Integrated Monitoring Programme's official web page – http://www.syke.fi/nature/icpim. Accessed on 01.10.2017.

ICP IM Programme Centre (2004) Manual for Integrated Monitoring. ICP IM Programme Centre, Helsinki.

ICP Vegetation Coordination Centre (2005) ICP Vegetation Manual. Heavy Metals in European Mosses: 2005/2006 Survey. Heavy Metals in European Mosses: 2005/ 2006 Survey Monitoring Manual. ICP Vegetation Coordination Centre, Bangor.

ICP Vegetation (2017) ICP Vegetation Programme's official web page – https://icpvegetation.ceh.ac.uk/. Accessed 24.09.2017.

Ilyin I, Rozovskaya O, Travnikov O, Varygina M, Aas W, Pfaffhuber KA (2016) EMEP Status Report 2/2016. Assessment of heavy metal transboundary pollution, progress in model development and mercury research. Joint MSC-E & CCC Report, Moscow and Kjeller.

Jobbagy EG, Jackson RB (2004) The uplift of soil nutrients by plants: Biogeochemical consequences across scales. Ecology 85: 2380–2389. doi: 10.1890/03-0245.

Kaasik M, Liiv S (2007) Spatial and temporal variability of trace metals in mosses in Estonia. Forestry Studies 46: 35–44.

Kabata-Pendias A (2011) Trace Elements in Soils and Plants. CRC Press, Florida.

Kabral N (2017a) Kompleksseire Saarejärvel ja Vilsandil 2016.a. Eesti Keskkonnauuringute Keskus OÜ, Tallinn.

Kabral N (2017b) Sademete seire 2016. Eesti Keskkonnauuringute Keskus OÜ, Tallinn.

Kaila A, Asam ZUZ, Sarkkola S, Xiao LW, Lauren A, Vasander H, Nieminen M (2012) Decomposition of harvest residue needles on peatlands drained for forestry – Implications for nutrient and heavy metal dynamics. Forest Ecology and Management 277: 141–149. doi: 10.1016/j.foreco.2012.03.024.

Kiikkilä O, Nieminen TM, Starr M, Makila M, Loukola-Ruskeeniemi K, Ukonmaanaho L (2014) Leaching of Dissolved Organic Carbon and Trace Elements After Stem-Only and Whole-Tree Clear-cut on Boreal Peatland. Water, Air, and Soil Pollution 225: 1767. doi: 10.1007/s11270-013-1767-y.

Klaminder J, Bindler R, Emteryd O, Renberg I (2005) Uptake and recycling of lead by boreal forest plants: Quantitative estimates from a site in northern Sweden. Geochimica Et Cosmochimica Acta 69: 2485–2496. doi: 10.1016/j.gca.2004.11.013.

Klaminder J, Bindler R, Laudon H, Bishop K, Emteryd O, Renberg I (2006) Flux rates of atmospheric lead pollution within soils of a small catchment in northern Sweden and their implications for future stream water quality. Environmental Science & Technology 40: 4639–4645. doi: 10.1021/es0520666.

Klaminder J, Bindler R, Renberg I (2008) The biogeochemistry of atmospherically derived Pb in the boreal forest of Sweden. Applied Geochemistry 23: 2922–2931. doi: 10.1016/j.apgeochem.2008.04.007.

Klaminder J, Farmer JG, MacKenzie AB (2011) The origin of lead in the organic horizon of tundra soils: Atmospheric deposition, plant translocation from the mineral soil or soil mineral mixing? Science of the Total Environment 409: 4344–4350. doi: 10.1016/j.scitotenv.2011.07.005.

Kohv N, Link A, Mandel E, N-B. P (2009a) Õhku eraldunud saasteainete heitkogused paiksetest saasteallikatest aastail 2004–2007. Keskkonnaministeeriumi Info- ja Tehnokeskus, Tallinn.

Kohv N, Mandel E, Heintalu H (2009b) 1990.–2007. aastal õhku eraldunud saasteainete heitkogused paiksetest ja hajussaasteallikatest Eestis In: K Kaukver (ed) "Eesti keskkond". Keskkonnaministeeriumi Info- ja Tehnokeskus, Tallinn.

Kohv N, Mandel, E., Ljamtsev, A. (2002) 2001. aasta Õhku paisatud saasteainete heitkogused Eestis (paiksed saasteallikad) ja 2000. aasta lõpparuanne Keskkonnaministeeriumi Info- ja Tehnokeskus, Tallinn.

Kvietkus K, Sakalys J, Valiulis D (2011) Trends of atmospheric heavy metal deposition in Lithuania. Lithuanian Journal of Physics 51: 359–369.

Kyllönen K, Karlsson V, Ruoho-Airola T (2009) Trace element deposition and trends during a ten year period in Finland. Science of the Total Environment 407: 2260–2269. doi: 10.1016/j.scitotenv.2008.11.045.

Liblik V, Pensa M (2001) Specifics and temporal changes in air pollution in areas affected by emissions from oil shale industry, Estonia. Water, Air, and Soil Pollution 130: 1787–1792. doi: 10.1023/a:1013936825342.

Liiv S, Kaasik M (2004) Trace metals in mosses in the Estonian oil shale processing region. Journal of Atmospheric Chemistry 49: 563–578. doi: 10.1007/s10874-004-1266-z.

Liiv S, Kösta H (2017) Eesti riikliku keskkonnaseire välisõhu allprogrammi seiretöö. Raskmetallide sadenemise bioindikatsiooniline hindamine. 2016.a. aruanne. Cd, Cr, Cu, Fe, Ni, Pb, V, Zn, N, As, Hg, Al ja Ti sisaldus samblas. Tallinna Botaanikaaed, Tallinn.

Lomander A, Johansson MB (2001) Changes in concentrations of Cd, Zn, Mn, Cu and Pb in spruce (*Picea abies*) needle litter during decomposition. Water, Air, and Soil Pollution 132: 165–184. doi: 10.1023/a:1012035620480.

Lundin L, Forsius M (2016) ICP Integrated Monitoring of Air Pollution Effects on Ecosystems – ICP IM Achievements & Priorities 2016–2017. PowerPoint presentation available at https://www.google.ee/url?sa=t&rct=j&q=&esrc=s&source=web&cd=1&cad=rja&uact=8&ved=0ahUKEwi4jfDPm77WAhVHApoKHW9zBjsQFggnMAA&url=http%3A%2F%2Fwww.syke.fi%2Fdownload%2Fnoname%2F%257BBCB38ED2-1171-41FC-9BC3-943D88A24EFB%257D%2F127757&usg=AFQjCNFudOaW7uO_WF1r202dDepZkTspLA. Accessed 12.08.2017.

Mander Ü, Ostonen I, Niinemets Ü (2017) Indicators of climate change adaptation from molecules to ecosystems. Regional Environmental Change 17: 2055–2059. doi.org/10.1007/s10113-017-1215-4

Márquez-García B, Fernández-Recamales MÁ, Córdoba F (2012) Effects of Cadmium on Phenolic Composition and Antioxidant Activities of *Erica andevalensis*. Journal of Botany 2012, Article ID 936950: 1–6. doi: 10.1155/2012/936950.

McClaugherty CA, Aber JD, Melillo JM (1984) Decomposition dynamics of fine roots in forested ecosystems. Oikos 42: 378–386. doi: 10.2307/3544408.

Meyer M, Schroder W, Pesch R, Steinnes E, Uggerud HT (2015) Multivariate association of regional factors with heavy metal concentrations in moss and natural surface soil sampled across Norway between 1990 and 2010. Journal of Soils and Sediments 15: 410–422. doi: 10.1007/s11368-014-0999-9.

Ministry of the Environment (2007) Estonian Environmental Strategy 2030. Ministry of the Environment, Tallinn.

Nikodemus O, Brumelis G, Tabors G, Lapina L, Pope S (2004) Monitoring of air pollution in Latvia between 1990 and 2000 using moss. Journal of Atmospheric Chemistry 49: 521–531. doi: 10.1007/s10874-004-1263-2.

Pajuste K, Frey J (2003) Nitrogen mineralisation in podzol soils under boreal Scots pine and Norway spruce stands. Plant and Soil 257: 237–247. doi: 10.1023/a:1026222831694.

Persson HA (1983) The distribution and productivity of fine roots in boreal forests. Plant and Soil 71: 87–101. doi: 10.1007/bf02182644.

Prapagdee S, Piyatiratitivorakul S, Petsom A, Tawinteung N (2014) Application of Biochar for Enhancing Cadmium and Zinc Phytostabilization in *Vigna radiata* L. Cultivation. Water, Air, and Soil Pollution 225:2233. doi: 10.1007/s11270-014-2233-1.

Raukas A (2010) Sustainable development and environmental risks in Estonia Agronomy Research. Estonian University of Life Sciences, Tartu.

Reinik J, Irha N, Steinnes E, Urb G, Jefimova J, Piirisalu E (2014) Release of 22 elements from bottom and fly ash samples of oil shale fueled PF and CFB boilers by a two-cycle standard leaching test. Fuel Processing Technology 124: 147–154. doi: 10.1016/j.fuproc.2014.03.011.

Reinik J, Irha N, Steinnes E, Urb G, Jefimova J, Piirisalu E, Loosaar J (2013) Changes in trace element contents in ashes of oil shale fueled PF and CFB boilers during operation. Fuel Processing Technology 115: 174–181. doi: 10.1016/j.fuproc.2013.06.001.

Romkens PF, Guo HY, Chu CL, Liu TS, Chiang CF, Koopmans GF (2009) Prediction of Cadmium uptake by brown rice and derivation of soil-plant transfer models to improve soil protection guidelines. Environmental Pollution 157: 2435–2444. doi: 10.1016/j.envpol.2009.03.009.

Roots O, Nõmmsalu, H. (2011) Aruanne veekeskkonnale ohtlike ainete sõeluurngu tulemustest Eestis.Baltic Actions for Reduction of Pollution of the Baltic Sea from Priority Hazardous Substances. Project LIFE07 ENV/EE/000122 – BaltActHaz. Eesti keskkonnauuringute Keskus OÜ and MTÜ Balti Keskkonnafoorum Eesti, Tallinn.

Rühling Å, Tyler G (2001) Changes in Atmospheric Deposition Rates of Heavy Metals in Sweden A Summary of Nationwide Swedish Surveys in 1968/70 – 1995. Water, Air and Soil Pollution 1: 311–323. doi: 10.1023/a:1017584928458.

Salmi T, Määttä A, Anttila A, Ruoho-Airola T, Amnell T (2002) Detecting Trends of Annual Values of Atmospheric Pollutants by the Mann-Kendall Test and Sen's Slope Estimates – The Excel Template Application MAKESENS. Publication on Air Quality 31: 26. Finnish Meteorological Institute, Helsinki.

Schroder W, Nickel S, Schonrock S, Schmalfss R, Wosniok W, Meyer M, Harmens H, Frontasyeva MV, Alber R, Aleksiayenak J, Barandovski L, Blum O, Carballeira A, Dam M, Danielsson H, De Temmermann L, Dunaev AM, Godzik B, Hoydal K, Jeran Z, Karlsson GP, Lazo P, Leblond S, Lindroos J, Liiv S, Magnusson SH, Mankovska B, Nunez-Olivera E, Piispanen J, Poikolainen J, Popescu IV, Qarri F,

Santamaria JM, Skudnik M, Spiric Z, Stafilov T, Steinnes E, Stihi C, Suchara I, Thoni L, Uggerud HT, Zechmeister HG (2017) Bioindication and modelling of atmospheric deposition in forests enable exposure and effect monitoring at high spatial density across scales. Annals of Forest Science 74:31. doi: 10.1007/s13595-017-0621-6.

Shahid M, Dumat C, Khalid S, Schreck E, Xiong TT, Niazi NK (2017) Foliar heavy metal uptake, toxicity and detoxification in plants: A comparison of foliar and root metal uptake. Journal of Hazardous Materials 325: 36–58. doi: 10.1016/j.jhazmat.2016.11.063.SOER (2015) The European environment – state and outlook 2015 (SOER 2015). Countries and regions: Estonia. European Environment Agency (EEA), Copenhagen.

Statistics Estonia (2017) Quarterly Bulletin of Statistics Estonia. Statistics Estonia, Tallinn.

Statistics Estonia databases (2017). Online databases available at: https://www.stat.ee/database. Accessed 01.10.2017.

Steinnes E, Friedland AJ (2006) Metal contamination of natural surface soils from long-range atmospheric transport: Existing and missing knowledge. Environmental Reviews 14: 169–186. doi: 10.1139/a06-002.

Talve S, Riipulk V (2001) Inventory analysis of oil shale energy produced on a small thermal power plant. Journal of Cleaner Production 9: 233–242. doi.org/10.1016/S0959-6526(00)00056-1

Tangahu BV, Abdullah SRS, Basri H, Idris M, Anuar N, Mukhlisin M (2011) A Review on Heavy Metals (As, Pb, and Hg) Uptake by Plants through Phytoremediation. International Journal of Chemical Engineering, Article ID 939161: 1–31. doi: 10.1155/2011/939161.

Ter Braak CJF, Šmilauer P (1998) CANOCO Reference Manual and User's Guide to Canoco for Windows: Software for Canonical Community Ordination (Version 4). Microcomputer Power, Ithaca.

Treier K, Kabral N, Frey J (2008) Trends in precipitation of air pollutants at Estonian monitoring stations 1994–2005. Oil Shale 25: 276–290. doi: 10.3176/oil.2008.2.09.

Tyler G (1984) The impact of heavy-metal pollution on forests – A case study of Gusum, Sweden. Ambio 13: 18–24.

Tyler G (1992) Critical concentrations of heavy metals in the mor horizon of Swedish forests. Report 4078. Swedish Environmental Protection Agency, Solna.

Ukonmaanaho L, Starr M, Mannio J, Ruoho-Airola T (2001) Heavy metal budgets for two headwater forested catchments in background areas of Finland. Environmental Pollution 114: 63–75. doi: 10.1016/s0269-7491(00)00207-4.

Venegas A, Rigol A, Vidal M (2016) Effect of ageing on the availability of heavy metals in soils amended with compost and biochar: evaluation of changes in soil and amendment properties. Environmental Science and Pollution Research 23: 20619–20627. doi: 10.1007/s11356-016-7250-8.

Wang JJ, Tharayil N, Chow AT, Suseela V, Zeng H (2015) Phenolic profile within the fine-root branching orders of an evergreen species highlights a disconnect in root tissue quality predicted by elemental- and molecular-level carbon composition. New Phytologist 206: 1261–1273. doi: 10.1111/nph.13385.

Yoon J, Cao XD, Zhou QX, Ma LQ (2006) Accumulation of Pb, Cu, and Zn in native plants growing on a contaminated Florida site. Science of the Total Environment 368: 456–464. doi: 10.1016/j.scitotenv.2006.01.016.

SUMMARY IN ESTONIAN

Raskmetallid Eesti okasmetsades – analüüs seireprogrammide andmete põhjal

Töö peamiseks eesmärgiks oli teha kokkuvõte keskkonnaseire riikliku programmi raames kogutud raskmetallide andmestiku baasil meie looduslike okasmetsade raskmetallidega saastatuse tasemest. Seireandmestik võimaldas analüüsida kuut erinevat raskmetalli: Zn, Cu, Cr, Ni, Cd ja Pb. Okasmetsade erinevatest keskkondadest kogutud raskmetallide andmed pärinevad peamiselt Genfi konventsiooni rahvusvahelistest seireprogrammidest: metsaseire (*ICP Forests*) ja kompleksseire (*ICP Integrated Monitoring*) andmebaasidest. Lisaks kasutati raskmetallide andmestikku sammalde kohta (*ICP Vegetation subprogram: Atmospheric Heavy Metal Deposition in Europe – estimation based on moss analysis*). Viimane on parim olemasolev andmebaas Eesti kohta (analüüsid on tehtud Soomes ja Rootsis) ja ajaliselt pikim raskmetallide seirerida (alates 1989 aastast). Kohalik sademete seire võrgustiku andmebaas raskmetallide osas on võrreldav alates 1999-st aastast. Eelnimetatud andmebaase kasutati selleks, et saada ülevaade raskmetallide kontsentratsioonidest, nende liikumisest okasmetsa erinevate osade vahel (muld, peenjuured, elusokkad, varis), peetumisest ja akumuleerumisest okasmetsa mulla orgaanilises osas ehk kõdukihis. Raskmetallide sadestumise ja akumuleerumise territoriaalset varieerumist iseloomustati kasutades kohalikku sademete seire võrgustiku andmestikku, sammalde seire andmeid ja okasmetsade kõdukihtide analüüse 75-st metsaseire I astme seire vaatluspunktist.

Euroopa Keskkonnaagentuuri ametlike andmete järgi on raskmetallide heitkoguste üldine vähenemine alates 1990. aastatest toimunud kõigis Euroopa Liidu riikides (EEA, 2014). Seda eriti plii, kaadmiumi, kroomi, nikli ja vähemal määral ka tsingi heitkoguste osas (EEA, 2014). Näiteks kõige toksilisema raskmetalli Pb heitkogused on langenud kahe aastakümnega kuni 90% (EEA, 2015), mis viitab, et raskemetallide heite vähendamiseks vastu võetud määruste ja protokollide rakendamine on olnud Euroopas edukas.

Raskemetallide peamisteks allikateks Eestis on olnud ja on ka praegusel hetkel paiksed antropogeensed saasteallikad: põlevkivil töötavad elektrijaamad, põlevkiviõli-, tsemendi- ning keemiatööstus, mis asuvad Kirde-Eesti tööstuspiirkonnas (Kohv *et al.,* 2002).

Põlevkivi on Eestis kõige olulisem maavara ning alates 1960. aastatest on Eesti olnud maailma suurim põlevkivi tootja ja tarbija (Raukas, 2010). Põlevkivitööstusest pärineva lendtuha ja tahkete osakestega on ökosüsteemidesse kantud mitmete aastakümnete jooksul raskmetalle, peamiselt Cr, Fe, Ni ja Pb (Liiv & Kaasik, 2004). Kõige kõrgema õhusaaste tasemega perioodil 1980-ndatel, mil põlevkivi kasutamine ulatus 30 milj. tonnini aastas, küündis lendtuha ja tahkete osakeste emissioon Eestis 280 000 tonnini aastas (Liblik & Pensa 2001). Statistikaameti andmetel oli 2014. aastal tahkete osakeste emissioon Eestis 21845 tonni (Statistics Estonia databases, 2017). Samuti on tunduvalt vähenenud ka

põlevkivi energeetikast pärineva lendtuha kogus – 2011. aastal oli see 28100 tonni, kuid 2015.aastal oli lendtuha emissioon vähenenud 3500 tonnini (Eesti Energia AS, 2016).

Alates 1990. aastatest on raskmetallide heitkogused Eestis märkimisväärselt vähenenud (Pb 81–99%, Cd 85%, Cr 44%, Cu 52%, Ni 77%, Zn 47%) (Kohv *et al.* 2009b). Suurim langus raskmetallide emissioonides toimus Eestis seoses majanduslike muutustega, eriti elektritootmise drastilise vähenemisega 1990. aastate alguses. Koos uute tehnoloogiate kasutuselevõtmisega põlevkivi põletamisel kui ka suitsugaaside puhastamisel ning uute rahvusvaheliste keskkonnaalaste eeskirjade rakendamisega, suuremate investeeringutega puhastesse tehnoloogiatesse aastatel 2005–2015 on ülaltoodud emissioonide vähenemine saavutatud (Treier *et al.,* 2008; Statistics Estonia, 2017). Raskmetallide heitkoguste alanemine on Eestis jätkunud ka peale 2000. aastat, kuid väiksemas mahus, seda näitavad emissiooniandmete kõrval ka sademete depositsiooni andmed: statistiliselt usaldusväärsed alanevad trendid sademetes saadi aastatel 2003–2013 Cd ja Cu puhul enamikes jaamades, kuid mõnedes jaamades kehtisid need ka Pb ja Zn kohta (artikkel IV). Keskmine aastane raskmetallide deponeerumine sademetega aastatel 2003–2013 oli: Cd 0,5 g ha^{-1}, Cu 27 g ha^{-1}, Pb 5,2 g ha^{-1} ja Zn 387 g ha^{-1} (artikkel IV).

Vaatamata alanenud raskmetallide emissioonidele ja depositsioonidele on Eesti metsaökosüsteemid olnud varasemalt pikka aega eksponeeritud raskmetallide saastele.

Zn, Cu, Cr, Ni, Cd ja Pb kontsentratsioone analüüsiti põhjalikult avamaasadametes, elusokastes, varises, sammaldes, mulla ülemistes orgaanilistes kihtides (OL ja OF), peenjuurtes ja juurtega seotud mütseelis (artiklid I ja II). Massivoo tasemel hinnati ka raskmetallide sissekannet metsadesse, peetumist ja akumuleerumist metsaökosüsteemi erinevates osades (artikkel IV). Uuriti ka võimalikke territoriaalseid erinevusi raskmetallide deponeerumisel ja peetumisel Eesti okasmetsades (artikkel I). Erinevad teadusartiklid on näidanud peenjuurte olulisust raskmetallide ringes ja peetumisel (Gordon & Jackson, 2000; Prapagdee *et al.,* 2014) ning seeläbi mõju raskmetallide kontsentratsioonidele mullas (Jobbagy & Jackson, 2004). Seetõttu pöörati selle doktoritöö raames erilist tähelepanu peenjuurtele ja peenjuurtega seotud ektomükoriisse seeneniidistiku rollile seoses raskmetallide peetumisega metsakõdus. Peenjuurte ja nendega seotud seeneniidistik ning mikroobide kooslus on oluline, sest võrreldes Lääne-Euroopa okaspuude peenjuurestikuga on siinsete okaspuude peenjuured potentsiaalselt võimelised rohkem ja kauem siduma raskmetalle (artikkel III).

Selle doktoritöö eesmärkideks oli 1) hinnata erinevusi raskmetallide kontsentratsioonides ja akumuleerumisel erivanuselistes metsaökosüsteemi osades; 2) hinnata kui paju raskmetallide lisandus metsaökosüsteemi depositsiooni ja varisega ning kui palju võeti raskmetalle ringlusesse peenjuurte vahendusel metsakõdust võrreldes raskmetallide varuga metsakõdus 3) hinnata ja võrrelda territoriaalseid erinevusi praeguste raskmetallide depositsioonide ja varasemalt deponeerinud ja nüüd metsakõdus akumuleerunud raskmetallide vahel.

Doktoritöö peamised hüpoteesid olid 1) raskmetallide peetumisel ja akumuleerumisel okasmetsade mulla orgaanilises osas on piirkondlikud erinevused 2) peenjuurtel on oluline roll raskmetallide ringes. Mulla orgaanilises osas akumuleerunud raskmetallid võetakse peenjuurtesse pikendades seeläbi raskmetallide peetumist mullas ja takistades metsaökosüsteemide isepuhastumist varasemalt deponeerinud raskmetallide saastest 3) raskmetallide kõrgeimad kontsentratsioonid ja suurimad varud uuritud metsaökosüsteemi osadest on mulla orgaanilistes kihtides 4) depositsioon raskmetallide allikana on tänapäeval vähem oluline kui minevikus.

Raskmetallide kõrged kontsentratsioonid peenjuurtes ja märkimisväärsed korrelatsioonid raskmetallide kontsentratsioonide vahel mulla orgaanilises horisondis ning peenjuurtes viitavad, et raskmetallid metsakõdus pärinevad eelkõige varasemast kõrge õhusaastetasemega ajaperioodist. Osaliselt transporditakse varasemalt akumuleerunud raskmetalle mulla orgaanilisest osast okaspuude biomassi. Töö tulemused näitasid, et nii kontsentratsioonide osas kui ka massivoos eristusid taimedele vajalikud raskmetallid – mikroelemendid Zn ja Cu saasteaineitest (Pb, Cd, Cr ja Ni). Zn ja Cu kontsentratsioonid olid kõrgemad taimses materjalis, eriti aga okaspuude peenjuurtes ja juurtega seotud seeneniidistikus ehk mütseelis mis võiks viidata Zn ja Cu bioloogilisele nõudlusele ja isegi aktiivsele juurtoitumisele. Kõrged kontsentratsioonid peenjuurtes leiti ka Pb ja Cd puhul, kuid erinevalt nt tsingist oli eriti Pb translokatsioon puude maapealsetesse osadesse äärmiselt madal.

Vaatamata sellele, et tänapäeval on raskmetallide saastekoormus Eestis pigem madal, on sademed endiselt jäänud oluliseks raskmetallide allikaks okasmetsa raskmetallide ringes – seda eriti Cu ja Zn aastase sisendvoo puhul (avamaasademete ja varisega). Tõeliste saastemetallide Cd ja Pb puhul olid tulemused erinevad: raskmetallide vood olid kõrged juurtes ja jooksva aasta elusokastes võrreldes samal perioodil varise ja sademetega lisandunud raskmetallide koguseid. See tulemus näitab, et saasteained omastati nii mulla orgaanilisest osast peenjuurte kaudu kui ka okaste kaudu välisõhust (samas oli translokatsioon väga madal, eriti just Pb puhul).

Raskmetallide kontsentratsioonide ja varude territoriaalsed erinevused Eestis avaldusid 75 okasmetsa leetunud- ja leedemuldade kõdude andmete võrdluses. Loodusliku okasmetsa aeglaselt lagunevas kõdukihti on raskmetallid mitmete aastakümnete jooksul akumuleerunud. Võrreldes raskmetallide andmeid sammaldes (peegeldavad sademetega deponeerumist) 1990ndatel aastatel kümme aastat hilisemate tulemustega (2005/06), on selgelt näha, et varasemate andmete põhjal koondus raskmetallidega seotud saaste peamiselt Kire-Eestisse. 2005/06 aasta tulemuste põhjal Kirde-Eesti üldisest foonist enam ei eritunud ja pigem tõusis esile Loode-Eesti, seda eelkõige pealinna mõju tõttu.

Raskmetallide varud metsamulla ülemises orgaanilises osas peegeldavad suure tõenäosusega veel põlevkivitööstuse hiigelaegadel (1980. aastatel) deponeerinud raskmetallide saastet. Seda eriti just vanemates kõdukihtides (OF ja OH). Uuritud raskmetallidest eristusid Ni ja Cr. Ni ja Cr omavaheline tugev korrelatsioon näitas nende ühtset päritolu, statistiliselt olulised kõrgemad

kontsentratsioonid ja ka varud paiknesid Lõuna-Eesti metsamuldades. Kirjanduse põhjal on tegemist raskmetallidega, mis pärinevad peamiselt kohalikest saasteallikatest (Brumelis *et al.,* 2002; Steinnes & Friedland, 2006), seetõttu võib oletada nende päritolu kohalikust põlevkivitööstusest.

Ökosüsteemi tasemel kõige enam ringleva raskmetalli Zn osas statistiliselt usaldusväärseid piirkondlikke erinevusi välja ei tulnud. Küll aga on endiselt Zn osas kõige suuremad varieeruvused depositsioonides eelkõige Kirde-Eesti tööstuspiirkonnas.

Seetõttu võib väita, et esimene hüpotees raskmetallide sadenemise ja sellega seotud varude territoriaalsete erinevuste osas leidis kinnitust. Samuti saab kinnitada ka teist hüpoteesi – peenjuured on olulised raskmetallide uuesti ringlusesse võtmisel. Raskmetallid võetakse peentesse juurtesse, kus nad peetuvad. Kõige rohkem peetuvad taimedele mittevajalikud Pb, Cd ja Cr. Peenjuured paiknevad oma peamise massiga mulla orgaanilises kihis, seega aeglustavad peenjuured raskmetallide liikumist mulla alumistesse kihtidesse ning pikendavad okasmetsade muldade ülemiste orgaaniliste kihtide puhastumist raskmetallidest mullaprotsesside kaudu. Kolmas hüpotees raskmetallide varude ja kontsentratsioonide kohta leidis osalise kinnituse, sest vaatamata sellele, et uuritud metsaökosüsteemide osadest paiknesid raskmetallide suurimad varud mulla ülemises orgaanilises kihis, ei olnud seal alati kõige kõrgemad raskmetallide kontsentratsioonid. Peenjuurtes ja eriti peenjuurtega seotud mütseelis olid näiteks Cu ja Zn kontsentratsioonid kordades kõrgemad. Mütseelis olid kõrgeimad ka Pb, Ni ja Cr kontsentratsioonid. Neljas hüpotees ei leidnud kinnitust – depositsioon on endiselt oluline raskmetallide allikas metsaökosüsteemis, seda eriti Cu ja Zn puhul.

Rahvusvaheliste seireprogrammide poolt pakuvad kvaliteetsed raskmetallide andmebaasid sobivad kasutamiseks ja ülevaate saamiseks nii praegusest keskkonnaseisundist kui ka eelnevalt akumuleeritud saasteainete mõju hindamiseks. Eriti oluline on see muutuvate keskkonnatingimuste korral, nt. lageraiete, metsatulekahjude, raskmetallide heitkoguste muutuste või kliimamuutuste kontekstis. Seetõttu on oluline ka tulevikus raskmetallide seireandmete kogumine ja analüüsimine ning see peaks jääma oluliseks osaks keskkonnaseireprogrammides.

AKNOWLEDGEMENTS

I am very grateful to my supervisors Dr. Jane Frey and Dr. Ivika Ostonen-Märtin as they provided me inspiration, guidance and support through my studies. I would also like to acknowledge the co-authors of my publications for provided data, feedback and support through publication processes. I am very grateful also for gaining the experience of working with Estonian forest monitoring team – your valuable support with practical experiences, data and knowledge was priceless. I would also like to stress the importance of the work of laboratories – Estonian Environmental Research Centre and fine root laboratory in University of Tartu. I also acknowledge my current colleagues at Estonian Research Council who have been very supportive. Finally, I would like to thank my family and friends who have supported me during my long studies.

This study has been financially supported by the target projects SF0180025s12 and IUT2-16 of the Ministry of Education and Research of Estonia and by the EU via the European Regional Development Fund (Centres of Excellence ENVIRON and EcolChange) for financial support. Fine root and soil organic horizon chemical analyses were supported by the Environmental Investment Centre projects No. 3793 and 6250. This study was also supported by Estonian Science Foundation grant No. 7452. Analyses of environmental monitoring programmes were supported by Estonian Ministry of the Environment via National Monitoring Programmes activities.

PUBLICATIONS

CURRICULUM VITAE

Name:	Ülle Napa
Data of birth:	20.04.1984
Citizenship:	Estonian
Address:	Department of Geography, Institute of Ecology and Earth Sciences, University of Tartu, Vanemuise 46, 51014 Tartu, Estonia
E-mail:	ulle.napa@ut.ee
Current position:	Estonian Research Council, Department of International Research Cooperation (senior adviser), Department of Research Programmes (RITA Programme consultant)

Education

2011–2017: University of Tartu, Faculty of Science and Technology, Institute of Ecology and Earth Sciences, Department of Geography, PhD student in geography

2007–2009: University of Tartu, Faculty of Science and Technology, Institute of Ecology and Earth Sciences, Department of Geography, MSc in environmental technology

2005–2006: University of Turku, Erasmus programme

2003–2007: University of Tartu, Faculty of Biology and Geography, Institute of Geography, BSc in environmental technology

2000–2003 Hugo Treffner Gymnasium

Professional employment

2013– Estonian Research Council, Department of International Research Cooperation (senior adviser), Department of Research Programmes (RITA Programme consultant).

2007–2013 Estonian Environment Agency, forest monitoring leading specialist

2006–2007 AS Tallink Group, travel consultant

Research interests

Heavy metals in different environmental samples from forest monitoring

Publications

Napa Ü, Kabral N, Ostonen I, Kriiska K, Asi E, Apuhtin V, Timmusk T, Frey J (201X) Heavy metal fluxes at coniferous monitoring stands in Estonia. Manuscript will be submitted for publication to journal of Environmental Monitoring and Assessment.

Napa Ü, Ostonen I, Kabral N, Kriiska K, Frey J (2017) Biogenic and contaminant heavy metal pollution in Estonian coniferous forests. Regional Environmental Change (2017) 17: 2111–2120.

Ostonen I, Truu M, Helmisaari HS, Lukac M, Borken W, Vanguelova E, Godbold DL, Lõhmus K, Zang U, Tedersoo L, Preem JK, Rosenvald K, Aosaar J, Armolaitis K, Frey J, Kabral N, Kukumägi M, Leppälammi-Kujansuu J, Lindroos AJ, Merilä P, **Napa Ü**, Nöjd P, Parts K, Uri V, Varik M, Truu J (2017) Adaptive root foraging strategies along a boreal–temperate forest gradient. New Phythologist (2017) 215: 977–991.

Napa Ü, Kabral N, Liiv S, Asi E, Timmusk T, Frey J (2015) 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. Ecological Indicators (2015) 52: 31–39.

Waldner P, Marchetto A, Thimonier A, Schmitt M, Rogora M, Granke O, Mues V, Hansen K, Pihl Karlsson G, Žlindra D, Clarke N, Verstraeten A, Lazdins A, Schimming C, Iacoban C, Lindroos AJ, Vanguelova E, Benham S, Meesenburg H, Nicolas M, Kowalska A, Apuhtin V, **Napa U**, Lachmanová Z, Kristoefel F, Bleeker A, Ingerslev M, Vesterdal L, Molina J, Fischer U, Seidling W, Jonard M, O'Dea P, Johnson J, Fischer R, Lorenz M (2014) Detection of temporal trends in atmospheric deposition of inorganic nitrogen and sulphate to forests in Europe. Atmospheric Environment (2014) 95: 363–374

Publications in Estonian

Napa Ü, Kabral N, Liiv S, Asi E, Timmusk T, Frey J. Raskmetallide sissekanne okasmetsadesse, peetumised samblarindes ja metsakõdus Eesti keskkonna-seire andmete põhjal. In "95 years of Estonian geography": selected studies: published for the 95th anniversary of the Department of Geography, University of Tartu. 2014; 317–329.

First author conference presentations

Napa Ü, Kabral N, Ostonen I, Frey J. Input of heavy metals, accumulation in organics and retention in fine roots of coniferous stands at ICP IM areas in Estonia.Poster. BIOGEOMON 2014: 8th International Symposium on Eco-system Behavior. 13.–18.07.2014, Bayreuth, Germany.

Napa Ü, Kabral N, Frey J. Load of heavy metals (Cd, Cu, Pb, Zn) in Estonia: based on data collected from ICP Forests, ICP Integrated Monitoring and local precipitation network sites. Poster. The 2nd Conference of Doctoral School of Earth Sciences and Ecology: Down to Earth. 16.–17.05.2013, Tallinn, Estonia.

Napa, Ü, Kabral, N., Hansen, R., Asi, E. and Frey, J. Trends of Na/Cl ratio in bulk precipitation and throughfall in Estonian ICP Forests and ICP Integrated Monitoring stations 1997–2011. Poster. BIOGEOMON 2012: The 7th International Symposium on Ecosystem Behavior. 15.–20.07.2012, Northport, Maine, USA.

Napa, Ü. Raskmetallid Eesti metsaseire andmetes. Oral presentation. LOTE Doctoral student conference: Mis mõttes?! 21.–22.05.2015, Tartu, Estonia.

Napa Ü, Kabral N, Ostonen I, Frey J.Zn as a heavy metal and bio-element. Poster. 7th International Workshop on Biomonitoring of Atmospheric Pollution (BIOMAP 7). 16.–20.06.2016, Lisbon, Portugal.

Napa, Ü. 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. Oral presentation. Baltic Earth Doctoral Students Conference. 10.–14.08.2015, Vilsandi, Estonia.

Napa Ü, Kabral N, Kriiska K, Ostonen I, Frey J. Cd, Cu, Pb, and Zn concentrations and accumulation in soil organics and retention in fine roots of coniferous stands. Poster. IUFRO Landscape Ecology Conference. 23.–30.08.2015, Tartu Estonia.

Napa Ü, Kabral N, Kriiska K, Ostonen I, Frey J. Cd, Cu, Pb, and Zn concentrations and accumulation in soil organics and retention in fine roots of coniferous stands. Poster. Environmental Adaptation: from Molecules to the Planet: The Estonian Centre of Excellence of Environmental Adaptation ENVIRON. Final Conference. 01.– 03.10.2015, Tartu Estonia.

Grants and projects

Short Term Scientific Mission (STSM) of COST Action FP0903. 03.09.2012–21.09.2012. Oulu and Rovaniemi Units of the Finnish Forest Research Institute (METLA) (http://cost-fp0903.ipp.cnr.it/images/stories/scientific_report_ulle_napa_copy.pdf)

Participation in Environmental Investment Centre project: KIK 2012.a metsandusprogrammi projekt nr 3793: Kasvuhoonegaaside heitkoguste inventuuri uuringud riikliku aruandluse täitmiseks maakasutuse ja metsandussektoris.

Improvement of skills

Courses on teaching (P2AV.TK.219 Interaktiivsed õppemeetodid and SHHI.TK.302 Akadeemilise kirjutamise õpetamise metoodika) at University of Tartu, 2014.

Internship in Estonian Liaison Office for EU RTD in Brussels, 02.09.2013–27.09.2013.

Internship in the Malta Council for Science & Technology 24.11.2013–05.12.2013.

Practical course on mosses and lichens (Eesti samblad ja samblikud) at University of Tartu, Natural History Museum. 12.10.12–13.10.2012.

Practical course on sampling (20-tunnine väljaõppe kursus heit-, reo-, pinna- ja põhjaveest ning reoveesettest proovivõtu valdkonnas) at Estonian Environmental Research Centre. 23.10.2012–25.10.2012.

ELUKOOKIRJELDUS

Nimi:	Ülle Napa
Sünniaeg:	20.04.1984
Kodakondsus:	Eesti
Adress:	Geograafia osakond, Ökoloogia- ja Maateadusteinstituut, Tartu Ülikool, Vanemuise 46, 51014 Tartu, Eesti.
E-post:	ulle.napa@ut.ee
Praegune töökoht, amet:	SA Eesti Teadusagentuur, välisteaduskoostöö osakond (vanemkonsultant), teadusprogrammide osakond (RITA vanemkonsultant)

Haridus

2011–2017: Tartu Ülikool, Loodus- ja tehnoloogiateaduskond, Ökoloogia- ja maateaduste instituut, Geograafia osakond, geograafia doktorant

2007–2009: Tartu Ülikool, Loodus- ja tehnoloogiateaduskond, Ökoloogia- ja maateaduste instituut, Geograafia osakond, MSc keskkonna-tehnoloogias

2005–2006: Turu Ülikool, Erasmus prorgammis osalemine

2003–2007: Tartu Ülikool, Bioloogia-georaafiateaduskond, Geograafiainstituut, BSc keskkonnatehnoloogias

2000–2003 Hugo Treffneri gümnaasium

Teenistuskäik

2013– SA Eesti Teadusagentuur välisteaduskoostöö osakond (vanem-konsultant), teadusprogrammide osakond (RITA vanemkonsultant)

2007–2013 Keskkonnaagentuur, metsaseire peaspetsialist

2006–2007 AS Tallink Group, reisikonsultant

Peamised uurimisvaldkonnad

Raskmetallid metsaökosüsteemis, metsaseire

Publikatsioonid

Napa Ü, Kabral N, Ostonen I, Kriiska K, Asi E, Apuhtin V, Timmusk T, Frey J (201X) Heavy metal fluxes at coniferous monitoring stands in Estonia. Saadetud avaldamiseks ajakirja Environemntal Monitoring and Assessment.

Napa Ü, Ostonen I, Kabral N, Kriiska K, Frey J (2017) Biogenic and contaminant heavy metal pollution in Estonian coniferous forests. Regional Environmental Change (2017) 17: 2111–2120.

Ostonen I, Truu M, Helmisaari HS, Lukac M, Borken W, Vanguelova E, Godbold DL, Lõhmus K, Zang U, Tedersoo L, Preem JK, Rosenvald K, Aosaar J, Armolaitis K, Frey J, Kabral N, Kukumägi M, Leppälammi-Kujansuu J, Lindroos AJ, Merilä P, **Napa Ü**, Nöjd P, Parts K, Uri V,

Varik M, Truu J (2017) Adaptive root foraging strategies along a boreal–temperate forest gradient. New Phythologist (2017) 215: 977–991.

Napa Ü, Kabral N, Liiv S, Asi E, Timmusk T, Frey J (2015) 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. Ecological Indicators (2015) 52: 31–39.

Waldner P, Marchetto A, Thimonier A, Schmitt M, Rogora M, Granke O, Mues V, Hansen K, Pihl Karlsson G, Žlindra D, Clarke N, Verstraeten A, Lazdins A, Schimming C, Iacoban C, Lindroos AJ, Vanguelova E, Benham S, Meesenburg H, Nicolas M, Kowalska A, Apuhtin V, **Napa U**, Lachmanová Z, Kristoefel F, Bleeker A, Ingerslev M, Vesterdal L, Molina J, Fischer U, Seidling W, Jonard M, O'Dea P, Johnson J, Fischer R, Lorenz M (2014) Detection of temporal trends in atmospheric deposition of inorganic nitrogen and sulphate to forests in Europe. Atmospheric Environment (2014) 95: 363–374

Publikatsioonid eesti keeles

Napa Ü, Kabral N, Liiv S, Asi E, Timmusk T, Frey J. Raskmetallide sissekanne okasmetsadesse, peetumised samblarindes ja metsakõdus Eesti keskkonna-seire andmete põhjal. In "95 years of Estonian geography": selected studies: published for the 95th anniversary of the Department of Geography, University of Tartu. 2014; 317–329.

Konverentsiettekanded

Napa Ü, Kabral N, Ostonen I, Frey J. Input of heavy metals, accumulation in organics and retention in fine roots of coniferous stands at ICP IM areas in Estonia. Posterettekanne. BIOGEOMON 2014: 8th International Symposium on Ecosystem Behavior. 13.–18.07.2014, Bayreuth, Saksamaa.

Napa Ü, Kabral N, Frey J. Load of heavy metals (Cd, Cu, Pb, Zn) in Estonia: based on data collected from ICP Forests, ICP Integrated Monitoring and local precipitation network sites. Posterettekanne. The 2nd Conference of Doctoral School of Earth Sciences and Ecology: Down to Earth. 16.–17.05.2013, Tallinn, Eesti.

Napa, Ü, Kabral, N., Hansen, R., Asi, E. and Frey, J. Trends of Na/Cl ratio in bulk precipitation and throughfall in Estonian ICP Forests and ICP Integrated Monitoring stations 1997–2011. Posterettekanne. BIOGEOMON 2012: The 7th International Symposium on Ecosystem Behavior. 15.–20.07.2012, Northport, Maine, Ameerika Ühendriigid.

Napa, Ü. Raskmetallid Eesti metsaseire andmetes. Suuline ettekanne. LOTE doktorantide konverents: Mis mõttes?! 21.–22.05.2015, Tartu, Eesti.

Napa Ü, Kabral N, Ostonen I, Frey J.Zn as a heavy metal and bio-element. Posterettekanne. 7th International Workshop on Biomonitoring of Atmospheric Pollution (BIOMAP 7). 16.–20.06.2016, Lissabon, Portugal.

Napa, Ü. 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. Suuline ettekanne. Baltic Earth Doctoral Students Conference. 10.–14.08.2015, Vilsandi, Eesti.

Napa Ü, Kabral N, Kriiska K, Ostonen I, Frey J. Cd, Cu, Pb, and Zn concentrations and accumulation in soil organics and retention in fine roots of coniferous stands. Posterettekanne. IUFRO Landscape Ecology Conference. 23.–30.08.2015, Tartu, Eesti.

Napa Ü, Kabral N, Kriiska K, Ostonen I, Frey J. Cd, Cu, Pb, and Zn concentrations and accumulation in soil organics and retention in fine roots of coniferous stands. Posterettekanne. Environmental Adaptation: from Molecules to the Planet: The Estonian Centre of Excellence of Environmental Adaptation ENVIRON. Final Conference. 01.–03.10.2015, Tartu Estonia.

Stipendiumid ja projektid

COST programmi noorteadlase stipendium uurimistööks Soome metsainstituudi METLA Oulu ja Rovaniemi keskustes (Stipendiumi nr: FP0903). 03.09.2012–21.09.2012. (http://cost-fp0903.ipp.cnr.it/images/stories/scientific_report_ulle_napa_copy.pdf).

Keskkonna Investeeringute Keskuse 2012.a metsandusprogrammi projektis nr 3793 osalemine: Kasvuhoonegaaside heitkoguste inventuuri uuringud riikliku aruandluse täitmiseks maakasutuse ja metsandussektoris.

Erialane enesetäiendus

Täiendõppekursused õpetamisest (P2AV.TK.219 "Interaktiivsed õppemeetodid" ja SHHI.TK.302 „Akadeemilise kirjutamise õpetamise metoodika"), Tartu Ülikool, 2014.

Stažeerimine SA Eesti Teadusagentuuri Brüsseli büroos, 02.09.–27.09.2013.

Stažeerimine Malta teaduse- ja tehnoloogia agentuuris, 24.11–05.12.2013.

Täiendõppekursus "Eesti samblad ja samblikud" Tartu Ülikooli Loodusmuuseumis, 12.–13.10.2012.

20-tunnine väljaõppe kursus heit-, reo-, pinna- ja põhjaveest ning reoveesettest proovivõtu valdkonnas Eesti Keskkonnauuringute Keskuses, 23.–25.10.2012.

DISSERTATIONES GEOGRAPHICAE UNIVERSITATIS TARTUENSIS

1. **Вийви Руссак.** Солнечная радиация в Тыравере. Тарту, 1991.
2. **Urmas Peterson.** Studies on Reflectance Factor Dynamics of Forest Communities in Estonia. Tartu, 1993.
3. **Ülo Suursaar.** Soome lahe avaosa ja Eesti rannikumere vee kvaliteedi analüüs. Tartu, 1993.
4. **Kiira Aaviksoo.** Application of Markov Models in Investigation of Vegetation and Land Use Dynamics in Estonian Mire Landscapes. Tartu, 1993.
5. **Kjell Weppling.** On the assessment of feasible liming strategies for acid sulphate waters in Finland. Tartu, 1997.
6. **Hannes Palang.** Landscape changes in Estonia: the past and the future. Tartu, 1998.
7. **Eiki Berg.** Estonia's northeastern periphery in politics: socio-economic and ethnic dimensions. Tartu, 1999.
8. **Valdo Kuusemets.** Nitrogen and phosphorus transformation in riparian buffer zones of agricultural landscapes in Estonia. Tartu, 1999.
9. **Kalev Sepp.** The methodology and applications of agricultural landscape monitoring in Estonia. Tartu, 1999.
10. **Rein Ahas.** Spatial and temporal variability of phenological phases in Estonia. Tartu, 1999.
11. **Эрки Таммиксаар.** Географические аспекты творчества Карла Бэра в 1830–1840 гг. Тарту, 2000.
12. **Garri Raagmaa.** Regional identity and public leaders in regional economic development. Tartu, 2000.
13. **Tiit Tammaru.** Linnastumine ja linnade kasv Eestis nõukogude aastatel. Tartu, 2001.
14. **Tõnu Mauring.** Wastewater treatment weltlands in Estonia: efficiency and landscape analysis. Tartu, 2001.
15. **Ain Kull.** Impact of weather and climatic fluctuations on nutrient flows in rural catchments. Tartu, 2001.
16. **Robert Szava-Kovats.** Assessment of stream sediment contamination by median sum of weighted residuals regression. Tartu, 2001.
17. **Heno Sarv.** Indigenous Europeans east of Moscow. Population and Migration Patterns of the Largest Finno-Ugrian Peoples in Russia from the 18th to the 20th Centuries. Tartu, 2002.
18. **Mart Külvik.** Ecological networks in Estonia — concepts and applications. Tartu, 2002.
19. **Arvo Järvet.** Influence of hydrological factors and human impact on the ecological state of shallow Lake Võrtsjärv in Estonia. Tartu, 2004.
20. **Katrin Pajuste.** Deposition and transformation of air pollutants in coniferous forests. Tartu, 2004.

21. **Helen Sooväli.** *Saaremaa waltz*. Landscape imagery of Saaremaa Island in the 20th century. Tartu, 2004.
22. **Antti Roose.** Optimisation of environmental monitoring network by integrated modelling strategy with geographic information system — an Estonian case. Tartu, 2005.
23. **Anto Aasa.** Changes in phenological time series in Estonia and Central and Eastern Europe 1951–1998. Relationships with air temperature and atmospheric circulation. Tartu, 2005.
24. **Anneli Palo.** Relationships between landscape factors and vegetation site types: case study from Saare county, Estonia. Tartu, 2005.
25. **Mait Sepp.** Influence of atmospheric circulation on environmental variables in Estonia. Tartu, 2005.
26. **Helen Alumäe.** Landscape preferences of local people: considerations for landscape planning in rural areas of Estonia. Tartu, 2006.
27. **Aarne Luud.** Evaluation of moose habitats and forest reclamation in Estonian oil shale mining areas. Tartu, 2006.
28. **Taavi Pae.** Formation of cultural traits in Estonia resulting from historical administrative division. Tartu, 2006.
29. **Anneli Kährik.** Socio-spatial residential segregation in post-socialist cities: the case of Tallinn, Estonia. Tartu, 2006.
30. **Dago Antov.** Road user perception towards road safety in Estonia. Tartu, 2006.
31. **Üllas Ehrlich.** Ecological economics as a tool for resource based nature conservation management in Estonia. Tartu, 2007.
32. **Evelyn Uuemaa.** Indicatory value of landscape metrics for river water quality and landscape pattern. Tartu, 2007.
33. **Raivo Aunap.** The applicability of gis data in detecting and representing changes in landscape: three case studies in Estonia. Tartu, 2007.
34. **Kai Treier.** Trends of air pollutants in precipitation at Estonian monitoring stations. Tartu, 2008.
35. **Kadri Leetmaa.** Residential suburbanisation in the Tallinn metropolitan area. Tartu, 2008.
36. **Mare Remm.** Geographic aspects of enterobiasis in Estonia. Tartu, 2009.
37. **Alar Teemusk.** Temperature and water regime, and runoff water quality of planted roofs. Tartu, 2009.
38. **Kai Kimmel.** Ecosystem services of Estonian wetlands. Tartu, 2009.
39. **Merje Lesta.** Evaluation of regulation functions of rural landscapes for the optimal siting of treatment wetlands and mitigation of greenhouse gas emissions. Tartu, 2009.
40. **Siiri Silm.** The seasonality of social phenomena in Estonia: the location of the population, alcohol consumption and births. Tartu, 2009.
41. **Ene Indermitte.** Exposure to fluorides in drinking water and dental fluorosis risk among the population of Estonia. Tartu, 2010.

42. **Kaido Soosaar.** Greenhouse gas fluxes in rural landscapes of Estonia. Tartu, 2010.
43. **Jaan Pärn.** Landscape factors in material transport from rural catchments in Estonia. Tartu, 2010.
44. **Triin Saue.** Simulated potato crop yield as an indicator of climate variability in Estonia. Tartu, 2011.
45. **Katrin Rosenvald.** Factors affecting EcM roots and rhizosphere in silver birch stands. Tartu, 2011.
46. **Ülle Marksoo.** Long-term unemployment and its regional disparities in Estonia. Tartu, 2011, 163 p.
47. **Hando Hain.** The role of voluntary certification in promoting sustainable natural resource use in transitional economies. Tartu, 2012, 180 p.
48. **Jüri-Ott Salm.** Emission of greenhouse gases CO_2, CH_4, and N_2O from Estonian transitional fens and ombrotrophic bogs: the impact of different land-use practices. Tartu, 2012, 125 p.
49. **Valentina Sagris.** Land Parcel Identification System conceptual model: development of geoinfo community conceptual model. Tartu, 2013, 161 p.
50. **Kristina Sohar.** Oak dendrochronology and climatic signal in Finland and the Baltic States. Tartu, 2013, 129 p.
51. **Riho Marja.** The relationships between farmland birds, land use and landscape structure in Northern Europe. Tartu, 2013, 134 p.
52. **Olle Järv.** Mobile phone based data in human travel behaviour studies: New insights from a longitudinal perspective. Tartu, 2013, 168 p.
53. **Sven-Erik Enno.** Thunderstorm and lightning climatology in the Baltic countries and in northern Europe. Tartu, 2014, 142 p.
54. **Kaupo Mändla.** Southern cyclones in northern Europe and their influence on climate variability. Tartu, 2014, 142 p.
55. **Riina Vaht.** The impact of oil shale mine water on hydrological pathways and regime in northeast Estonia. Tartu, 2014, 111 p.
56. **Jaanus Veemaa.** Reconsidering geography and power: policy ensembles, spatial knowledge, and the quest for consistent imagination. Tartu, 2014, 163 p.
57. **Kristi Anniste.** East-West migration in Europe: The case of Estonia after regaining independence. Tartu, 2014, 151 p.
58. **Piret Pungas-Kohv.** Between maintaining and sustaining heritage in landscape: The examples of Estonian mires and village swings. Tartu, 2015, 210 p.
59. **Mart Reimann.** Formation and assessment of landscape recreational values. Tartu, 2015, 127 p.
60. **Järvi Järveoja.** Fluxes of the greenhouse gases CO_2, CH_4 and N_2O from abandoned peat extraction areas: Impact of bioenergy crop cultivation and peatland restoration. Tartu, 2015, 171 p.

61. **Raili Torga.** The effects of elevated humidity, extreme weather conditions and clear-cut on greenhouse gas emissions in fast growing deciduous forests. Tartu, 2016, 128 p.
62. **Mari Nuga.** Soviet-era summerhouses On homes and planning in post-socialist suburbia. Tartu, 2016, 179 p.
63. **Age Poom.** Spatial aspects of the environmental load of consumption and mobility. Tartu, 2016, 141 p.
64. **Merle Muru.** GIS-based palaeogeographical reconstructions of the Baltic Sea shores in Estonia and adjoining areas during the Stone Age. Tartu, 2017, 132 p.