UK Centre for Ecology & Hydrology

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LRTAP
Long-range Transboundary Air Pollution

MOSSES AS BIOMONITORS OF AIR POLLUTION:

2015 / 2016 survey on heavy metals, nitrogen and POPs in Europe and beyond

Marina Frontasyeva, Harry Harmens, Alexander Uzhinskiy,
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ICP VEGETATION

wge Working Group on Effects of the Convention on Long-range Transboundary Air Pollution

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April 2020

*The International Cooperative Programme on Effects of Air Pollution on Natural Vegetation and Crops. The ICP Vegetation reports to the Working Group on Effects of the Convention on Long-range Transboundary Air Pollution.

Acknowledgements

We wish to thank Juha Piispanen (National Resources Institute Finland (Luke), Oulu), who made moss reference material available to all participants for quality assurance purposes, and Eiliv Steinnes for his valuable advice. Data from previous moss surveys were collated and disseminated by Åke Rühling (1990/1 and 1995/6), Eiliv Steinnes (1995/6), Alan Buse (2000/1) and Harry Harmens (2005/6 and 2010/11).

The ICP Vegetation Coordination Centre received financial support from the UK Department for Environment, Food and Rural Affairs (Defra, contract AQ0833 and AQ0846) and the UNECE (Trust Fund of the LRTAP Convention).

The Moss Coordination Centre thanks JINR for financial support through grants of the Plenipotentiaries of the JINR member states.

We also thank all national funding bodies who have provided financial support to participants of the surveys.

This report should be quoted as:

Frontasyeva M., Harmens H., Uzhinskiy A., Chaligava, O. and participants of the moss survey (2020). Mosses as biomonitors of air pollution: 2015/2016 survey on heavy metals, nitrogen and POPs in Europe and beyond. Report of the ICP Vegetation Moss Survey Coordination Centre, Joint Institute for Nuclear Research, Dubna, Russian Federation, 136 pp. ISBN 978-5-9530-0508-1.

The cover was designed by Valentina Tamonova (JINR, Dubna).

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Executive summary

Background

The first moss survey at the European scale was conducted in 1990 and has been repeated every five years since then. At first, the survey focussed on monitoring the concentration of selected heavy metals as an indication of atmospheric heavy metal pollution and deposition. In 2005, determination of the nitrogen concentration in mosses was included for the first time. Since 2010, some countries also determined the concentration of selected persistent organic pollutants (POPs), particularly polycyclic aromatic hydrocarbons (PAHs), at a selected number of sites. The idea of using mosses as biomonitors of atmospheric deposition is based on the fact that carpet forming, ectohydric mosses obtain most elements and other compounds directly from precipitation and dry deposition; there is little uptake from the substrate they grow on.

From the start, the European moss survey has provided data on concentrations of ten heavy metals (arsenic, cadmium, chromium, copper, iron, lead, mercury, nickel, vanadium and zinc) in naturally-growing mosses. Since 2005, the concentration of aluminium (a good indicator of wind-blown dust as it is present in high concentrations in the earth's crust), antimony (a good indicator of anthropogenic pollution as it is present in very low concentrations in the earth's crust) and nitrogen were also determined. The moss data provide a complementary measure of elemental deposition from the atmosphere to terrestrial systems, it is easier and cheaper than conventional precipitation analysis, and therefore enables a high sampling density to be achieved. The aim of the survey is to identify the main polluted areas and further develop the understanding of long-range transboundary air pollution of heavy metals and nitrogen. Apart from spatial patterns, the repeated surveys also provide an indication of temporal trends of heavy metal and nitrogen deposition.

Originally funded by the Nordic Council of Ministers, coordination of the 2000 European moss survey was handed over to the ICP Vegetation[1] Programme Coordination Centre at the UK Centre for Ecology and Hydrology (UKCEH) in Bangor. The UNECE ICP Vegetation was established in the late 1980s to consider the science for quantifying the impacts of air pollutants on vegetation. It reports to the Working Group on Effects (WGE) of the Convention on Long-range Transboundary Air Pollution (LTRAP). The WGE monitors, models and reviews the effects of atmospheric pollutants on different components of the environment and health. In an attempt to extend the moss survey to countries in Eastern Europe, Caucasus and Central Asia (EECCA), coordination of the moss survey was passed on in 2014 to the Joint Institute for Nuclear Research (JINR) in Dubna, Russian Federation, with reporting continuing as part of the ICP Vegetation.

Moss survey 2015

Here we report on the results of the 2015 moss survey, when mosses were sampled at about 5,100 sites across Europe and beyond, either in 2015, 2016 or both. In 2015, reporting for metals has greatly increased from about 28 countries in previous surveys to 36 countries, mainly due to participation of more countries in the EECCA region. Nitrogen and POPs data were reported for 14 and 8 countries respectively. As in previous surveys, mosses were sampled according to a standardised protocol and concentrations were determined in the

[1] The International Cooperative Programme on Effects of Air Pollution on Natural Vegetation and Crops

last two to three years' growth segments using a range of analytical techniques. *Pleurozium schreberi* was the most frequently sampled moss species (39.6% for heavy metals), followed by *Hypnum cupressiforme* (23.1%), *Hylocomium splendens* (19.9%), *Pseudoscleropodium purum* (6.3%) and other species (11.2%). For quality assurance purposes moss reference material was included in the analyses and where necessary, correction factors were applied to outliers and in some cases, severe outliers were excluded from further data processing. Data were mapped for metals and nitrogen and temporal trends were determined.

Spatial patterns (2015) and temporal trends (1990 – 2015)

Heavy metals

As in previous surveys, the lowest concentrations of heavy metals in mosses were generally found in northern and western Europe and the highest concentrations in (south-)eastern Europe, resulting in a north-west to south-east gradient. This gradient was more evident in 2015 with the enhanced participation of countries in the EECCA region. For the majority of metals, the concentration of heavy metals in mosses is highest in (parts of) the EECCA region and in south-eastern Europe (SEE), with highest median country values often being a factor ten or more higher than in other parts of Europe. This is particularly the case for metals associated with mineral particles (i.e. aluminium, arsenic, chromium, iron, nickel and vanadium). SEE and the EECCA region are characterised by mineral soils, which tend to have no or hardly any humus layer that could protect the region from wind-blown dust. Antimony concentrations in mosses also tend to be highest in the EECCA region and SEE (although this is not true for all the countries in this area). This would indicate that anthropogenic emission sources for heavy metals are highest in this area, hence metal concentrations in mosses are expected to be highest there, contributing to the north-west to south-east gradient in heavy metals in mosses across Europe and beyond.

The decline in emission and subsequent deposition of heavy metals across Europe has resulted in a decrease in the heavy metal concentration in mosses since 1990, with the decrease continuing for some but not all metals since 2010. Between 2010 and 2015, country and metal-specific changes have been observed, with increases, decreases or no changes found, depending on metal and country. Since 1990, the metal concentration in mosses has declined the most for lead (82%), cadmium (63%) and vanadium (57%), followed by copper (30%), nickel (25%), chromium (24%), zinc (23%) and iron (22%). For arsenic and mercury, the concentration in mosses has declined by 13% and 2% respectively since 1995. Clearly, mercury pollution remains a problem of global concern. Since 2005, the average concentration of aluminium and antimony in mosses has declined by 24% and 38%, respectively.

Nitrogen

Hardly any changes were observed in the nitrogen concentration in mosses since 2005 (decline of 1.5%). As in previous surveys, areas most at risk from high nitrogen deposition are located in parts of western (except Ireland) and central Europe. However, the risk in many northern, eastern and Mediterranean countries could not be assessed as those countries did not report on nitrogen concentrations in mosses. Previously it was found that the relationship between nitrogen concentrations in mosses and measured or modelled nitrogen deposition starts to show saturation between deposition rates of 15 - 20 kg ha^{-1} y^{-1}. Although this makes it difficult to assess the magnitude of risk in areas with medium to high

nitrogen deposition, the moss technique still allows the identification of the areas potentially most at risk.

Persistent organic pollutants (POPs)

Only a limited number of countries submitted data on POPs concentrations in mosses, with the majority reporting on polycyclic aromatic hydrocarbons (PAHs). Hence, it is difficult to assess spatial trends across Europe. In 2015, the highest median values of PAHs sums were reported for Sweden, Austria and Switzerland, the lowest median values were reported for Ireland. For Norway and Switzerland, the median values for 'SUM EPA 16' are considerably lower than those for 'SUM EPA 13' reported in 2010. The highest sum PCB 7 (polychlorinated biphenyls) values were reported for Germany, followed by Switzerland and Ireland, with the lowest median values found in Norway. The sum of dioxin-like PCBs and DDT (dichlorodiphenyltrichloroethane) were only reported by Germany and Norway, respectively.

Conclusions and recommendations

- Moss biomonitoring continues to provide a cheap, complementary method to deposition analysis to identify areas at risk from high atmospheric deposition fluxes of heavy metals and nitrogen and for monitoring changes with time.
- For cadmium and lead, temporal changes in concentrations in mosses across Europe are in agreement with those reported for EMEP modelled atmospheric deposition. Mercury pollution remains a problem in Europe and globally.
- Country-specific trends were observed, with concentrations declining for some but rising or showing no change for other metals since 2010.
- Despite the apparent success of the implementation of air pollution abatement techniques in large areas of Europe, further measures are required in (south)-eastern Europe to reduce the apparent high emissions of heavy metals. For nitrogen, more stringent air pollution abatement strategies are required across Europe to reduce the areas at risk from adverse effects of elevated atmospheric nitrogen deposition, especially from reduced nitrogen.
- There is a need to further investigate whether mosses are suitable as biomonitors of heavy metal pollution in areas dominated by mineral soils as found in southern and eastern Europe, especially bearing in mind the enhanced participation of countries from the EECCA region. Further detailed statistical analysis of the 2015 moss survey data is recommended in an effort to understand better the factors primarily contributing to the variation of heavy metal and nitrogen concentrations in mosses across Europe and beyond. Machine learning and linking with earth observation data might also provide further insight.
- There is a need to improve the spatial coverage of data on nitrogen and POPs in future surveys. In 2020, some countries will conduct a pilot study on the use of mosses as biomonitors of atmospheric deposition of microplastics.

1 Introduction

Mosses as biomonitors of atmospheric deposition

The heavy metals in mosses biomonitoring network was originally established as a Swedish initiative (Rühling and Skärby, 1979). The idea of using mosses to measure atmospheric heavy metal deposition is based on the fact that carpet forming, ectohydric mosses obtain most trace elements and nutrients directly from precipitation and dry deposition; there is little uptake of metals from the substrate (Tyler, 1970). In recent decades, mosses have been applied successfully as biomonitors of heavy metal deposition (e.g. Harmens et al., 2007, 2008, 2010; 2015, Zechmeister et al., 2003) across Europe. The technique of moss analysis provides a surrogate, time-integrated measure of metal deposition from the atmosphere to terrestrial systems, at least for the metals cadmium and lead (Aboal et al., 2010). It has been shown that at the European scale atmospheric deposition is the main factor determining the accumulation of cadmium and lead in mosses (Holy et al., 2010; Schröder et al., 2010b). The moss technique is easier and cheaper than conventional precipitation analysis as it avoids the need for deploying large numbers of precipitation collectors with an associated long-term programme of routine sample collection and analysis. Therefore, a much higher sampling density can be achieved than with conventional precipitation analysis. Heavy metals deposited from the atmosphere tend to be retained by the mosses. Although the heavy metal concentration in moss provides no direct quantitative measurement of deposition, this information can be derived by using regression or correlation approaches relating moss and precipitation monitoring data (e.g. Berg and Steinnes, 1997; Berg et al., 2003; Schröder and Pesch, 2010; Thöni et al., 2011). However, Boquete et al. (2011; 2015) recommended that the results of moss biomonitoring studies should be regarded as qualitative or semi-qualitative, rather than attempting to provide absolute data, which may not be temporally representative, and may have a high degree of uncertainty associated with them, at least in Spain. A more detailed review of the moss technique and its applications has been provided by Zechmeister et al. (2003), Frontasyeva et al. (2016) and Steinnes (2016).

During 2001, responsibility for the coordination of the European moss survey was handed over from the Nordic Working Group on Monitoring and Data, Nordic Council of Ministers, to the UNECE ICP Vegetation Coordination Centre at the UK Centre for Ecology & Hydrology (UKCEH) in Bangor. The ICP Vegetation was established in the late 1980s to consider the science of the effects of air pollution on vegetation. It is one of seven ICPs/Task Forces that report to the Working Group on Effects (WGE) of the Convention on Long-range Transboundary Air Pollution (LRTAP). The WGE monitors and reviews the effects of atmospheric pollutants on different components of the environment (e.g. forests, fresh waters, vegetation, buildings) and human health (UNECE, 2014). The ICP Vegetation provides information for the review and possible revision of the Protocols of the LRTAP Convention. In 1998, the first Protocol for the control of emissions of heavy metals was adopted in Aarhus. The Protocol states that “an effects-based approach should integrate information for formulating future optimized control strategies taking account of economics and technological factors”. Cadmium, lead and mercury emissions were targeted as they are the most toxic of metals. The Joint World Health Organization/Convention Task Force on the Health Aspects of Air Pollution (Task Force on Health) has evaluated the potential health risks of the priority metals cadmium, lead and mercury in Europe in more detail (WHO, 2007).

The European moss survey has been repeated at five-yearly intervals and the number of participating countries has expanded greatly since 1990 (Table 1.1). As mentioned in the

2014–2015 workplan of the Convention (UNECE, 2014), increased ratification and related implementation is particularly important for countries of Eastern Europe, the Caucasus and Central Asia and South-Eastern Europe to improve air quality. In 2015, attempts to increase participation in countries in the EECCA region was successful through participation in Armenia, Azerbaijan, Georgia, Kazakhstan, Moldova, Mongolia and Tajikistan.

Table 1.1. History of moss biomonitoring surveys in Europe.

Year	Surveys	Coordinators
1968	Moss technique was first proposed	Åke Rühling and Germund Tyler (Lund University, Sweden)
1975	First nationwide survey in Sweden	Åke Rühling (Lund University, Sweden)
1977	First nationwide survey in Norway	Eiliv Steinnes (Trondheim University, Norway)
1985	First joint Nordic Survey (Denmark, Finland, Norway, Sweden)	Åke Rühling (supported by Nordic Council of Ministers)
1990	First European survey (Joint Nordic/Baltic survey)	Åke Rühling (Lund University, Sweden)
1995	Second European survey, 28 countries	Åke Rühling and Eiliv Steinnes
2000	Third European survey, 28 countries	Alan Buse (ICP Vegetation, CEH Bangor, UK)
2005	Fourth European survey, 28 countries	Harry Harmens (ICP Vegetation, CEH Bangor, UK)
2010	Fifth European survey, 27 countries	Harry Harmens
2015	Sixth European survey, 36 countries	Harry Harmens and Marina Frontasyeva (JINR, Russian Federation)

The most recent moss survey in Europe and beyond was conducted in 2015/2016 with 36 countries participating (Table 1.2), sampling mosses from about 5,100 sites. The survey provides data on concentrations of 12 metals in naturally-growing mosses: aluminium (Al), antimony (Sb), arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), iron (Fe), mercury (Hg), nickel (Ni), lead (Pb), vanadium (V) and zinc (Zn). Aluminium is a good indicator of mineral particles, mainly windblown soil dust (Berg and Steinnes, 1997; Zechmeister et al., 2003) as it is present at high concentrations in the earth's crust. Antimony is present at very low concentrations in the earth's crust and generally considered as a good indicator of long-range transport of anthropogenic pollution (Berg and Steinnes, 1997). The increase in production and use of antimony in recent decades has resulted in enrichment of Arctic air by more than 50%. Given that the toxicity of antimony is comparable to that of lead, antimony has now replaced lead in the rank of potentially toxic trace metals in the Arctic atmosphere, which might have broader implications worldwide for ecosystem and human health in the future (Krachler et al., 2005). Some countries determined many more additional elements in

mosses, including set of rare-earth elements, uranium (U) and thorium (Th), but these are not included in this report and some limitations have been highlighted by Steinnes (2016).

Table 1.2. Countries (-regions) that submitted data for the 2015/2016 moss survey.

Note: *all countries submitted data for heavy metals; N and POPs: countries that also submitted data for nitrogen and POPs respectively.*

Rest of Europe (16)		SEE Europe (8)	EECCA (9)	Others (3)
Austria[N,POPs]	Latvia[N,POPs]	Albania	Armenia	Canada
Czech Rep.	Norway[POPs]	Bulgaria	Azerbaijan	Mongolia
Denmark-Faroe Islands	Poland[N]	Greece-North	Belarus	Vietnam
Estonia[N]	Slovakia[N]	North Macedonia	Georgia	
France[N]	Spain-Rioja[N,POPs]	Romania[N]	Kazakhstan	
Germany[N,POPs]	Sweden[N,POPs]	Serbia	Moldova	
Iceland	Switzerland[N,POPs]	Slovenia[N]	Russian Fed.	
Ireland[N,POPs]		Turkey-North	Tajikistan	
Italy-Bolzano[N]			Ukraine	

About a third of participating countries also provided data on nitrogen (N) concentrations. Previous studies have shown that there is a good linear relationship between the total nitrogen concentration in mosses and atmospheric nitrogen deposition rates for areas with bulk atmospheric nitrogen deposition rates up to about 20 kg ha^{-1} y^{-1} (Harmens et al., 2011; 2014). Nitrogen was included in the moss survey for the first time in 2005. Synthetic fertilizer production together with industrialization, population growth and associated demand for food has resulted in a five-fold increase in emission of reactive nitrogen compounds. Nitrogen tends to stimulate plant growth up to a certain level, above which detrimental effects occur. However, enhanced nitrogen deposition is known to reduce plant diversity in areas and habitats were plants are adapted to low atmospheric nitrogen input. The total nitrogen concentration in mosses can be used to identify areas at risk from nitrogen pollution at a high spatial resolution. Potentially it can also be used as a complementary method to estimate total nitrogen deposition, particularly in lower nitrogen deposition areas (Harmens et al., 2011; 2015). Due to the high local variation in nitrogen deposition, the relationship between total nitrogen deposition and the nitrogen concentration in mosses is most robust when deposition rates are measured at the moss sampling sites rather than modelled over a larger area.

Eight countries reported on POPs concentrations in mosses at a selection of sites for a selection of POPs as mosses are also suitable organisms for monitoring spatial patterns and temporal trends of atmospheric concentrations or deposition of some POPs (Harmens et al., 2013a). Worldwide there is concern about the continuing release of POPs into the environment. POPs possess toxic characteristics, are persistent, bioaccumulate, are prone to long-range transboundary atmospheric transport and deposition, and can cause significant adverse human health or environmental effects near to and distant from their source (UNECE, 2009). They show weak degradability and consequently are accumulating in the environment across the globe, including in remote areas such as the polar regions (Lead et al., 1996; Harmens et al., 2013a). Examples in the literature show that mosses are suitable organisms to monitor spatial patterns and temporal trends of atmospheric concentrations or deposition of POPs (Harmens et al., 2013a; Wu et al. 2014). These examples include polycyclic aromatic hydrocarbons (PAHs), polychlorobiphenyls (PCBs), dioxins and furans (PCDD/Fs), and polybrominated diphenyl ethers (PBDEs). So far, a majority of studies report on PAHs concentrations in mosses and relative few studies have been conducted on other POPs. Many studies have focused on spatial patterns around pollution sources or the concentration in mosses in remote areas such as the polar regions, as an indication of long-range transport of POPs. Very few studies have determined temporal trends or have directly related the concentrations in mosses with measured atmospheric concentrations and/or deposition fluxes (Harmens et al., 2013a).

2 Methodology for the 2015/16 survey

Moss species

As in previous surveys, moss samples were collected according to a standardized protocol (Frontasyeva et al., 2014) and the heavy metal concentrations were determined in the last two-three years' growth segments using a range of analytical techniques (**Annex 2**).

For heavy metals in 5,156 moss samples, *Pleurozium schreberi* was the most frequently sampled species (39.6%), followed by *Hypnum cupressiforme* (23.1%), *Hylocomium splendens* (19.9%), *Pseudoscleropodium purum* (6.3%) and other species (11.2%).

For nitrogen in 1,667 moss samples*, Pleurozium schreberi* was the most frequently sampled species (33.4%), followed by *Hypnum cupressiforme* (29.8%), *Pseudoscleropodium purum* (18%), *Hylocomium splendens* (13.1%), and other species (5.6%).

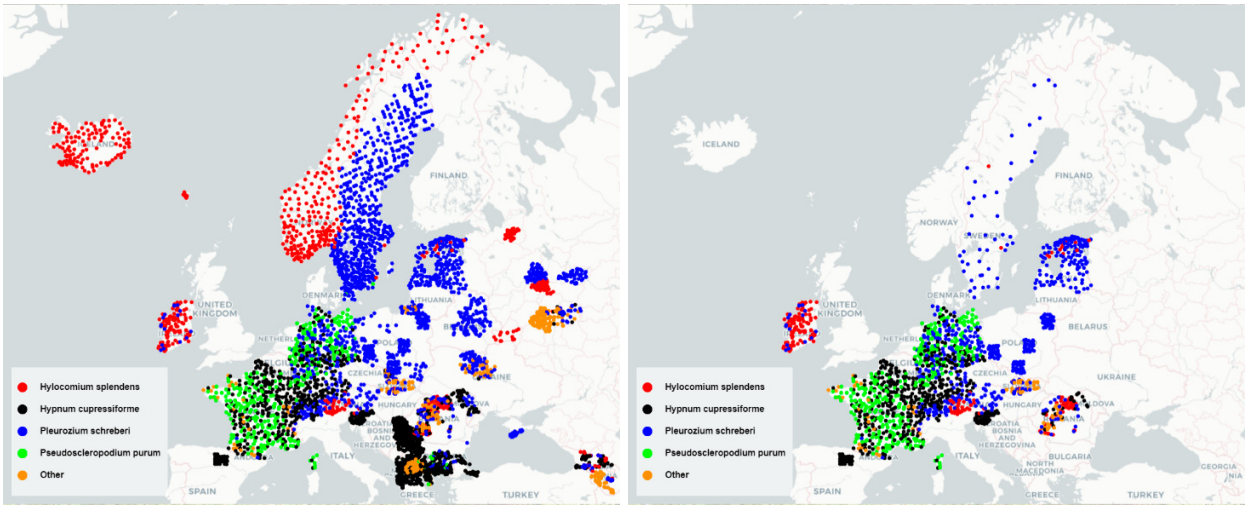

Figure 2.1. Sites where mosses were sampled for heavy metals (left) and nitrogen analysis (right).

Field sampling

The distribution of the sampling sites throughout Europe is shown in Figure 2.1. Moss sampling was according to the guidelines set out in the experimental protocol for the 2015/2016 survey (Frontasyeva et al., 2014). The procedure was similar to that used in previous European moss surveys. Each sampling site was located at least 300 m from main roads and populated areas and at least 100 m from any road or single house (Note: In some EECCA countries these rules were not always followed). In forests or plantations, samples were collected as far as possible in small open spaces to preclude any significant effect of canopy drip. Sampling and sample handling were carried out using plastic gloves and bags. Each sample was a composite of about ten sub-samples. Dead material and litter were removed from the samples and only the last two to three years' growth segments were used for the analyses. Samples were refrigerated, frozen or dried at room temperature, and stored under those conditions until chemical analysis.

Chemical analysis

For the determination of metal concentrations, sorted material (ca. last two to three years' growth) was dried at 40 ºC (room temperature for Hg) and either decomposed in concentrated nitric acid (with or without hydrogen peroxide or perchloric acid) or not dissolved before analysis. Acid-digestion of samples was performed in a microwave oven (majority of countries) or a hotplate using a range of temperatures. The metal concentrations were determined by a range of analytical techniques, under the broad headings of atomic absorption spectrometry, inductively coupled plasma spectrometry (both ICP optical emission spectrometry and ICP mass spectrometry), fluorescence spectrometry, neutron activation analysis and advanced mercury analysis (see **Annex 2** for details). All metal concentrations (including mercury) are expressed as mg kg^{-1} dry weight at 40 ºC. For the determination of nitrogen, moss tissue was dried at 40 ºC and concentrations were determined according to either the Kjeldahl method or via elemental analysis following the Dumas method (see **Annex 2** for details). Nitrogen concentrations are expressed as percentage (based on dry weight).

Quality control

For quality assurance purposes, moss reference materials were included in the analyses and where necessary, correction factors were applied to outliers and in some cases, severe outliers were excluded from further data processing. Moss reference materials M2 and M3, first prepared for the 1995/6 European moss survey (Steinnes et al., 1997), were distributed amongst the laboratories. In addition, some laboratories used other certified reference materials for quality assurance. For determination of the elemental concentrations in the reference materials, laboratories followed the same analytical procedure as used for the collected moss samples. Generally, data obtained indicated acceptable agreement between laboratories. However, outliers were identified for some laboratories for selected metals (not for nitrogen). This was the case when the values were outside the range of two standard deviations (as determined for the 2015/16 survey) from the mean recommended value for reference material M2 and/or M3 (Steinnes et al., 1997; Harmens et al., 2010). In consultation with the participating country correction factors were applied when both M2 and M3 values were outliers for a specific metal, and sometimes corrections factors were also agreed and applied when only one reference value was identified as an outlier. Although applying correction factors enhanced compatibility of data between countries, it had minimal effect on the overall European mean and median values for elements. As a consequence, it did not significantly affect the temporal trends reported for the whole of Europe (but might have affected the temporal trends per country). The accuracy of data received by the Moss Survey Coordination Centre was assessed by inspecting them for extremes and by sending summarized data and the relevant draft maps to individual contributors for checking and approval before incorporating the final data into the maps, figures and tables in this report. Summary data for each country are presented in **Annex 3.**

Data Management System (DMS)

At JINR, a cloud platform Data Management System (DMS) was created to collect experimental data (elemental concentrations, geographical coordinates of sampling sites to provide statistical analysis and create distribution maps (Ososkov et al., 2016). The web address of DMS is http//:moss.jinr.ru. To submit data one should receive a login and

password from DMS administrator at JINR (verkn@mail.ru or marina@nf.jinr.ru), register and upload the EXCEL file with data format standardized according the instruction on the website. The reported data are checked for anomalies before maps are produced. Detailed information can be found in recent papers by (Uzhinskiy et al., 2018a; 2018b; 2019).

Mapping

The maps were produced using OpenLayer, an open-source JavaScript library and a set of simple base maps (https://openlayers.org/). Each point displays heavy metal or nitrogen concentration in mosses for each sampling site. The maps don't show the data for the far eastern countries (i.e. Kazakhstan, Mongolia, Tajikistan and Vietnam) in order not to compromise the resolution; in those far eastern countries, mosses were often sampled in a very small region. Data for those countries are included in the bar graphs comparing 2010 and 2015 results and/or in Annex 3.

Temporal trend analysis

For assessing temporal trends of the average of median values per country, data were only included for those countries that had reported heavy metal data in four out of the five (As, Hg) or six surveys (all other metals) since the first European-wide survey in 1990. Hence, these trends differ from previous trends reported up to the 2010 survey (Harmens et al., 2015) as the countries included for each metal were different then. More countries were included in the current trend analysis as more were compliant with the rule applied. None of the data from countries that participated in the moss survey for the first time were included in trend analyses. For elements only included in the survey since 2005 (Al, Sb and N), only data for countries that submitted data for at least two out of the three survey years were used to calculate the European average (of the median values per country).

For comparing changes in elemental concentrations in mosses since 2010, it should be noted that some countries have sampled mosses in different areas in 2015 compared to 2010. Hence, any changes in concentrations are confounded by a change in sampling strategy. For example, in the Czech Republic, mosses were sampled in the heavy polluted region of the Black Triangle, which explains the increase of many heavy metals in mosses in 2015 compared to 2010; 2010 data were therefore not included in the bar charts. In Spain, mosses were only sampled in Rioja in 2015, whilst in 2010 mosses were also sampled in Galicia and Navarra. To be consistent, only 2010 data from Rioja were included in comparing data between 2010 and 2015. In the Russian Federation and the Ukraine, additional regions were included in 2015.

3 Spatial patterns and temporal trends in Europe

Introduction

The 2015/2016 data on the concentration of each element in moss samples from each country are summarized in **Annex 3**. Extreme values are often for single hot spots. The emphasis of this chapter is on Europe-wide spatial patterns and temporal trends. One should bear in mind that changes with time for emissions in Europe are not necessarily of a similar magnitude as trends in deposition due to the contribution of long-range transport outside Europe to deposition of elements in Europe and the contribution of wind-blown dust to deposition, representing historic deposition of heavy metals. Many contributors to the survey have reported national trends in greater detail elsewhere, including local emission sources of the pollutants and the relationship between concentration in mosses and measured or modelled atmospheric deposition (see **Annex 5** for details). Elevated concentrations of heavy metals in mosses sampled in a particular region can arise in several ways; hot spots can be associated with either contemporary or historical industrial and mining activities, or with large conurbations, whereas widespread effects can be due to widely scattered sources, particularly vehicle emissions along major roads or geological sources, or to long-range atmospheric transport of pollutants. Important sources for elevated concentrations of nitrogen in mosses are combustion of fossil fuel and agricultural activities. Elements such as copper, zinc (micronutrients), and nitrogen (macronutrient) are essential for moss growth and development and are therefore to some extent recycled from dying tissues to new growth. Therefore, these nutrients have a baseline concentration in moss tissue. When comparing changes since 2010 or earlier years, one should bear in mind that many countries have not consistently sampled mosses from the same sites each year and/or might have changed the sampling density or strategy between years. In addition, the application of different analytical techniques and/or improvements in the performance of analytical instruments might have contributed to the variation in element concentrations in mosses between years.

Aluminium

Away from local pollution sources, aluminium is a good indicator of mineral particles, mainly windblown soil dust, as it is present at high concentrations in the earth's crust. Therefore, the spatial pattern of aluminium concentrations in mosses might provide an indication of the contribution of wind re-suspension of soil particles to the deposition of metals to mosses, reflecting to some extent historical deposition of heavy metals. Compared to other countries in northern Europe, aluminum concentrations in mosses are relatively high in Norway (Figure 3.1). There is an east-west gradient across Europe, indicating that in the dryer regions of Europe with mosses directly growing on mineral soil the deposition of soil dust on mosses is higher. For some metals, this might explain the higher concentration in mosses in certain regions of Europe, for example, the high concentrations of chromium, iron, and vanadium in south-eastern European countries and in the EECCA region. Strong linear relationships (R^2 > 0.77) were found between aluminium and iron, aluminium and vanadium and iron and vanadium concentrations in mosses. A higher accumulation of soil dust does not necessarily translate into a higher deposition flux for all metals in the same way.

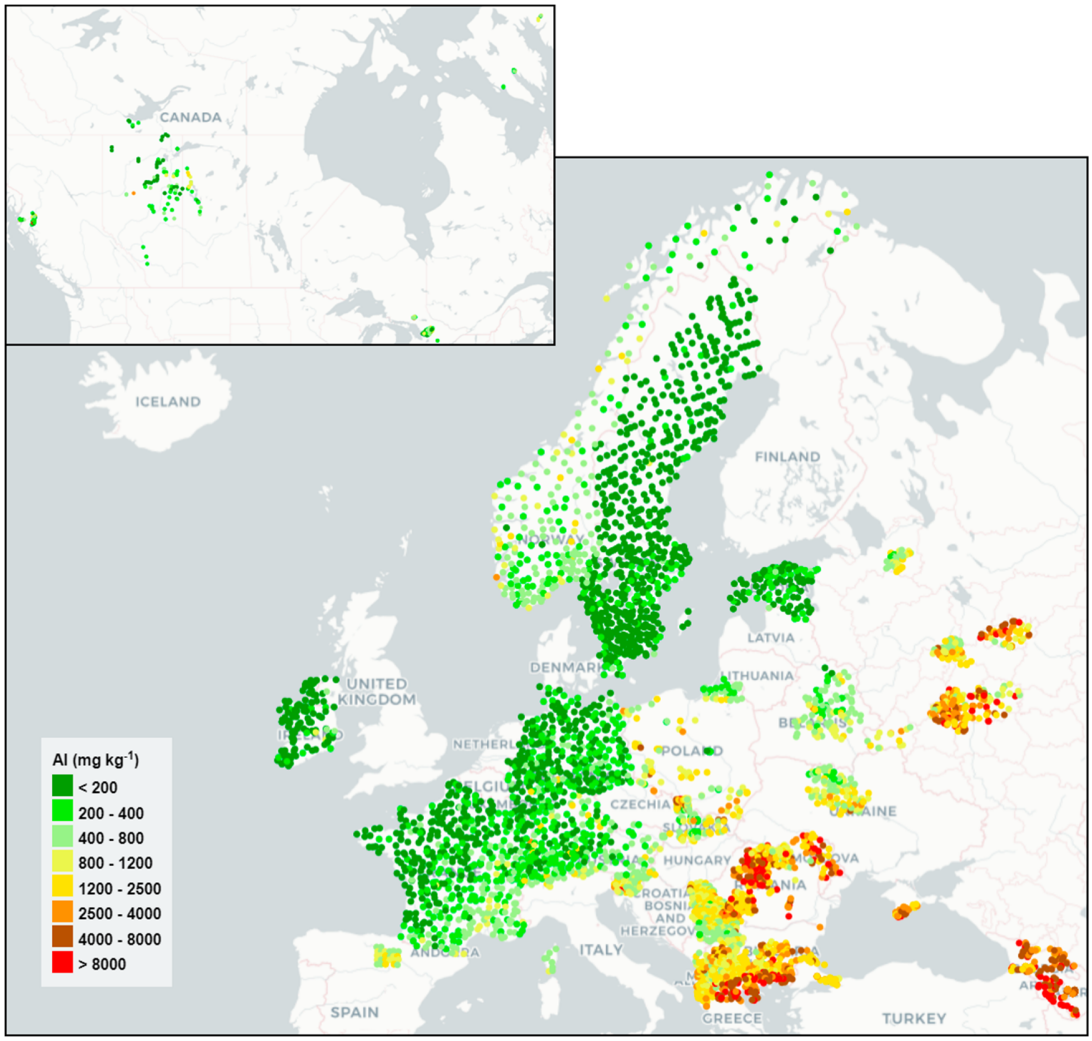

Figure 3.1. Aluminium concentration in mosses in 2015/16.

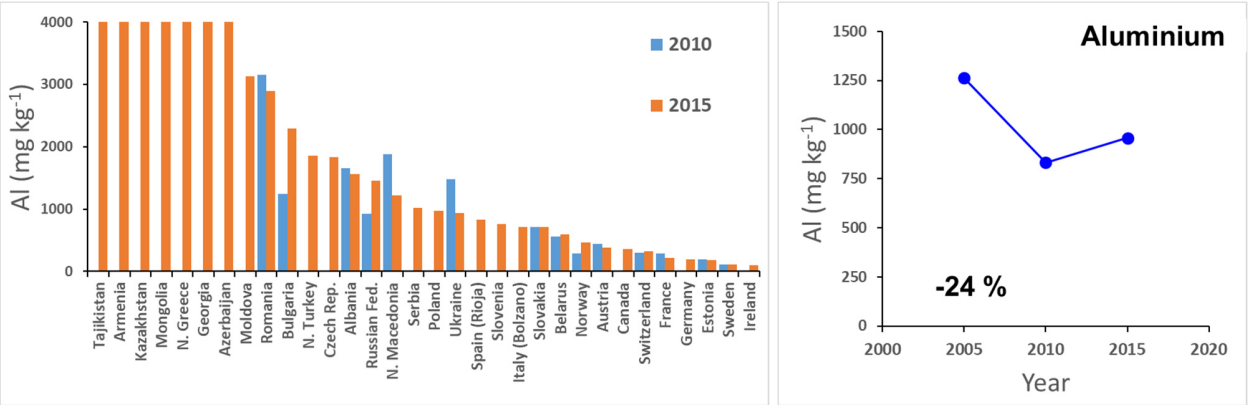

Figure 3.2. Median aluminium concentrations in mosses in 2010 and 2015 (left) and average median aluminium concentrations in mosses for countries (n = 16-19, depending on year) that reported data for at least two survey years between 2005 and 2015 (right); the percentage decline since 2005 is shown in bold. See **Annex 3** for median values per country in 2015.

The highest concentrations of aluminium are observed in countries characterized by mineral soils (Tajikistan, Armenia, Kazakhstan, Mongolia, northern Greece, Georgia, Azerbaijan and Republic of Moldova), indicating a high degree of soil dust re-suspension contributing to metal concentrations in mosses. In addition, many of the countries with high aluminum concentrations used INAA as the analytical technique, which tends to result in higher aluminium concentrations compared to other analytical techniques. INAA results in 56% and 80% higher aluminium values in the moss standards M3 and M2 respectively (Smodiš and Bleise, 2007), which have relatively low aluminium concentrations of 264 and 321 mg kg^{-1} respectively (as determined by INAA). Despite application of INAA for samples collected in Belarus and Slovakia, the values for aluminium are in the lower range. There is a clear need to analyse samples from countries with high aluminium concentrations with analytical techniques other than INAA (and vice versa for countries with low aluminium concentrations) to assess the influence on those techniques on the apparent aluminium concentrations in mosses. The lowest average aluminium value was reported in 2010 (832 mg kg^{-1}) and an increase was observed between 2010 and 2015 (957 mg kg^{-1}). Since 2005, the average concentration of aluminium in mosses has declined by 24%. The Canadian data are similar to low European data, except for one sampling site where aluminium concentration reached about 10,000 mg kg^{-1}, which can be explained by the nearby location of the Kitimat aluminium smelter.

Antimony

Antimony is present at very low concentrations in the earth's crust and is an indication of anthropogenic emissions. As for aluminium, high concentrations of antimony are observed in mosses in Tajikistan, Kazakhstan, Mongolia, Armenia, northern Greece, Georgia, Azerbaijan and Republic of Moldova (Figure 3.3 and 3.4). This could either indicate the nearby presence of heavy polluting industries, sampling near densely-populated areas, long-range transport or a combination of all. High antimony concentrations in mosses in the Czech Republic are due to sampling in the Black Triangle where industrial activity is high. Relatively high concentrations of antimony were also observed in Poland and Romania, indicating the presence of highly polluting industry in several areas. Hotspots of relatively high antimony concentrations were observed near urban areas in France (Paris), Germany and Norway (Oslo). The relatively high antimony concentrations in sourthern Norway is an indication of long-range transport from central Europe, however, the association of antimony with long-range transport of metals was less evident than in earlier Norwegian surveys (2005 and earlier). Whilst an increase in the median antimony concentration was observed in 2015 compared to 2010 in the Russian Federation, a decline of approximate 50% was found in Slovenia, France and Austria. The median value for antimony in Canada falls within the range of low concentrations reported in European countries. Whilst the average antimony concentration declined by 38% between 2005 (0.158 mg kg^{-1}) and 2015 (0.099 mg kg^{-1}), the decline had slowed down between 2010 (0.112 mg kg^{-1}) and 2015.

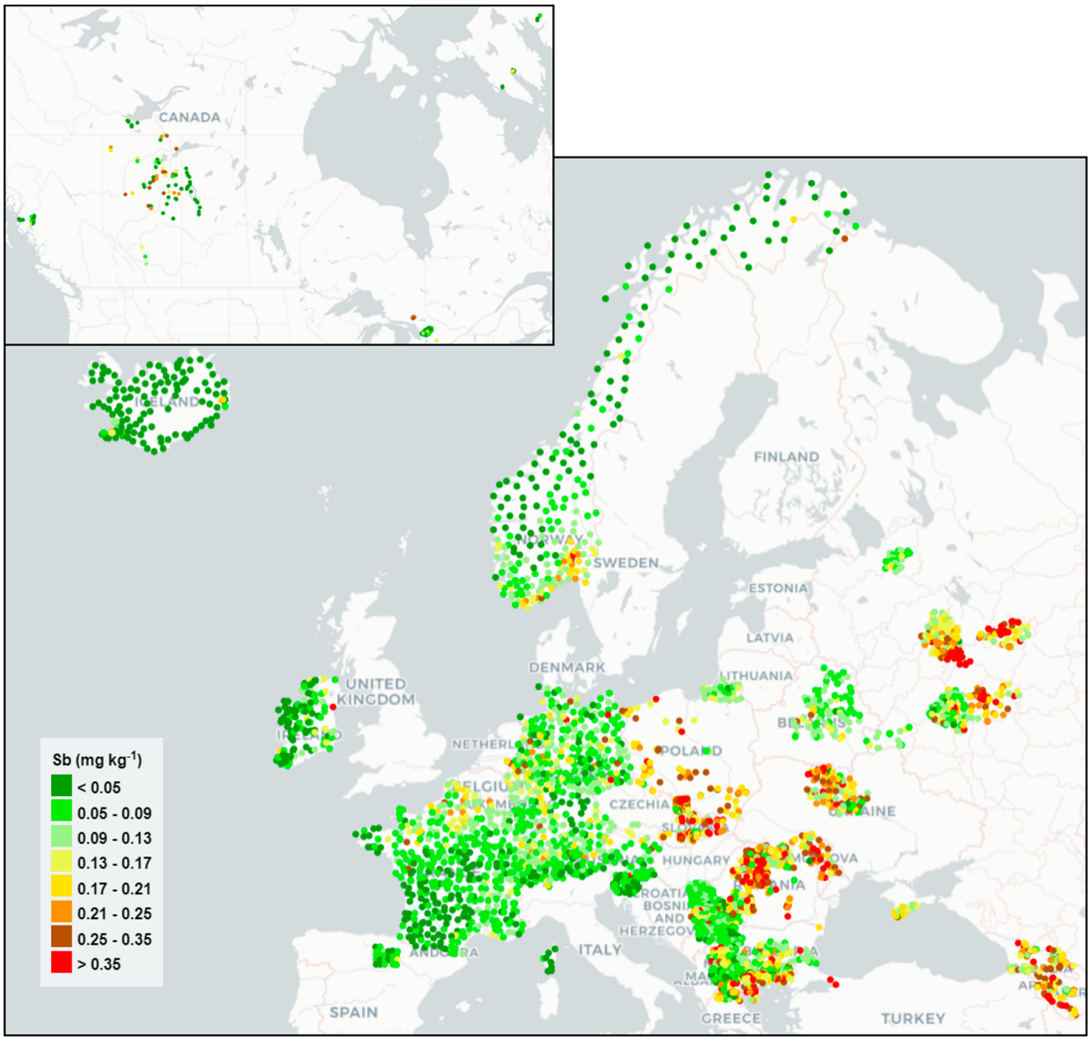

Figure 3.3. Antimony concentration in mosses in 2015/16.

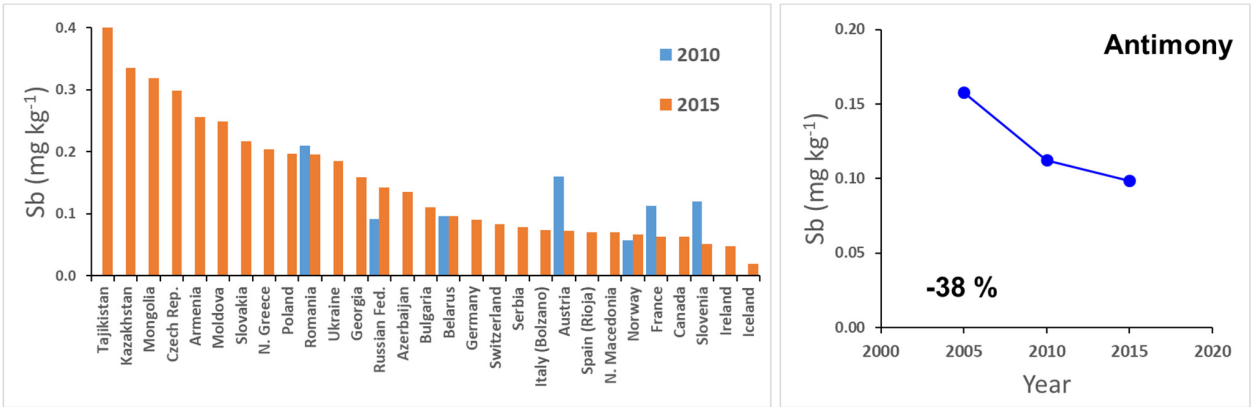

Figure 3.4. Median antimony concentrations in mosses in 2010 and 2015 (left) and average median antimony concentrations in mosses for countries (n = 9-12, depending on year) that reported data for at least two survey years between 2005 and 2015 (right); the percentage decline since 2005 is shown in bold. See **Annex 3** for median values per country in 2015.

Arsenic

Arsenic concentrations in mosses are generally low in northern Europe, Ireland and Germany (Figure 3.5 and 3.6). High levels of arsenic were observed in southern and eastern countries, with median levels above 1.0 mg kg^{-1} reported for Tajikistan, northern Turkey, Kazakhstan, Mongolia, Armenia, northern Greece, Azerbaijan and Romania. In western Europe, relatively high arsenic concentrations were reported for large parts of France, Rioja (Spain), southern Norway and eastern parts of Iceland. Compared to 2010, the median arsenic concentration increased in Albania, Belarus, Romania, Russian Federation (where mosses were sampled in additional regions compared to 2010) and Switzerland.

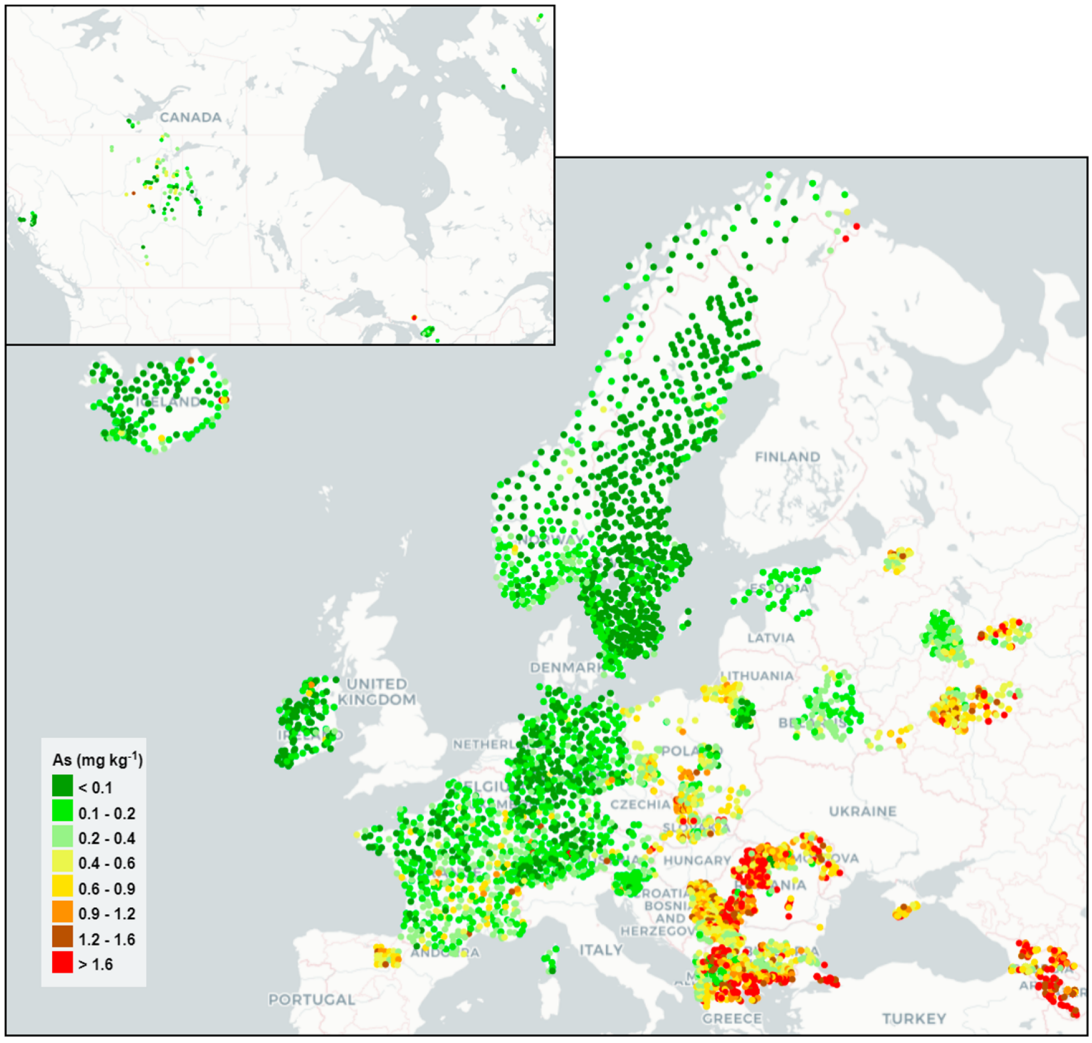

Figure 3.5. Arsenic concentration in mosses in 2015/16.

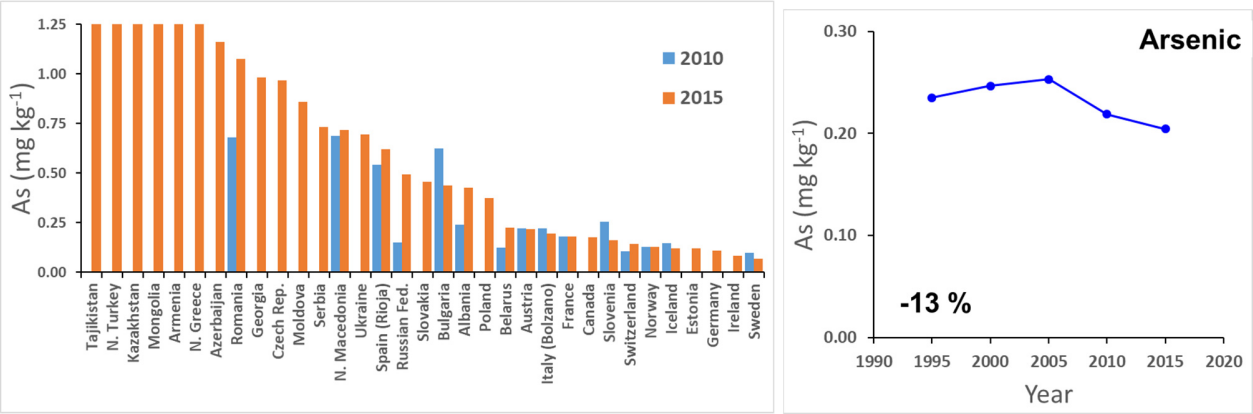

Figure 3.6. Median arsenic concentrations in mosses in 2010 and 2015 (left) and average median arsenic concentrations in mosses for countries (n = 10-14, depending on year) that reported data between 1995 and 2015 for at least four survey years (right); the percentage decline since 1995 is shown in bold. See **Annex 3** for median values per country in 2015.

The arsenic concentrations in mosses show a decline of 13% between 1995 (0.23 mg kg^{-1}) and 2015 (0.20 mg kg^{-1}), with the average median European value being highest in 2005 (0.25 mg kg^{-1}) and lowest in 2015. For the EU28, the European Environment Agency (2019) reported a reduction in emissions of arsenic across Europe of 33% for the same period, which is similar to a 38% reduction in the average median concentration in mosses when only including data reported by six EU28 Member States. The highest emission reductions in EU28 were observed between 1990 and 1995, in agreement with the moss data. However, in 1990, only three EU28 Member States and two other countries submitted data on arsenic concentrations in mosses, hence 1990 was not included in the trend analyses here. The Canadian data for arsenic, which were obtained for a very minor part of the country, are in line with the European results.

Cadmium

Industrial emissions of cadmium have fallen since 1990 in EU Member States largely because of improvement of abatement technologies for waste-water treatment, incinerators, metal-refining and metal-smelting facilities (EEA, 2019). Relatively high reductions have also been reported for public electricity and heat production. The main categories for cadmium emissions in recent years are residential, iron, steel and copper production. Cadmium is also present in organic and inorganic fertilizers. Cadmium concentrations in mosses were lowest in Iceland, Ireland and northwest Scandinavia, with elevated concentrations observed in southern Scandinavia due to long-range transport from continental Europe (Figure 3.7 and 3.8). Generally, intermediate concentrations were reported for central Europe. The highest concentrations of cadmium were observed in the Czech Republic (Black Triangle), followed by Mongolia, Tajikistan, Belarus, Moldova, and Ukraine. In comparison with 2010, cadmium had not changed or declined in most European countries in 2015, except in Iceland, Russian Federation (sampling in additional regions, with very high concentrations in Ivanova) and Rioja in Spain. In Canada, high concentrations in the Sudbury area can be explained by the presence of several mining companies.

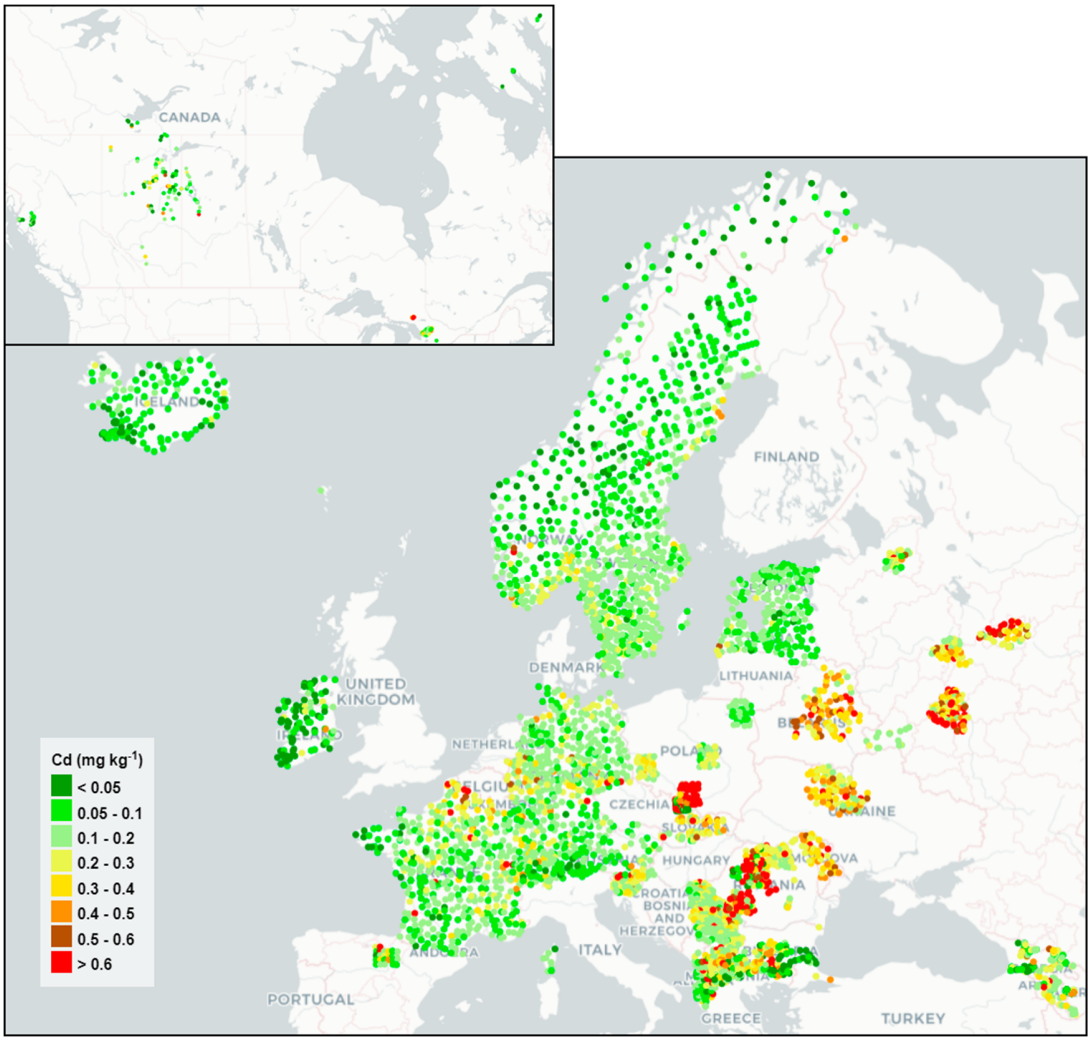

Figure 3.7. Cadmium concentration in mosses in 2015.

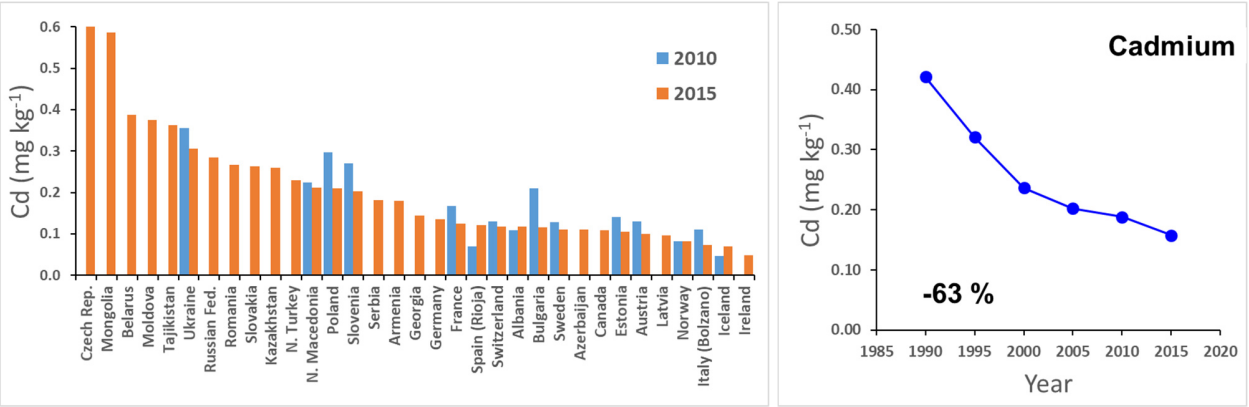

Figure 3.8. Median cadmium concentrations in mosses in 2010 and 2015 (left) and average median cadmium concentrations in mosses for countries (n = 16-23, depending on year) that reported data between 1990 and 2015 for at least four survey years (right); the percentage decline since 1990 is shown in bold. See **Annex 3** for median values per country in 2015.

The average median value across Europe has declined by 63% (from 0.42 to 0.16 mg kg^{-1}) between 1990 and 2015. This decline is similar to the decline in reported cadmium emissions in EU28 (65%; EEA, 2019) and modelled depositions in the EMEP region (53% between 1990 and 2014; EMEP, 2014), with a higher deposition decline reported for EU28 than the EECCA region. Both moss data and EMEP modelled deposition show the steepest decline between 1990 and 2000, with the decline slowing down since 2000. EMEP modelled cadmium deposition since 2012 showed some increase caused partly by higher emission values used in the modelling and partly by year-to-year variability of meteorological conditions (EMEP, 2016).

Chromium

Chromium concentrations in mosses show the highest levels in parts of in south-eastern Europe, with the highest median concentrations reported for Tajikistan, Armenia, northern Greece, Kazakhstan, Albania and Azerbaijan (Figure 3.9 and 3.10). Relatively high values were also observed in parts of France and Iceland, the Bolzano region in Italy, parts of Poland, Romania and Moldova. High values in countries that determined chromium using instrumental neutron activation analysis (INAA) might partly be explained by using INAA (see Annex 2), a technique that generally results in higher chromium concentrations than other techniques that require acid digestion of the samples; such digestion is generally not complete for chromium (Smodiš and Bleise, 2007). In general, the determination of chromium concentrations in mosses is associated with considerable uncertainty (Steinnes et al., 1997; Smodiš and Bleise, 2007). Changes in Ukraine and the Russian Federation since 2010 are confounded by the fact that mosses were sampled from different regions in 2010 and 2015. Since 2010, the median chromium concentration in mosses increased in some countries (e.g. Albania, Bulgaria, Italy – Bolzano region, Poland) whereas it decreased in other countries (e.g. North Macedonia, Slovenia, Faroe Islands and Sweden). Between 1990 and 2000, the chromium concentration in mosses was quite stable, then declined steadily until 2010 and showed a slight increase between 2010 and 2015. Since 1990, the average of median chromium concentration in mosses per country has declined by 24% (22% in EU28 Member States) across Europe (from 2.55 to 1.95 mg kg^{-1}; Figure 3.10). This decline is much lower than the 71% decline in emissions of chromium in EU28 (EEA, 2019). Chromium is among the elements where contribution from wind-blown dust to deposition might play a significant role, at least in some areas. Hence, a lower decline in depositions compared to emissions is to be expected. Chromium concentrations in mosses were generally low in Canada, with some hotspots observed in Saskathewan and Sudbury.

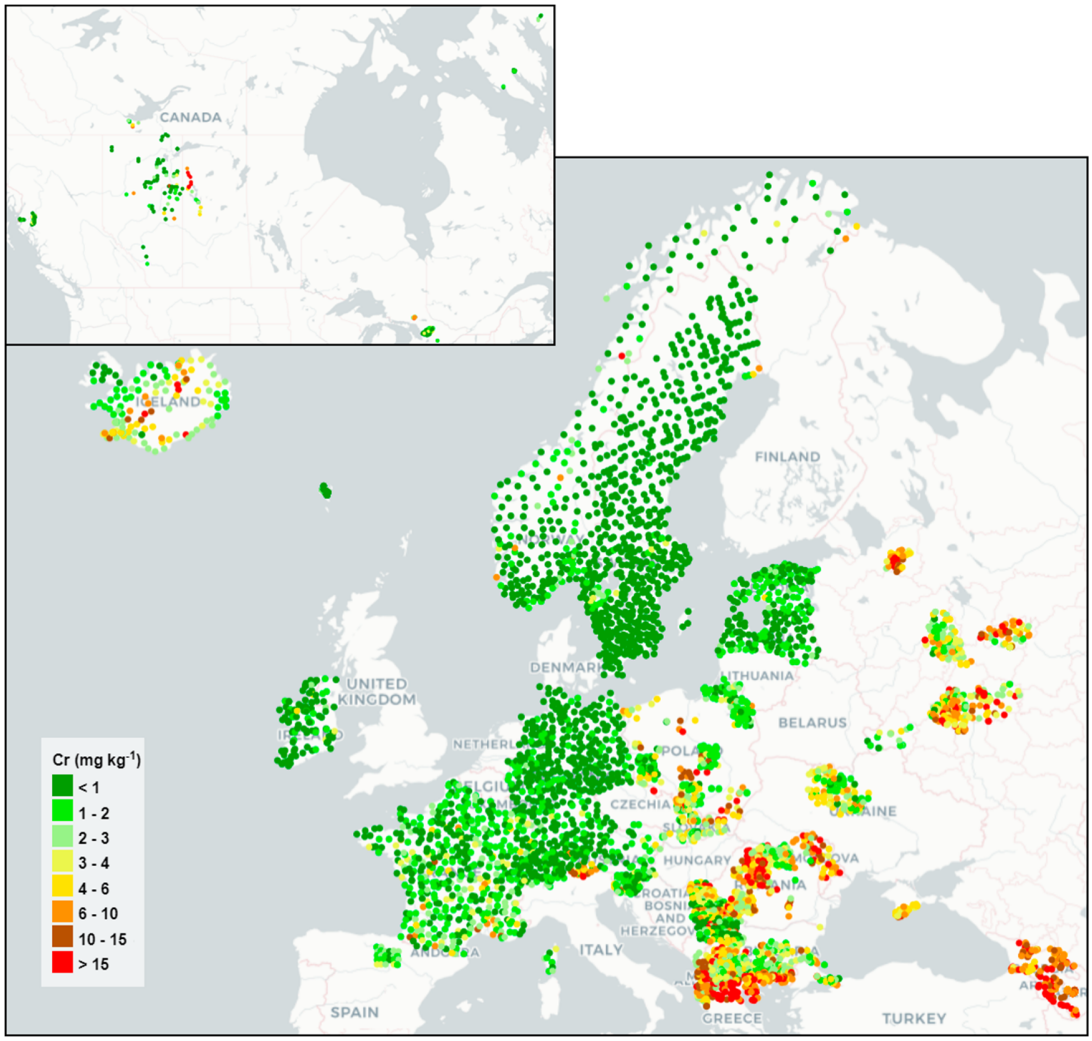

Figure 3.9. Chromium concentration in mosses in 2015/16.

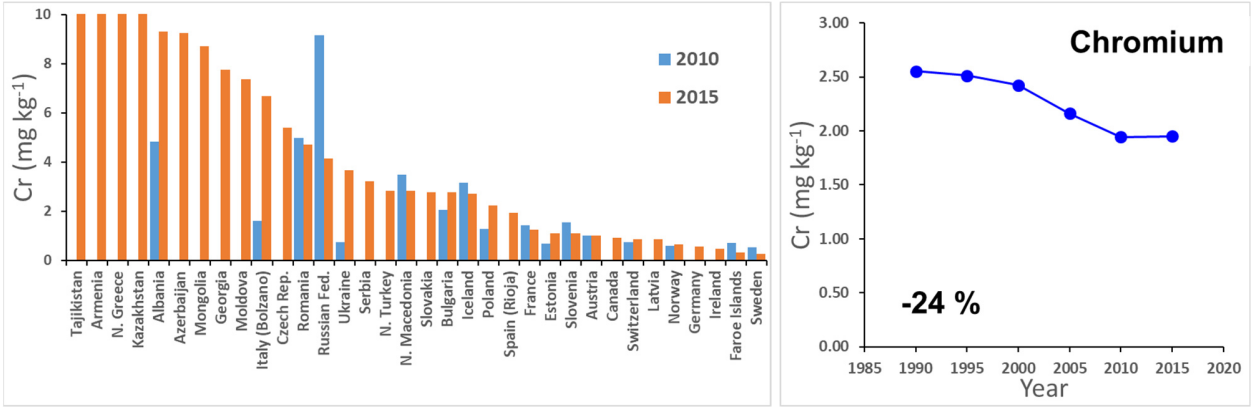

Figure 3.10. Median chromium concentrations in mosses in 2010 and 2015 (left) and average median chromium concentrations in mosses for countries (n = 16-23, depending on year) that reported data between 1990 and 2015 for at least four survey years (right); the percentage decline since 1990 is shown in bold. See **Annex 3** for median values per country in 2015.

Copper

The highest copper concentrations in mosses were found in parts of southern and eastern Europe (northern Turkey, Moldova, Tajikistan, Ukraine, Albania, Slovakia and Romania) and the Black Triangle in the Czech Republic. Hotpots were observed too in Iceland and at the Norwegian border with the Koala Peninsula, due to the presence of copper-nickel smelters in the northwest of the Russian Federation (Figure 3.11 and 3.12). Low copper concentrations were generally observed in northern Europe (Estonia, Norway and Sweden, with slightly higher levels in southern parts of Scandinavia), Ireland, Austria, Rioja (Spain), Canada and parts of France and Germany.

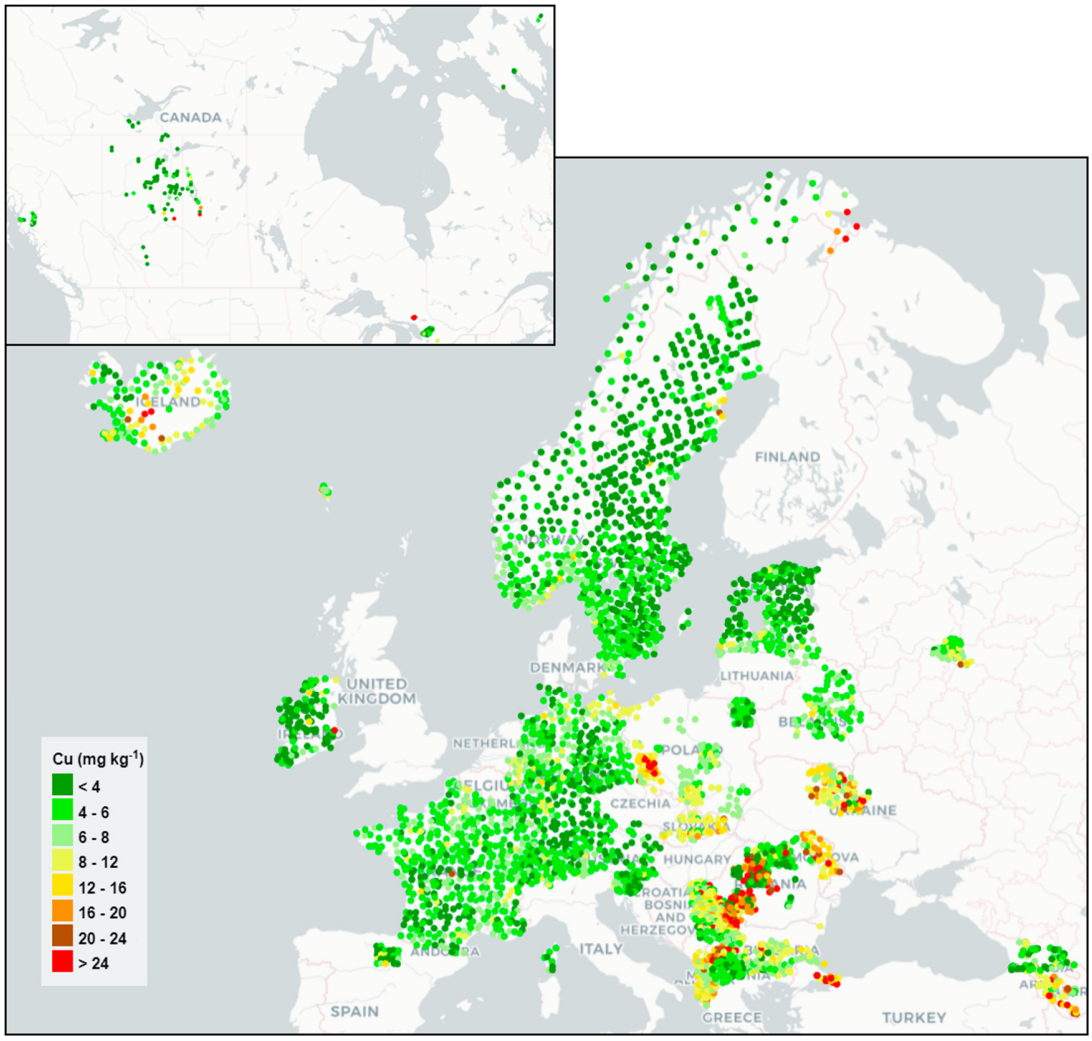

Figure 3.11. Copper concentration in mosses in 2015/16.

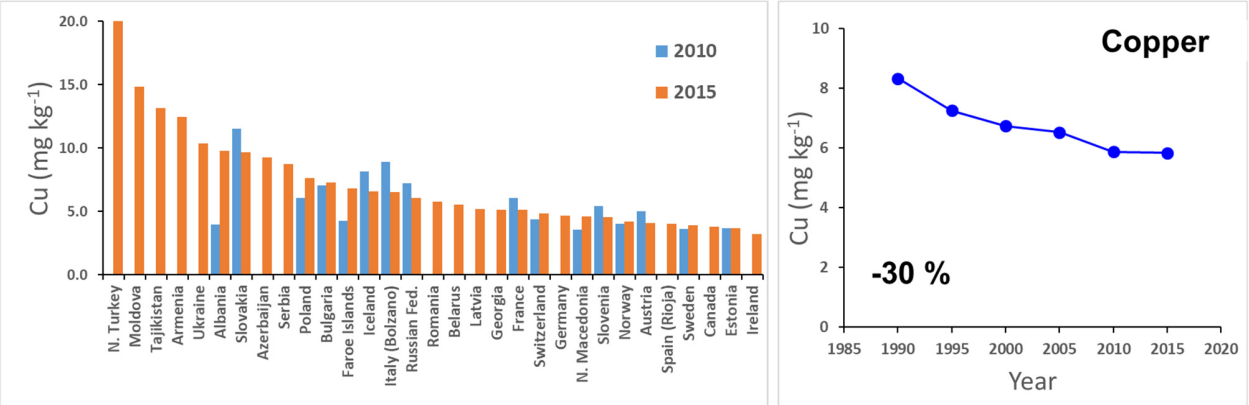

Figure 3.12. Median copper concentrations in mosses in 2010 and 2015 (left) and average median copper concentrations in mosses for countries (n = 16-22, depending on year) that reported data between 1990 and 2015 for at least four survey years (right); the percentage decline since 1990 is shown in bold. See **Annex 3** for median values per country in 2015.

Whilst the average of the median country values declined steadily across Europe from 8.3 to 5.8 mg kg^{-1} between 1990 and 2015, a decline of 30% (37% in EU28), the EEA (2019) reported an increase in copper emissions of 6.5% over the same period. In Germany, the Member State contributing the most to copper emissions in EU28, emissions have increased by 28% between 1990 and 2015.

Iron

As in previous years, there is a clear east-west gradient in Europe for the iron concentration in mosses (Figure 3.13 and 3.14), with median values above 2000 mg kg^{-1} being reported for Tajikistan, Armenia, Kazakhstan, northern Greece, Mongolia, Azerbaijan, Georgia, northern Turkey and Moldova. Median values between 1000 and 2000 mg kg^{-1} were reported for Albania, the Black Triangle (Czech Republic), Romania, Bulgaria and Serbia. The spatial patterns are similar to those for aluminium, indicating a significant contribution of soil-derived material, either from soil contamination or wind-resuspension. However, in some hotspots a significant contribution from pollution from mining or heavy metal industry can't be excluded. Compared to 2010, a considerable decline was observed in Ukraine (sampling in additional areas), North Macedonia and the Faroe Islands, whilst a considerable increase was observed in the Russian Federation (sampling in additional areas). The lowest median values were observed in Ireland, Sweden, Estonia, Germany, France, Faroe Islands and Latvia. For countries reporting iron data in at least four survey years, the average of median country values has declined by 22% from 612 mg kg^{-1} in 1990 to 479 mg kg^{-1} in 2015. The highest average values was observed in 2000 (661 mg kg^{-1}), dropping steeply between 2000 and 2005 and remaining rather stable since then.

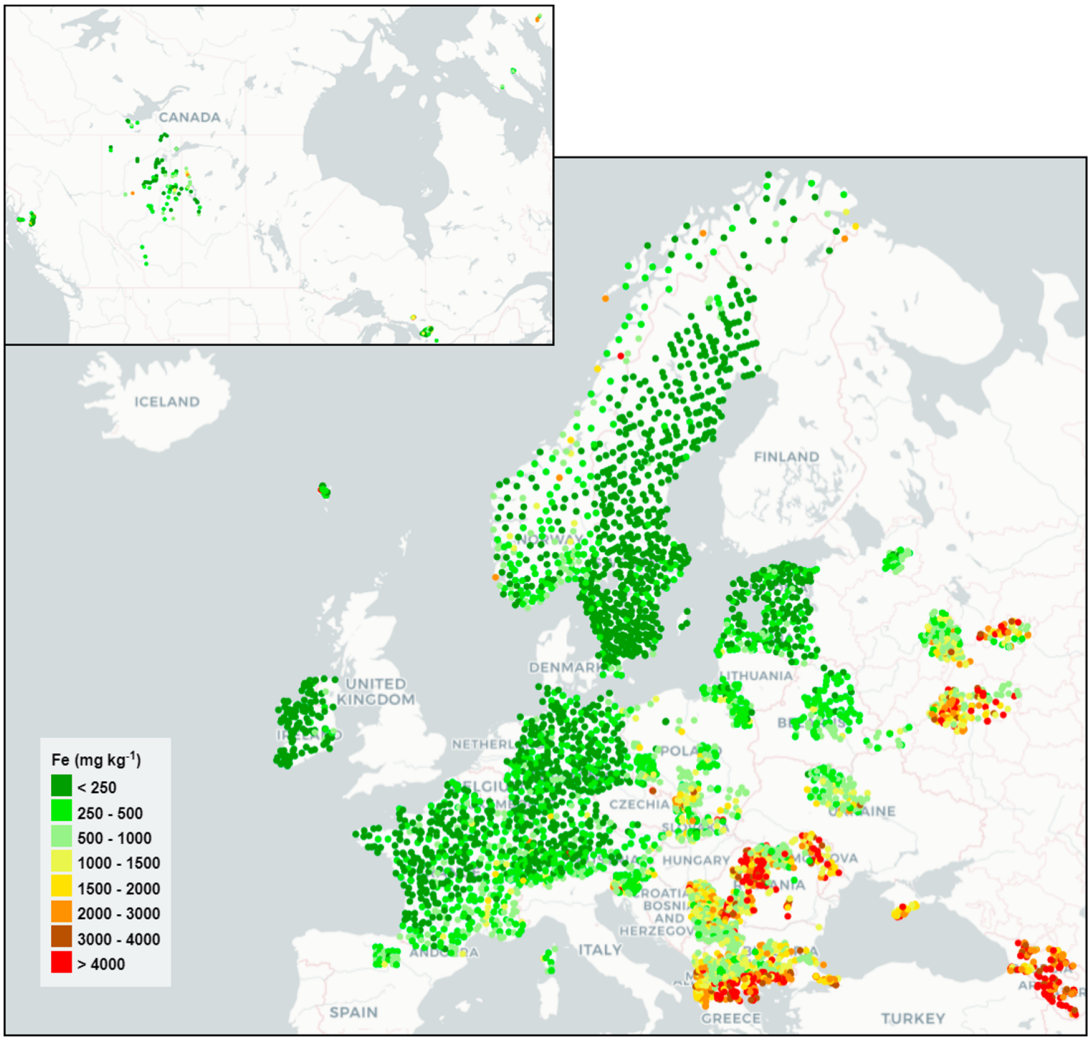

Figure 3.13. Iron concentration in mosses in 2015/16.

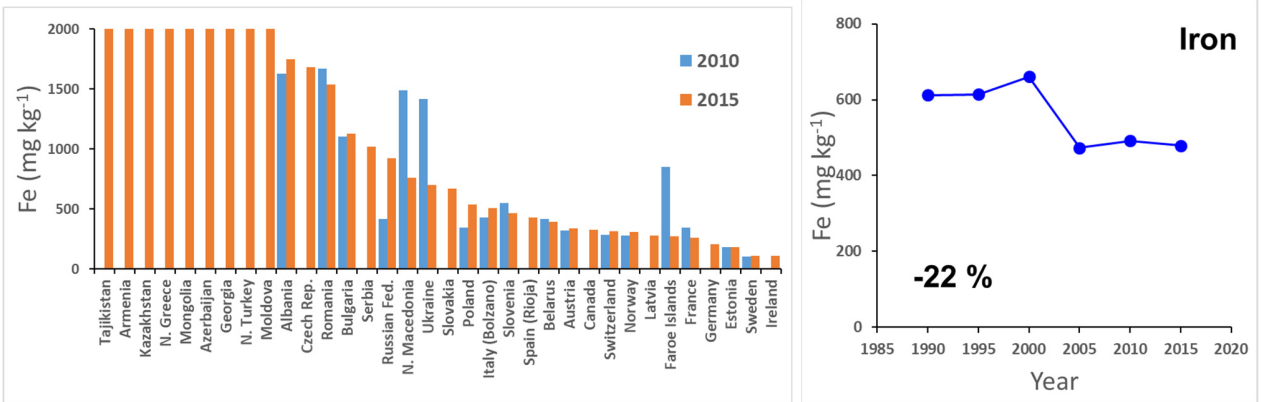

Figure 3.14. Median iron concentrations in mosses in 2010 and 2015 (left) and average median iron concentrations in mosses for countries (n = 12-22, depending on year) that reported data between 1990 and 2015 for at least four survey years (right); the percentage decline since 1990 is shown in bold. See **Annex 3** for median values per country in 2015.

Lead

In 2015, the highest median concentrations in mosses were generally found in eastern Europe (with the exception of Moscow region (Russian Federation) and Moldova), where phasing out of leaded petrol has not been fully implemented yet in some countries (Figure 3.15 and 3.16). The lowest concentrations in mosses were found in parts of Sweden, Iceland, Ireland, Rioja (Spain) and Canada, with elevated concentrations observed in particularly in southern Norway (due to long-range transport from central Europe) and Iceland. Intermediate concentrations were found in large parts of France and central Europe. The phasing out of leaded petrol across Europe has resulted in a considerable decline in the lead concentration in mosses since the first European moss survey in 1990, with the decline slowing down since 2000 (Figure 3.16).

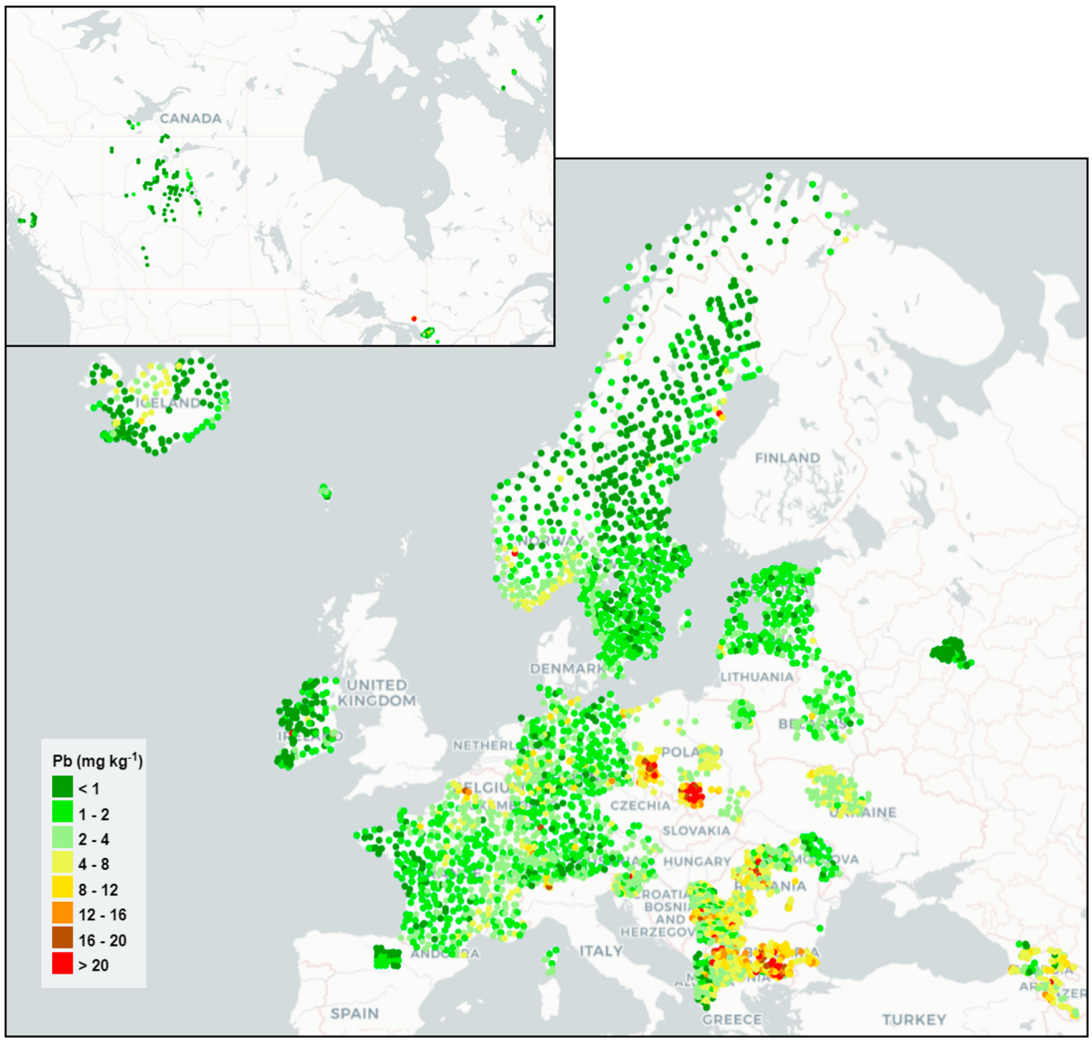

Figure 3.15. Lead concentration in mosses in 2015/16.

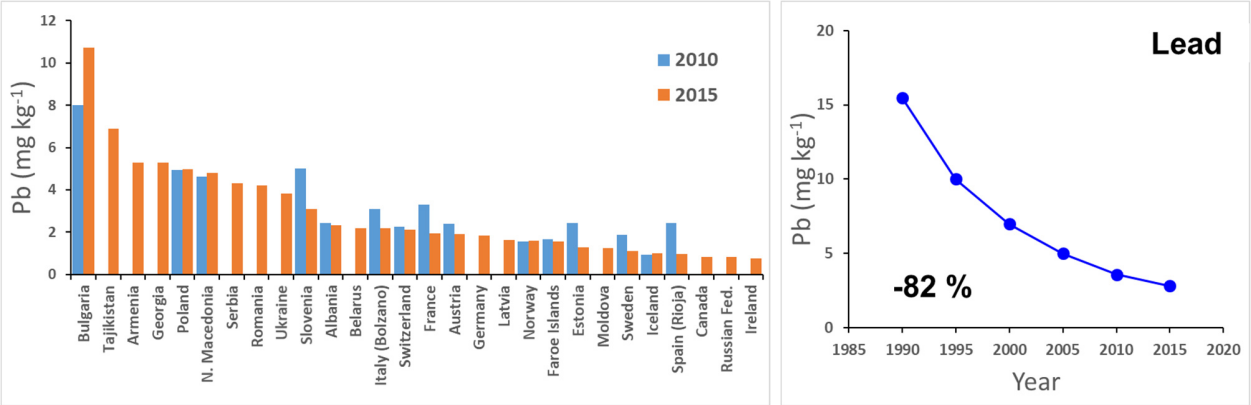

Figure 3.16. Median lead concentrations in mosses in 2010 and 2015 (left) and average median lead concentrations in mosses for countries (n = 17-22, depending on year) that reported data between 1990 and 2015 for at least four survey years (right); the percentage decline since 1990 is shown in bold. See **Annex 3** for median values per country in 2015.

Since 1990, the average of the country-specific median lead concentrations in mosses has declined by 82% from 15.5 to 2.82 mg kg^{-1}; in 2010 the value was 3.58 mg kg^{-1}. The decline is slightly lower than the decline in lead emissions reported for the EU28 in the same period (EEA, 2019). However, this is to be expected as a higher fraction of the lead deposition now originates from wind-resuspension, which also includes historically-deposited lead (EMEP, 2016). Indeed, the decline in modelled lead deposition in the EMEP region is 78% between 1990 and 2014, with a slightly higher decline observed in EU28 than the EECCA region. The most important emission categories in 2017 in the EU28 were iron and steel production, public electricity and heat production and automobile tyre and brake wear in road transport (EEA, 2019). Of these sectors, only the emissions from tyre and break wear have increased (36%) since 1990, whilst emissions in the other two sectors have decline significantly (74 – 82%).

Mercury

Mercury is a naturally, rarely occurring element, but has been mobilized by humans for thousands of years into aquatic and terrestrial ecosystems through mining (coal and metal ores), use in precious metal extraction, use in products (e.g. paint, electronic devices) and in industry (e.g. as a catalyst in chlor-alkali plants; Pacyna et al., 2009). Compared to many other metals, the spatial distribution of mercury concentrations in mosses is more homogenous across Europe (Figure 3.17 and 3.18). This is a result of the global nature and transport of mercury pollution due to the very long residence time of mercury in the atmosphere (EMEP, 2016). In most EMEP countries, the main contribution to mercury deposition is made by non-EMEP sources, i.e. from pollution originating outside the EMEP-region. In general, more than 80% of mercury emitted by a country is transported to other countries. The highest levels of mercury in mosses were found in the Black Triangle (Czech Republic), France and parts of Slovakia (Figure 3.17 and 3.18). In France, the mercury concentration in mosses increased considerably between 2010 and 2015, resulting in the highest median value in Europe in 2015. Relatively high levels of mercury were also reported for Norway and North Macedonia, and they did not change greatly since 2010. Arctic Mercury Depletion Events might be contributing to the elevated mercury concentrations in mosses in

northern Norway (Berg et al., 2008). Between 2010 and 2015, the mercury concentration in mossed declined by about one-third in Italy, Poland, Slovenia and Iceland.

Mercury concentrations in mosses have not changed (-2%) between 1995 and 2015, based on data from a limited number of countries (7 – 10, depending on survey year; Figure 3.18). Although EMEP (2016) reported a 23% decline in modelled mercury deposition between 1990 and 2014, the biggest decline occurred between 1990 and 1995; the decline between 1995 and 2014 was approximately 10%. Between 1995 and 2015, reported emissions in the EU28 declined by 57% (EEA, 2019), however as mentioned before, the main contribution to mercury deposition in Europe originates from sources outside Europe due to its long residence time in the atmosphere and global transport. The decline in mercury emissions in the industrial sector is mainly due to better emission controls on mercury cells, replacing them with diaphragm or membrane cells, and switching from coal to gas and other energy sources in many countries. In 2019, public electricity and heat production, iron and steel production and residential-stationary were the main sources for mercury emissions in EU28 (EEA, 2019).

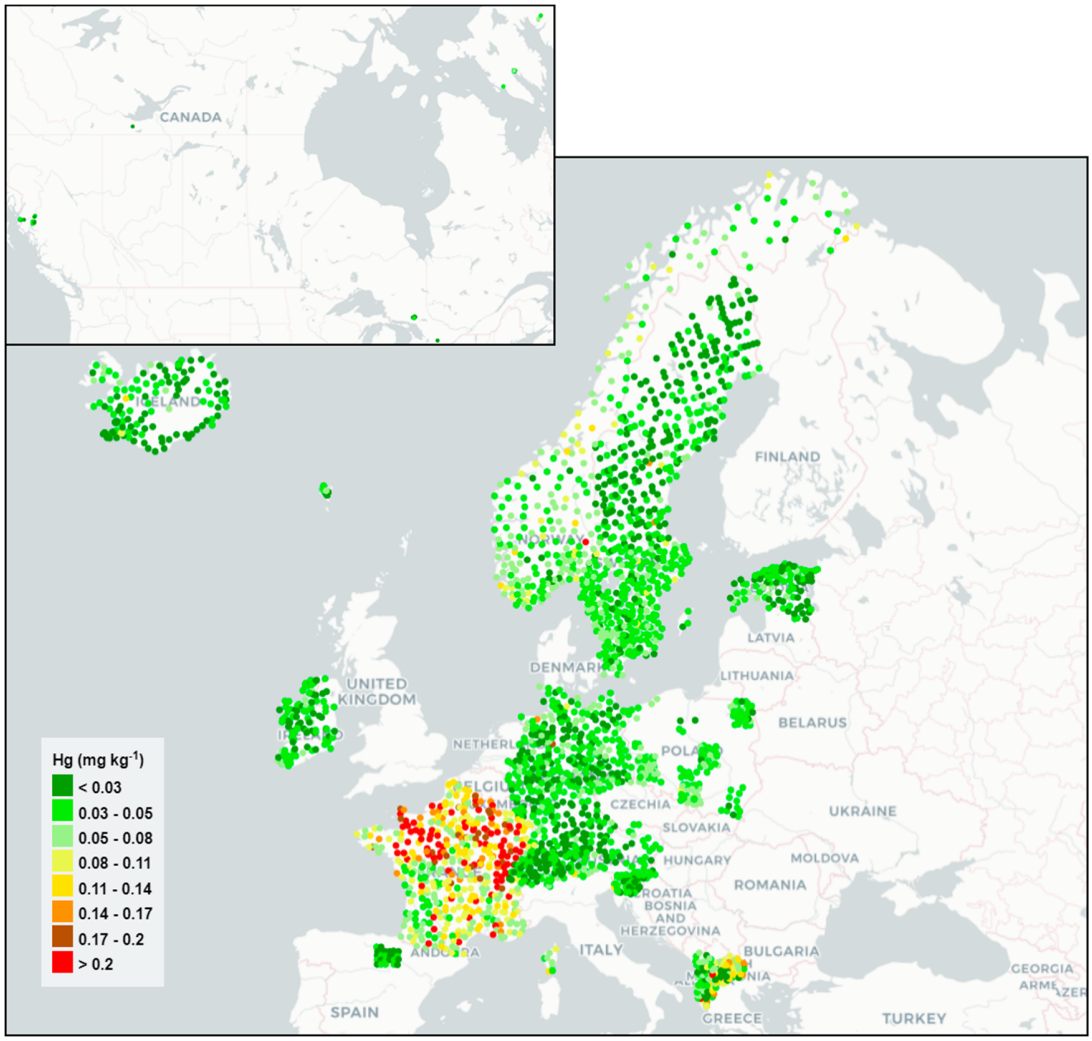

Figure 3.17. Mercury concentration in mosses in 2015/16.

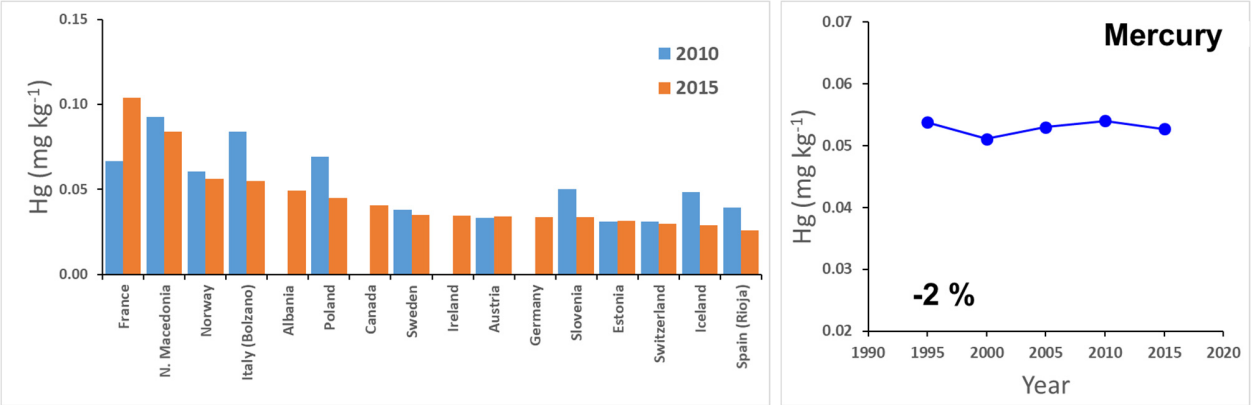

Figure 3.18. Median mercury concentrations in mosses in 2010 and 2015 (left) and average median mercury concentrations in mosses for countries (n = 7-10, depending on year) that reported data between 1995 and 2015 for at least four survey years (right); the percentage decline since 1995 is shown in bold. See **Annex 3** for median values per country in 2015.

Nickel

In general, the highest nickel concentrations were found in Armenia, Tajikistan, northern Greece, Albania, Kazakhstan, northern Turkey, Azerbaijan, Georgia, Republic of Moldova and at the Norwegian border with the Koala Peninsula (due to the presence of copper-nickel smelters in the northwest of the Russian Federation). Relatively high nickel concentrations were also observed in parts of Iceland (due to its volcanic origin), France and Canada (Figure 3.19 and 3.20). For Ukraine, the large decrease in nickel concentrations in comparison with 2010 is most likely due to sampling mosses in different areas in 2010 and 2015. Increases in median nickel concentrations in mosses were observed in Albania, Italy (Bolzano), Poland and Belarus; for Belarus the median nickel concentration was very low in 2010 compared to 2005 and 2015. Since 1990, the nickel concentration in mosses has declined by 25%, with the biggest decline occurring between 1990 and 1995 and concentrations remaining stable since then (Figure 3.20). In 1990 and 2015, the average of country-median nickel concentrations in mosses were 2.49 and 1.87 mg kg^{-1}, respectively. In EU28, the decline in average nickel concentrations in mosses between 1990 and 2015 was 35%, which is about half the decline (73%) in reported nickel emissions in EU28 (EEA, 2019).

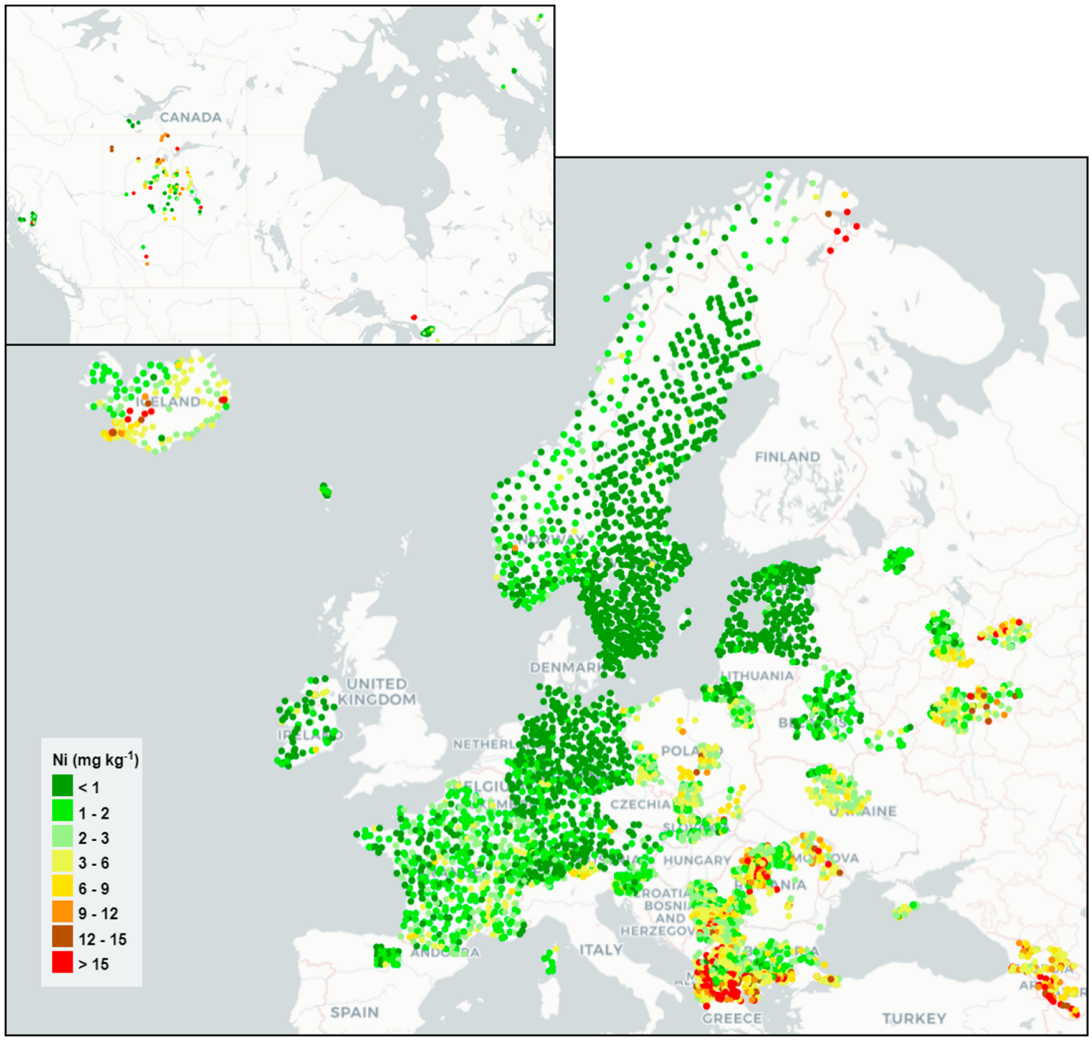

Figure 3.19. Nickel concentration in mosses in 2010/2015.

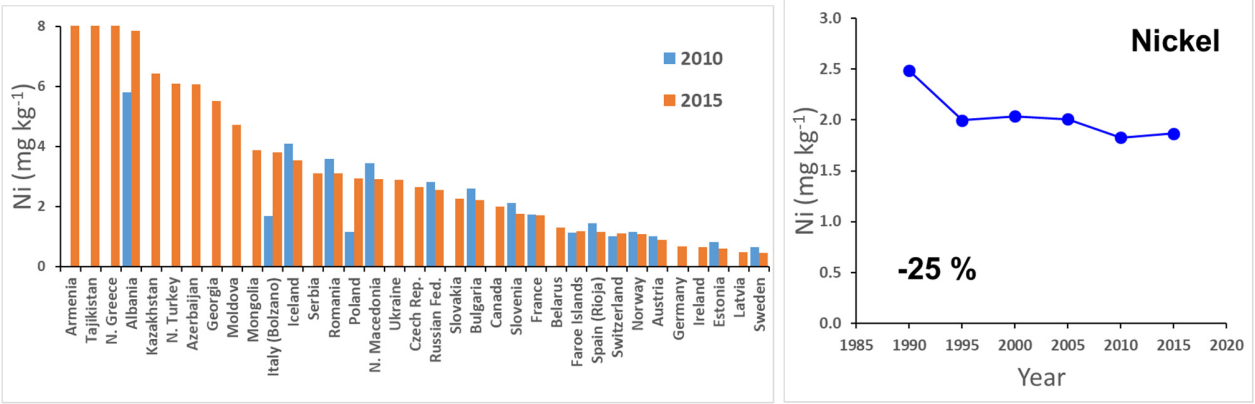

Figure 3.20. Median nickel concentrations in mosses in 2010 and 2015 (left) and average median nickel concentrations in mosses for countries (n = 17-23, depending on year) that reported data between 1990 and 2015 for at least four survey years (right); the percentage decline since 1990 is shown in bold. See **Annex 3** for median values per country in 2015.

Vanadium

In 2015, the spatial distribution of vanadium concentrations in mosses is very similar to that of aluminium and iron, and to a lesser extent also to arsenic, chromium and nickel. Highest vanadium concentrations were reported for mosses in south-eastern Europe, from Romania to Mongolia (Figure 3.21 and 3.22). Relatively high median concentrations were also observed in the Black Triangle (Czech Republic) and the Faroe Islands. The lowest vanadium concentrations were generally found in Sweden, Latvia, Estonia, Ireland, western France, Germany and Canada. Compared to 2010, the median vanadium concentration in mosses in 2015 has increased in Bulgaria and Switzerland and declined in Romania, North Macedonia, Faroe Islands, Slovenia, France, Estonia and Sweden. Since 1990, the average country-median concentration has declined by 57% (from 3.73 to 1.62 mg kg^{-1}), with concentrations being stable between 1995 and 2000, and the rate of decline slowing down since 2005 (Figure 3.22).

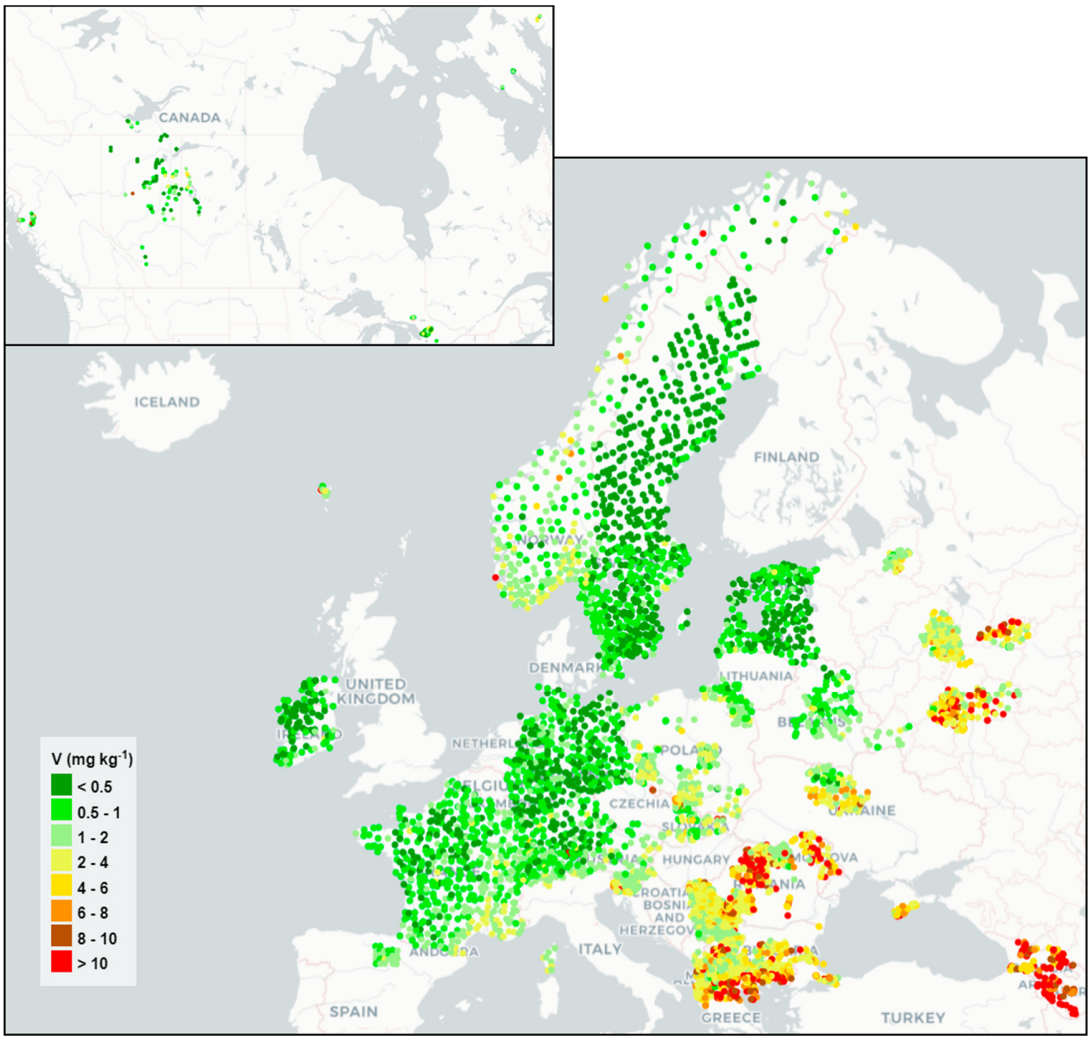

Figure 3.21. Vanadium concentration in mosses in 2015/16.

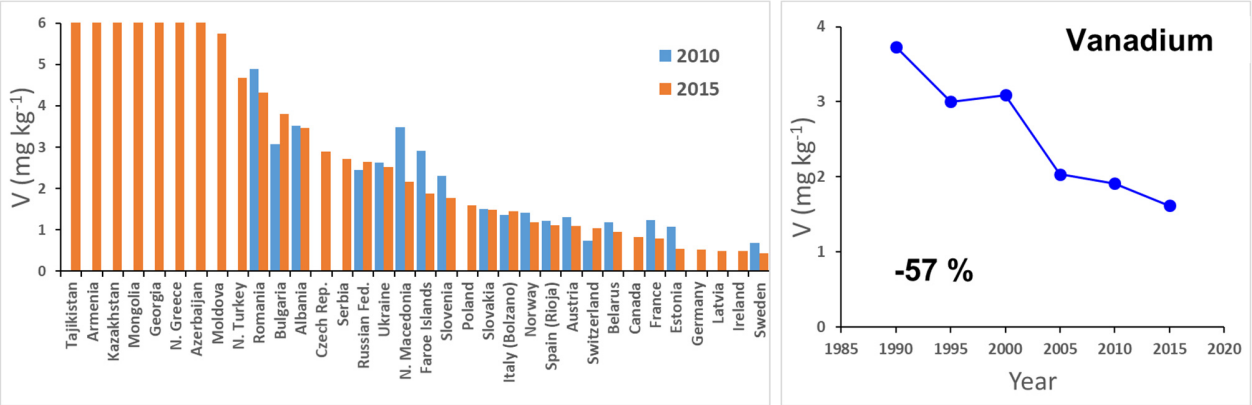

Figure 3.22. Median vanadium concentrations in mosses in 2010 and 2015 (left) and average median vanadium concentrations in mosses for countries (n = 13-21, depending on year) that reported data between 1990 and 2015 for at least four survey years (right); the percentage decline since 1990 is shown in bold. See **Annex 3** for median values per country in 2015.

Zinc

Of all metals, the zinc concentration in mosses has the most homogenous distribution across Europe, with locally or regionally elevated concentrations being observed (Figure 3.23 and 3.24). It should be noted that zinc is an essential element to plants (including mosses), meaning that there is a natural background concentration of zinc in mosses. In 2015, very high median values were found in northern Turkey and the Black Triangle (Czech Republic), followed by Kazahkstan, Tajikistan, Poland, Mongolia, Slovakia, the Russian Federation and Romania. The lowest median values (below 20 mg kg^{-1}) were found in the Faroe Islands, Rioja (Spain), Albania and Iceland. Low concentrations were also reported for parts of Ireland, southern France, Austria, Slovenia and Serbia. Since 1990, the zinc concentration in mosses has declined steadily from 39.6 mg kg^{-1} to 30.3 mg kg^{-1} in 2015, a decline of 23% across Europe. For the EU28, this decline is 29%, similar to the 39% decline in reported emission (EEA, 2019). Since 2010, the median zinc concentration in mosses declined in some countries (e.g. Ukraine, France, Italy (Bolzano), Estonia and Slovenia) whilst it increased in other countries (e.g. Russian Federation, North Macedonia, Bulgaria and Albania).

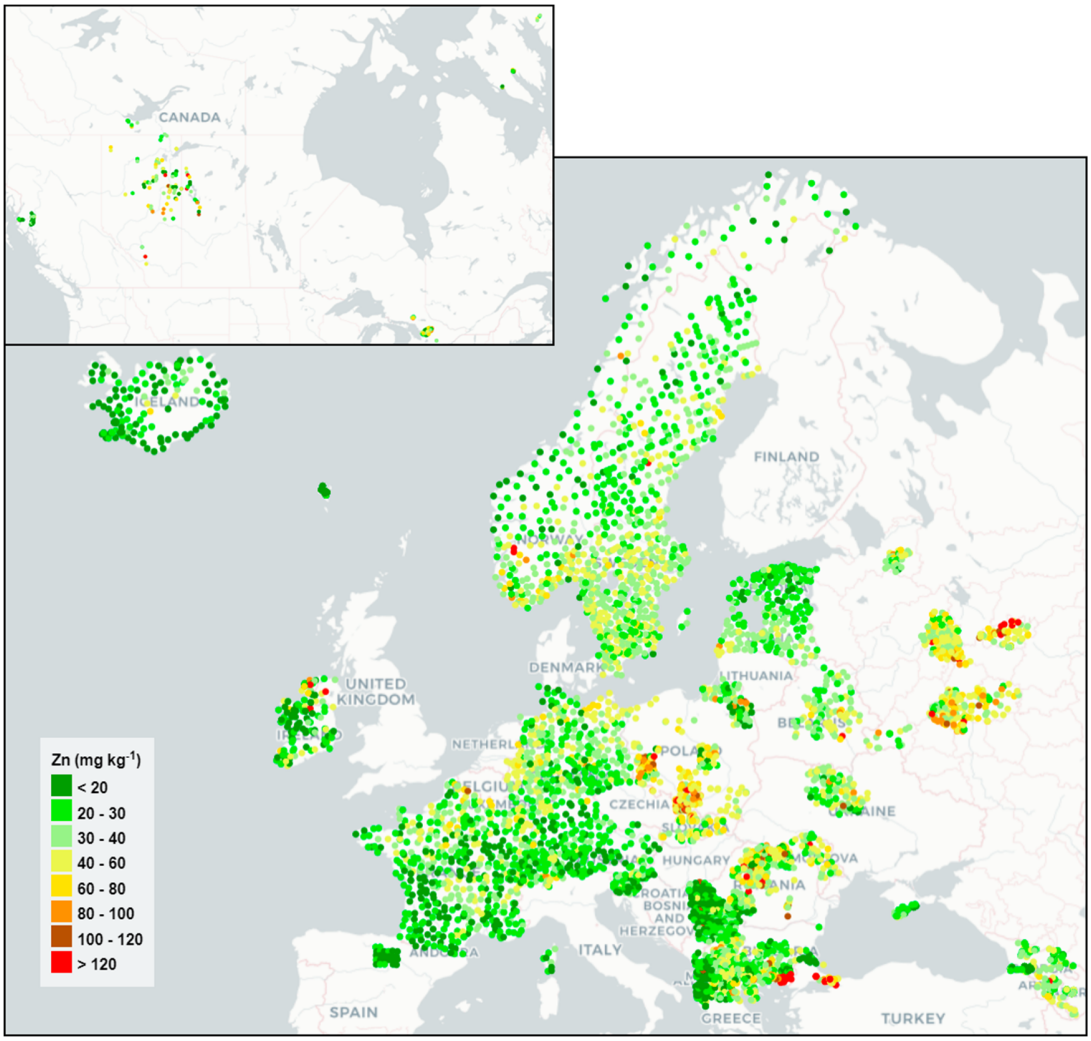

Figure 3.23. Zinc concentration in mosses in 2015.

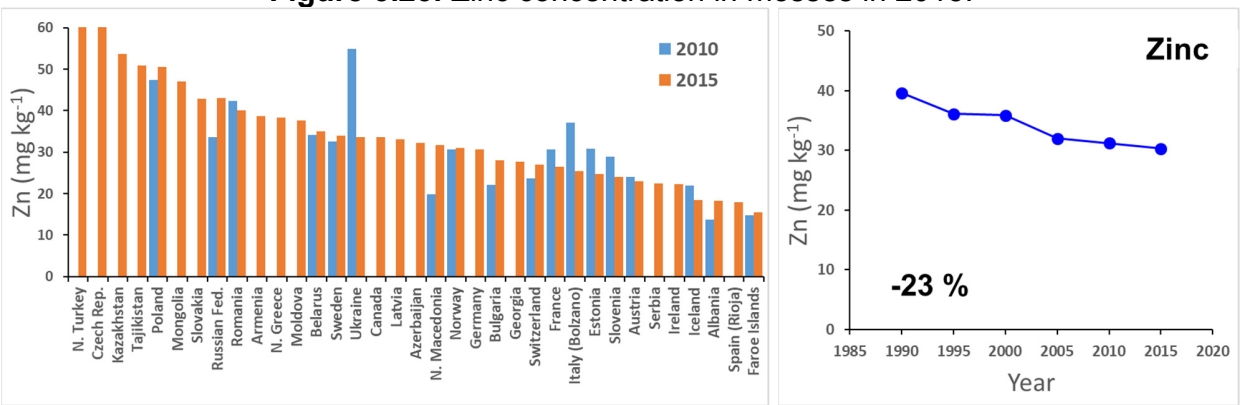

Figure 3.24. Median zinc concentrations in mosses in 2010 and 2015 (left) and average median zinc concentrations in mosses for countries (n = 16-24, depending on year) that reported data between 1990 and 2015 for at least four survey years (right); the percentage decline since 1990 is shown in bold. See **Annex 3** for median values per country in 2015.

Nitrogen

As in previous years, high concentrations of nitrogen were found in mosses in parts of France, central and south-eastern Europe (Figure 3.25 and 3.26). The highest median values (above 1.4%) were reported for Slovakia, Romania, Poland and Germany and the lowest median values (below 1%) in Ireland, Rioja (Spain), Sweden, Estonia and Austria. As nitrogen is an essential macronutrient for mosses, there is a natural background concentration in mosses of about 0.5% (Harmens et al., 2011; Schröder et al., 2010a). Compared to 2010, in 2015 the median nitrogen concentration in mosses increased slightly in Slovakia, Bolzano (Italy) and Switzerland, and decreased slightly in France, Austria and Slovenia. Across Europe, the average of the country-median values has hardly changed between 2005 and 2015 (1.5% decline).

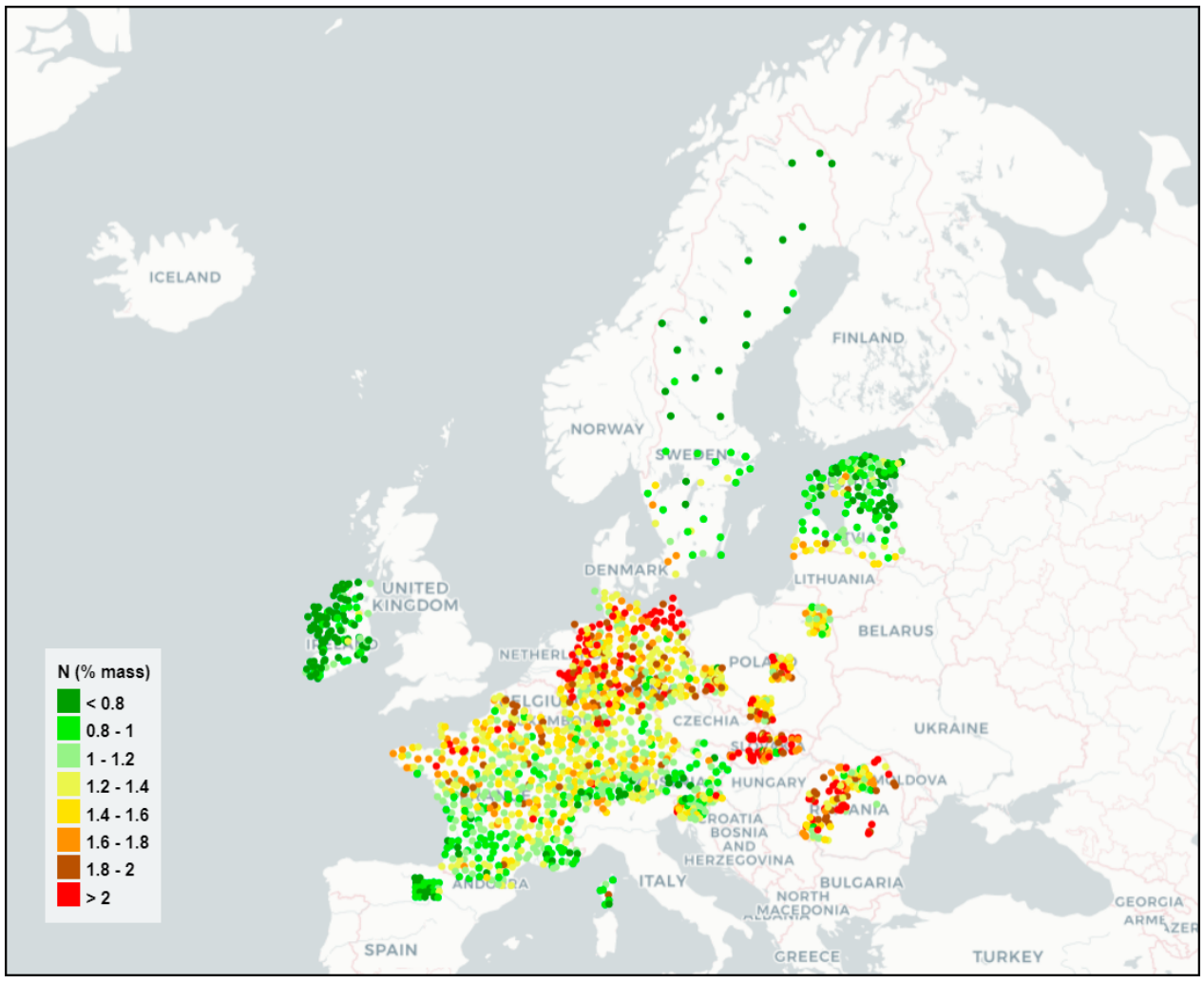

Figure 3.25. Total nitrogen concentration in mosses in 2015/16.

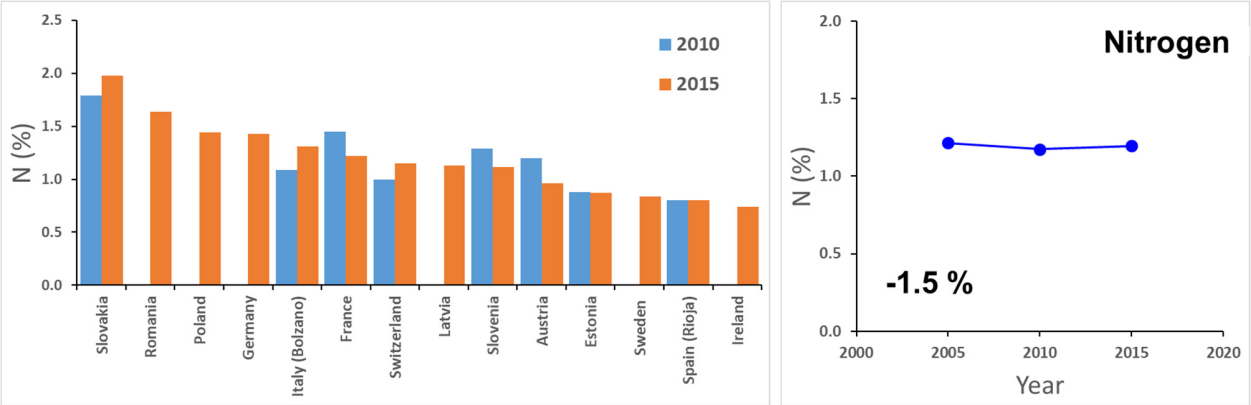

Figure 3.26. Median nitrogen concentrations in mosses in 2010 and 2015 (left) and average median nitrogen concentrations in mosses for countries (n = 10-14, depending on year) that reported data for at least two survey years between 2005 and 2015 (right); the percentage decline since 2005 is shown in bold. See **Annex 3** for median values per country in 2015.

Persistent Organic Pollutants (POPs)

In 2010, selected POPs were determined in mosses for the first time in a pilot study in selected countries (Harmens et al., 2013b; Foan et al., 2014). Mosses have been proposed in the past as biomonitors of POPs; polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs), in particular, at the local or national scale (Harmens et al., 2013a). For the 2015 survey, it was suggested to extend the pilot study conducted in 2010 to other countries and to focus on PAHs, PCBs, polybromodiphenylethers (PBDEs), dioxins, and perfluorooctane sulfonic acid and its salts (PFOS), but other POPs could also be included if there was a national interest. The recommended list of POPs can be found in the Moss Monitoring Manual 2020 (Frontasyeva et al., 2019). No specific analytical techniques were recommended at this stage due to the diverse nature of POPs. Here we report the SUM PAH EPA 16, because this is the most commonly published and therefore useful for comparison with other studies. SUM PAH EPA 16 is dominated by naphthalene, so in addition to this sum, it is useful to report SUM PAH 4 and SUM Borneff 6, which are specified as indicators for emission inventories in UNECE POPs Protocol (https://www.unece.org/environmental-policy/conventions/envlrtapwelcome/guidance-documents/protocol-on-pops.html).

In 2015, eight countries reported results on POPs (Table 3.1), mainly PAHs. Ireland has co-elution of triphenylene (not within EPA 16 for PAHs) with chrysene, which is included in the sum EPA 16, therefore there is some uncertainty introduced in the value of SUM PAH EPA 16 for Ireland. For PCBs, the most common compounds were reported such as the sum of PCB 7 and the 12 dioxin-like, most toxic congeners according to the World Health Organization (WHO, 2010). The SUM PCB 7 were calculated for Germany, Norway and Ireland. Ireland reported a co-elution of PCB 28 and 31, introducing some uncertainty in the SUM PCB 7. Germany and Norway also reported dioxin-like PCBs and DDT analogues, respectively.

The highest PAHs sums were reported for Austria, Switzerland, Latvia and Sweden, the lowest values were reported for Ireland (Table 3.1). For Ireland and Rioja (Spain), the detection frequency was rather low, ranging from 25% for SUM PAH 4 in Ireland to 48% for

SUM EPA 16 in Rioja (**Annex 4**). For the other countries, the detection frequency ranged from 63% (SUM EPA 16, Norway) to 100% (SUM PAH 4, Norway and Germany; SUM Borneff 6, Germany. For Norway and Switzerland, the values for SUM EPA 16 are considerably lower than the values for SUM EPA 13 reported in 2010 (Harmens et al., 2013b). The same is true for Spain, however, in 2010 PAHs were reported for Navarra whilst in 2015 PAHs were reported for Rioja. The highest sum PCB 7 values were reported for Sweden and the lowest values were found in Norway.

Table 3.1. Median values of PAHs (SUM EPA 16, SUM PAH 4 and SUM Borneff 6), PCBs (SUM PCB 7, SUM Dioxin-like PCBs) and DDT analogues (SUM DTT) in mosses in 2015/2016, sampled at selected sites in Europe. See annex 4 for further details.

Countries		Austria	Germany[1]	Ireland[2]	Latvia	Norway	Spain[3]	Sweden	Switzerland[4]
Number of sites		26	8	9	20	20	25	20	22
Median values	SUM EPA 16 [ng/g]	121	24.3	23.4	80.3	40.2	44.7	77.3	138
	SUM PAH 4 [ng/g]	8.40	6.07	1.21	15.2	4.31	2.99	21.1	14.8
	SUM Borneff 6 [ng/g]	27.7	11.0	6.11	26.8	8.27	6.30	38.5	28.8
	SUM PCB 7 [pg/g]		429	222		117		1275	464
	SUM Dioxin-like PCBs [pg/g]		26.5						
	SUM DDT [pg/g]					386			

[1] Benzo(b/j)fluoranthenes was taken into calculation instead Benzo(b)fluoranthenes;
[2] Chrysene/Triphenylene was taken into calculation instead of Chrysene; PCB-31/28 was taken into calculation instead of PCB 28;
[3] Benzo(b/j)fluoranthenes was taken into calculation instead of Benzo(b)fluoranthenes;
[4] Benzo(b/k)fluoranthen was taken into calculation instead of Benzo(b)fluoranthenes and Benzo(k)fluoranthenes.

4 Discussion, conclusion and recommendations

Discussion

Heavy metals

The decline in emission and subsequent deposition of most heavy metals across Europe and beyond has resulted in a decrease in the heavy metal concentration in mosses since 1990 for most metals, with the decrease continuing for some but not all metals since 2010. Between 2010 and 2015, country and metal-specific changes have been observed, with increases, decreases or no changes found, depending on metal and country. Many emission sources have become cleaner, for example by using filters or other best available technologies, by changing from coal to gas as fuel source or phasing out leaded petrol in many parts of Europe (EEA, 2019; Ilyin et al., 2016). In addition, some very polluting local emission sources have been shut down since 1990, in particular in eastern Europe. For cadmium and lead the decline in the concentration in mosses since 1990 was in good agreement with the decline in atmospheric deposition rates modelled by EMEP (EMEP, 2016). However, for mercury the decline in modelled deposition rates was not reflected in the trend in concentrations in mosses, which hardly changed since 1995. With emissions declining in Europe, the contribution to heavy metal deposition from secondary sources (e.g. wind re-suspension of historic deposition or from sources originating outside Europe) tends to become larger (EMEP, 2016).

Since 1990, the metal concentration in mosses has declined the most for lead (82%), cadmium (63%) and vanadium (57%), followed by copper (30%), nickel (25%), chromium (24%), zinc (23%) and iron (22%). For arsenic and mercury, the concentration in mosses has declined by 13% and 2% respectively since 1995. Clearly, mercury pollution remains a problem of global concern. Aluminium and antimony concentrations in mosses were reported for the first time in 2005 to provide an indication of the potential contribution of soil-derived material, either through wind re-suspension or soil contamination during sampling (aluminium), and anthropogenic sources (antimony) to metal concentrations in mosses. Since 2005, the average concentration in mosses has declined by 24% and 38% for aluminium and antimony, respectively. Even in times of generally decreasing metal deposition across Europe, temporal trends are different for different geographical scales, i.e. temporal trends were country or region-specific with no changes or even increases in metal concentrations in mosses observed. For some countries a comparison between 2010 and 2015 data is confounded by sampling in different (e.g. Czech Republic, Spain) or additional regions (Russian Federation, Ukraine) or sampling at a lower number of sites (e.g. Austria, Norway, Poland, Slovenia, Switzerland). In the Czech Republic, sampling in 2015 was limited to the highly polluted Black Triangle.

As in previous surveys, the lowest concentrations of heavy metals in mosses were generally found in northern and western Europe and the highest concentrations in (south-)eastern Europe, resulting in a north-west to south-east gradient. In 2015, participation in the moss survey from countries in the EECCA region has greatly increased. For the majority of metals, the concentration of heavy metals in mosses is highest in (parts of) the EECCA region and in south-eastern Europe (SEE), with median country values often being a factor ten or more higher than in other parts of Europe. This is particularly the case for metals associated with mineral particles (i.e. aluminium, arsenic, chromium, iron, nickel and vanadium), thought to be mainly originating from wind-blown dust (Harmens et al., 2015). High correlations (R^2 > 0.77) were found between the moss concentrations of aluminium, iron and vanadium. SEE

and the EECCA region are characterised by mineral soils, which tend to have no or hardly any humus layer that could protect the region from wind-blown dust. There is a need to investigate whether mosses sampled in (parts of) the EECCA region and SEE can be used as biomonitors of atmospheric heavy metal deposition given the rather high contribution of mineral particles to the metal concentration in mosses. As a start, for cadmium and lead the spatial distribution of their concentrations in mosses should be compared in more detail with the spatial distribution of their EMEP-modelled atmospheric deposition (EMEP, 2016). This could provide an indication whether the concentrations in mosses are overestimated in the EECCA region and SEE in comparison with EMEP-modelled deposition and can provide an estimate of the contribution of modelled wind-resuspension in those areas. However, it should be noted that cadmium and lead concentrations in mosses are not strongly associated with mineral particles (Harmens et al., 2015) and that there is a lack of EMEP monitoring stations in those areas for model validation (EMEP, 2016).

Antimony concentrations in mosses also tend to be highest in the EECCA region and SEE (although this is not true for all the countries in this area). This could indicate that anthropogenic emission sources for heavy metals are highest in this area, hence metal concentrations in mosses are expected to be highest there, contributing to the north-west to south-east gradient in heavy metals in mosses across Europe. For some metals such as aluminium and chromium, analysis of their concentration using instrumental neutron activation analysis (INAA), also contributes to a higher concentration in mosses in the EECCA region and SEE (Smodiš and Bleise, 2007). There is a need to analyse moss samples from this area, combining sample digestion with different analytical techniques (e.g. ICP-MS) to assess how much the application of INAA contributes to higher heavy metal concentrations in mosses. At the same time, mosses sampled in other parts of Europe should be analysed using INAA for comparison. This should be done at a range of heavy metal concentrations in mosses.

Nitrogen

Hardly any changes were observed in the nitrogen concentration in mosses since 2005. As in previous years, areas most at risk from adverse effects of nitrogen on terrestrial ecosystems are located in parts of western (except Ireland) and central Europe. However, the risk in many northern, eastern and Mediterranean countries could not be assessed as the majority of countries from those regions did not report on nitrogen concentrations in mosses. The relationship between nitrogen concentrations in mosses and measured (Harmens et al., 2014) or modelled nitrogen deposition (Harmens et al., 2011) starts to show saturation between deposition rates of 15 - 20 kg ha^{-1} y^{-1}. Although this makes it difficult to assess the magnitude of risk in areas with medium to high nitrogen deposition, the moss technique still allows the identification of the areas potentially most at risk.

POPs

Only a limited number of countries submitted data on POPs concentrations in mosses, with the majority reporting on PAHs. Hence, it is difficult to assess spatial trends across Europe. In 2015, the highest median values of PAHs sums were reported for Austria, Switzerland, Latvia and Sweden, the lowest median values were reported for Ireland. For Norway and Switzerland, the median values for SUM EPA 16 are considerably lower than those for SUM EPA 13 reported in 2010 (Harmens et al., 2013b). The highest sum PCB 7 values were reported for Sweden and the lowest median values were found in Norway.

Conclusions

- Moss biomonitoring continues to provide a cheap, complementary method to deposition analysis for the identification of areas at risk from high atmospheric deposition fluxes of heavy metals and nitrogen and for monitoring changes with time.
- For cadmium and lead, the temporal changes in concentrations in mosses across Europe are in agreement with those reported for EMEP modelled atmospheric deposition. Mercury pollution remains a problem in Europe and globally.
- Country-specific trends were observed, with concentrations declining for some but rising or showing no change for other metals since 2010.
- Despite the apparent success of the implementation of air pollution abatement techniques in large areas of Europe, further measures are required in (south)-eastern Europe to reduce the apparent high emissions of heavy metals. For nitrogen, more stringent air pollution abatement strategies are required across Europe to reduce the areas at risk from adverse effects of elevated atmospheric nitrogen deposition, especially of reduced nitrogen.

Recommendations

Whilst we welcome the increased participation of countries in the EECCA region and SEE, there is a need to unravel factors primarily contributing to the very high metal concentrations in mosses reported for 2015. Especially the role of wind-blown dust and/or soil contamination in this area dominated by mineral soils requires further investigation. It might be that the moss technique is less suitable in (parts of) this region for providing an indication of the contribution of current primary anthropogenic emission sources to atmospheric metal deposition and to long-range transboundary air pollution. For the survey in 2020, there is a need to ensure that sampling of mosses in this region is conducted strictly according to the guidelines described in the moss survey manual (Frontasyeva et al., 2019), including sampling in remote areas away from point sources of anthropogenic pollution. To achieve this, a training workshop on moss sampling and processing led by moss experts is recommended. In addition, analyses of moss samples using other analytical techniques than INAA is recommended as part of an intercalibration exercise. In this exercise, moss samples from other parts of Europe should be included in INAA analysis too, as well as moss reference material (Smodiš and Bleise, 2007). We encourage more countries to include the analysis of nitrogen and selected POPs in future surveys. In 2020, some countries will also include a pilot study on using mosses as biomonitors of atmospheric microplastic deposition (Roblin and Aherne, 2020).

Further detailed statistical analysis of the 2015 moss survey data is recommended in an effort to understand better the factors primarily contributing to the variation of heavy metal and nitrogen concentrations in mosses. The contribution of atmospheric deposition might well be less pronounced for heavy metals such as cadmium and lead with deposition levels continuing to decline. The application of satellite data to predict atmospheric deposition of heavy metals to mosses should be explored too (Uzhinskiy et al., 2018b).

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Annex 2. Analytical techniques used in 2015/16

Country	As	Cd	Cr	Cu	Fe	Hg	Ni	Pb	V	Zn	Al	Sb	N
Albania	ETAAS	ETAAS	ICP-ES	ETAAS	ICP-ES	CVAAS	ICP-ES	ETAAS	ICP-ES	ICP-ES	ICP-ES	-	-
Armenia	INAA	ETAAS	INAA	ETAAS	INAA	-	INAA	ETAAS	INAA	INAA	INAA	INAA	-
Austria	GFAAS	ICP-MS	ICP-ES	ICP-ES	ICP-ES	CVAAS	ICP-MS	ICP-MS	ICP-MS	ICP-ES	ICP-ES	GFAAS	EA
Azerbaijan	INAA	INAA	INAA	INAA	INAA	-	INAA	-	INAA	INAA	INAA	INAA	-
Belarus	INAA	ETAAS	-	ETAAS	INAA	-	INAA	ETAAS	INAA	INAA	INAA	INAA	-
Bulgaria	INAA	ICP-ES	INAA	ICP-ES	INAA	-	INAA	ICP-ES	INAA	INAA	INAA	INAA	-
Canada	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	DMA	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	-
Czechia	INAA	INAA	INAA	INAA	INAA	-	INAA	-	INAA	INAA	INAA	INAA	-
Denmark													
- Faroe Islands	-	-	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	-	-	-
Estonia	ICP-ES	ICP-ES	ICP-ES	ICP-ES	ICP-ES	CVAFS	ICP-ES	ICP-ES	ICP-ES	ICP-ES	ICP-ES	-	Kjeldahl
France	ICP-MS	ICP-MS	ICP-MS	ICP-ES	ICP-MS	CVAAS	ICP-MS	ICP-MS	ICP-MS	ICP-ES	ICP-ES	ICP-MS	EA
Georgia	INAA	ETAAS	INAA	ETAAS	INAA	-	INAA	ETAAS	INAA	INAA	INAA	INAA	-
Germany	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	CVAAS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	EA
Greece	INAA	-	INAA	-	INAA	-	INAA	-	INAA	INAA	INAA	INAA	-
Iceland	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	DMA	ICP-MS	ICP-MS	ICP-MS	ICP-MS	-	ICP-MS	-
Ireland	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	DMA	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	EA
Italy	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	DMA	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	EA
Kazakhstan	INAA	INAA	INAA	-	INAA	-	INAA	-	INAA	INAA	INAA	INAA	-
Latvia	-	FAAS	FAAS	FAAS	FAAS	-	FAAS	FAAS	FAAS	FAAS	-	-	EA
Mongolia	INAA	INAA	INAA	-	INAA	-	INAA	-	INAA	INAA	INAA	INAA	-
North Macedonia	INAA	ICP-ES	INAA	ICP-ES	INAA	CVAAS	INAA	ICP-ES	INAA	INAA	INAA	INAA	-
Norway	ICP-HRMS	ICP-HRMS	ICP-HRMS	ICP-HRMS	ICP-HRMS	CVAFS	ICP-HRMS	ICP-HRMS	ICP-HRMS	ICP-HRMS	ICP-HRMS	ICP-HRMS	-
Poland	ETAAS/ INAA	FAAS/ ETAAS/ INAA	FAAS/ INAA	FAAS/ INAA	FAAS/ INAA	DMA	FAAS/ ETAAS/ INAA	FAAS/ ETAAS/ INAA	ETAAS/ INAA	FAAS/ INAA	INAA	INAA	Kjeldahl
Republic of Moldova	INAA	ETAAS	INAA	ETAAS	INAA	-	INAA	ETAAS	INAA	INAA	INAA	INAA	-
Romania	INAA	ICP-MS	INAA	ICP-MS	INAA	-	INAA	ICP-MS	INAA	INAA	INAA	INAA	Kjeldahl
Russian Federation													
- Moscow region	INAA	ETAAS	INAA	ETAAS	INAA	-	INAA	ETAAS	INAA	INAA	INAA	INAA	-
- Bryansk region	INAA	INAA	INAA	-	INAA	-	INAA	-	INAA	INAA	INAA	INAA	-
- Ivanovo region	INAA	INAA	INAA	-	INAA	-	INAA	-	INAA	INAA	INAA	INAA	-
- Kalinigrad	INAA	-	INAA	-	INAA	-	INAA	-	INAA	INAA	INAA	INAA	-
- Ryazan region	INAA	-	INAA	-	INAA	-	INAA	-	INAA	INAA	INAA	INAA	-
- Tikhvin region	INAA	INAA	INAA	-	INAA	-	INAA	-	INAA	INAA	INAA	INAA	-
- Tula region	INAA	INAA	INAA	-	INAA	-	INAA	-	INAA	INAA	INAA	INAA	-
- Tver region	INAA	-	INAA	-	INAA	-	INAA	-	INAA	INAA	-	INAA	-
- Udmurtia	INAA	-	INAA	-	INAA	-	INAA	-	INAA	INAA	INAA	INAA	-
Serbia	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-ES	-	ICP-ES	ICP-MS	ICP-MS	ICP-ES	ICP-ES	ICP-MS	-
Slovakia	INAA	ETAAS	INAA	ETAAS	INAA	-	INAA		INAA	INAA	INAA	INAA	EA
Slovenia	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	DMA	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	EA
Spain	INAA	ICP-MS	INAA	INAA	INAA	DMA	INAA	ICP-MS	INAA	INAA	INAA	INAA	?
Sweden	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	-	Kjeldahl
Switzerland	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	DMA	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	EA
Tajikistan	INAA	ETAAS	INAA	ETAAS	INAA	-	INAA	ETAAS	INAA	INAA	INAA	INAA	-
Turkey	ICP-ES	ICP-ES	ICP-ES	ICP-ES	ICP-ES	-	ICP-ES	-	ICP-ES	ICP-ES	ICP-ES	ICP-ES	-
Ukraine													
- Kyiv region	-	ICP-ES	ICP-ES	ICP-ES	ICP-ES	-	ICP-ES	ICP-ES	ICP-ES	ICP-ES	ICP-ES	ICP-ES	-
- Zhytomyr region	-	ICP-ES	ICP-ES	ICP-ES	ICP-ES	-	ICP-ES	ICP-ES	ICP-ES	ICP-ES	ICP-ES	ICP-ES	-
- Crimea	INAA	-	INAA	-	INAA	-	INAA	-	INAA	INAA	INAA	INAA	-
Vietnam	INAA	INAA	INAA	INAA	INAA	-	INAA	-	INAA	INAA	INAA	INAA	-

Abbreviations

CVAAS	Cold vapour atomic absorption spectrometry
CVAFS	Cold vapour atomic fluorescence spectrometry
EA	Elemental analysis (Dumas method)
ETAAS	Electrothermal atomic absorption spectrometry
FAAS	Flame atomic absorption spectrometry
GFAAS	Graphite furnace atomic absorption spectrometry
ICP-ES	Inductively coupled plasma emission spectrometry
ICP-MS	Inductively coupled plasma mass spectrometry
INAA	Instrumental neutron activation analysis
DMA	Direct mercury analyzer
ICP-HRMS	Inductively coupled plasma-high resolution mass spectrometry

Annex 3. Metal (mg kg^{-1}) and nitrogen concentrations (mass %) in mosses in 2015/16

	As	Cd	Cr	Cu	Fe	Hg	Ni	Pb	V	Zn	Al	Sb	N (%)
Albania													
Number	58	58	58	58	58	58	58	58	58	58	58		
Min	0.13	0.045	2.21	6.10	685	0.013	0.68	0.51	0.56	10.3	486		
Max	3.18	1.02	66.2	22.4	6956	0.21	108	14.5	26.2	108	9022		
Mean	0.63	0.22	10.6	10.7	1899	0.060	16.9	2.98	4.27	23.0	1788		
Median	0.43	0.12	9.31	9.74	1749	0.049	7.85	2.34	3.46	18.4	1562		
90th percentile	1.25	0.54	19.3	15.2	2789	0.11	40.2	5.91	6.89	30.3	2803		
Armenia													
Number	37	37	37	37	37		37	37	37	37	37	37	
Min	0.96	0.089	5.64	5.29	1840		2.01	2.52	6.53	27.4	3520	0.10	
Max	11.9	1.97	132	38.6	13900		33.5	23.1	62.6	149	35600	1.22	
Mean	2.61	0.25	25.6	15.1	6572		14.2	6.22	23.6	46.8	11112	0.34	
Median	2.14	0.18	18.1	12.4	6130		11.4	5.29	23.5	38.6	10600	0.26	
90th percentile	3.58	0.33	52.3	30.2	12380		25.9	10.8	38.1	71.6	18020	0.72	
Austria													
Number	50	50	50	50	50	50	50	50	50	50	50	50	50
Min	0.074	0.028	0.39	2.80	120	0.022	0.40	0.74	0.42	14.0	126	0.024	0.43
Max	2.54	0.65	9.50	8.50	3400	0.057	4.90	5.30	11.0	43.0	2331	0.26	1.78
Mean	0.38	0.13	1.49	4.59	435	0.036	1.15	1.94	1.42	24.0	473	0.093	0.98
Median	0.22	0.099	1.00	4.10	340	0.034	0.90	1.90	1.10	23.0	378	0.072	0.97
90th percentile	0.70	0.21	2.60	7.01	631	0.046	2.04	2.60	2.13	33.1	756	0.17	1.26
Azerbaijan													
Number	84	84	84	84	84		84		84	84	84	84	
Min	0.44	0.020	2.71	1.99	921		2.16		2.02	12.9	1070	0.033	
Max	5.48	0.65	20.7	42.4	6800		11.1		18.9	64.7	13300	0.44	
Mean	1.29	0.17	9.32	12.6	3267		6.00		8.67	32.7	4539	0.15	
Median	1.16	0.11	9.24	9.26	3045		6.08		8.29	32.3	4225	0.14	
90th percentile	1.96	0.42	13.3	25.8	4895		8.29		12.3	45.5	6836	0.24	
Belarus													
Number	86	86		86	86		86	86	86	86	86	86	
Min	0.11	0.15		3.41	232		0.55	0.92	0.30	20.0	102	0.050	
Max	0.50	1.09		14.9	1470		4.84	8.47	4.00	157	3230	0.35	
Mean	0.25	0.41		5.92	429		1.46	2.29	1.06	39.2	656	0.10	
Median	0.23	0.39		5.52	392		1.30	2.18	0.95	35.0	595	0.096	
90th percentile	0.39	0.60		7.81	607		2.33	3.10	1.66	50.5	982	0.13	
Bulgaria													
Number	130	130	130	130	130		130	130	130	130	130	130	
Min	0.092	0.020	0.22	3.20	201		0.45	1.62	0.54	9.52	347	0.022	
Max	12.8	1.56	19.0	46.9	7240		14.6	103	18.2	101	10700	0.51	
Mean	0.71	0.21	3.85	7.96	1408		2.91	15.0	4.52	32.0	2745	0.13	
Median	0.44	0.12	2.76	7.28	1125		2.21	10.7	3.81	28.1	2290	0.11	
90th percentile	0.89	0.40	7.60	10.8	2463		6.00	26.6	7.73	51.0	4740	0.21	

	As	Cd	Cr	Cu	Fe	Hg	Ni	Pb	V	Zn	Al	Sb	N (%)
Canada													
Number	400	400	411	414	414	108	400	412	413	412	414	336	
Min	0.0001	0.002	0.01	0.41	28	0.013	0.005	0.060	0.051	0.89	41.2	0.001	
Max	10.5	5.55	74.8	1628	15628	0.095	1211	94.8	57.6	288	9229	1.55	
Mean	0.28	0.18	2.53	12.2	634	0.042	11.9	1.89	1.97	41.1	580	0.11	
Median	0.18	0.11	0.92	3.77	327	0.041	2.01	0.83	0.83	33.5	362	0.063	
90th percentile	0.48	0.34	5.02	8.61	1282	0.064	13.2	2.57	3.76	74.5	1135	0.26	
Czech Republic													
Number	93	93	93		93		93		93	93	93	93	
Min	0.30	0.020	1.10		338		1.00		0.55	30.6	305	0.049	
Max	3.75	7.09	34.1		6930		8.26		14.9	587	11000	1.31	
Mean	1.07	1.18	6.84		2022		2.90		4.01	111	2530	0.34	
Median	0.97	0.60	5.40		1680		2.64		2.90	85.4	1830	0.30	
90th percentile	1.70	3.55	14.7		4284		4.66		8.70	161	5718	0.60	
Denmark (Faroe Islands)													
Number			14	14	14	10	14	13	14	14			
Min			0.19	5.13	158	0.039	0.63	1.08	0.95	11.0			
Max			2.36	16.5	4552	0.067	5.89	2.60	10.0	26.4			
Mean			0.47	7.29	599	0.050	1.53	1.70	2.32	16.1			
Median			0.32	6.79	270	0.048	1.19	1.57	1.89	15.5			
90th percentile			0.47	8.15	648	0.061	1.84	2.46	2.51	18.3			
Estonia													
Number	33	99	99	99	99	99	99	99	99	99	99		99
Min	0.10	0.042	0.47	2.12	72.2	0.006	0.32	0.65	0.18	13.5	73.3		0.63
Max	0.24	0.27	4.80	10.2	553	0.069	2.26	3.12	2.38	46.1	548		1.86
Mean	0.13	0.11	1.21	3.79	208	0.034	0.68	1.43	0.60	25.2	194		0.93
Median	0.12	0.11	1.09	3.69	181	0.031	0.60	1.27	0.54	24.7	178		0.87
90th percentile	0.17	0.15	1.82	4.83	322	0.049	0.98	2.08	0.87	31.9	292		1.21
France													
Number	441	441	441	441	441	441	441	441	441	441	441	441	441
Min	0.048	0.025	0.23	2.08	64.7	0.032	0.31	0.62	0.23	9.92	51.2	0.022	0.61
Max	1.31	1.07	14.7	20.8	1870	0.63	7.91	19.2	3.98	113	1180	0.34	3.18
Mean	0.24	0.16	1.72	5.34	353	0.13	1.90	2.41	0.99	29.0	293	0.077	1.26
Median	0.18	0.13	1.23	5.13	261	0.10	1.70	1.95	0.79	26.5	220	0.064	1.22
90th percentile	0.50	0.28	3.42	7.31	682	0.23	3.16	4.03	1.81	45.3	594	0.14	1.69
Georgia													
Number	111	111	111	111	111		111	111	111	111	111	111	
Min	0.18	0.010	2.04	0.13	404		1.92	0.18	1.71	7.15	759	0.049	
Max	83.3	0.58	39.0	11.9	14100		24.2	19.1	54.0	75.2	20800	1.36	
Mean	2.04	0.17	10.2	5.25	3659		6.70	5.36	11.8	30.7	5019	0.20	
Median	0.98	0.14	7.74	5.15	2720		5.52	5.29	9.47	27.7	4240	0.16	
90th percentile	2.46	0.35	18.6	8.91	7310		11.4	8.70	23.3	47.8	9080	0.33	

	As	Cd	Cr	Cu	Fe	Hg	Ni	Pb	V	Zn	Al	Sb	N (%)
Germany													
Number	398	398	399	400	400	397	400	400	400	400	400	397	400
Min	0.018	0.035	0.051	1.68	75.0	0.005	0.068	0.47	0.030	11.8	41.3	0.007	0.80
Max	1.51	1.76	4.95	13.9	2505	0.20	7.42	19.3	5.25	92.4	2965	0.41	3.49
Mean	0.14	0.17	0.71	5.16	257	0.037	0.84	2.37	0.64	33.0	273	0.099	1.55
Median	0.11	0.14	0.57	4.66	206	0.034	0.68	1.83	0.52	30.7	197	0.090	1.43
90th percentile	0.23	0.26	1.24	7.77	433	0.054	1.46	4.33	1.08	48.2	461	0.16	2.13
Greece (North)													
Number	105		105		105		105		105	105	105	105	
Min	0.52		2.04		1010		1.72		2.61	14.6	1350	0.020	
Max	17.9		222		28700		138		33.4	282	46100	3.23	
Mean	3.31		33.0		6345		19.8		11.1	55.7	8240	0.31	
Median	1.62		14.7		4630		10.0		8.66	38.3	6160	0.20	
90th percentile	9.39		84.7		13860		50.2		20.8	119	16000	0.58	
Iceland													
Number	146	146	146	146	146	146	146	146	146	146		146	
Min	0.028	0.015	0.56	2.95	841	0.007	0.63	0.14	2.37	10.6		0.002	
Max	2.23	0.25	65.7	33.1	15639	0.12	58.2	8.05	45.9	75.9		0.59	
Mean	0.20	0.077	4.18	7.96	4405	0.032	6.03	1.95	12.8	20.7		0.050	
Median	0.12	0.069	2.72	6.59	3666	0.029	3.54	0.99	10.7	18.4		0.020	
90th percentile	0.37	0.13	6.61	12.6	8171	0.047	13.7	5.24	23.6	30.9		0.14	
Ireland													
Number	127	108	109	131	131	130	61	131	131	131	131	130	131
Min	0.0002	0.0002	0.037	1.34	42.0	0.010	0.050	0.14	0.14	4.86	22.4	0.010	0.45
Max	0.97	0.43	5.31	47.7	874	0.074	7.42	65.8	2.01	167	815	0.44	1.33
Mean	0.12	0.071	0.76	4.30	148	0.036	1.30	2.18	0.56	30.6	133	0.065	0.78
Median	0.082	0.049	0.46	3.23	107	0.034	0.64	0.74	0.49	22.3	100	0.048	0.74
90th percentile	0.19	0.17	1.68	5.92	228	0.052	3.61	2.31	0.99	59.6	223	0.13	1.04
Italy (Bolzano)													
Number	26	26	26	26	26	26	26	26	26	26	26	26	26
Min	0.13	0.040	1.84	4.19	313	0.031	1.40	1.06	0.94	17.5	437	0.038	0.97
Max	0.58	0.13	17.6	11.5	900	0.12	9.63	4.16	2.52	36.7	1339	0.16	1.68
Mean	0.21	0.078	8.18	6.81	518	0.056	4.43	2.39	1.51	25.7	750	0.081	1.33
Median	0.20	0.072	6.67	6.49	506	0.055	3.81	2.17	1.45	25.4	714	0.074	1.31
90th percentile	0.30	0.10	15.8	9.20	626	0.074	7.70	3.52	2.04	33.4	943	0.13	1.57
Kazakhstan													
Number	93	61	91		93		88		91	92	92	93	
Min	0.091	0.005	3.19		884		1.68		2.63	0.93	33.8	0.11	
Max	17.1	4.40	60.7		25900		36.6		64.0	1500	40300	1.77	
Mean	3.17	0.44	16.7		6252		8.06		16.7	87.9	11381	0.45	
Median	2.47	0.26	12.9		5090		6.44		13.0	53.7	9260	0.34	
90th percentile	6.14	0.83	30.5		13600		15.7		34.4	99.9	24890	0.90	

	As	Cd	Cr	Cu	Fe	Hg	Ni	Pb	V	Zn	Al	Sb	N (%)
Latvia													
Number		101	101	101	101		101	101	101	101			40
Min		0.044	0.032	2.37	77.5		0.20	0.54	0.17	22.4			0.75
Max		0.55	2.70	12.3	1234		1.67	12.0	2.54	99.8			1.83
Mean		0.11	0.91	5.45	331		0.57	1.85	0.56	34.2			1.21
Median		0.10	0.85	5.17	279		0.48	1.64	0.49	33.1			1.13
90th percentile		0.17	1.54	7.84	560		0.90	2.63	0.81	41.5			1.55
Moldova													
Number	34	34	34	34	34		34	34	34	34	34	34	
Min	0.38	0.22	2.02	5.98	1010		2.25	0.54	2.88	20.2	1560	0.11	
Max	4.06	0.95	32.9	28.3	9520		17.1	2.71	29.5	124	17200	1.14	
Mean	1.29	0.40	10.9	15.4	3485		6.25	1.37	10.1	42.1	5912	0.31	
Median	0.86	0.38	7.37	14.8	2180		4.73	1.23	5.75	37.6	3135	0.25	
90th percentile	2.50	0.59	22.4	20.7	7375		12.2	2.15	21.8	54.8	12980	0.47	
Mongolia													
Number	39	30	39		39		39		39	39	39	39	
Min	1.31	0.16	3.90		1960		1.50		4.41	26.2	3510	0.14	
Max	7.90	1.00	22.0		11000		11.8		23.1	69.6	19300	0.81	
Mean	2.63	0.54	9.10		4582		4.27		10.4	46.1	8524	0.31	
Median	2.30	0.59	8.70		4310		3.88		10.0	47.1	8070	0.32	
90th percentile	4.10	0.87	13.3		6750		5.86		14.7	60.7	12160	0.44	
North Macedonia													
Number	72	72	72	72	72	72	72	72	72	72	72	72	
Min	0.079	0.018	1.05	3.03	236	0.020	0.64	2.18	0.68	15.4	533	0.028	
Max	1.66	0.88	17.3	8.28	1780	0.25	52.6	13.6	5.52	59.1	4280	0.32	
Mean	0.71	0.25	3.55	4.74	833	0.085	5.12	5.34	2.44	33.3	1440	0.080	
Median	0.72	0.21	2.83	4.57	761	0.084	2.91	4.79	2.17	31.8	1220	0.071	
90th percentile	1.26	0.49	5.13	6.11	1354	0.15	6.66	8.41	3.80	47.4	2110	0.14	
Norway													
Number	228	228	228	228	228	228	228	228	228	228	228	228	
Min	0.036	0.016	0.19	1.80	78.4	0.021	0.44	0.28	0.31	8.07	98.4	0.007	
Max	4.72	1.33	16.9	374	8125	0.27	547	22.2	14.4	409	3048	0.38	
Mean	0.17	0.12	1.08	7.24	488	0.060	5.11	2.15	1.64	36.3	569	0.081	
Median	0.13	0.082	0.66	4.20	307	0.056	1.09	1.58	1.19	31.1	461	0.067	
90th percentile	0.23	0.23	1.98	7.26	811	0.088	2.41	4.70	2.56	56.1	907	0.17	
Poland													
Number	197	117	197	196	197	166	167	196	197	197	80	80	117
Min	0.0007	0.050	0.45	3.20	119	0.027	1.23	1.35	0.32	5.54	105	0.052	0.68
Max	15.8	11.6	21.5	197	4600	0.091	13.7	206	10.1	238	4780	0.75	2.38
Mean	0.51	0.58	3.87	10.1	698	0.047	3.62	10.9	1.79	54.7	1249	0.21	1.48
Median	0.38	0.21	2.22	7.60	535	0.045	2.94	4.98	1.59	50.6	967	0.20	1.44
90th percentile	0.83	1.26	10.0	15.2	1133	0.068	6.59	19.7	2.78	87.6	2833	0.30	1.98

	As	Cd	Cr	Cu	Fe	Hg	Ni	Pb	V	Zn	Al	Sb	N (%)
Romania													
Number	214	203	214	203	214		214	203	214	214	214	214	112
Min	0.027	0.024	0.92	0.81	150		0.68	0.33	0.73	10.8	548	0.027	0.81
Max	9.33	3.10	55.4	122	23900		27.8	63.7	65.1	393	40000	3.78	2.88
Mean	1.65	0.48	9.75	11.9	3360		5.16	5.51	8.87	47.7	5694	0.30	1.67
Median	1.08	0.27	4.72	5.77	1535		3.11	4.20	4.32	40.1	2895	0.20	1.64
90th percentile	3.74	0.94	26.5	27.1	8715		11.4	9.72	20.8	78.1	13870	0.59	2.27
Russian Federation													
Number	419	252	403	51	419		400	51	404	419	374	419	
Min	0.028	0.044	0.050	1.55	56		0.52	0.12	0.15	18.1	81.9	0.016	
Max	5.11	4.78	301	20.7	16200		23.6	7.94	50.3	342	27100	13.2	
Mean	0.66	0.44	9.44	6.61	1683		3.78	1.05	4.75	50.3	2866	0.25	
Median	0.49	0.28	4.13	6.03	925		2.55	0.81	2.65	43.1	1450	0.14	
90th percentile	1.25	0.92	17.5	9.96	3402		7.68	1.77	10.3	78.6	6918	0.38	
Serbia													
Number	212	212	212	212	190		212	212	212	212	212	212	
Min	0.16	0.050	0.006	3.25	275		0.62	0.36	0.91	8.33	358	0.02	
Max	71.1	0.99	60.8	213	10119		90.6	460	21.5	115	11000	2.20	
Mean	1.35	0.21	4.64	12.7	1280		5.59	9.69	3.49	25.6	1419	0.11	
Median	0.73	0.18	3.21	8.75	1019		3.12	4.31	2.72	22.4	1021	0.078	
90th percentile	1.78	0.32	8.75	22.8	2184		7.56	12.6	5.88	40.3	2442	0.16	
Slovakia													
Number	68	62	68	68	68		68		68	68	68	68	68
Min	0.15	0.092	0.73	4.56	149		0.76		0.60	25.6	251	0.067	0.85
Max	2.62	0.89	26.6	67.5	5850		21.8		10.2	161	5580	1.06	3.96
Mean	0.62	0.30	3.81	10.8	859		2.77		2.03	47.2	1037	0.29	2.07
Median	0.46	0.26	2.78	9.65	673		2.26		1.50	43.0	706	0.22	1.98
90th percentile	1.18	0.47	5.87	15.0	1315		4.42		3.37	67.4	1922	0.49	2.82
Slovenia													
Number	55	55	55	55	55	55	55	55	55	55	55	55	55
Min	0.099	0.065	0.62	3.24	288	0.021	0.62	1.57	1.06	13.4	449	0.008	0.043
Max	1.14	0.76	10.8	11.2	4459	0.11	7.59	48.9	11.9	44.7	8194	0.39	2.10
Mean	0.22	0.24	1.86	4.79	691	0.037	2.06	4.47	2.34	25.0	1106	0.059	1.21
Median	0.16	0.20	1.08	4.53	465	0.034	1.75	3.10	1.77	24.1	760	0.051	1.11
90th percentile	0.37	0.36	3.66	6.35	1218	0.049	3.20	6.52	3.83	33.7	1894	0.076	1.59
Spain (Rioja)													
Number	25	25	25	25	25	25	25	25	25	25	25	25	25
Min	0.39	0.045	0.28	1.51	236	0.018	0.37	0.57	0.70	11.5	490	0.031	0.60
Max	1.45	0.77	3.41	12.9	1150	0.038	5.91	1.58	2.36	28.4	2020	0.15	1.20
Mean	0.70	0.20	2.03	4.90	502	0.027	1.31	0.98	1.25	18.5	928	0.067	0.80
Median	0.62	0.12	1.92	3.99	428	0.026	1.16	0.97	1.12	18.0	834	0.071	0.80
90th percentile	1.11	0.42	2.99	8.76	748	0.035	1.61	1.29	1.92	25.7	1394	0.087	0.90

	As	Cd	Cr	Cu	Fe	Hg	Ni	Pb	V	Zn	Al	Sb	N (%)
Sweden													
Number	610	611	585	611	611	594	607	611	611	611	611		48
Min	0.016	0.031	0.080	1.40	32.0	0.020	0.15	0.190	0.066	15.0	19.0		0.50
Max	0.59	0.55	9.70	21.0	940	0.16	4.10	22.0	3.30	140	930		1.72
Mean	0.074	0.12	0.39	4.16	137	0.037	0.49	1.27	0.50	34.8	127		0.90
Median	0.069	0.11	0.26	3.90	110	0.035	0.45	1.10	0.44	34.0	110		0.84
90th percentile	0.12	0.18	0.66	5.60	230	0.054	0.70	2.00	0.86	46.0	210		1.38
Switzerland													
Number	73	73	73	73	73	73	73	73	73	73	73	73	55
Min	0.058	0.028	0.36	3.54	155	0.015	0.33	0.61	0.39	14.1	154	0.038	0.71
Max	1.49	0.48	3.89	10.9	1573	0.079	4.99	19.6	3.97	95.1	1887	0.23	2.03
Mean	0.19	0.14	1.07	5.25	417	0.031	1.32	2.90	1.23	30.3	454	0.088	1.21
Median	0.14	0.12	0.85	4.84	314	0.030	1.12	2.13	1.05	27.0	318	0.083	1.15
90th percentile	0.33	0.23	1.97	6.86	691	0.043	2.17	4.35	2.06	47.3	783	0.13	1.63
Tajikistan													
Number	29	29	29	29	29		29	29	29	29	29	29	
Min	1.10	0.14	7.06	6.13	1260		2.85	0.61	5.28	22.2	2680	0.21	
Max	51.6	2.61	68.5	54.0	21400		25.4	18.7	57.0	98.3	34400	24.5	
Mean	10.9	0.60	24.2	16.0	8889		11.9	7.59	27.7	52.5	17029	3.10	
Median	6.42	0.36	23.2	13.2	8280		11.4	6.90	27.0	50.9	15700	1.50	
90th percentile	23.3	1.23	34.5	22.8	16700		18.2	13.2	42.6	76.9	31980	6.61	
Turkey (North)													
Number	42	3	67	67	67		67		67	67	67	2	
Min	1.20	0.22	0.45	11.2	843		2.28		1.63	40	704	2.12	
Max	20.7	0.42	117	239	11098		18.0		17.8	945	12977	2.37	
Mean	3.77	0.29	9.05	39.9	3050		6.41		5.44	139	2440	2.25	
Median	3.21	0.23	2.84	28.3	2239		6.10		4.68	97	1860	2.25	
90th percentile	4.94	0.38	15.2	78.5	5558		10.2		10.6	248	3831	2.35	
Ukraine													
Number	26	91	116	91	117		117	91	116	117	117	117	
Min	0.39	0.10	0.082	2.97	245		0.65	1.51	0.268	14.5	221	0.034	
Max	3.09	0.70	19.9	29.6	7260		11.9	9.83	21.8	106	14000	0.50	
Mean	0.91	0.33	3.90	12.5	1075		3.52	4.12	3.49	35.8	1692	0.20	
Median	0.70	0.31	3.65	10.4	700		2.89	3.81	2.52	33.7	938	0.19	
90th percentile	1.70	0.51	6.33	21.2	1922		5.77	6.75	6.26	50.4	3526	0.31	
Vietnam													
Number	31	31	31	6	31		31		31	31	31	31	
Min	0.99	0.25	2.12	37.2	1120		1.09		2.55	75.8	1010	0.32	
Max	11.6	3.77	31.2	83.6	19600		12.6		57.4	786	15300	2.06	
Mean	3.13	1.96	12.9	53.4	4446		5.27		11.7	212	5275	1.21	
Median	2.74	2.03	13.1	49.5	3730		4.82		8.15	167	4260	1.20	
90th percentile	4.65	3.34	21.2	71.1	6630		9.58		16.6	456	8760	1.65	

Annex 4. POPs concentrations in mosses in 2015/2016

	SUM EPA 16 [ng/g]	SUM PAH 4 [ng/g]	SUM Borneff 6 [ng/g]	SUM PCB 7 [pg/g]	SUM Dioxin-like PCBs [pg/g]	SUM DDT [pg/g]
Austria						
Sampling points	26	26	26			
Min	81.9	3.04	7.32			
Max	183	17.8	46.8			
Mean	122	9.11	25.5			
Median	121	8.40	27.7			
90th percentile	146	16.5	38.5			
½ LOD	7.43	1.25	2.50			
Quantification frequency (%)	95.9	90.4	93.6			
Germany [1]						
Sampling points	8	8	8	8	8	
Min	7.56	1.44	2.40	328	16.5	
Max	53.7	13.0	25.7	594	41.9	
Mean	25.4	6.74	11.7	448	27.7	
Median	24.3	6.07	11.0	429	26.5	
90th percentile	37.1	11.4	19.4	557	38.9	
½ LOD	1.37	0.20	0.30	163	7.09	
Quantification frequency (%)	78.1	100	100	17.9	49.0	
Ireland [2]						
Sampling points	9	9	9	9		
Min	9.01	0.78	1.72	140		
Max	42	2.01	9.86	495		
Mean	23.9	1.38	6.13	288		
Median	23.4	1.21	6.11	222		
90th percentile	40.2	1.89	9.79	489		
½ LOD	0.80	0.20	0.30	70.0		
Quantification frequency (%)	47.2	25.0	33.3	39.7		
Latvia						
Sampling points	20	20	20			
Min	49.3	4.15	10.9			
Max	226	36.9	64			
Mean	90.3	16.2	29.5			
Median	80.3	15.2	26.8			
90th percentile	109	21.9	38.6			
½ LOD						
Quantification frequency (%)	98.4	100	100			

[1] Benzo(b/j)fluoranthenes was taken into calculation instead Benzo(b)fluoranthenes

[2] Chrysene/Triphenylene was taken into calculation instead of Chrysene; PCB-31/28 was taken into calculation instead of PCB 28

	SUM EPA 16 [ng/g]	SUM PAH 4 [ng/g]	SUM Borneff 6 [ng/g]	SUM PCB 7 [pg/g]	SUM Dioxin-like PCBs [pg/g]	SUM DDT [pg/g]
Norway						
Sampling points	20	20	20	20		20
Min	31.2	1.19	3.79	94.4		386
Max	171	64.1	103	747		477
Mean	57.9	12.3	21.8	159		395
Median	40.2	4.31	8.27	117		386
90th percentile	105	33.5	55.9	194		416
½ LOD	14.7	0.12	1.23	36.3		192
Quantification frequency (%)	62.2	100	92.5	65.0		4.17
Spain (Rioja) [1]						
Sampling points	25	25	25			
Min	22.9	1.41	4.29			
Max	74.9	10.9	15.8			
Mean	47.6	3.89	7.94			
Median	44.7	2.99	6.30			
90th percentile	63.0	7.60	13.2			
½ LOD	4.75	0.71	1.58			
Quantification frequency (%)	47.8	31.0	48.0			
Sweden						
Sampling points	20	20	20	20		
Min	23.4	3.14	5.80	830		
Max	132	38.3	69.3	2150		
Mean	74.3	18.8	34.7	1342		
Median	77.3	21.1	38.5	1275		
90th percentile	125	33.6	62.2	1859		
½ LOD						
Quantification frequency (%)	83.8	98.8	98.3	25.0		
Switzerland [2]						
Sampling points	22	22	22	22		
Min	105	5.88	13.0	299		
Max	235	46.6	84.8	2009		
Mean	147	17.4	35.5	548		
Median	138	14.8	28.8	464		
90th percentile	194	30.8	60.4	808		
½ LOD	43.3	1.50	5.00	75.5		
Quantification frequency (%)	85.2	98.5	97.3	87.7		

[1] Benzo(b/j)fluoranthenes was taken into calculation instead of Benzo(b)fluoranthenes
[2] Benzo(b/k)fluoranthen was taken into calculation instead of Benzo(b)fluoranthenes and Benzo(k)fluoranthenes

	SUM EPA 16	SUM PAH 4	SUM Borneff 6	SUM PCB 7	SUM Dioxin-like PCBs	SUM DDT
Compounds	Naphtalene	benzo[b]fluoranthene	Fluoranthene	PCB 28	PCB 77	o.p'-DDE
	Acenaphthylene	benzo[k]fluoranthene	Benzo(b)fluoranthenes	PCB 52	PCB 81	p,p'-DDE
	Acenaphthene	benzo[a]pyrene	Benzo(k)fluoranthenes	PCB 101	PCB 105	o,p'-DDD
	Fluorene	indeno[123-cd]pyrene	Benzo(a)pyrene	PCB 118	PCB 114	p,p'-DDD
	Phenanthrene		Indeno(1,2,3-cd)pyrene	PCB138	PCB 118	o,p'-DDT
	Anthracene		Benzo(ghi)perylene	PCB153	PCB 123	p,p'-DDT
	Fluoranthene			PCB180	PCB 126	
	Pyrene				PCB 156	
	Benzo(a)anthracene				PCB 157	
	Chrysene				PCB 167	
	Benzo(b)fluoranthenes				PCB 169	
	Benzo(k)fluoranthenes				PCB 189	
	Benzo(a)pyrene					
	Indeno(1,2,3-cd)pyrene					
	Dibenzo(ah)anthracene					
	Benzo(ghi)perylene					

Annex 5. Country reports

This part brings together the reports from national experts participating in the moss survey. The content of the reports are the sole responsibility of the national experts. The content of national reports have not been checked or edited by the Moss Survey Coordination Centre or the ICP Vegetation Programme Coordination Centre.

Albania

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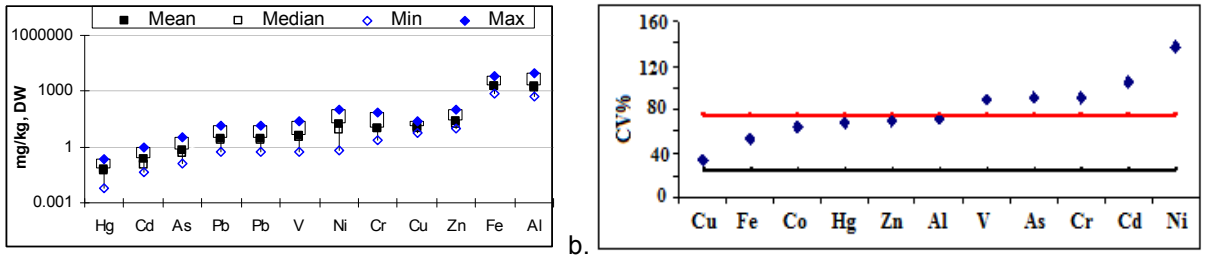
Background

Moss biomonitoring in Albania started with 2010/2011 when researchers from Albania joined the European Moss Survey conducted within the framework of the International Cooperative Programme on Effects of Air Pollution on Natural Vegetation and Crops, ICP Vegetation. 20 elements were analyzed by ICP/AES and 46 by ENAA methods in mosses (*Hypnum cupressiforme and Pseudoscleropodium purum*) collected in a regular grid (25 km x 25 km) once a year (beginning of autumn) from 44 monitoring sites in whole territory of Albania. The results of moss samples have been reported in several publications. Only Al, As, Cd, Cr, Cu, Fe, Hg, Ni, Pb, V are reported to ICP Vegetation Programme. The survey is done each five years (from 2010 to 2015) to study general patterns of air pollution by using the moss as biomonitor. The number of sampling sites is increased to 56 during 2015 moss survey of Albania. This survey was done without specific funding and under the lack of a national supporting budget. It was overcome by Ph.D. Programme of University of Tirana and the collaboration with other Institute of Chemistry, Faculty of Science, Ss. Cyril and Methodius University, Skopje, Macedonia and Frank Laboratory of Neutron Physics, Joint Institute for Nuclear Research, Dubna, Russian Federation for the analysis of moss samples.

Metal concentrations in mosses

The target elements in this study were Al, As, Cd, Cr, Cu, Fe, Hg, Ni, Pb, V and Zn. The results of the descriptive statistical analysis of the trace elemental concentrations are shown in Figure 1.



a. b.

Figure 1. The Box Plot of the data of descriptive statistical analysis of the trace elemental concentrations (a) and CV% data (b).

The metal concentration in moss samples based on the mean values follows the trend Hg<Cd<As<Li<Pb<V<Cr< Ni<Cu<Zn< Fe<Al. V, As, Cr, Cd and Ni show high variation (CV % > 75 %). The distribution maps of some important metals are shown in Figure 2.

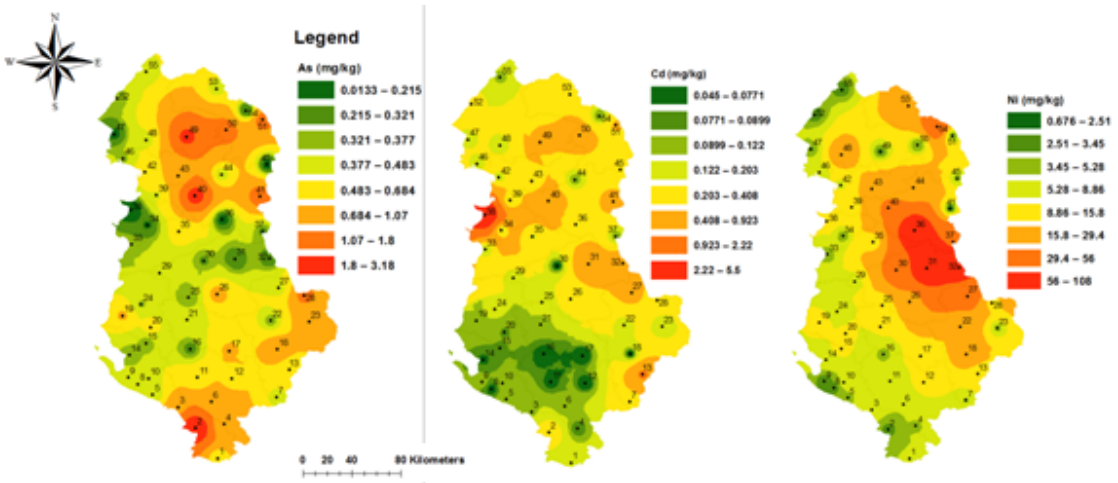


Figure 2. GIS distribution maps of As, Cd and Ni in 2015 mosses sampled of Albanai (Note: Black dots on the map are the sampling sites).

Temporal trends: The 2010 European moss survey has demonstrated that median heavy metal concentrations on mosses between 1990 and 2010 have declined for As, V, Cd, Cr, Zn, Ni, Fe, and Pb, whilst it remained high particularly in Eastern Europe and the Balkan countries. The concentration level of Hg in moss samples of Albania is highly decreased on 2015 compared to 2010. The concentration level of Co, Pb, Li, V and Al is decreased on 2015 compared to 2010; whilst the concentrations of Cd, As, Ni, Cr, Cu and Fe in 2015's moss samples of Albania is increased compared with 2010's.

Discussion and conclusions

The spatial distribution of metals in moss samples is used to investigate the extent of the national background level and the areas with high concentration of the elements. In general, the highest levels of metals concentrations correspond to the East part of the country. The presence of mining industry and the loss of landscape due to mining, processing and mineral transport are important factors in determining metal distributions. The lower level of trace metals concentrations is located in the coastal area (Western part of the country). It is polluted mostly by elements linked mostly with oil and gas industry, shipping activity and traffic emission. Higher level of elements (Cd, As, Ni, Cr, Cu and Fe) on 2015 compared to 2010 indicates high emission level of these elements in environment. For environmental and human health protection, the monitoring of trace elements atmospheric deposition should be continued.

Further reading

Lazo P, Steinnes E, Qarri F, Allajbeu Sh, Kane S, Stafilov T, Frontasyeva, Harmens H (2017) Origin and spatial distribution of metals in moss samples in Albania: A hotspot of heavy metal contamination in Europe. Chemosphere. //doi.org/10.1016/j.chemosphere.2017.09.132

Allajbeu Sh, Qarri F, Marku E, Bekteshi L, Ibro V, Frontasyeva MV, Stafilov T, Lazo P (2017) Contamination scale of atmospheric deposition for assessing air quality in Albania evaluated from most toxic heavy metal and moss biomonitoring. Air Qual. Atmos. Health 10, 587-599.

Bekteshi L, Lazo P, Qarri F, Stafilov T (2015). Application of normalization process in the survey of atmospheric deposition of heavy metals in Albania by usingmoss biomonitoring. Ecol. Indic. 56, 48-59.

Harmens H, Norris DA, Sharps K, Mills G, Alber R, Aleksiayenak Y, Blum O, Cucu-Man SM, Dam M, De Temmerman L, Ene A, Fernandez JA, Martinez-Abaigar J, Frontasyeva M, Godzik B, Jeran Z, Lazo P, Leblond S, Liiv S, Magnússon SH, Mankovska B, Pihl Karlsson G, Piispanen J, Poikolainen J, Santamaria JM, Skudnik M, Spiric Z, Stafilov T, Steinnes E, Stihi C, Suchara I, Thoni L, Todoran R, Yurukova L, Zechmeister HG (2015). Heavy metal and nitrogen concentrations in mosses are declining across Europe whilst some "hotspots" remain in 2010. Environ. Pollut. 200, 93-104

Qarri, F., Lazo, P., Stafilov, T., Frontasyeva, M., Harmens, H., Bekteshi, L., Baceva, K., Goryainova, Z., 2013. Multi-elements atmospheric deposition study in Albania. Environ. Sci. Pollut. Res. 21, 2486-2518.

Armenia

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Background

The Republic of Armenia (38°51´- 41°18´N and 43°27´- 46°37´E) is situated in the South-West of Asia between the Black Sea and the Caspian Sea, and northeast of the Armenian Highlands. The country occupies the north-eastern part of Armenian plateau - between Caucasus and Nearest Asia (the inter-river territory between the middle flows of Kur and Araks rivers). The total territory of the country is 29743 km^2 of which 11.2 % are forests, 11.3 % are areas of special preservation, 68.8 % are agricultural lands, and 8.7 % are classified as other lands. The highest elevation of the country is the Peak of Aragats Mountain (4090 m), the deepest landslide - the Debed river canyon (379 m). In the north and east, it borders with Georgia and Azerbaijan, and in the west and south - Turkey and Iran. The longest extension from northwest to the southeast is 360 km, and from west to east - 200 km.

In the Republic of Armenia environmental studies using mosses started in 2016 based on the agreement signed between The Center for Ecological-Noosphere Studies (CENS), NAS RA and Sector of Neutron Activation Analysis and Applied Research (SNAA&AR) of the Frank Laboratory of Neutron Physics (FLNP) of Joint Institute for Nuclear Research (JINR), Dubna, Russia.

During the September-December of 2016, 37 moss samples (*Homalothecium philippeanum, Syntrichia ruralis, Ptilium crista castrensis, Brachythecium rutabulum, Brachythecium reflexum)* were collected. Among all studied moss species the most abundant was *Syntrichia ruralis* (22 samples). This study was done in order to establishing moss monitoring network and reveal the spatial distribution peculiarities of atmospheric deposition of trace elements in Armenia.

Concentrations of chemical elements

Totally 42 elements were determined from which 39 (*Na, Mg, Al, Cl, Ca, K, Sc, Ti, V, Cr, Fe, Mn, Co, Ni, Zn, As, Se, Br, Rb, Sr, Mo, Sb, I, Cs, Ba, La, Ce, Nd, Sm, Eu, Tb, Dy, Tm, Ta, W, Au, Th, U and Hf*) by instrumental epithermal neutron activation analysis and 3 (*Cu, Cd and Pb*) using atomic absorption spectrometry. From all studied elements *K, Ca, Dy and Eu* follow normal and *Na, Mg, Al, Cl, Sc, Ti, V, Cr, Fe, Mn, Co, Ni, Cu, Rb, Sr, Sb, Cs, Ba, La, Ce, Sm, Tb, Tm, Ta, W, Th, U and Hf* lognormal distribution. Zn, As, Se, Br, Mo, Cd, Sb, I, Nd and Au showed abnormal distribution indicating the presence of outliers and extreme values.

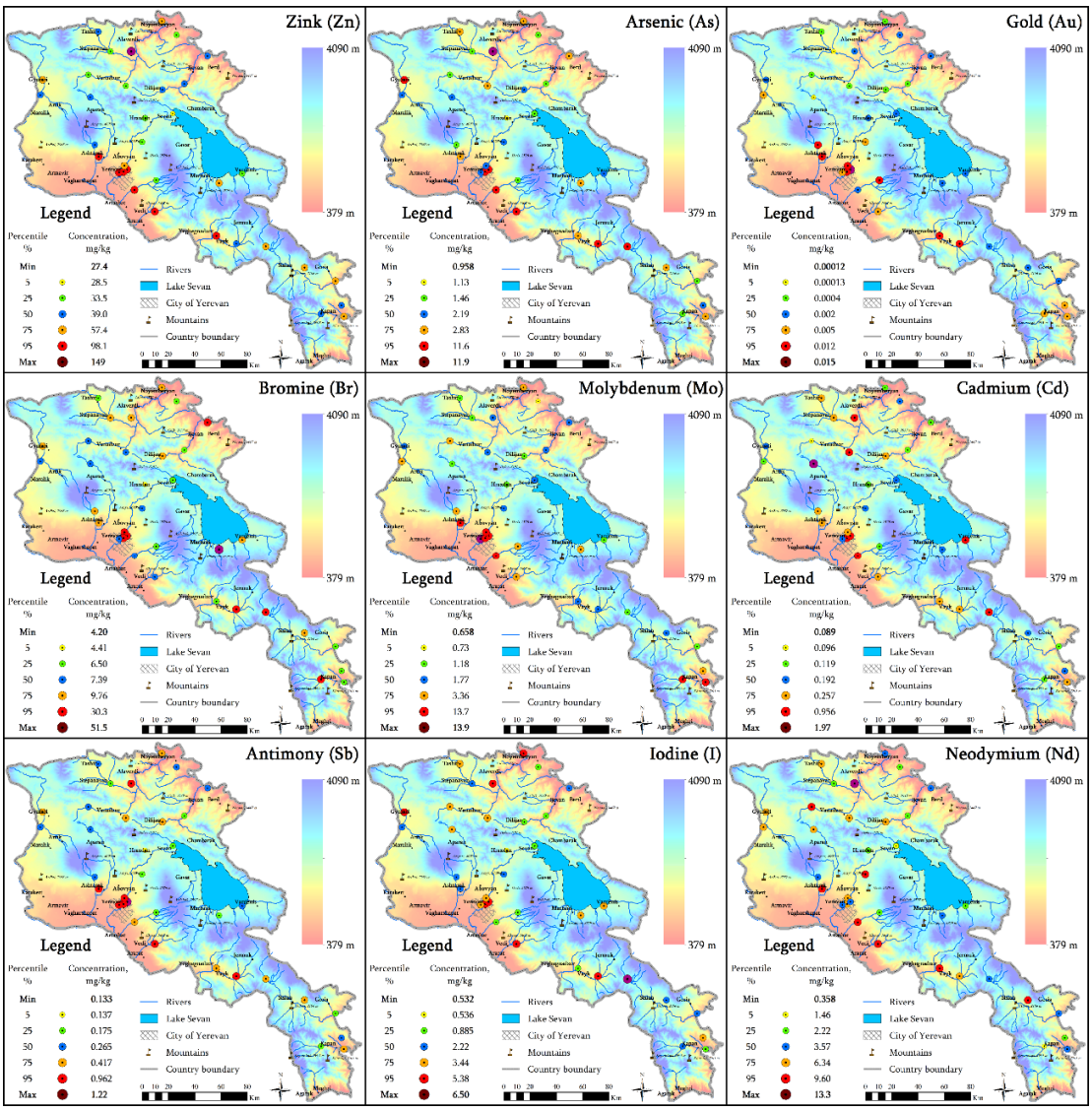

Figure 1. Spatial distribution of Zn, As, Se, Br, Mo, Cd, Sb, I and Nd in mosses in Armenia.

The spatial distribution patterns of these elements (Fig. 1) showed that the high (>95%) values Mo are spatially allocated near and in city Yerevan area where Mo concentrate smelting plant is operating, as well as in the southern part of Armenia where is located Kajaran Cu-Mo open pit mine. High (>95%) values of Zn, As, Sb, Nd and Au are mainly located in the southern central part of the country where the geological base of sampling sites characterized by sandstones, limestones and clay facies to the volcanogenic rocks of Palaeogenic system. In addition to the natural concentrations of these elements the southern central part of Armenia are known by the diatomite, marble, limestone, travertine, phosphorite mining, gold extraction plant, as well as deposits of Zn, As and Sb. In the case of Br and I values >75% are spatially located in the northern part of Armenia and supposed to be the results of atmospheric precipitations from the Black Sea and in the southeastern part influenced by the Caspian Sea.

According to the Cluster Analysis three distinct groups were observed. Cluster I included La, Ce, Sm, Tb, Hf, Ta, Cs, Th, Ba, Tm, As, Nd, Cr, Eu, Co, Fe, W, Ni, U, Rb, K, Na, Dy, Sr, Mg, Al, Ti, V and Sc which supposed to be associated with the soils mineral particles suggesting that elements in the cluster I are naturally distributed.

Cluster II included Zn, Sb, Cu, Pb, I and Cd while cluster III consisted of Cl, Br, Mo, Au, Se and Ca. Elements included in II and III clusters supposed to have a mixed origin as Zn, Sb, Cu, Pb, Cd and Mo are included in the long-range atmospheric transport and Cl, Br, I, Se and Ca in the natural cycling processes categories, as well as may have some contribution from the local sources of pollution.

Discussion and conclusions

The study revealed that from all studied elements only Zn, As, Se, Br, Mo, Cd, Sb, I, Nd and Au do not follow the normal distribution. Moreover, the boxplots of these elements confirms the presence of outliers and extreme values. The detailed inspection of spatial distribution maps showed that manmade sources of elements in Armenia are mainly associated with the mining industry. Therefore, the moss biomonitoring technique allows revealing the spatial distribution peculiarities of atmospheric deposition of trace elements in Armenia and identifies their possible sources. The latter highlight the need to expand moss monitoring network to efficiently investigate the atmospheric deposition of chemical elements in Armenia.

Austria

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Background and Methods

Austria has been participating in the European monitoring of atmospheric heavy metal pollution since 1991, starting with a pilot study, testing various parameters like differences in moss species or altitudes of sampling sites. Since 1995, 220 sampling sites were investigated every five years. For cost reasons in 2015 a reduction of the sampling points from 220 to 75 was made. For 50 sampling sites the relevant selection was made based on statistical procedures in order to make this sampling period comparable to previous studies. Data of these 50 sites were passed on to ICP Vegetation. Additionally, 25 points were subjectively selected, focusing on locations that were striking in previous sampling periods. The collection of samples was carried out from July 20 to September 10, 2015. For monitoring the moss species *Pleurozium schreberi* was primarily (26 samples) used, additionally used species were *Hylocomium splendens* (19), *Hypnum cupressiforme* (18), *Abietinella abietina* (8) and *Pseudscleropodium purum* (4).

Heavy metals, aluminium, nitrogen and sulfur were investigated. A microwave-assisted total digestion with nitric acid, hydrogene peroxide, hydrofluoric acid followed by boric acid complexation for analysis of elements (except nitrogen) was performed. Digests were analyzed for aluminum (Al), chromium (Cr), copper (Cu), iron (Fe), sulfur (S) and zinc (Zn) by means of ICP-OES, cadmium (Cd), cobalt (Co), nickel (Ni), molybdenum (Mo), lead (Pb), vanadium (V), by ICP-MS, mercury (Hg) by CV-AAS, arsenic (As) by FI-GF-AAS and antimony (Sb) by GF-AAS. Total nitrogen was determined by elemental analysis.

For the first time all 16 EPA-PAHs as well as coronene, retene and nitro-pyrene were analyzed. For this purpose, Soxhlet extraction (n-Hexane) was used, followed by analysis using GC-MS-MS.

Results

At large a decline of metal depositions could be observed in Austria. Except for As and Cr all the elements showed a significant decrease since 1995 (see e.g. Cd in Fig.1). However, this should not cover, that certain elements have increased at least slightly since 2010 (Co, Fe, Mo – Figure 1).

In general, current atmospheric metal deposition in Austria is low. Concern is however, that in some locations, with far above average highs in Austria, and some of these values are maximum values even in Europe, for many years these values exhibit unchanged and in some cases they were even increased. These regions are around Treibach/Althofen (metallurgical industry) and the region in the Northeast of Vienna with intensive agriculture, oil production and inputs from the capitals Vienna and Bratislava. There are some other regions like the densely populated Rhein-Valley and Inn Valley or areas with well known industrial complexes, too.

Due to these incoherencies to the general trend, a continuation of the moss-monitoring would be of high relevance because it delivers the underlying data evidence to apply appropriate measures to protect their habitats.

The results of the PAH analysis were affected by extremely deviating and diverse climatic conditions before and during the collection (heat, heavy rainfall, photodegradation by very high levels of ozone). Nevertheless, the PAHs showed plausibly explainable distribution pattern. The determination of the sources of PAHs on ratio calculations brought good results in many cases too. The comparability with other Austrian studies or international studies was difficult due to the comparatively very low values, which were a result of processes given above. Despite all the problems in this part of the investigation PAH monitoring by mosses would be desirable in future repetitions because these toxic organic substances are a valuable addition to the metals and their human- and eco-toxicological relevance in many other studies was demonstrated.

All results of the 2015 collection have been already published in detail by Umweltbundesamt (2016).

Moss monitoring – what else?

It should not be forgotten that the moss monitoring is a comparable inexpensive method compared to technical measurements. It is the only dense, nationwide monitoring network that has a long time series of data in the case of heavy metals. In terms of results moss monitoring is comparable to technical measurements and is sometimes even superior because of the long accumulation time-space and therefore better analytical accuracy. This applies in particular also for PAHs, where there is currently no comparable, dense measuring network and the existing measuring sites are limited on BaP. Also for this reason, a consolidation of sampling sites would be desirable to levels as there were in the previous studies. This would facilitate the identification of problem regions and the results of these studies can therefore serve as a starting point for regional follow-up studies (in terms of environmental policy, technical or health related).

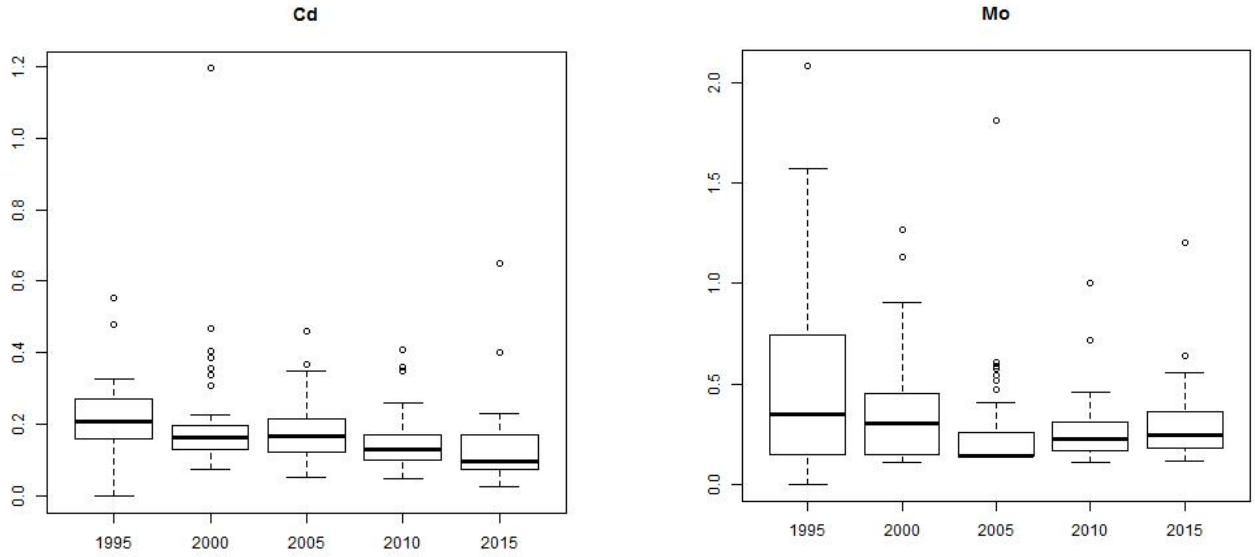

Figure 1. Boxplots of concentrations of Cd and Mo in Austria from 1995 to 2015.

Reference

UMWELTBUNDESAMT (2016): Zechmeister H., Kropik M., Moser D., Denner M., Hohenwallner D., Hanus-Illnar A., Scharf S., Riss A., Mirtl M.: Moos-Monitoring in Österreich. Aufsammlung 2015. Reports, Bd. REP-0595. Umweltbundesamt, Wien. ISBN 978-3-99004-409-4. http://www.umweltbundesamt.at/fileadmin/site/publikationen/REP0595.pdf

Belarus

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Background

For the third time Belarus is participating in the moss survey carried out in the framework of the UNECE ICP ICP Vegetation (Aleksiayenak et al., 2015). Samples of moss species of *Hylocomium splendens* and *Pleurozium schreberi* were collected at 86 sites over the Mogilev, Vitebsk and Minsk Regions in the summer of 2015. Out of 86 sample sites 30 samples were collected in the previously studied areas, other samples covered some new regions. A total of 30 elements were determined by epithermal neutron activation analysis. In general, moss was sampled at 250 sites evenly distributed over nearly the whole territory of the country (Figure 1).

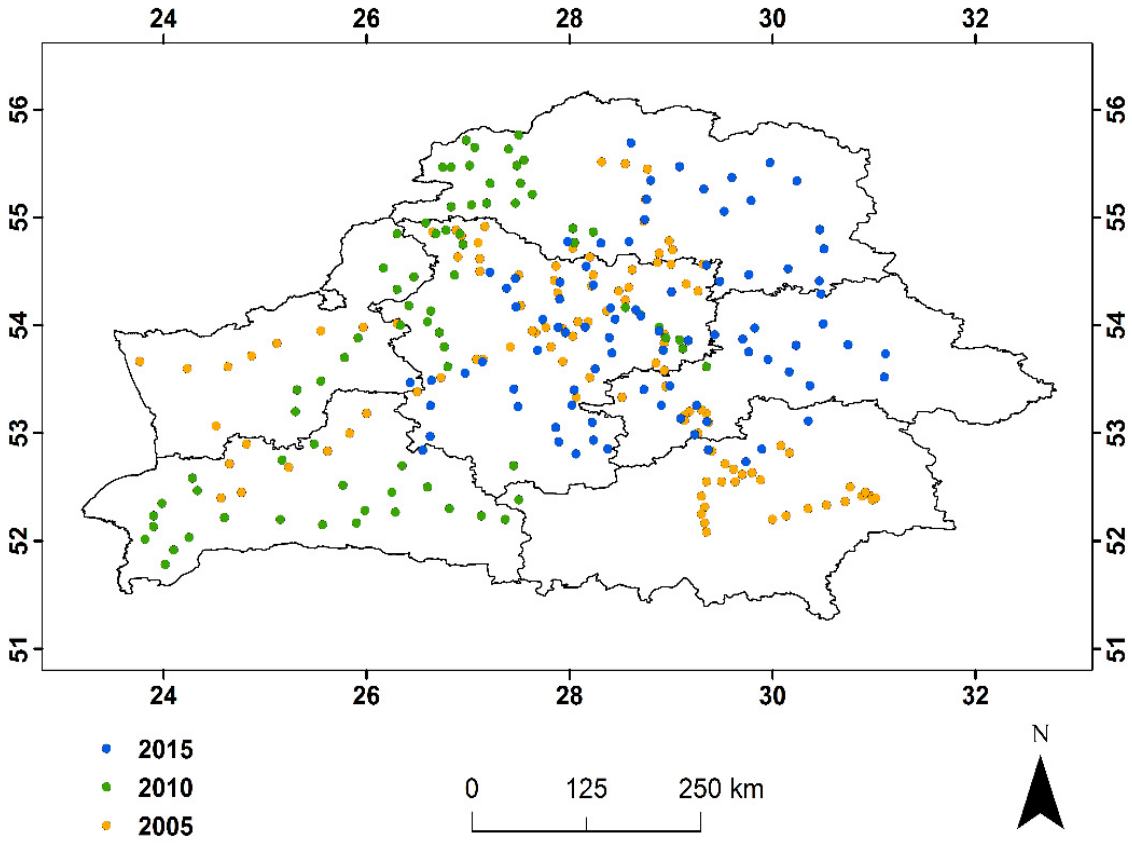


Figure 1. Distribution of the sampling sites.

Results and discussion

Comparison of the median values for V, Cr, Fe, Ni, Zn, As, Al, Sb from the three surveys in Belarus (in 2005/6, 2010/11 and 2015/16), showed a decrease of the content of V and As in the mosses and increase of Cr in 2010. Other elements are mostly at the same levels (Fig.2). Although we noticed the increase of metal concentration at some sampling sites (Fig.3), the comparison of the results for Belarus with the analogous data for the other European countries showed relatively low contamination levels for the most of heavy and toxic elements.

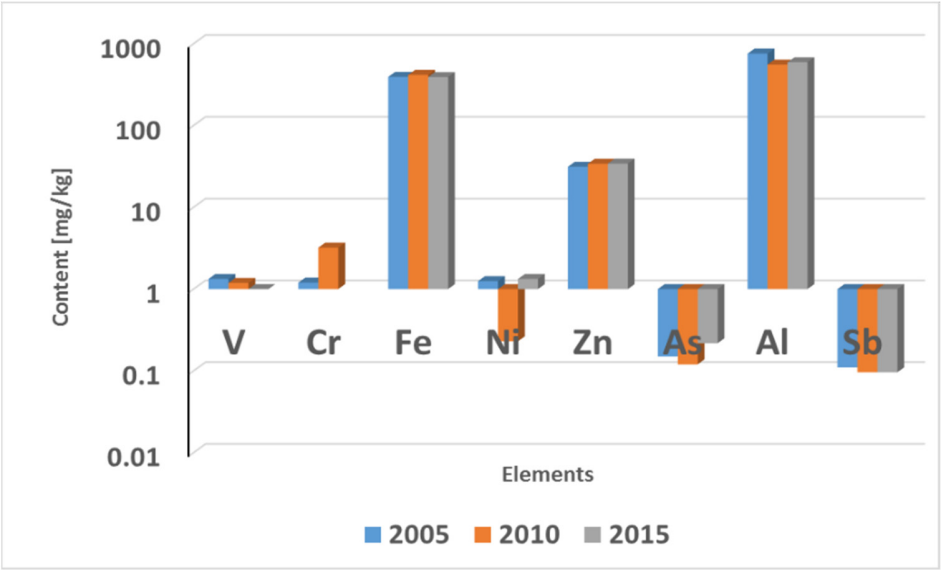
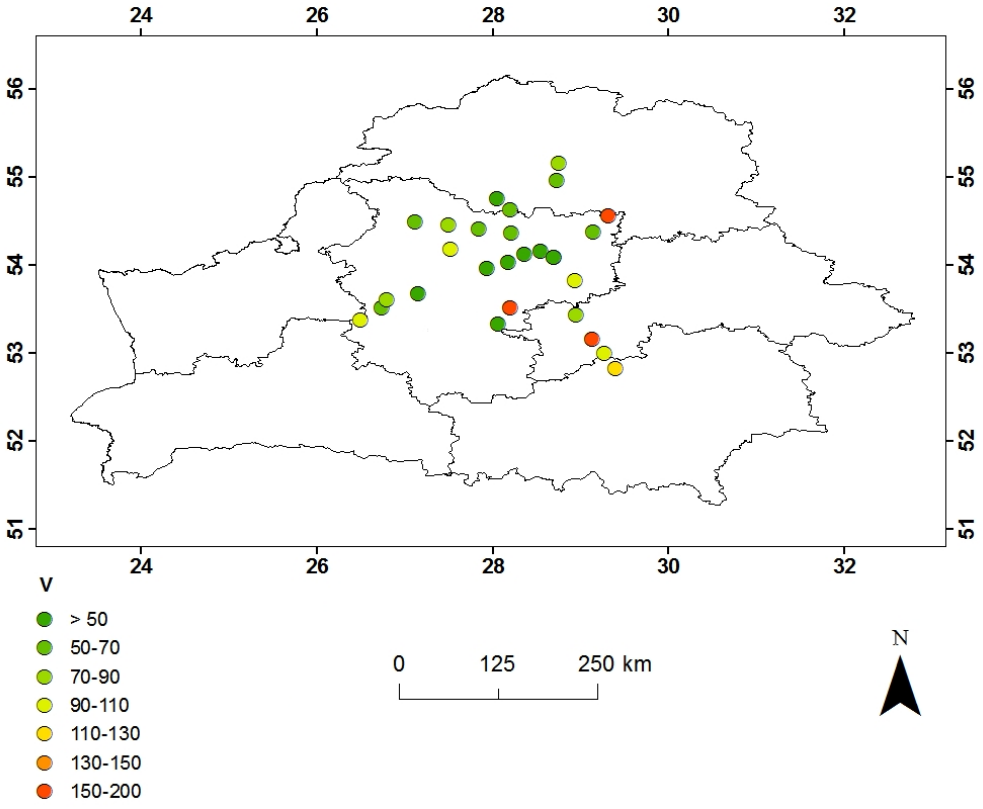


Figure 2. Comparison of the median concentration values [mg/kg] for selected elements determined in 2005, 2010 and 2015 (log scale)



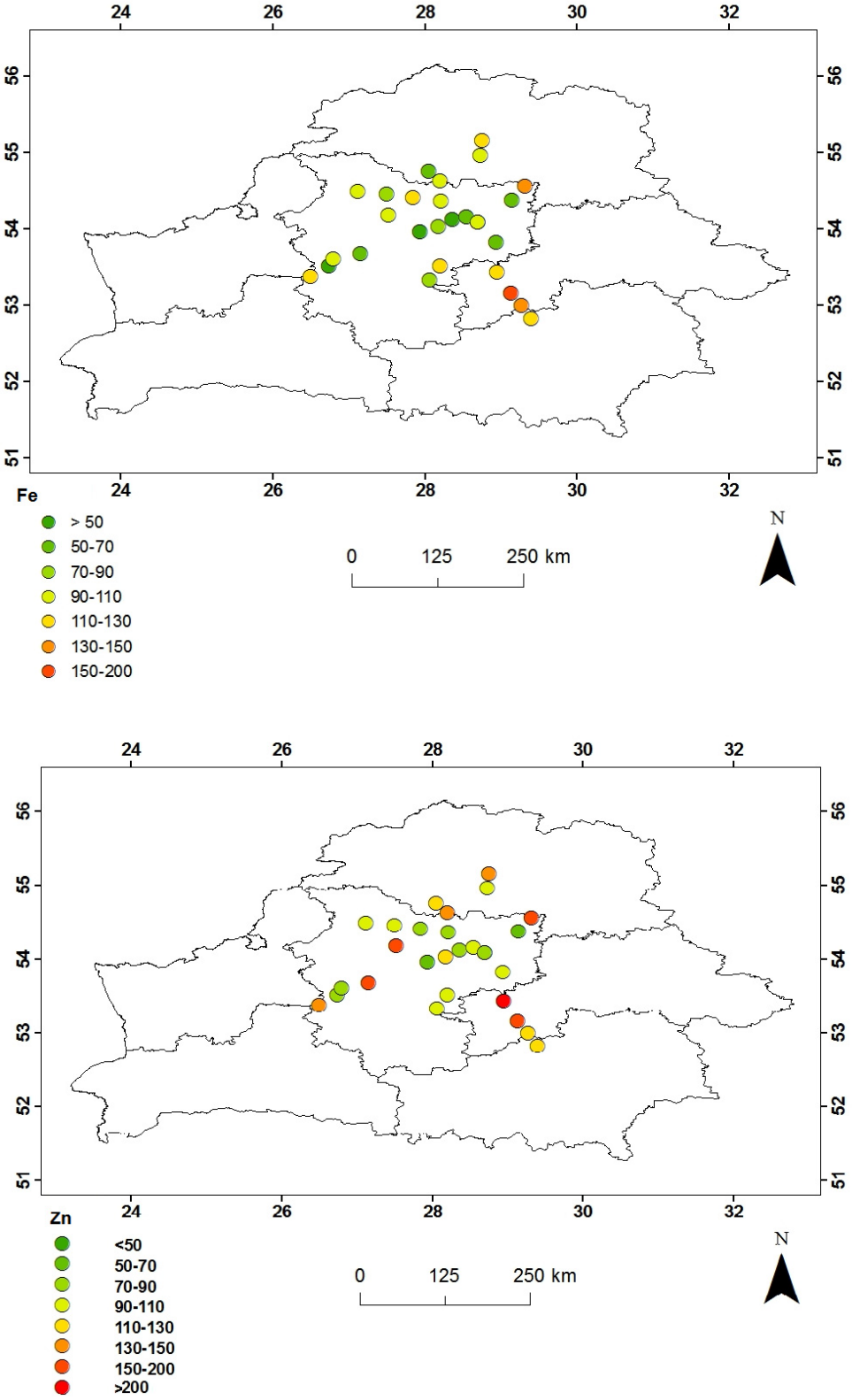


Figure 3. Concentration of V, Fe, Zn in 2015 expressed as percentage of the values in 2005 (% of 2005) at the same sample site

Conclusion

During our ten-year research all Belarusian regions were studied, based on these studies convenient sample net was created for the next moss survey in 2020/21. Median concentrations of the most observed elements has not changed significantly between 2005 and 2015. The exception is average median value of V that has declined by 30 %. What concerns spatial distribution the increase of the element concentrations was observed at some sample sites since 2005. These sample sites are located close to the cities with the machinery and metalworking industries. In general, in comparison with the European data, median concentrations of the studied elements in Belarus are low. Deposition levels for some elements observed in Belarus are comparable with Norwegian data. Still, it is important to continue monitoring heavy metal deposition in order to see long-term spatial and temporal trends.

Reference

Aleksiayenak YuV, Frontasyeva MV, Ostrovnaya TM, Okina OI. Moss biomonitoring technique, NAA and AAS in studying air pollution in Belarus. Problems of regional ecology. 2015;4:126-134 [in Russian].

Bulgaria

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Background

Bulgaria is a participant in the European moss surveying programme since 1995. Sampling has been performed regularly, and the predominant biomonitoring species is *Hypnum cupressiforme*. Due to the typically hot and dry summers, the mountainous terrains, and different member groups partaking in sampling throughout the years, the sampling networks were non-uniform.

Over the past three decades, the country has undergone a shift from a highly centralized, planned economy to an open market-based economy, characterized by slow economic restructuring and growth. The largest industrial enterprises have been closed down, which has greatly reduced local pollution emissions. At present, there are several local hotspots corresponding to contemporary and historical non-ferrous and ferrous facilities, mining and smelting activities.

Still, air quality data collected from state monitoring stations show continuous and systematic exceeding of daily and annual limit values for particulate matter concentrations (PM10) in 25 towns. This is attributed to domestic heating, especially burning wood and coal, vehicle emissions, mainly due to obsolete fleets lacking catalytic converters, and to a lesser extent, electricity production and industrial activities.

Concentrations of heavy metals in mosses

In 2015, 115 moss samples were collected. Concentrations of 34 elements in total were determined using instrumental epithermal neutron activation analysis (NAA) (Al, As, Ba, Br, Ca, Ce, Cl, Co, Cr, Cs, Eu, Fe, Hf, I, K, La, Lu, Mg, Mn, Na, Nd, Ni, Rb, Sb, Sc, Se, Sr, Ta, Tb, Th, Ti, Tm, U, V, W, Yb, and Zn). Three additional elements (Cd, Cu, and Pb) were analysed by means of inductively coupled plasma atomic emission spectroscopy (ICP-ES). Multivariate statistics (factor analysis) was applied to identify associations between the determined elements. Four factors were determined, of which one was interpreted as anthropogenic. Factor 1 was mixed, characterized by earth crust elements (Na (0.66), Mg (0.81), Al (0.74), Sc (0.80), Ti (0.65), V (0.84,) and Fe (0.82)), and marine aerosols (Cl (0.53), Br (0.53), and I (0.61)). Factor 2 contained REEs, U (0.61), and Th (0.84) – typical crust components, indicating presence of soil particles in the samples. Factor 3 had high loadings for As (0.75), Se (0.73), Sb (0.72), and Cu (0.74), which are found in ores. The highest loadings for this factor were for sites located near Cu-Ag mines. Factor 4 had high values for K (0.67) and Ca (0.65), characterizing wet deposition by higher vegetation.

Bulgarian mosses had the highest concentration of Pb (maximal values) for the European moss survey in 1995. Since then, leaded petrol has been phased out. Open quarries and tailings, and an explosion in an ordnance plant in Iganovo (VMZ Sopot) explain the observed maximal values for Pb in 2015. In 2015, the highest concentrations for the elements Al, V, Ni and Fe were determined in three of the border crossing posts with Greece (Kulata, Ivaylovgrad, Zlatograd), along the nearest major roads, and in a site located relatively close to a fossil fuel power station.

Figure 1 shows the temporal trends for metals reported in the moss surveys, with the exception of Sb. Data for this element determined in mosses using INAA in 2000/2001 is available elsewhere, and in 2005/2006 – in the ICP Vegetation thematic report, listed as additional data. Median values have decreased by 52% (from 0.23 mg/kg in 2000, 0.29 mg/kg in 2005, to 0.11 mg/kg in 2015).

A comparison between the reported median values shows that with the exception of As, all reported metals have decreased atmospheric depositions between 1995 and 2010. The median value for As increased sharply in 2010 but has decreased again in 2015 (from 0.2 mg/kg in 1995, 0.21 mg/kg in 2000, 0.2 mg/kg in 2005, 0.63 mg/kg in 2010 and 0.44 mg/kg in 2015). The maximal values for As in 2015 could be attributed to operation activities in cement plants and fossil fuel power stations.

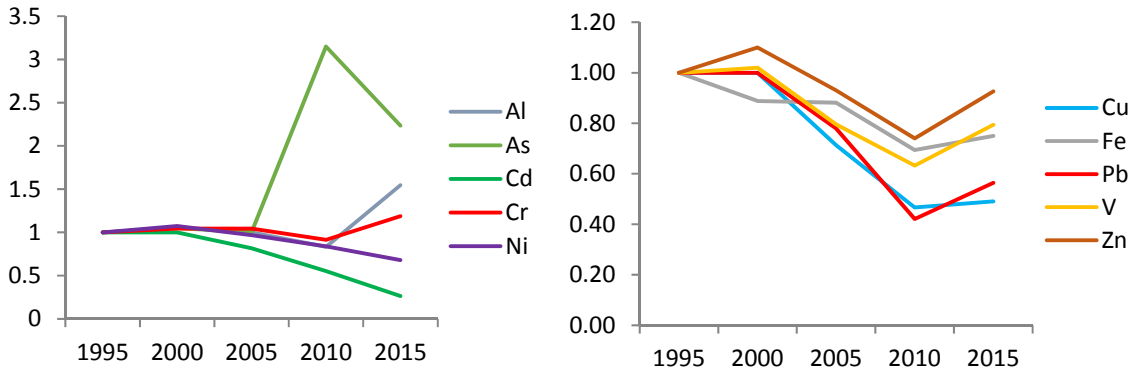

Figure 1. Temporal trends – median values for concentrations of 10 metals, normalized to their values for 1995.

It should be noted that due to the analytical methods applied (ICP-ES until 2010, NAA in 2015), some differences in the results are anticipated. They arise from the sample preparation and sensitivities, and in ICP-ES, refractory compounds in the samples may potentially be omitted. Still, the decreasing trends for Ni and Cd atmospheric depositions are retained in 2015. Fe and Cu have a slightly higher median value in 2015 than in 2010.

Conclusion

In 2010 there was an observation that, in general, since the beginning of Bulgaria's participation in the ICP Vegetation programme in 1995, concentrations of metals deposited from the atmosphere have steadily decreased by about 30%. The most recent survey data do not show continuation of that trend for all elements reported. Following the shutdown of several major industrial facilities and the implementation of better filtering technologies, vehicle fleet renewal and stricter environmental and safety regulations are required to improve air quality.

Further reading

Judgement of the Court (Third Chamber) of 5 April 2017. *European Commission v Republic of Bulgaria*, C-488/15, ECLI:EU:C:2017:267

J. Stamenov et al. New results from air pollution studies in Bulgaria (moss survey 2000-2001). E14-2002-204, JINR, Dubna, Russia, 2002

Canada

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Introduction

This report outlines the Canadian submission to the ICP Vegetation 2015 call for data, and the first time North America is represented under the ICP Vegetation moss biomonitoring program. Three moss species, *Hylocomium splendens*, *Pleurozium schreberi*, and *Isothecium stoloniferum,* were sampled between 2014 and 2016 in the provinces of British Columbia (BC), Alberta (AB), Saskatchewan (SK), Nunavut (NU), and Ontario (ON), and the Northwest Territories (NT). Only *H. splendens* and *P. schreberi* are reported here; all moss tissues were analysed for heavy metal concentrations and a subset (n = 108) were analysed for total mercury (Hg).

Methods

Moss tissues were collected in conjunction with graduate research projects at Trent University, and largely followed survey protocols described in the ICP Vegetation moss monitoring manual. Note that in the dense forests of British Columbia, canopy cover is nearly ubiquitous; where possible mosses were sampled away from canopy. Surveys were conducted between 2014–2015 (123 samples in AB, 20 samples in SK, and eight in the NT, and between 2015–2016 (104 samples in the Kitimat Valley and Prince Rupert, BC, as well as 61 on Baffin Island, NU, and 98 in Muskoka, Sudbury and Warsaw, ON. In total, 414 samples were taken at 327 unique plots (Figure 1).

Unwashed samples were stored in paper bags and oven-dried at 57°C for 70 hours. Dried samples were analyzed for heavy metal and Hg concentrations. Heavy metal concentrations were determined for all samples using a Triple-Quad ICP-MS analyzer following acid digestion (Mars 6 microwave digester). Total Hg was determined for 108 samples using a mercury analyzer (Milestone DMA-80).

Results and discussion

Sample sites with *H. splendens* and *P. schreberi* are evenly split (48% and 52% respectively), although the spatial distribution of dominant species was quite different across the provinces (Figure 1). There was some overlap in distribution, with both species sampled at 86 sites. However, only *H. splendens* was found on Baffin Island, NU. In contrast, *P. schreberi* was the dominant species found at the sites sampled in ON, while both species were sampled in relatively equal proportions in the western provinces.

Since sampling coincided with focused research projects, some of the observed high metal concentrations were due to proximity to smelters. The Sudbury, ON, and Kitimat, BC, sampling regions were near point sources of metals from mining and smelting, while many of the AB and SK sites were in proximity to the Athabasca oil sands. The observed vanadium and cadmium concentrations were generally lower than the European averages reported in 2010–2011 (see Appendix 1, and Harmens et al., 2013). Aluminum and lead concentrations were typically lower, but did have a few high values, particularly elevated aluminum in Kitimat in proximity to the aluminum smelter located in the same valley. Zinc and antimony concentrations were quite consistent with European averages, while arsenic, chromium, and iron means were similar to European values, with elevated values near Sudbury. Mean copper and nickel concentrations were quite high, but averages were driven by high values at some sites (particularly near the nickel and copper roast beds in the Sudbury samples); median values for these two metals were consistent with average European results. Mercury was not analysed in all samples (n=108) but showed elevated values on Baffin Island compared to other regions, likely due to northward movement of Hg. High values of Hg were also found in the Prince Rupert area and Kitimat, likely as a result of proximity to the shipping port in Prince Rupert and the aluminium smelter in Kitimat. Median Hg values across all sites surveyed were slightly lower than the median reported by all European countries in 2010; Hg concentrations had been on a downward trend in Europe from 1995 (Harmens et al. 2013).

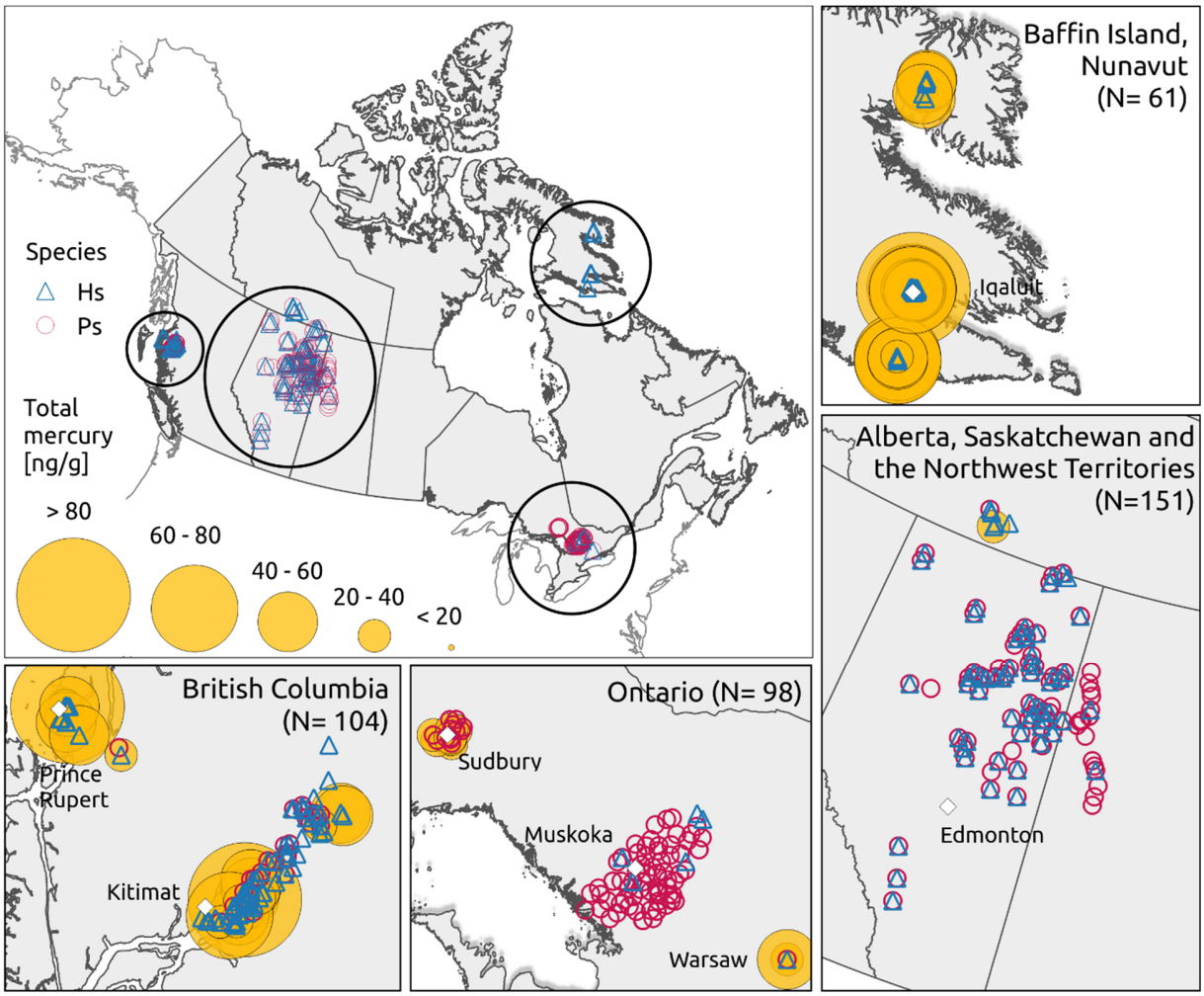

Figure 1. Spatial distribution of *Hylocomium splendens* and *Pleurozium schreberi* sampled between 2014–2016 in British Columbia, Alberta, Saskatchewan, the Northwest Territories, Nunavut, and Ontario. Concentrations of total mercury are shown for each region (insets).

Reference

Harmens, H., Norris, D., Mills, G., and the participants of the moss survey. (2013). Heavy metals and nitrogen in mosses: spatial patterns in 2010/2011 and long-term temporal trends in Europe. *ICP Vegetation Programme Coordination Centre, Centre for Ecology and Hydrology, Bangor, UK*, 63 pp.

Appendix 1. Summary data Canada

Table A1. Summary of trace element concentrations in moss tissue (n = 414) sampled between 2014–2015.

	n	min	max	mean	median	90th percentile
Ag [µg/g]	315	0.00	2.73	0.13	0.08	0.20
Al [µg/g]	414	41.20	9229.43	579.78	361.76	1135.44
As [µg/g]	400	0.00	10.47	0.28	0.18	0.48
Ba [µg/g]	413	0.17	855.41	29.27	20.95	54.41
Ca [µg/g]	414	572.48	27441.01	3882.33	3348.03	6380.92
Cd [µg/g]	400	0.00	5.55	0.18	0.11	0.34
Co [µg/g]	371	0.00	36.28	0.61	0.25	0.95
Cr [µg/g]	411	0.01	37.40	1.27	0.46	2.51
Cu [µg/g]	414	0.41	1628.26	12.19	3.77	8.61
Fe [µg/g]	414	27.94	15628.06	633.61	327.30	1282.34
K [µg/g]	414	637.16	29974.37	4462.34	4264.10	6592.47
Mg [µg/g]	414	173.37	10017.40	1130.92	1053.71	1757.14
Mn [µg/g]	414	5.96	2007.56	266.58	192.57	615.60
Mo [µg/g]	269	0.00	17.28	1.00	0.36	2.31
Na [µg/g]	414	9.12	3517.44	192.44	111.57	388.68
Ni [µg/g]	400	0.00	1211.23	11.87	2.01	13.19
Pb [µg/g]	412	0.06	94.83	1.89	0.83	2.57
Sb [µg/g]	336	0.00	1.55	0.11	0.06	0.26
Se [µg/g]	393	0.00	16.23	0.25	0.11	0.35
Sr [µg/g]	414	2.03	58.03	12.57	10.60	23.99
V [µg/g]	413	0.05	57.57	1.97	0.83	3.76
Zn [µg/g]	412	0.89	287.79	41.05	33.54	74.51
Hg [ng/g]	108	12.94	94.63	41.79	40.65	64.33

Estonia

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Background

The relative deposition of Cd, Cr, Cu, Fe, Ni, Pb, V and Zn has been monitored, based on epigeic mosses *Pleurozium schreberi* and *Hylocomium splendens* since 1989, when Estonia (area 45 227 km²) joined the air pollution monitoring programme of the European Nordic countries. From 2000 the same network of sampling sites was used as a part of the European moss survey. An international moss study was carried out in Estonia in every fifth year (1989/1990; 1995; 2000/2001; 2005/2006; 2010/2011; 2015/2016). The moss samples were collected from 99 sampling sites nearly 30 km apart. A denser moss sampling network as a part of Estonian monitoring network was applied in the areas where pollution loads were critically high (around some cities or towns, eg capital Tallinn and industrial pollution sources in SE Estonia) (Liiv and Kaasik, 2007).
There is no significant interspecies difference in the uptake of Cd, Cr, Cu, Fe, Ni, Pb, V and Zn by *P. schreberi* and *H. splendens* in Estonia (Liiv and Kaasik, 2004).

Element concentrations in mosses

Between 1992 and 2011, the median value of the concentration of Ni in mosses in the sampling sites around two large oil-shale-fired thermoelectric power stations and a cement factory in the north-eastern part of Estonia has declined the most – 5.23 times, the median value of Pb – 3.8 times, the median value of Cr – 3.7 times and the median value of V – 3.6 times. A clear spatial pattern and temporal trends dependence of the concentrations of the trace metals in mosses on the deposition fluxes of fly ash has been found in this industrial region in Estonia (Kösta and Liiv, 2011).
The content of Al, Hg, Cd, Cr, Cu, Fe, Ni, Pb, V, Zn and N in the mosses collected from sampling sites was generally uniformly low in 2015/2016, and the content of As was even below the limit of determination. Comparing to year 2010/2011, the concentration of heavy metals and N in mosses in 2015/2016 has decreased or remained at the same level or within the range of local variability (Liiv and Kaasik, 2007). Most significant changes are met only at single sampling points.
Raster maps of concentrations of the elements were generated from the moss data, using the Kriging algorithm (Figures 1-11).

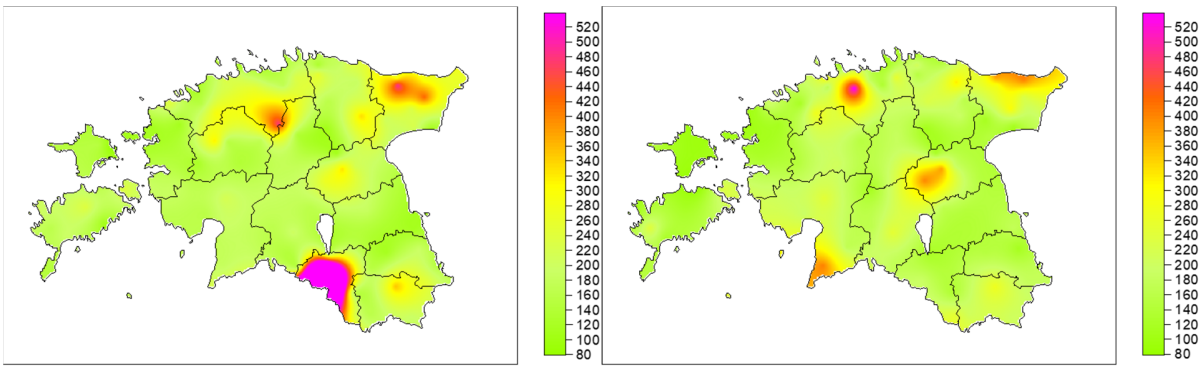

Figure 1. Distribution of aluminium concentrations (µg/g) in mosses in Estonia in 2010 (left) and 2015 (right).

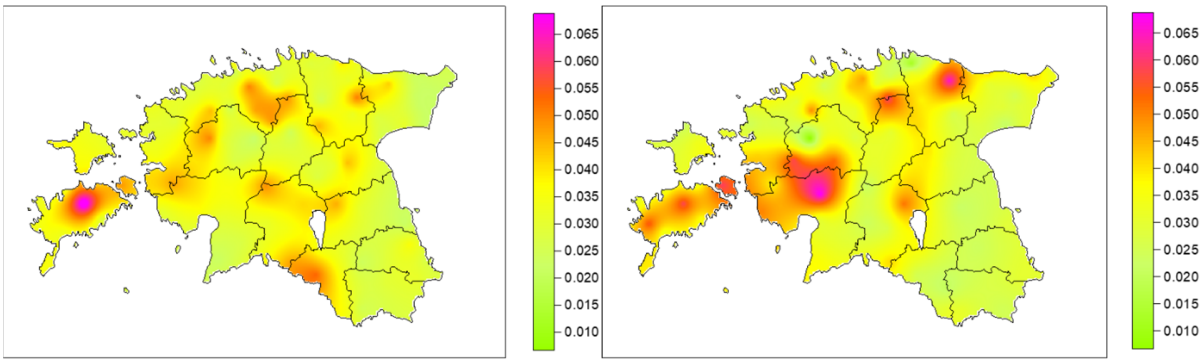

Figure 2. Distribution of mercury concentrations (µg/g) in mosses in Estonia in 2010 (left) and 2015 (right).

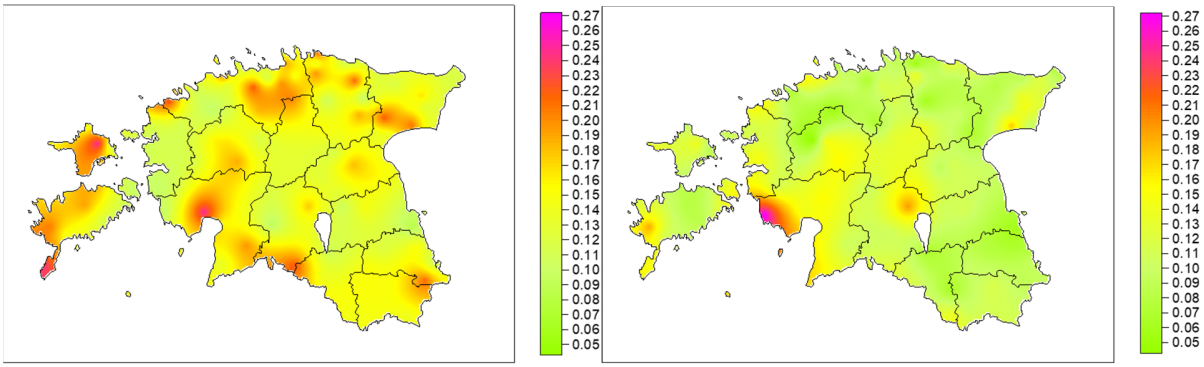

Figure 3. Distribution of cadmium concentrations (µg/g) in mosses in Estonia in 2010 (left) and 2015 (right).

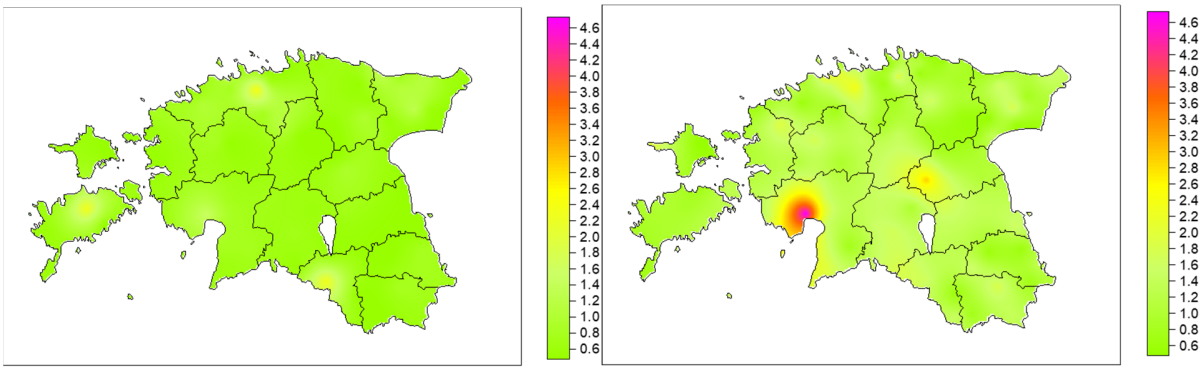

Figure 4. Distribution of chromium concentrations (µg/g) in mosses in Estonia in 2010 (left) and 2015 (right).

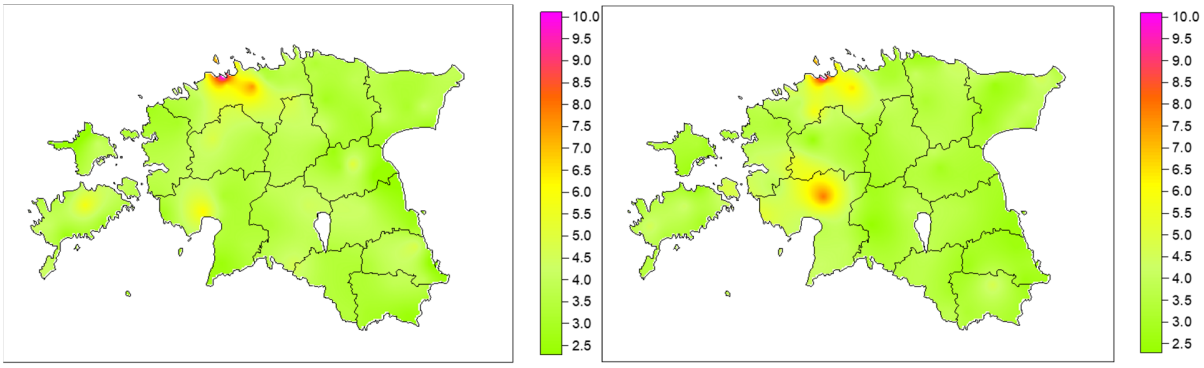

Figure 5. Distribution of copper concentrations (µg/g) in mosses in Estonia in 2010 (left) and 2015 (right).

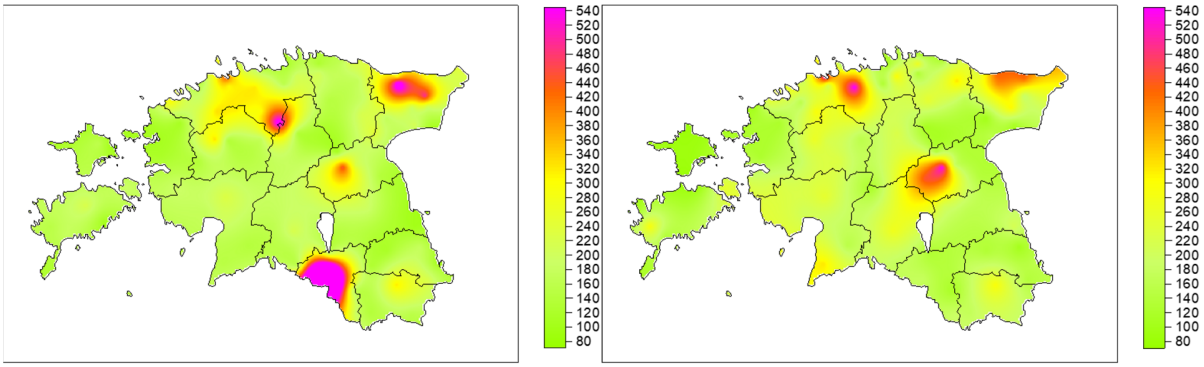

Figure 6. Distribution of iron concentrations (µg/g) in mosses in Estonia in 2010 (left) and 2015 (right).

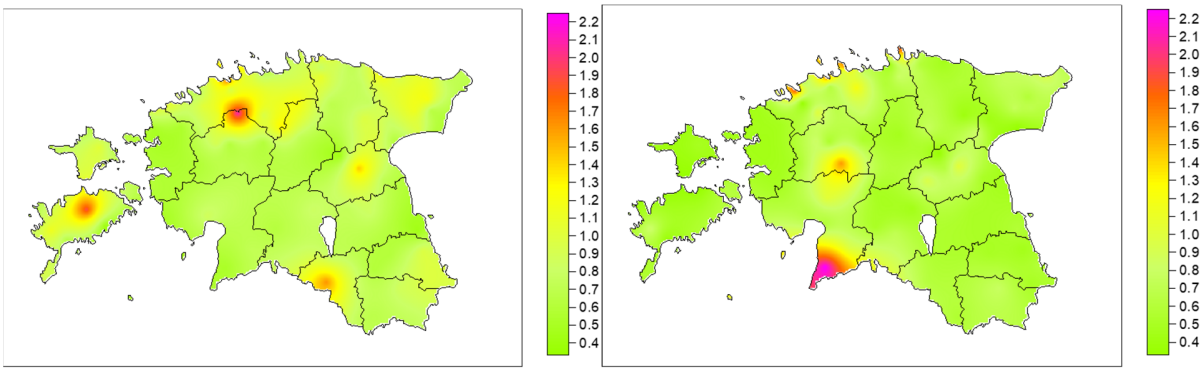

Figure 7. Distribution of nickel concentrations (µg/g) in mosses in Estonia in 2010 (left) and 2015 (right).

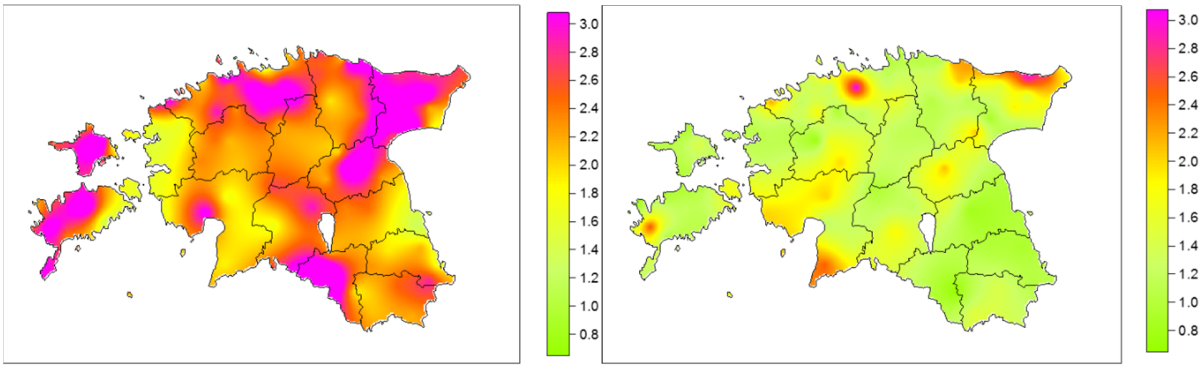

Figure 8. Distribution of lead concentrations (µg/g) in mosses in Estonia in 2010 (left) and 2015 (right).

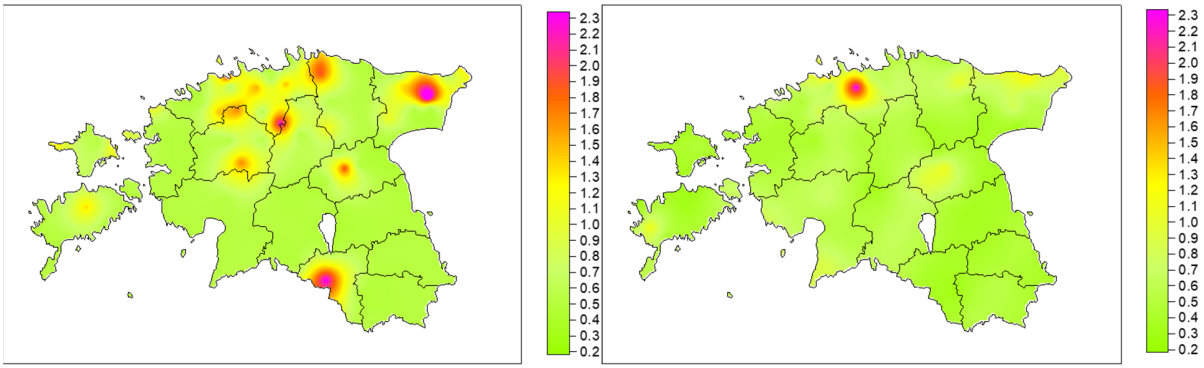

Figure 9. Distribution of vanadium concentrations (µg/g) in mosses in Estonia in 2010 (left) and 2015 (right).

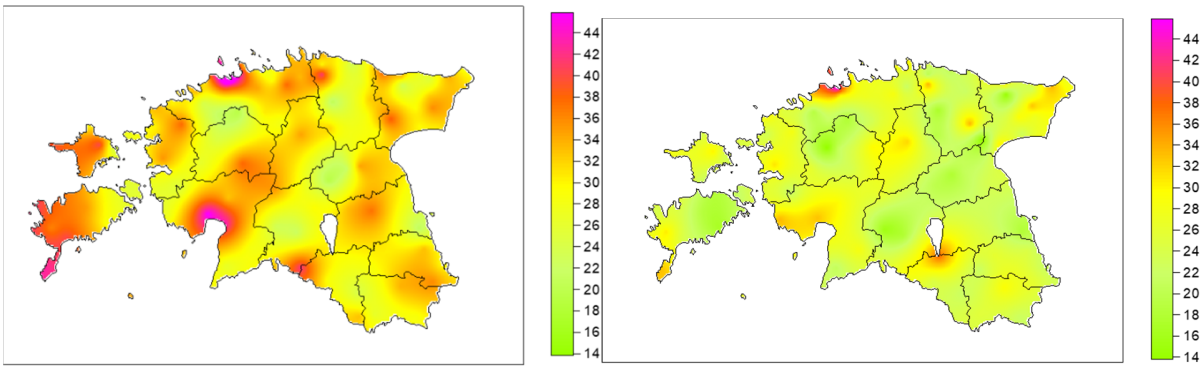

Figure 10. Distribution of zinc concentrations (µg/g) in mosses in Estonia in 2010 (left) and 2015 (right).

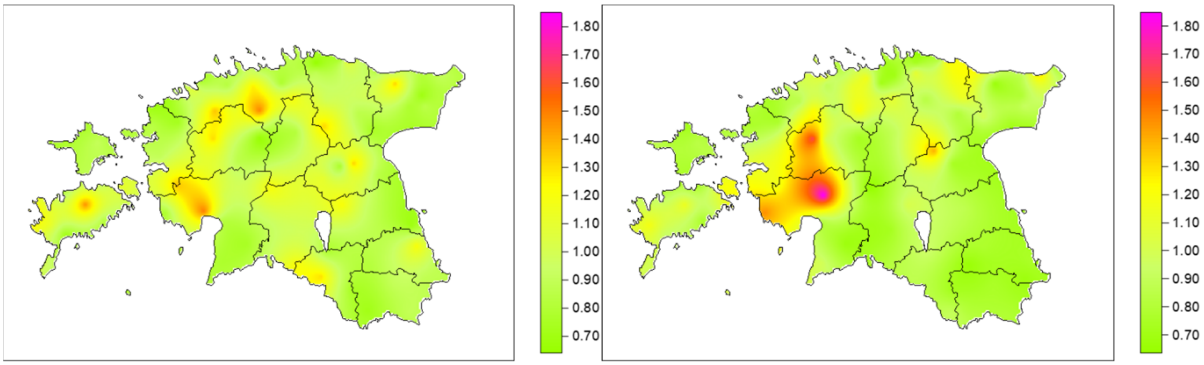

Figure 11. Distribution of nitrogen concentrations (%) in mosses in Estonia in 2010 (left) and 2015 (right).

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Kösta, H., Liiv, S. (2011). Spatial and temporal trends of heavy metal accumulation in mosses in Estonia. WIT Transactions on Ecology and the Environment, Vol 144: 133–144.

Liiv, S., Kaasik, M. (2004). Trace metals in mosses in the Estonian oil shale processing region. Journal of Atmospheric Chemistry 49: 563–578.

Georgia

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Background
Georgia participates in the moss biomonotoring program of UNECE ICP Vegetation since 2014, when a preliminary collection of Georgian moss (16 samples from different sites around the country) was investigated in collaboration with JINR. It was the first time for the western Caucasus, when the moss biomonitoring method of atmospheric deposition of trace elements was used. The investigation showed that this method is an efficient technique for studying the environmental situation in a country with specific geographic conditions and climate. In 2015-2016 the research was continued and moss samples were collected on a larger territory of Georgia. *Pleurozium schreberi, Hypnum cupressiforme, and Hylocomium splendens* were chosen for the study due to their characteristic and occurrence. Overall, during these surveys, 111 moss samples were collected from different altitudes, from 161 m to 2763 m above the sea level, covering nearly the whole territory of the country. The sampling was performed in compliance with the UNECE ICP Vegetation guidelines.

Concentrations of heavy metals in mosses
The analysis of moss samples was carried out at the reactor IBR-2 of FLNP JINR by means of epithermal neutron activation analysis: concentrations of 39 elements (Na, Mg, Al, Cl, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Zn, As, Se, Br, Sr, Zr, Mo, Pb, Sb, I, Cs, Ba, La, Ce, Nd, Sm, Eu, Tb, Yb, Hf, Ta, W, Au, Th, and U) were determined. Concentrations of Cu, Cd and Pb were obtained by atomic absorption spectrometry. For graphical data presentation, GIS tools were used. As an example, the spatial pattern of arsenic, chromium, lead and vanadium content in mosses are shown in Figure 1. Multivariate statistics was applied to find associations of chemical elements and to characterize the sources of element-pollutants determined in the samples. Factor analysis revealed mineral dust, industrial and marine components, as well as high-traffic roads.

Discussion and conclusions
The obtained results evidence that there is a considerable problem in the Western Georgia, due to metal processing industry and mining enterprises allocated there, like machine-building factory in Kutaisi, Zestaponi Ferroalloy Plant, Tsana and Uravi arsenic mining sites, Chiatura mine complex, and others. A comparison of determined values of elements with corresponding data from other Europe countries showed that the concentrations of heavy metals in mosses collected in Georgia are mostly higher. The performed investigations show that the moss biomonitoring technique is an efficient technique to study the environmental situation in Georgia. There is a clear need to continue the moss survey in Georgia, to evaluate the air quality in whole country, and see long-term trends.

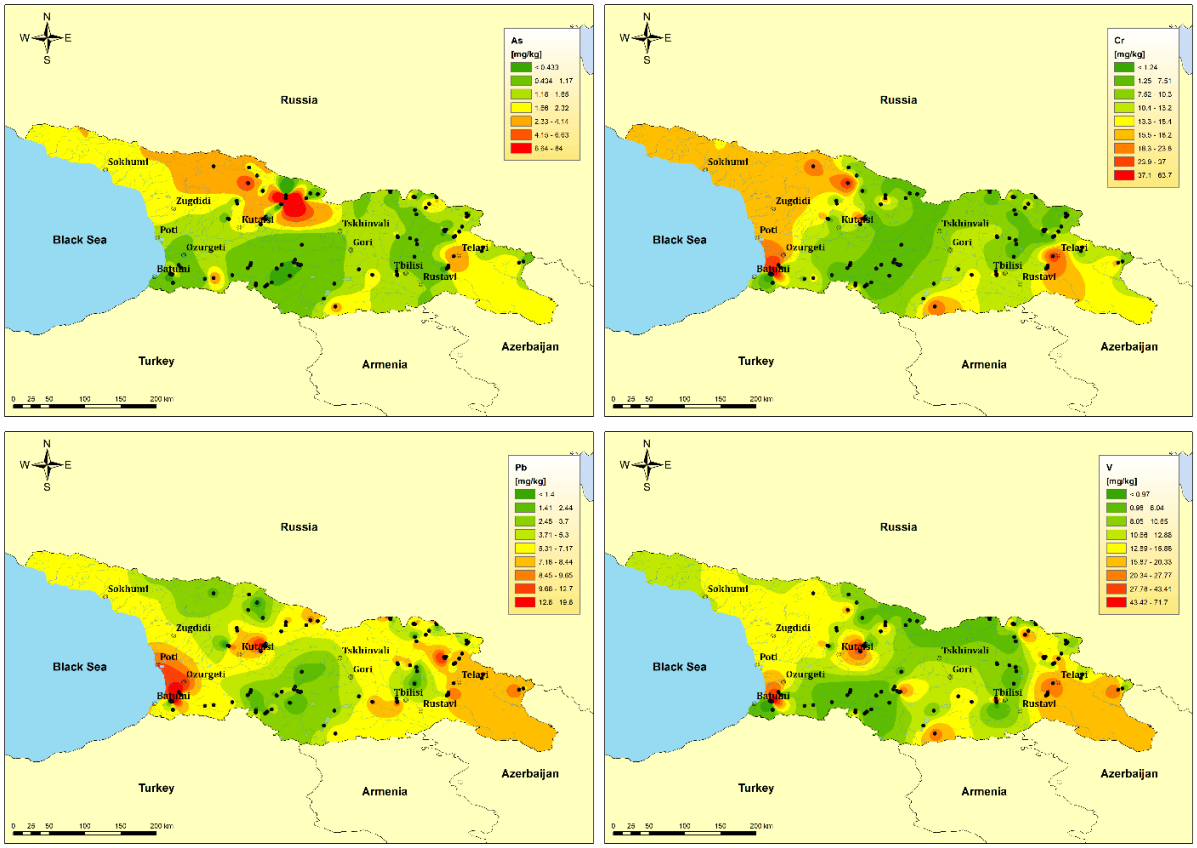

Figure 1. Arsenic (As), Chromium (Cr), Lead (Pb), and Vanadium (V) distribution in mosses samples.
Note: Black dots on the map are the sampling sites.

Acknowledgement. This research was performed in the frame of Shota Rustaveli National Science Foundation grant AR/198/9-240/14 (28.04.2015-28.04.2017) and Grant of Plenipotentiary of Georgia in JINR, Order # 18 of 15.01.2016 and Order # 44 of 26.01.2018.

Further reading

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Shetekauri S., et al. (2018). Biomonitoring Air Pollution Using Moss in Georgia. Polish Journal of Environmental Studies, 27(5), 2259-2266.

Germany

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Background

Since 1990, Germany has been part of the European moss survey with exception of 2010. The number of sampling sites amounted to 592 (1990), 1026 (1995), 1028 (2000), and 726 (2005). For the 2015 survey, the spatial sampling network was further reduced to 400 sites following a transparent and statistically sound methodology (Nickel & Schröder 2017). In 2015, chemical analysis was carried out for aluminium (Al), arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), iron (Fe), mercury (Hg), nickel (Ni), lead (Pb), antimony (Sb), vanadium (V), zinc (Zn), nitrogen (N) in moss specimens collected from about 400 sites throughout Germany and selected persistent organic pollutants (POP) at eight sites. Additionally, a special focus was laid on examining canopy drip effects on element concentrations in moss and on adjusting and mapping respective values by relating them to vegetation structure measures (Schröder & Nickel 2018 c).

Concentrations in mosses

The German Moss Surveys 1990-2015 reveal a clear and statistically significant decrease of concentrations of most heavy metals in moss but not for nitrogen (Table 1). Spatio-temporal trends of the elements relevant for CLRTAP (Cd, Hg, Pb, and N) are characterised as follows (Figure 1; Schröder & Nickel 2018 a, b):

Table 1. Development of median values of heavy metal and N concentrations in moss [%]

	Al	As	Cd	Cr	Cu	Fe	Hg	Ni	Pb	Sb	V	Zn	N
Change of median concentrations in moss 2015 compared to that in 2005	**-31.8**	**-32.5**	**-35.2**	**-75.8**	**-36.0**	**-37.2**	**-4.0**	**-41.3**	**-50.4**	**-43.8**	**-52.1**	**-34.2**	-2.0
Change of median concentrations in moss 2015 compared to that in the year of first sampling*	**-54.2**	**-68.0**	**-52.6**	**-74.0**	**-47.0**	**-66.7**	**-20.0**	**-71.1**	**-85.9**	**-48.0**	**-83.2**	**-29.4**	-2.0

Bold = Significant ($p \leq 0.05$); * = Year of first sampling (1990: As, Cd, Cr, Cu, Fe, Ni, Pb, V, Zn; 1995: Al, Hg, Sb; 2005: N)

Cadmium. In the 2015 survey, the measured concentrations of Cd in 398 moss samples reveal values between 0.035 and 1.760 µg/g and a median of 0.136 µg/g. Between 1990 and 2015 the Germany-wide median of Cd concentrations decreased by -52.5 %. Between 1990 and 1995 the median Cd accumulation in moss increased by +2.1 %, and from 1995 to 2005 it decreased by -28.3 %. Changes of the median Cd values throughout Germany could not be measured between 2000 and 2005, while from 2005 to the median Cd concentrations in moss decreased significantly by -35.2 %. No increase of median Cd concentrations could be detected during the years 2005 to 2015.

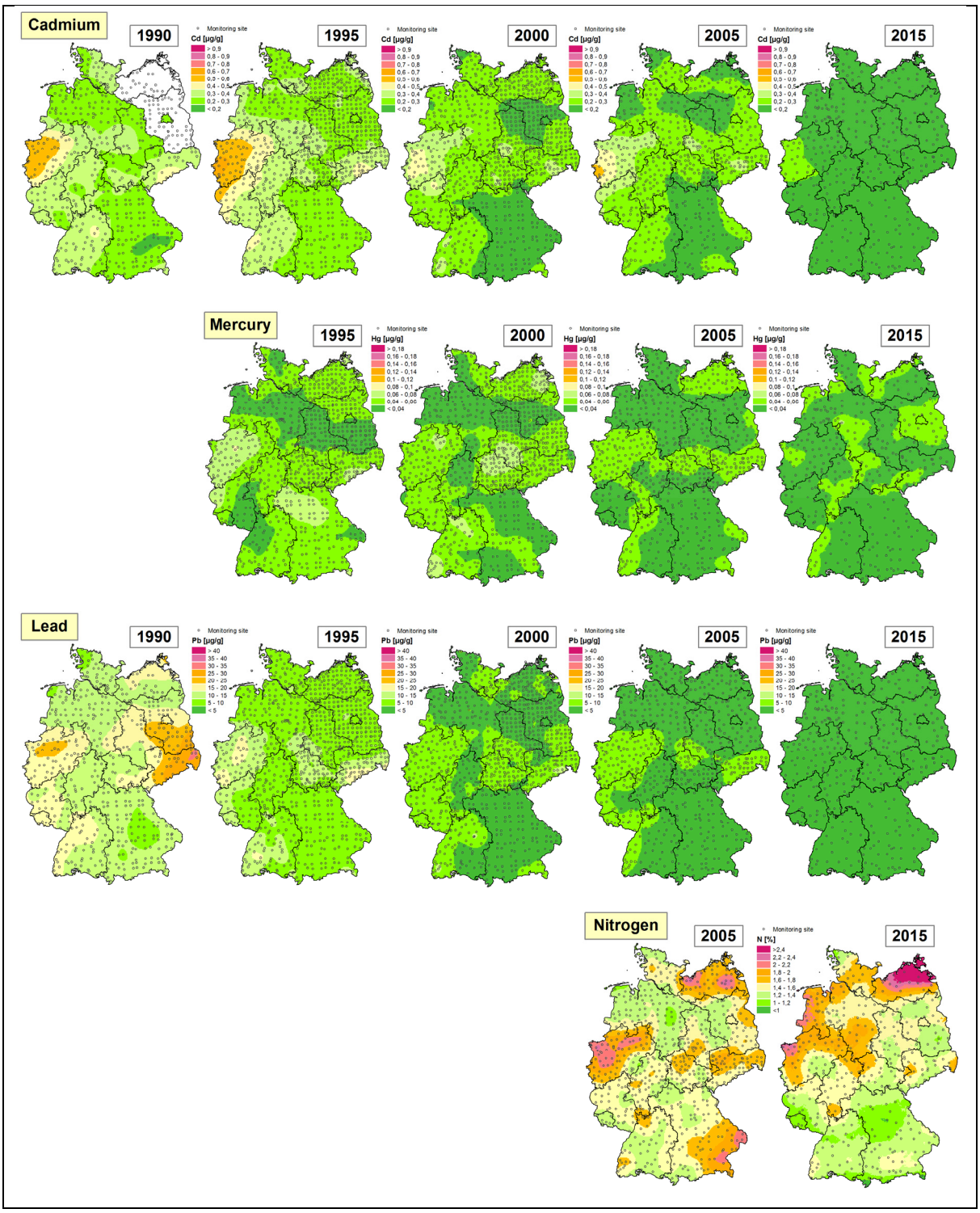

Figure 1. Spatio-temporal trends of Cd, Hg, Pb, and N concentrations in moss (1990-2015).

Mercury. In 2015, 397 Hg measurements ranged between 0.0047 µg/g and 0.196 µg/g, and the median throughout Germany was 0.0446 µg/g. The medians measured from 1995 to 2000 increased significantly in four federal states (= 26 % of Germany's territory). Across Germany, no such statistically significant trend could be corroborated. From 2000 to 2005 the median of Hg measurements sank in almost all federal states, and the median decreased by -14.6 %. During 2005 to 2015 the reduction of Hg concentrations in moss accounted for another -4 % ($p < 0.05$). Eight

federal states (= 40 % of Germany´s territory) did not show any significant decline since 1995 (Schröder & Nickel 2018 a).

Lead. The 2015 survey yielded Pb concentrations in moss collected at 400 sites across Germany ranging from 0.47 µg/g to 19.34 µg/g with a median of 1.830 µg/g. The Germany-wide trend of median Pb bioaccumulation exhibits a continuous decrease throughout time (1990-2015). Since 1990, the Pb conc. in moss declined by -85.9 %. A similar tendency could be found for most of the federal states.

Nitrogen. From the measured concentrations of N in 400 moss specimens, ranging between 0.80 % and 3.49 %, a median value of 1.431 % was computed. The Kriging maps for 2005 and 2015 indicate that the N bioaccumulation did not change significantly during the last ten years. Permanent N hot spots existed between 2005 and 2015 in North Rhine-Westphalia and Mecklenburg-West Pomerania. Inference statistical tests corroborate that the N concentrations did not change significantly between 2005 and 2015, neither Germany-wide nor in most of the federal states.

POPs. Within the 2015 European moss survey, selected POP have been analysed in eight moss samples from Germany (Dreyer et al. 2018). Overall, 17 polychlorinated dibenzo dioxins and -furans (PCDD/F), 18 polychlorinated biphenyls (PCB), 16 polycyclic aromatic hydrocarbons (PAH), 17 perfluoroalkyl substances (PFAS), 3 isomers of hexabromocyclododecane (HBCD), 7 polybrominated biphenyls (PBB), 24 polybrominated diphenyl ethers (PBDE), and 19 alternative halogenated flame retardants (HFR) such as Dechlorane Plus were determined by gas chromatography coupled to mass spectrometry (GC-MS), high resolution GC coupled to high resolution MS (HRGC-HRMS), liquid chromatography coupled to tandem mass spectrometry (LC-MS/MS), or GC-atmospheric pressure ionization (API) -MS/MS. Except for PBBs and PFASs, POPs of all substance groups could be quantified, although to different extents. Highest levels of PCDD/F and PAH in moss were observed at sites close to the Belauer See (Northern Germany, agricultural land-use), dl-PCB values were highest at the Saarland (conurbation). Total concentrations of HBCD and PBDEs (including BDE 209) were highest at the Harz National Park, those for alternative flame retardants at one Saarland site (conurbation) and at the Harz site. Levels of individual substances may differ from the spatial distribution of substance group-specific findings. I.e. concentrations for Dechlorane Plus were highest at the Harz site followed by sites locates at Solling (forestry) and Scheyern (agricultural) and were lowest at the site in the Halle-Leipzig conurbation.

Investigation of canopy drip effect on element concentrations in moss

Based on 71 moss samplings in North-western Germany the ratio between Leaf area indices (LAI) of sampling sites from neighbouring forest stands and open fields was found as an important factor for respective ratios of element concentrations in moss (Schröder & Nickel 2018 b). Four elements (Cu, Hg, Pb, Sb) reveal correlation coefficients (spearman) between 0.6 and 0.8, nitrogen a very strong relationship (rs = 0.81). Given the availability of observed LAI, regression models for Cu, Pb, and N ($R^2 > 0.5$) can be used for converting element concentrations in moss for any target LAI representing a standardized vegetation structure / land use.

Discussion and conclusions

The calculated maps reveal a clear and statistically significant decrease of concentrations in moss of most heavy metals in moss but not of nitrogen. Due to decreasing element concentrations and the unchanged application of the element concentration classification for the mapping, the heavy metals maps for the survey 2015 do no longer depict much spatial variation. Therefore, the standard classification of ICP Vegetation needs to be complemented for the heavy metals by mapping percentile statistics (Schröder & Nickel 2018 b).

For POPs, results show the widespread distribution of organic contaminants across Germany as well as the suitability of moss as bioaccumulation monitor for most of these compound classes. The general surrounding land-use does not seem to be the (only) driving force determining the POPs

burden in moss samples. Observations for PAHs or dioxins lie well in the range of concentrations found at other Central European and/or German sites. PBDE moss concentrations observed in this study were similar to those observed at background sites in Spain and lower than those of background/remote sites in Norway (Dreyer et al. 2018). Alternative flame retardants were dominated by DBDPE, DPTE and Dechlorane Plus with concentrations usually being lower than those reported by very few studies from Nordic countries or the Arctic (Dreyer et al. 2018).

In further studies of canopy drip effects, the Leaf Area Index and coverage of trees should be determined more precisely. The spatial sampling network should be enhanced to regions with lower deposition of N and higher deposition of heavy metals.

Acknowledgement
The project was funded by the German Environment Agency (Fkz . 3715 63 212 0).

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Greece (North)

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Background

During the 2015/2016 moss survey, ninety-five (95) samples of *Hypnum cupressiforme* Hedw., were collected in the region of Northern Greece during the end of summer 2016, covering a regular grid of 30 km x 30 km. The sampling sites were located from 39.97° to 41.65° North and from 20.97° to 26.26° East. The morphology of the surface crust of Greece varies from place to place, providing a very challenging collection of moss samples, with samples collected from different altitudes, from 30 m to 1450 m above the mean sea level. The regions from where samples were collected were open regions in most of the sampling sites, avoiding possible contact of mosses with surface water. All the samples were collected according to the instructions of the Protocol of the European Survey ICP Vegetation (Harmens et al., 2008). The most common moss species present was *Hypnum cupressiforme* Hedw., with the exception of only three stations where in absence of *Hypnum*, samples of *Homalothecium lutescens*, *Scleroporodium tourettii* and *Pseudoscleropodium purum* were available for collection. All samples were analyzed to the content of heavy metals (using INAA) and of natural and artificial radionuclides (using low energy gamma ray measurements). Studying the concentrations of heavy metals in mosses in the region of Northern Greece, provide information about the air quality, the identification of possible local pollution sources and transboundary transport of heavy metals, and finally assessing possible health risks in the region of investigation.

Heavy metals concentrations in mosses

The concentrations of 33 elements were determined in all moss samples by using INAA performed in Frank Laboratory of Neutron Physics, Joint Institute for Nuclear Research, Dubna, Russia (Frontasyeva 2011; Pavlov et al., 2014). Descriptive statistic of ten (10) element concentrations in mosses is presented in Table 1. Spatial distribution of the heavy metals concentration (Al, As, Cr, Ni, V, Zn) across the region of Northern Greece is presented in Figure 1. The concentration of Zn is higher in the region close to the Bulgarian boarders, indicating the transboundary transfer of Zn from the zinc-lead smelter in the region of Kardzhali in Bulgaria. Higher concentrations of Al and V are observed in regions where there are metal industries and in regions close to coal fired power plants and lignite mining. Areas with manufacturing industries, as well as electricity and heat production activities, present also a rise in concentrations of As, Cr and Ni elements.

Table 1. Heavy metal concentrations (μg g^{-1}) in moss *H. cupressiforme* in Greece in 2015/2016 survey.

	Al	*As*	*Cr*	*Fe*	*Ni*	*Sb*	*V*	*Zn*	*Ba*	*Co*
Min	1350	0.52	2.04	1010	1.72	0.02	2.61	14.60	15.90	0.43
Max	46100	17.90	222.00	28700	138.00	3.23	33.40	282.00	519.00	20.30
Median	6160	1.62	14.70	4630	10.00	0.20	8.66	38.30	76.30	1.99

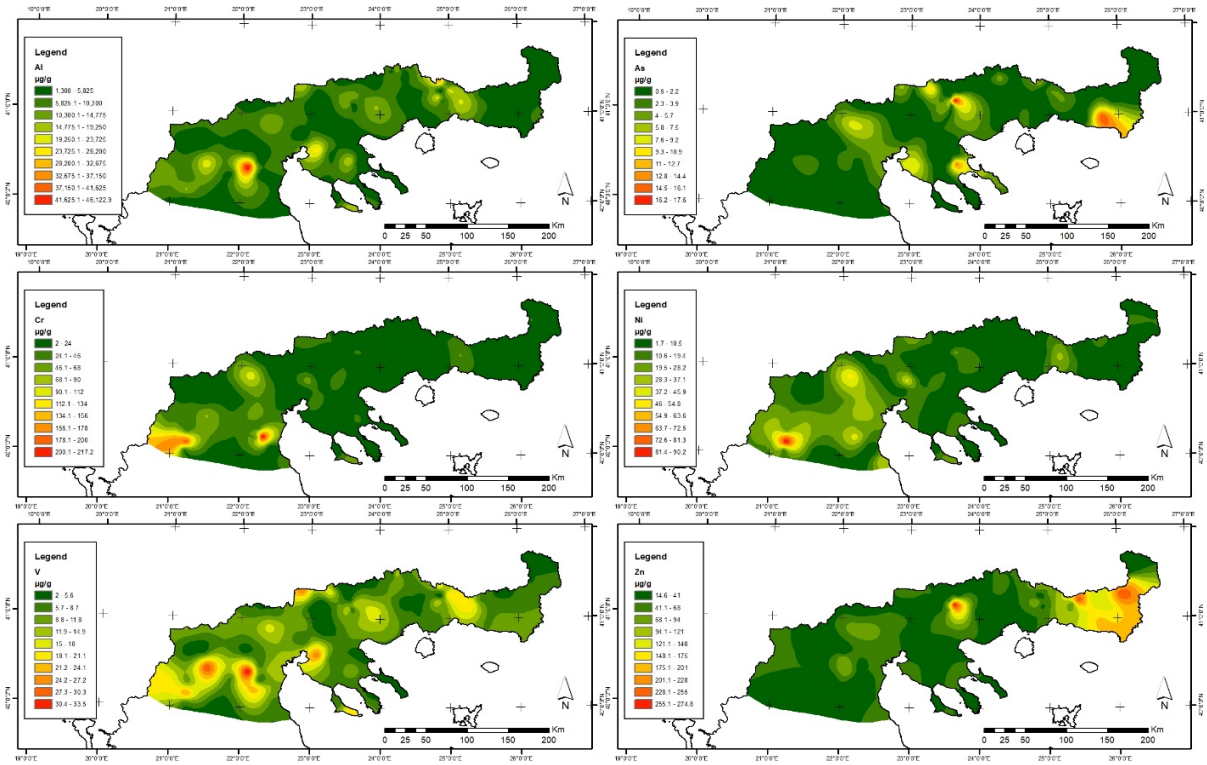

Figure 1. The concentrations of heavy metals (Al, As, Cr, Ni, V, Zn) in μg g^{-1} in moss samples of *H. cupressiforme* in the region of Northern Greece.

Discussion and Conclusion

This study has shown that the relatively cheap moss method can be used to determine regional differences and temporal changes in the atmospheric deposition of several elements. This enables the effectiveness of emission-reduction measures to be assessed.

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Italy (province of Bolzano)

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Background

The province of Bolzano, Italy, has been participating in the European monitoring of atmospheric heavy metal pollution since 1995 (Harmens et al. 2015). From that year were investigated at 20 sampling sites every five years the concentrations in *Hylocomium splendens* of the following elements: aluminium (Al), barium (Ba), strontium (Sr), copper (Cu), zinc (Zn), cadmium (Cd), lead (Pb), vanadium (V), chromium (Cr), manganese (Mn), iron (Fe), nickel (Ni), arsenic (As), selenium (Se), cobalt (Co), antimony (Sb), mercury (Hg) and nitrogen (N, only since 2005).

Concentrations in mosses

The concentrations of different heavy metals at the sampling sites are generally highly correlated with precipitation amount, which in turn is connected to the exposition and altitude.
The concentrations of the different heavy metals found in mosses at the sampling sites in the province of Bolzano in the past 20 years are mostly in line with the European mean. For most of the heavy metals a steadily decline could be recorded during the last 20 years (e.g. cadmium and lead, Figure 1 and 2).

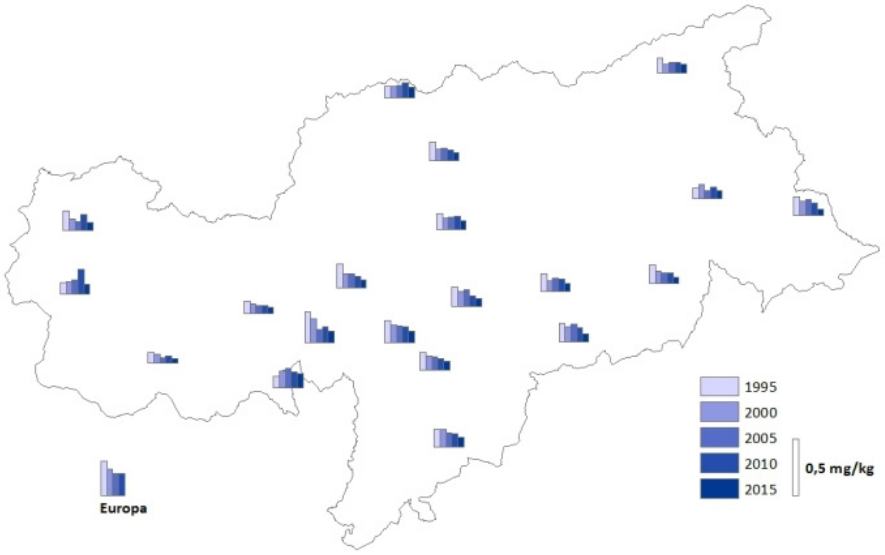

Figure 1. Cadmium (Cd) concentrations (mg/kg) at different sampling sites in South Tyrol from 1995 to 2015. The European mean of the respective year is shown in the lower left corner

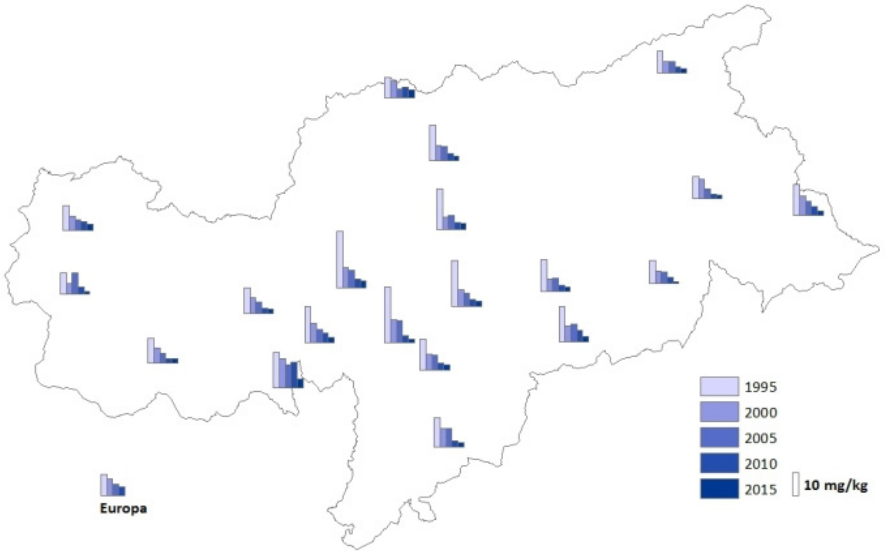

Figure 2. Lead (Pb) concentrations (mg/kg) at different sampling sites in South Tyrol from 1995 to 2015. The European mean of the respective year is shown in the lower left corner

For South Tyrol, this decline might be linked to the decrease of fine particles during the last decade, which are known to transport heavy metals and cause their deposition. However, for some elements like chromium and nitrogen raising concentrations could be registered at most sampling sites in South Tyrol (Fig. 3 and 4).

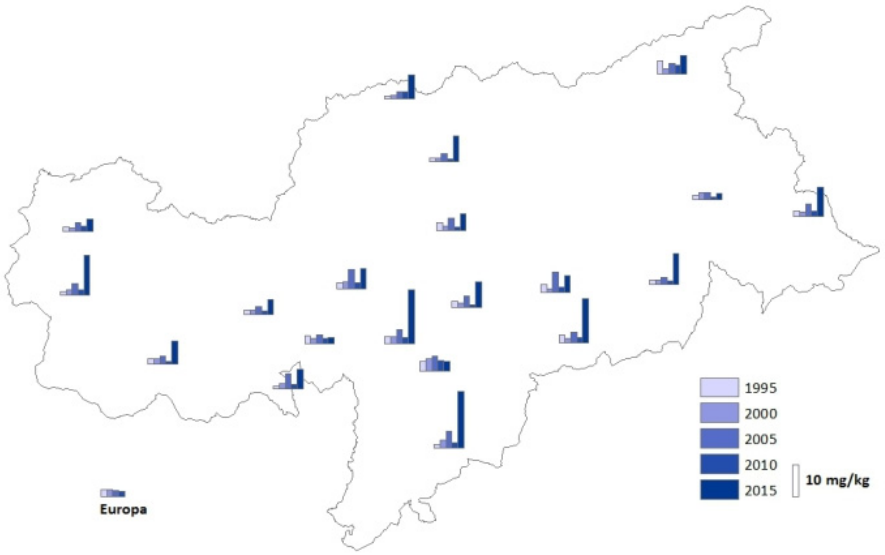

Figure 3. Chromium (Cr) concentrations (mg/kg) at different sampling sites in South Tyrol from 1995 to 2015. The European mean of the respective year is shown in the lower left corner.

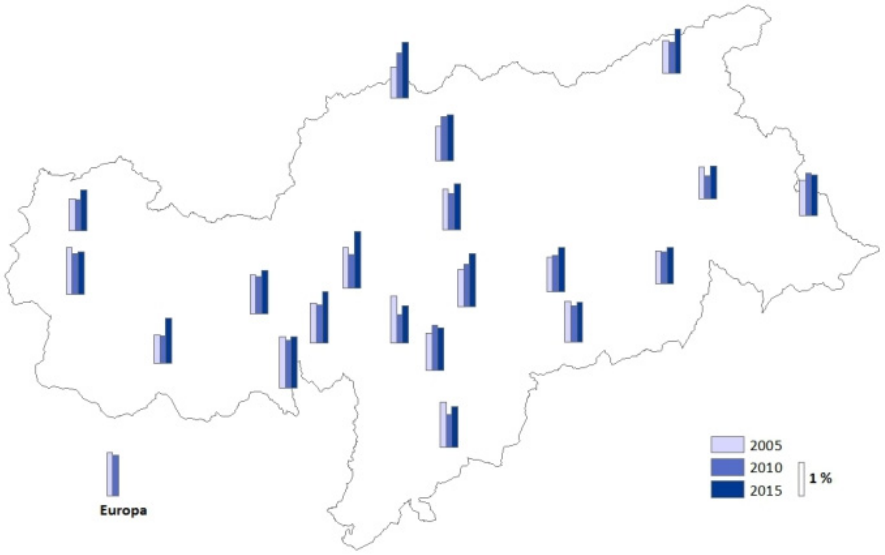

Figure 4. Nitrogen (N) concentrations (%) at different sampling sites in South Tyrol from 2005 to 2015. The European mean of the respective year is shown in the lower left corner**.**

This could be connected with the transport of heavy metals with southern winds from the industrialised Po plain.

Reference and website

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Latvia

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Background

Latvia is one of the Baltic countries and located in northern Europe with a total territory of 64 589 km^2. Latvia has participated in the European moss survey since 1990. Bioimonitoring of atmospheric heavy metal distributions has been conducted using moss in five national surveys: in 1990, using *Hylocomium splendens* collected in 81 plots, in 1995, 2000, 2005 and 2015 using *Pleurozium schreberi* in 101 plots. Change from one to other species was made because *P. schreberi* has wider distribution in Latvia. Moss samples were collected during the period from middle August to middle October 2015. Concentrations of eight heavy metals (Cd, Cr, Cu, Fe, Ni, Pb, V, Zn), nitrogen and persistent organic pollutants (POPs) were analysed in *P. schreberi* moss to estimate atmospheric pollutions in the whole territory of Latvia.

Concentrations in moss

In 2015, the median concentrations of heavy metals (mg kg^{-1}) and nitrogen (%) were as follows: Cd – 0.10, Cr – 0.33, Cu – 5.17, Fe – 133.02, Ni – 0.48, Pb – 1.26, V – 0.49, Zn – 33.13 and N – 1.13.

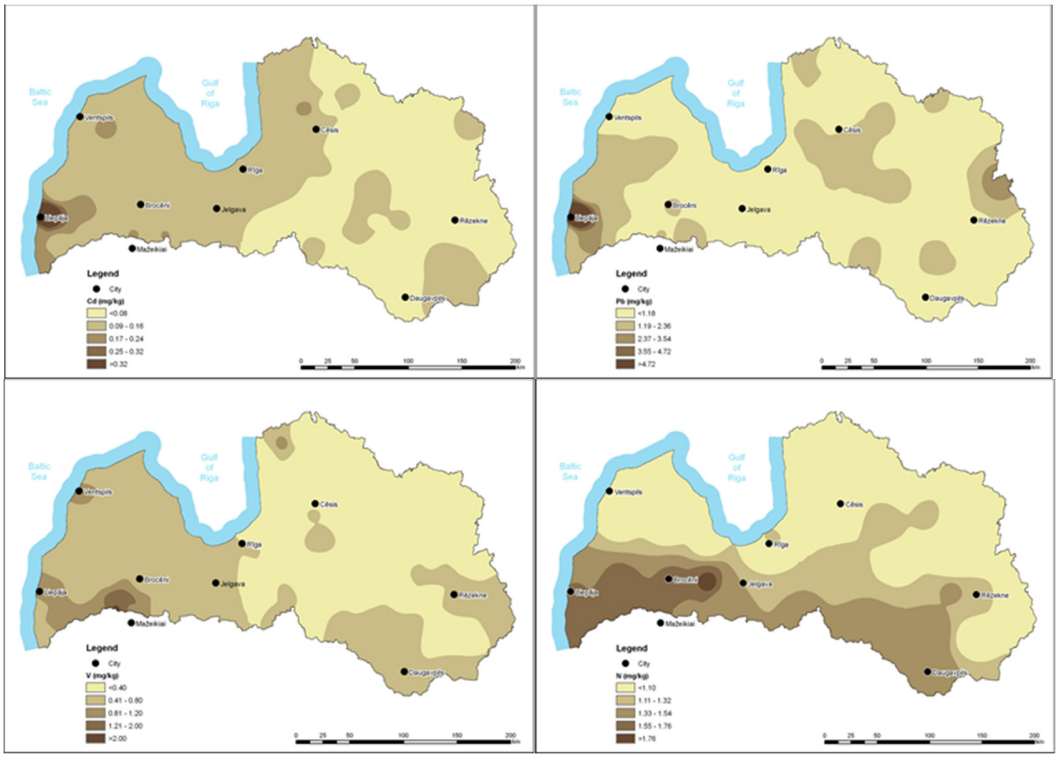

Figure 1. Heavy metal (Cd, Pb, V) (mg kg^{-1}) and nitrogen (%) concentration in *Pleurozium schreberi* moss in 2015 in Latvia.

Increased concentrations in the western part of Latvia (Figure 1) are due to the long-range transboundary transport of pollution from Western Europe (Tabors et al. 2017). Higher concentrations near the Lithuanian border are associated with pollution impact from Naujoji Akmene cement factory (Cu, Fe, Ni) and Mažeikiai oil refinery (Ni, V) (Figure 1). The highest N concentrations in *P. schreberi* moss in 2015 were determined in the south-western part of Latvia (1.74-1.83%), the lowest N concentrations (< 1.10%) were determined in the northern part of Latvia (Figure 1). The higher N

concentrations are in the south-western area of Latvia due to the long-range transboundary transport of pollution, as well as in the intensive agriculture areas and territories close to the industrial cities. The results of POPs of the median concentration (µg/kg) in Latvia were as follows: Naphthalene – 3.11, Acenaphthylene – 6.82, Acenaphthene – 1.13, Fluorene – 3.46, Phenanthrene – 24.03, Anthracene – 0.36, Fluoranthene – 8.75, Pyrene – 8.57, Benzo [a] anthracene – 1.46, Chrysene – 2.29, Benzo[b]fluoranthene – 2.17, Benzo[k/j]fluoranthene – 3.96, Benzo[a]pyrene – 2.86, Indeno[1,2,3-c,d]pyrene – 6.21, Dibenz[a, h]anthracene – 1.72, Benzo[g,h,i]perylene – 3.29. POPs results shows that the higher concentration in moss was found in the western part of Latvia.

Discussion and conclusion

In Latvia since 1990 until 2015, concentration in mosses in all plots as a whole has declined the most for Pb (89%), V (85%), Cr (78%), Fe (71%), Cd (69%) and Ni (66%), followed by Zn (21%) and Cu (14%) (Tabors et al. 2017). Decrease of V and Ni concentrations in moss can be explained with the fact that many thermal power plant have substituted oil products with gas or bio-fuel (Nikodemus et al. 2004) that is more environmental friendly. Decrease of Pb concentration could be related not only to the decrease in the intensity of industrial manufacturing, but also to an improved emission control and improvement of road transport quality (EEA 2012). Decrease of Cr concentration can be explained with a rapid decrease in operational intensity of heavy metallurgy and cement factory industries. In Latvia the atmospheric pollution is not so high and it has observed a decreasing tendency (Tabors et al. 2017). Median concentrations of heavy metals and nitrogen in mosses in Latvia are generally relatively low compared to the concentrations in other parts of Europe (Harmens et al. 2013). 2015 mapping results of heavy metal distribution in atmosphere in Latvia by using moss confirmed their efficiency in atmospheric air quality change control.

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Ireland

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Background

Ireland, situated on the western periphery of Europe, has a temperate oceanic climate dominated by relatively clean westerly Atlantic winds and high annual rainfall. Ireland participated in the European moss biomonitoring survey for the first time in 2015. *Hylocomium splendens* and *Pleurozium schreberi* moss tissue was collected at 113 sites during two field campaigns following survey protocols described in the ICP Vegetation moss monitoring manual. All samples were analyzed for heavy metal concentrations including total mercury, percent carbon (C), nitrogen (N), and sulphur (S), and a sub-set were analysed for radionuclides (n = 23) and persistent organic pollutants (POPs; n = 9).

Methods

Sampling took place during two field campaigns in 2015 (27 May–05 June and 28 July–05 August). In an effort to ensure national coverage, sampling sites were selected from a 25 km × 25 km grid across the country. More than 170 plots were surveyed; species of interest (i.e., *H. splendens* and *P. schreberi*) were found at 113 sites (Figure 1). Unwashed samples were stored in paper bags and oven-dried at 57°C for 70 hrs. Dried samples were pulverized using a hand mill, and analysed for C, N and S content (%) using an Elementar vario Marco CNS analyzer. Heavy metal concentrations were determined using a Triple-Quad ICP-MS analyzer following acid digestion (Mars 6 microwave digester). Total mercury was determined using a mercury analyzer (Milestone DMA-80), and radionuclides were analysed by the Irish EPA's Office of Radiological Protection. In addition, moss tissue samples (n = 9) collected from three ICP Waters catchments were analysed for POPs and total and monomethylmercury. Relationships between moss tissue %N content and modelled total N deposition were explored using regression analysis. Spatial trends were explored for heavy metals, and autocorrelation was tested using the Moran's *I* test. Correlations between heavy metal concentrations, radionuclide concentrations, and climate variables were tested using a Pearson's correlation test.

Results and Discussion

The species *H. splendens* was found much more frequently (n = 109) than *P. schreberi* (n = 16); with both species sampled at 12 sites. Nitrogen content in the mosses (average = 0.78%) was correlated with modelled total N deposition (Figure 1a) and showed a slight regression trend (R^2 = 0.18, $p < 0.05$). The mosses showed lower average N content compared with all other European countries in the 2010/2011 surveys (Harmens et al., 2013) except Finland (average = 0.8%; n = 426). Concentrations of cadmium (Cd), antimony (Sb), lead (Pb) and mercury (Hg) (and all other metals, see Appendix Table A1) were low compared with other European countries participating in the moss survey. The position of Ireland on the extreme western coast of Europe and the prevailing winds from the Atlantic mean that Ireland receives relatively low transboundary air pollution from other European countries. A spatial trend was observed in the Pb samples, suggesting point sources of emissions within the country (Moran's *I* = 0.45, p=0) (Figure 1b). Ore deposits including Pb and associated mining have been historically associated with higher Pb concentrations in soils (Aslibekian and Moles, 2003).

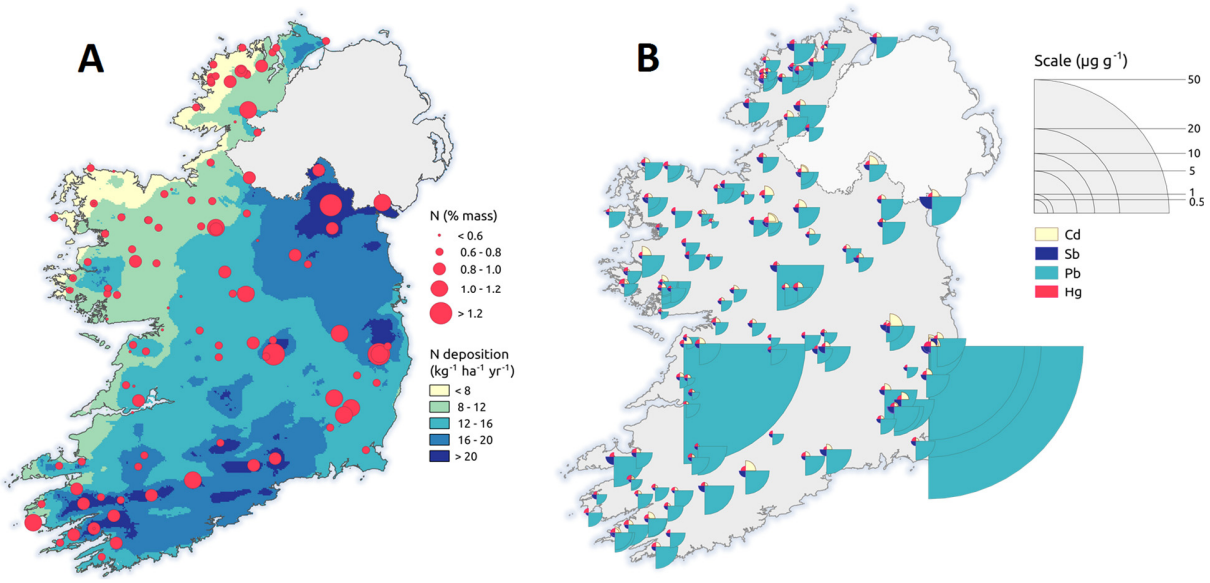

Figure 1. (a) Nitrogen content (% mass) and (b) tissue concentrations (µg g^{-1}) of cadmium (Cd), antimony (Sb), lead (Pb), and mercury (Hg) in *Hylocomium splendens* and *Pleurozium schreberi* at 113 sample sites across Ireland. The nitrogen concentrations are depicted with total nitrogen deposition (kg N ha^{-1} y r^{-1}) for grasslands (Henry and Aherne, 2014)

Naturally occurring lead 210 (^{210}Pb) activity was observed in every sample (550.4 Bq kg^{-1}; n = 23) and highly correlated with average annual rainfall as well as selenium and strontium concentrations, suggesting that deposition dominated by Atlantic air masses was the primary source. While only ^{210}Pb was found to be significantly correlated with rainfall, spatial clustering also suggested marine air masses as a source of cesium 137 (^{137}Cs). Increased ^{137}Cs deposition was recorded in Ireland after the Fukushina nuclear incident in 2011 (Environmental Protection Agency, 2015).

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Appendix. Summary data Ireland

Table A1: Summary of metal and nutrient concentrations (n=113) and radionuclide activity (n=23) in moss tissue sampled during 2015.

	n	min	max	mean	median	90th percentile
Al [µg/g]	113	22.36	815.36	132.55	100.94	219.43
V [µg/g]	113	0.14	2.01	0.56	0.50	0.98
Cr [µg/g]	95	0.02	2.65	0.38	0.23	0.83
Mn [µg/g]	113	6.30	797.46	187.33	150.19	363.78
Fe [µg/g]	113	41.96	798.87	146.27	107.50	229.47
Co [µg/g]	113	0.02	2.23	0.11	0.07	0.19
Ni [µg/g]	54	0.05	7.42	1.15	0.53	2.74
Cu [µg/g]	113	1.34	47.71	4.39	3.27	5.92
Zn [µg/g]	113	4.86	167.16	30.10	22.21	59.04
As [µg/g]	110	0.00	0.97	0.12	0.09	0.20
Se [µg/g]	113	0.11	1.20	0.44	0.38	0.77
Sr [µg/g]	113	4.73	81.29	18.56	16.39	29.59
Mo [µg/g]	111	0.01	5.51	0.39	0.21	0.86
Ag [µg/g]	91	0.00	0.25	0.05	0.05	0.09
Cd [µg/g]	92	0.00	0.43	0.08	0.05	0.18
Sb [µg/g]	112	0.01	0.44	0.07	0.05	0.13
Ba [µg/g]	113	1.63	178.29	14.16	9.90	22.54
Tl [µg/g]	101	0.00	0.24	0.02	0.01	0.04
Pb [µg/g]	113	0.14	65.78	2.39	0.72	2.33
Hg [µg/g]	113	0.01	0.07	0.04	0.03	0.05
%N	113	0.54	1.33	0.79	0.75	1.04
%S	113	0.13	0.24	0.17	0.16	0.21
^{210}Pb [Bq/kg]	23	225.51	968.04	550.38	511.93	868.78
^{137}Cs [Bq/kg]	16	3.06	41.38	14.05	10.41	23.94
^{7}Be [Bq/kg]	8	283.10	604.35	420.68	376.19	601.30
^{40}K [Bq/kg]	17	57.17	155.42	94.09	85.07	120.27

Moldova

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Background

Republic of Moldova took part for the first time in the European moss survey in 2015/2016 and attended the ICP Vegetation Task Force meeting for the first time in 2016. During the May 2015, 32 moss samples were collected at 33 sampling sites evenly distributed over the RM entire territory (Zinicovscaia et al., 2017). The most dominant moss species present were *Hypnum cupressiforme* and *Pleurozium schreberi.* This study was undertaken in order to i) provide an assessment of the air quality throughout Moldova, ii) generate information needed for better identification of pollution sources and iii) to create a database for future surveys.

Concentrations of heavy metals

A total of 41elements (Na, Mg, Al, Cl, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Br, Rb, Sr, Zr, Cd, Sb, Cs, Ba, La, Ce, Nd, Sm, Eu, Gd, Tb, Tm, Yb, Hf, Ta, W, Pb, Th, and U) were determined by instrumental epithermal neutron activation analysis and atomic absorption spectrometry. As an example, the spatial pattern of arsenic, chromium, copper and vanadium content in mosses in 2015 are shown in Figure 1. Principal component analysis was applied in order to show associations between the elements. Three factors were determined. Factor 1 is interpreted to represent a combined geogenic/anthropogenic association of elements. Factor 2 includes Cl-Se-Sr, which are most likely of vegetation origin. Factor 3 is dominated by Pb-Sb-Zn and is an anthropogenic factor.

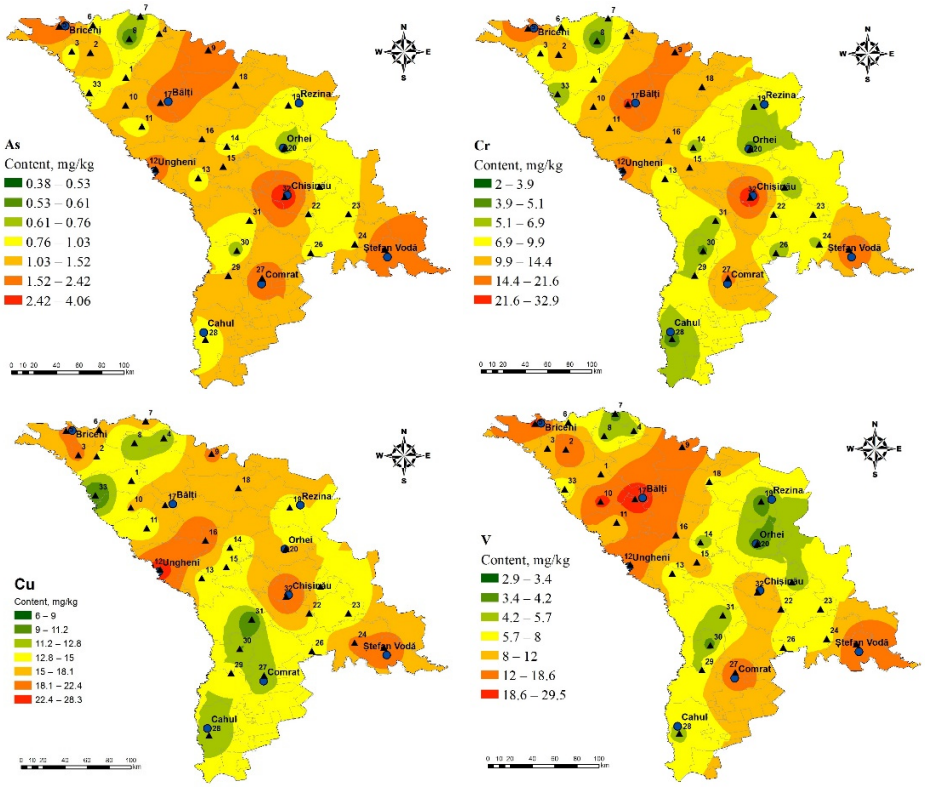

Figure1. Arsenic (As), chromium (Cr), copper (Cu), and Vanadium (V) distribution in mosses samples (Note: Black dots on the map are the sampling sites).

Discussion and conclusions

From the moss data it can be concluded that the main anthropogenic sources of heavy metals are thermoelectric plants, transport and industrial activity. Three different indices, contamination factor C_F, the geo-accumulation index I_{geo} and pollution load index, used to quantify the degree of contamination pointed toward a moderate to severely industrial pollution, localized around main urban and industrial centers – the municipalities of Chisinau and Balti. The median values obtained for the elements considered as main environmental pollutants (V, Cr, Fe, Ni, As) were very similar with those obtained for neighbouring country - Romania. The moss biomonitoring technique has proven to be an effective method for studying the atmospheric deposition of heavy metals as well as other trace elements and identification of pollution sources. There is a clear need to continue the moss survey in the Republic of Moldova.

Acknowledgement. The sampling in Moldova was supported by the Grant of International Organization for Migration, Mission in Moldova.

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North Macedonia

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Background

Studying air pollution with heavy metals in the Republic of Macedonia, using moss biomonitoring technique was applied for the first time in 2002, in the framework of United Nations Economic Commission for Europe International Co-operative Programme on Effects of Air Pollution on Natural Vegetation and Crops with heavy metals in Europe (UNECE ICP Vegetation) (Barandovski et al., 2008). Moss survey was also performed again in 2005 and 2010 using samples of terrestrial mosses *Camptothecium lutescens* and *Hypnum cupressiforme* Hedw. Moss samples were collected at 72 sites in 2002 and at 72 sites in 2005, 2010 and 2015 evenly distributed over the territory of the country using dense net of 17x17 km^2. The analyses of 43 elements were performed by using of neutron activation analysis (NAA), atomic emission spectrometry with inductively coupled plasma (ICP-AES) and atomic absorption spectrometry (AAS) as analytical techniques. It was concluded that the most important emission sources were near the mines, drainage systems and smelters near the towns of Veles, Tetovo, Kavadarci and Radoviš); some uranium deposition patterns were described by the activity of power plants using lignite coal as fuel. Results from the second and third moss survey in 2005 and 2010 confirmed the findings of the first survey and provided information on temporal deposition trends (Barandovski et al., 2012, 2013, 2015). In particular, the increase of Pb and Zn content in the eastern parts of Macedonia should be emphasized, especially due to reactivation of the mines and flotations of Pb and Zn ore. The first results of air pollution study with heavy metals have led to increased interest in the application of biomonitoring with mosses for extensive research in certain regions in Macedonia. Such investigations were carried out in the vicinity of copper mine "Bučim" near Radoviš, ferronickel smelter plant near Kavadarci, Pb and Zn mines and flotations near Kriva Palanka, Probištip, and Makedonska Kamenica, as well as in the surroundings of thermoelectric power plant REK "Bitola" using coal near the town of Bitola.

Material and methods

To determine the content of the various elements in the mosses collected in 2015, AAS, ICP-AES and NAA were used. Content of 23 elements (Al, As, Ba, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Li, Mg, Mn, Mo, Ni, Na, Ni, P, Pb, Sr, V and Zn) were determined by using AAS and ICP-AES. The analyses were performed at the Institute of Chemistry, Faculty of Natural Sciences and Mathematics, Skopje, Macedonia, while NAA was performed at the Joint Institute for Nuclear Research, Frank Laboratory of Neutron Physics, Department of Neutron Activation Analysis in Dubna, Russia. Using AAS, ICP-AES and NAA techniques the content of 43 elements was determined (Al, As, Au, Ba, Br, Ca, Cd, Ce, Cl, Co, Cr, Cs, Cu, Fe, Hf, Hg, I, In, K, La, Li, Mg, Mn, Na, Nd, Ni, Mo, P, Pb, Rb, Sb, Sc, Se, Sm, Sr, Ta, Tb, Th, Ti, U, V, W, Zn).

Results and discussion

From the obtained results it can be seen that almost all potentially toxic elements (As, Cd, Co, Cr, Cu, Hg, Ni, Pb and Zn) have increased content in moss samples collected in 2002 and 2005 and then in the samples collected in 2010 and 2015 is reduced with a slight increase again in the samples from 2015. The increased median values found in the last ten years were observed for Cd and Pb, compared to 2002, which is likely due to the reactivation of mining for lead and zinc in Eastern

Macedonia with large amounts of floatation tailings deposed to the landfills. However, the content of Cd and Pb in the last surveys (2010 and 2015) is reduced, resulting in the closure of the smelter in Veles and reduced use of petrol for cars that contain lead. The similar behavior was found for higher Ni with their content in the samples from 2005 (5.8 mg/kg) due to the increase in the capacity of the smelter for ferronickel near the city of Kavadarci, while in 2010 and 2015 these values are identical. It may be noted that in 2015 no significant changes were found in the content of the elements appearing in high content as a result of anthropogenic activity, compared to the value of 2010. The reason for this is that all mining and metallurgy activities in the country are in continuous operation and work with the same capacity in the last 5 years.

To explain the variation and to reveal associations of chemical elements the multivariate statistical cluster and factor analyses were performed. Four factors with the variability of the established elements of 75.4% have been identified: Factor 1 which includes elements As, Al, Ca, Fe, Mg, Li and V; Factor 2 including the elements Cd, Pb and Zn; Factor 3 with the elements Co, Cr, Ni and Mo, and Factor 4 with Ba and Sr. In the factor analysis 6 elements were excluded (Cu, Hg, K, Mn, Rb and Na).

The elements included in **Factor 1** (Al, As, Ca, Fe, Mg, Li, V) are naturally distributed in the soil in the country (Stafilov & Šajn 2016). High content of elements from this association has been found in samples taken from the areas where Paleozoic and Precambian shales prevail. High content of these elements were also found in the moss samples taken in Western Macedonia, where Mesozoic clastitic sediments dominate, then in the Kumanovo, Ovče Pole and the area of Kavadarci, where Neogene clastitic sediments predominate, then in moss samples taken from the vicinity of Galičica and Dojran due to the result of the Mesozoic carbonate rocks that are present in these areas. It could be concluded that all of the elements from F1 have the lithological origin except arsenic which shows both lithological and anthropogenic origin (Figure 1).

Factor 2 (Cd, Pb, Zn) is an anthropogenic factor and is associated with the industrial activity in the Republic of Macedonia. From Figure 1 it can be seen that the highest contents of these elements are found in the moss samples collected in the central and northern part of the country (Skopje, Veles and Tetovo), as well as in the central eastern part of the country. Elements included in Factor 2 are directly related to the dust from the surface layer of the floating tailings and from the polluted soil. In Veles and its surroundings the main source of pollution with these elements is the landfill of the former work of the Pb and Zn smelter in Veles. Although the smelter has stopped working in 2002, soil from the area in its vicinity is polluted and contributes to the high content of these elements in the air from this part of the country. The main source of pollution in the Tetovo region is the ferro-silicon smelter, while in the eastern part of the country there is an area with high content of Cd, Pb and Zn in the moss samples which is due to the emission of particles from the flotation landfills the Pb-Zn mines and flotations near the towns of Probištip, Makedonska Kamenica and Kriva Palanka.

The distribution map of the **Factor 3** (Ni, Cr, Co, Mo) scores show that the distribution of the particles with high content of the elements included in this factor are the highest in the Kavadarci region as a result of work of the smelter for ferronickel located neat the town of Kavadarci (Figure 1). Comparing this data with those obtained in the survey from 2010 it can be noted that there are no significant changes in the last 5 years in terms of pollution in this region. **Factor 4 (Ba, Sr)** is an association of elements that are naturally distributed and are not related to urban and industrial activities (Figure 1). The high content of Ba was found in the Polog region where the magmatic rocks are predominant, then in the Pelagonia region where the Quaternary alluvium is dominant. Districts with high content of Ba and Sr are representing also in mosses collected in the Eastern Macedonia and surrounding of Kavadarci where prevailing Neogene magmatic rocks.

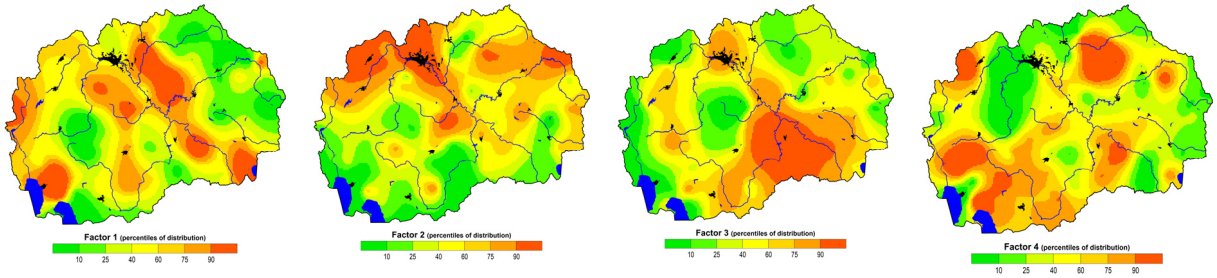

Figure 1. Spatial distribution of Factor 1 (Al, As, Ca, Fe, Mg, Li, V), Factor 2 (Cd-Pb-Zn), Factor 3 (Ni-Co-Mo-Cr) and Factor 4 scores (Ba-Sr).

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Norway

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Background

The first country-wide metal deposition surveys in Norway employing the moss technique was carried out in 1977, and was followed by corresponding surveys every five years starting in 1985. Since 1995, the same network of 465 sites has been used, and from 2000 the data have formed part of the European moss surveys coordinated by UNECE ICP vegetation. Currently the Norwegian survey includes 55 elements, including the heavy metals of concern in the European survey. This work is part of a national monitoring network organized and financed by the Norwegian Climate and Pollution Agency.

Spatial patterns and temporal trends of concentrations in mosses

The deposition patterns for most metals are dominated by long-range transport of aerosols from other parts of Europe. This is particularly evident for metals such as lead, zinc, arsenic, vanadium, antimony, tin, and bismuth, where the deposition in the far south of the country is substantially higher than in the middle and northern part. The deposition of these elements has decreased substantially over time, and in the case of lead the current deposition in the far south is only about 5% of the 1977 level. Calibrations of concentrations in moss against bulk deposition values from precipitation analysis prove that the moss survey reflect atmospheric deposition on Norway very well for most priority metals (Berg and Steinnes, 1997).

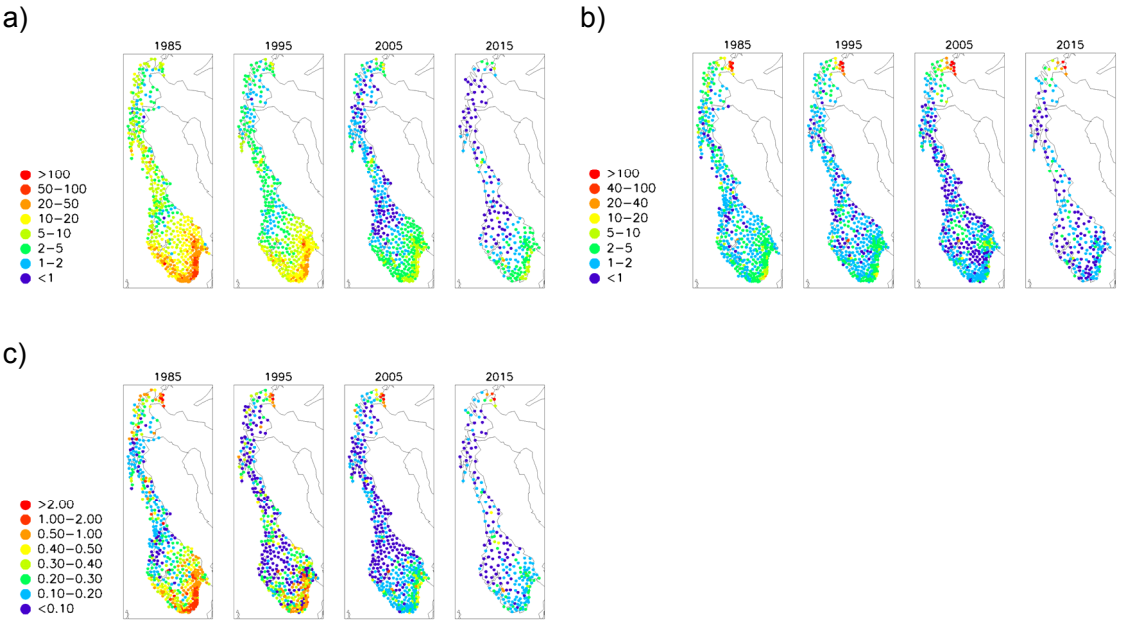

Figure 1. Concentration on a) lead, b) Nickel and c) Arsenic in moss in Norway (mg kg^{-1}) at four different years in the time period 1985-2015.

Other metals such as iron, copper, and nickel in moss are mainly related to emissions from industrial point sources. Examples are zinc and cadmium from the Odda zinc smelter and iron, manganese and chromium from the Mo i Rana industries. Because of topographic factors these point sources generally influence only limited areas near the source. The most severe influence from local point

sources is emissions of copper and nickel from Russian smelters situated close to the Norwegian border in the far northeast. In contrast to the emissions in Norway, the contribution from these copper-nickel smelters has increased steadily over time. The geographical trend of mercury in moss differs substantially from bulk deposition values calculated from precipitation monitoring, showing quite uniform values all over Norway. This is probably explained by retention of elemental mercury in the moss, as different from precipitation where only oxidised forms of the elements are found.
Since 2000, a more detailed moss survey has been conducted every five years around 15 main industrial pollution sources in the country. This survey was initiated by The Norwegian Climate and Pollution Agency and financed by the industries involved, and has become a useful instrument in assessing emission trends of metals from these industries.

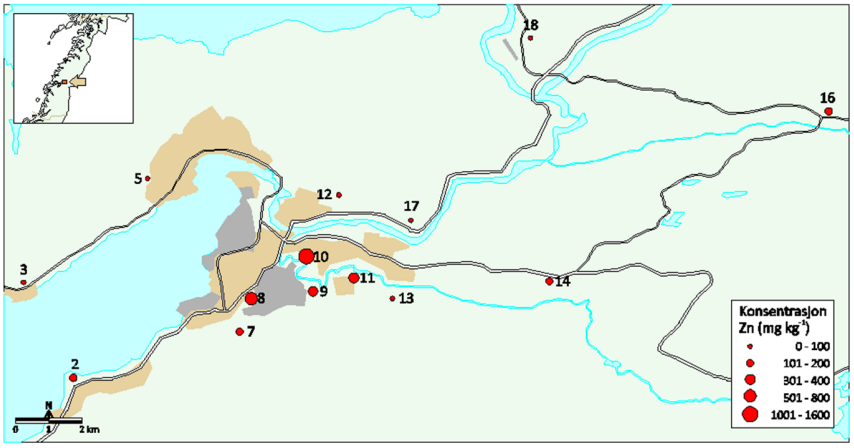

Figure 2. Concentration of Zinc in moss samples - Mo i Rana

In 2010, separate moss samples were collected at 20 sites distributed over the country, and the concentrations of several groups of persistent organic pollutants such as polychlorobiphenyl (PCB), polycyclic aromatic hydrocarbon (PAH), and polybrominated diphenyl ether (PBDE) were determined. These compounds are retained in the moss from the atmosphere, and moss samples may thus be a useful instrument for looking at time trends also for these compounds (Harmens et al., 2013). The geographical patterns are influenced by local sources as well as long-range transport, depending on the substance considered. The south to north distribution apparently depends on the volatility of the compounds.

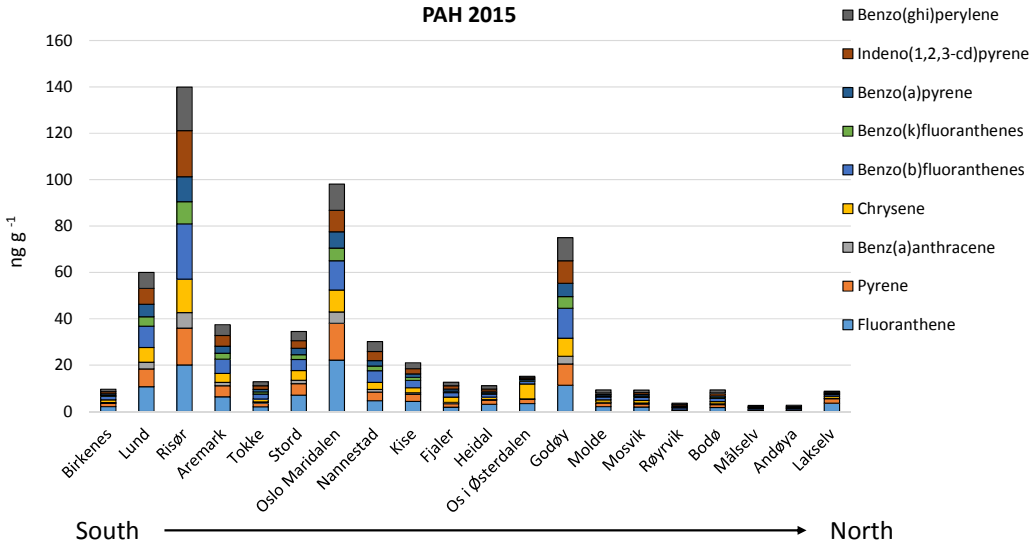

Figure 3. Distribution of selected PAH compounds from the 2015 study.

Conclusion

The nationwide moss survey has been conducted repeatedly since 1977, providing a detailed record of temporal and spatial trends of metal deposition over Norway (Steinnes et al, 2011). This is an important and valuable supplement to the national monitoring of trace metals in precipitation, which is limited to a small number of sites.

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Poland

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Background

Moss monitoring was initiated in Poland in the 1970s and became a part of the European monitoring programme in 1990. It is conducted every five years and utilizes a common moss species *Pleurozium schreberi* (Willd. Ex Brid.) Mitt. as a bioindicator. The aim of the 2015 Polish moss survey was to assess the air quality in four regions differing in the degree of urbanization and industrialization, and compare it with the state recorded in the past (2001). The selected regions were: 1) the Legnica-Głogów Copper District (LG) located in the west of the country, with copper mines and smelters, 2) the Silesian-Cracow Industrial District (SC) in the southern, heavily industrialized and urbanized part of the country, with coal mines, coal-based facilities, zinc-lead ore mines and smelters, and steelworks, 3) the central region (CEN) covering the Warsaw agglomeration (the capital of Poland), and 4) the reference area in north-east Poland (REF) away from large cities and industry. The sampling sites (N=117) were the same as in 2001. In green parts of mosses the concentration of 13 elements (N and As, Cd, Co, Cu, Cr, Fe, Hg, Mn, Mo, Ni, Pb, Zn) was determined. Four elements, Cd, Cu, Fe and Pb were analysed in both years.

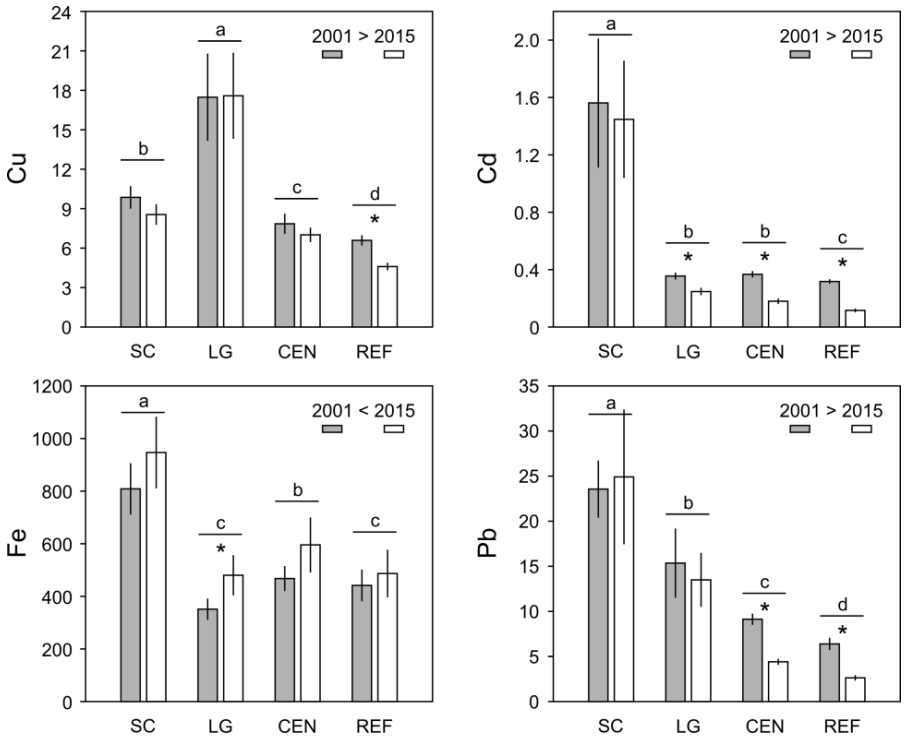

Figure 1. Concentration of four metals (mean and standard error) in mosses collected in four Polish regions in 2001 and 2015. Significant differences ($p<0.05$) were indicated by different letters (between regions), inequality signs (between years) and asterisks (between years within the regions).

Temporal and spatial patterns in element accumulation

The content of metals in mosses significantly differed between 2001 and 2015 (Figure 1). The levels of Cd, Cu and Pb decreased, while Fe showed the opposite trend. Significant differences were also found between the study regions. As expected, the most contaminated were industrial regions, i.e. **SC** (high concentrations of Cd, Fe and Pb) and **LG** (high concentrations of Cu and Pb), while the reference area was the cleanest. In the case of Cu, Cd and Pb, the year × region interaction was

found. This suggests that air quality has improved only in areas that were relatively clean in the past; on the contrary, in areas characterized by high levels of pollution in 2001, the poor condition of the environment persists.

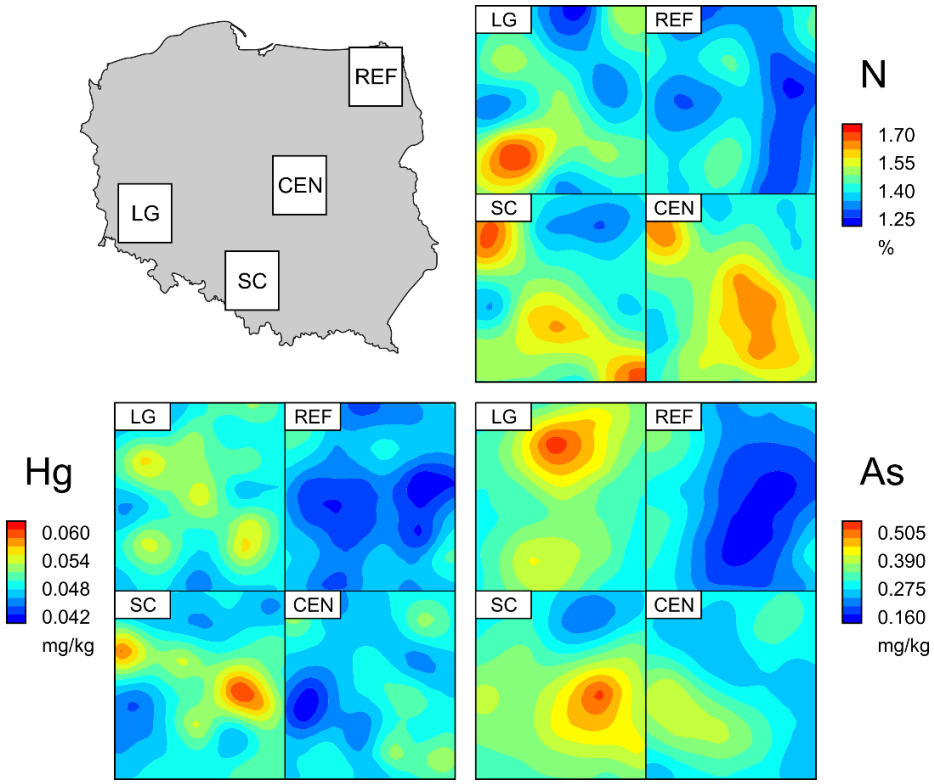

Figure 2. Spatial distribution of nitrogen, mercury and arsenic in 2015 in four studied regions as indicated by moss monitoring.

Other elements (N and As, Co, Cr, Hg, Mn, Mo, Ni, Zn, examined in 2015) were compared only between regions. Significant diferences were found for all with the exception of Co. The lowest levels were always observed in the reference area (Figure 2). As for the other regions, the pattern was element-specific. For example, the central urban region surpassed other regions in terms of the level of N and Ni, while As and Hg levels were highest in the industrial regions (Figure 2).

Acknowledgements: The study was financed by the statutory fund of the W. Szafer Institute of Botany of the Polish Academy of Sciences.

Romania

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Background

In the period 1995–2001 the first systematic study in Romania of atmospheric pollution from heavy metals and other toxic elements based on moss analysis was undertaken as a Romanian–Russian–Norwegian collaboration (Lucaciu et al., 2004). The results on moss samples collected in different regions of Romania in 1990, 1995 and 2000 were unified and reported by Harmens et al., 2008. Results for the nationwide moss survey undertaken in 2010/2011 by four Romanian Universities from Targoviste, Galati, Iasi and Baia Mare were compiled in Harmens et al., 2013; Harmens et al., 2015; Popescu et al., 2014; Stihi et al., 2017. The study continued with the campaign in 2015/2016, in order to complete the pollution database with nitrogen, besides the assessment of trends of heavy metal and toxic element pollution.

Results and discussion

The moss survey, undertaken in 2015/2016 by teams from Targoviste, Galati and Iasi universities, comprised 214 sampling sites over the Romanian territory (Fig. 1). A total of 29 elements (Na, Mg, Al, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu*, Zn, As, Rb, Sr, Cd*, Sb, Ba, Cs, La, Ce, Sm, Tb, Pb*, Th, and U) were determined in the large-scale concentration range — from 10000 mg/kg for Al, Fe, Ca and K to 0.001 mg/kg for some rare earths — by two complementary methods: instrumental epithermal neutron activation analysis (INAA) at the IBR-2 reactor in Joint Institute for Nuclear Research at Dubna, Russian Federation, and inductively coupled plasma mass spectrometry (ICP-MS)* in the Multidisciplinary Research Institute for Science and Technologies from Valahia University of Targoviste, Romania. Nitrogen was determined for the first time for Romania at National Institute for Research and Development in Forestry "Marin Dracea", Campulung Moldovenesc Station, Suceava County, Romania. Maps of nitrogen and metal load in mosses were generated by DATA MANAGEMENT SYSTEM (DMS) on the cloud platform of Joint Institute for Nuclear Research (Dubna, Russia) (Figure 1).

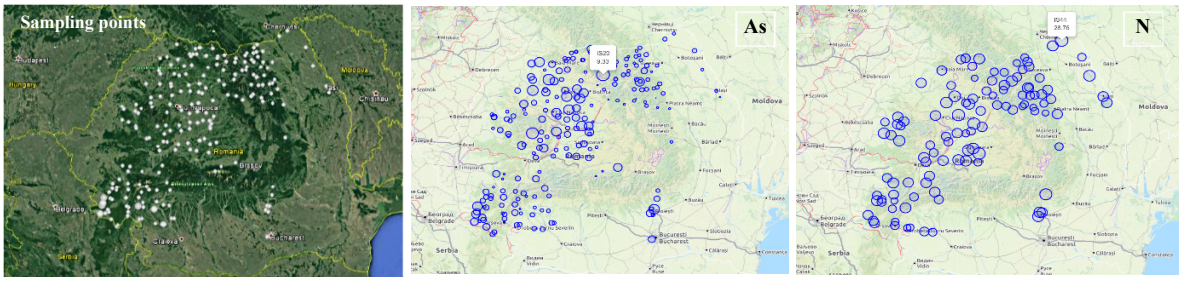

Figure 1. Sampling points and typical maps of element concentrations in mosses in Romania (2015).

Although the concentrations of heavy metals in mosses collected in Romania are high compared to other (Eastern-) European countries, the temporal trends presented in Figure 2 based on the reported (Harmens et al., 2008, 2013, 2015) and obtained values for mean and median concentration of selected metals reveal a decrease in 2015 for the majority of elements, with the exception of As, as well as Fe, V and Cr (mean value).

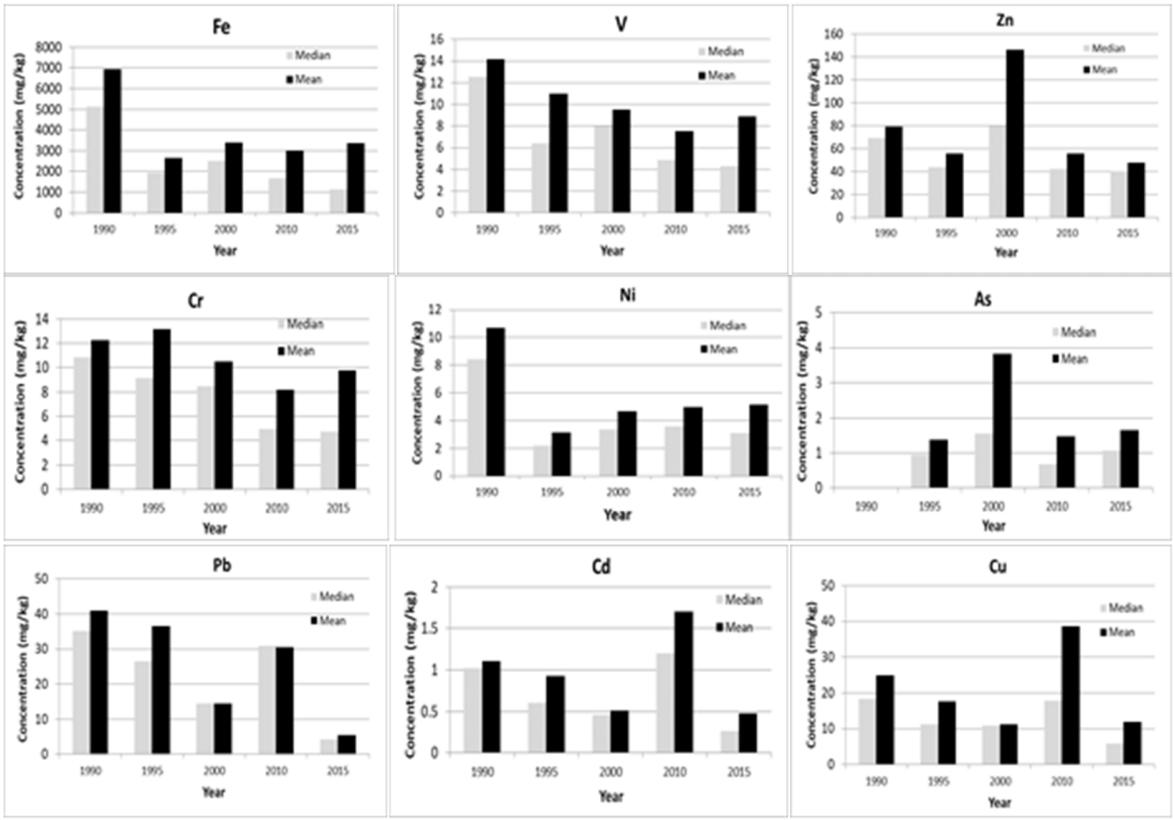

Figure 2. Temporal trends of 9 metal concentrations in moss in Romania since 1990.

Conclusions

From the presented results it can be concluded that atmospheric deposition of trace metals is a considerable problem in the northern and western parts of Romania. This study contributes to the national monitoring system of Romania for long-range transport of air pollutants, and along with epidemiological data it may serve for baseline human health risk assessments.

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Russian Federation

The Russian Federation is firmly entrenched in the list of countries with poor environmental status. The air quality complies with health standards in only 15 large cities of the Russian Federation and only 15% of the urban population breathe relatively clean air. In 125 cities, annually 5–10 times higher air pollution levels than the maximum permissible concentrations (MPC) are recorded.

The dirtiest cities include Norilsk, Moscow, St. Petersburg, Yekaterinburg, Novosibirsk, Omsk, Tomsk, Chelyabinsk, Kemerovo, Lipetsk, Novokuznetsk, Magnitogorsk, Nizhny Tagil, and Cherepovets. In all of them, 10-fold excesses of the maximum permissible concentrations of at least three pollutants at the same time are noted. Norilsk is one of the dirtiest cities in the world, having air pollution levels similar to Mexico City, Los Angeles, Athens, Bombay and Cairo.

However, it should be noted that it is customary to include only large Russian cities in the lists of environmentally disadvantaged places, while medium or even plants in small cities may be polluting the most. Indeed, 39% of the urban population of the Russian Federation lives in territories where the level of air pollution is not monitored at all (http://znakka4estva.ru/dokumenty/inostrannye-yazyki-yazykoznanie/air-pollution-in-russia/). Thus, the UNECE ICP Vegetation plays an important role in monitoring the air pollution situation in some areas where enthusiasts collected moss species in compliance with the Moss Manual of the UNECE ICP Vegetation.

During the 2015/2016 moss survey, the following territories were monitored for deposition of trace elements using the moss biomonitoring technique, neutron activation analysis, and atomic absorption spectrometry, providing results for 35-40 elements: Republic of Udmurtia, Ivanovo region, Tula region, Ryazan' region, Kaliningrad region, Tikhvin district of Leningrad region, Bryansk region, Moscow region, and Tver region. In addition, some reserves of the Russian Federation were included, i.e. Prioksko-Terrasny Biospheric Nature Reserve, an island of wilderness in the most densely populated region of the Russian Federation, the only reserve in the Moscow region, situated 12 km from Serpukhov town; the most protected Voronezh Biosheric Nature Reserve, one of the oldest nature reserves, located only 25 kilometers from the industrial town of Nikel in Murmansk Region; Reserve "Arctic Circle", and some others. Individual county reports are presented for Moscow, Ivanovo, Ryazan', and Tula region.

Moscow region

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Background

Moscow region is a federal subject of the Russian Federation. With a population of 7,095,120 living on a territory of 44,300 square kilometers it is one of the most densely populated zones in the country. The first attempt to apply moss biomonitoring technique in the north-eastern part of the Moscow region was made in 2004 (Vergel et al. 2009). The main pollution sources was determined to be industrial activity and transport. The aim of the present study was: i.- to present results from the 2015/2016 moss survey based on terrestrial moss analysis neutron activation analysis (NAA) and atomic absorption spectrometry (AAS) as analytical techniques; ii.- to compare the obtained results with data obtained in 2004; and iii.- to identify the possible sources of heavy metals.

Concentrations of heavy metals in mosses

Sampling was performed in June 2014 to a total of 39 sampling stations in the north-eastern part of the Moscow region in accordance with the CLRTAP (2015) manual for mosses sampling. A total of 33 elements (Na, Mg, Al Cl, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Zn, As, I, Se, Mo, Br, Rb, Sr, Sb, Cs, Ba, La, Ce, Sm, Hf, W, Th, and U) by using both short and long time activation. The concentration of Cd, Cu and Pb in the moss samples was determined by means of a Thermo Scientific™ iCE™ 3000 Series AA spectrometers with electrothermal (graphite furnace) atomization.

Multivariate statistics (factor analysis) was applied to identify associations between the determined elements. Three factors with the variability of the established elements of 70% have been identified. Factor 1 (Fig. 1) covers 43% of the total variability and can be defined as a geogenic/anthropogenic association. The contents of these elements in the moss samples are significantly influenced by mineral particles released to the atmosphere by wind, and their spatial distribution mainly depends on urban activities not related to industrial activities, for example transportation.

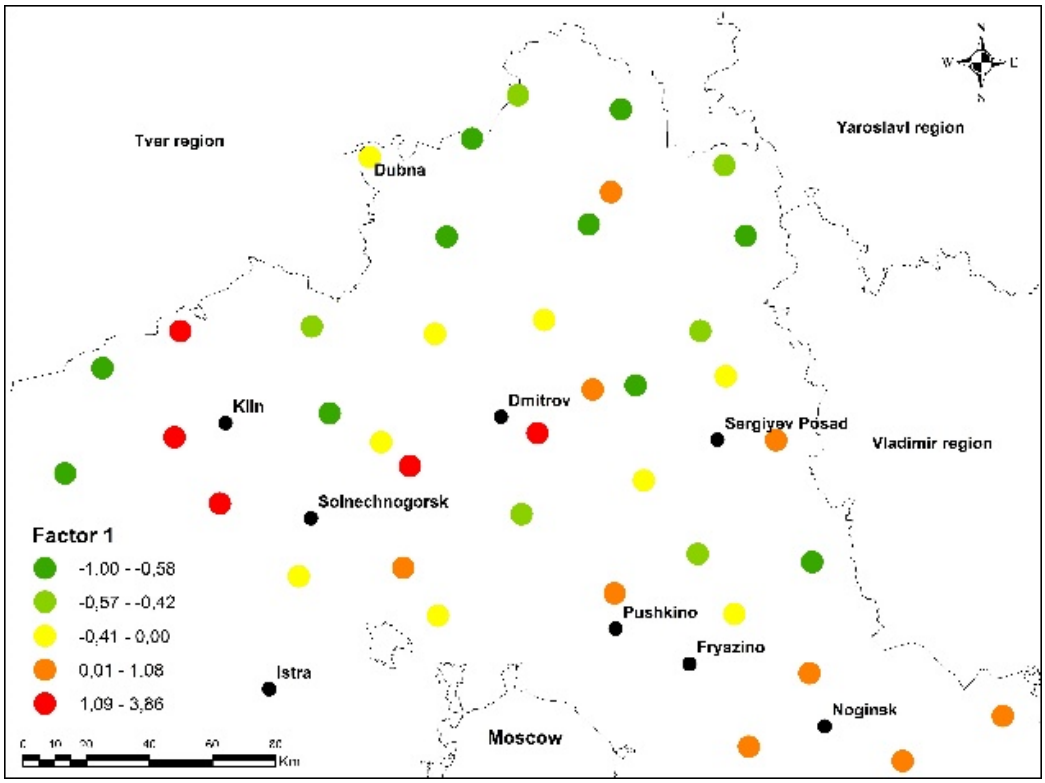

Figure 1. Distribution of Factor 1.

Factor 2 (Mo, Sb, and W) is an anthropogenic factor and is associated with urban and industrial activities. From Fig. 2 it appears that the highest contents of these elements are found in samples collected in the eastern part of Moscow where a main part of industrial enterprises is located. The enormous traffic density in this zone also contributes to the increased pollution of the region. Factor 3 (Fig. 3) represents 13 % of the total variance. This factor is loaded by Mn and Br and negatively loaded by Cs.

For a better interpretation of the results, various descriptors such as the contamination factor CF, was calculated (Zinicovscaia et al. 2017). According to the scales proposed by Fernández and Carballeira (2001) the content of Cr (2.36), V (1.62), Zn (1.22), Cu (2.44) and Fe (2.52) are associated with the third scale (slightly polluted areas), while Sb (3.81) and Co (3.56) are associated with the moderate pollution. CF value obtained for Pb (5.5) indicates on moderate pollution, while value obtained for W (13) point at severe pollution.

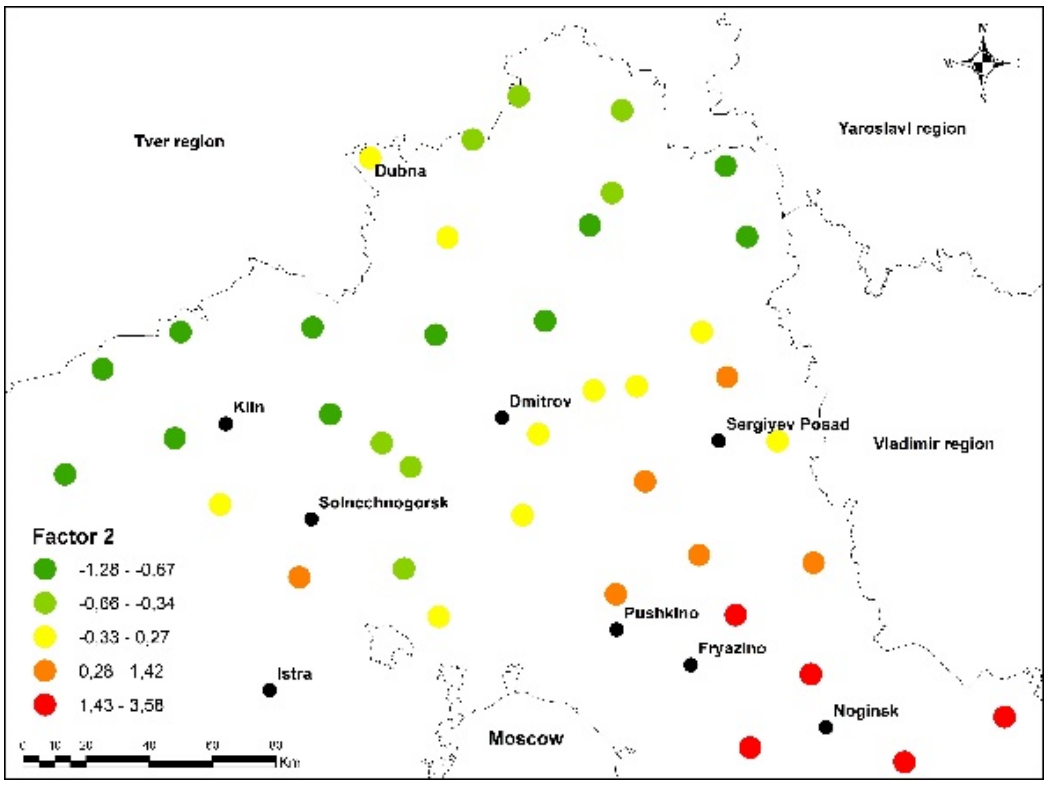

Figure 2. Maps showing the distribution of Factors 2.

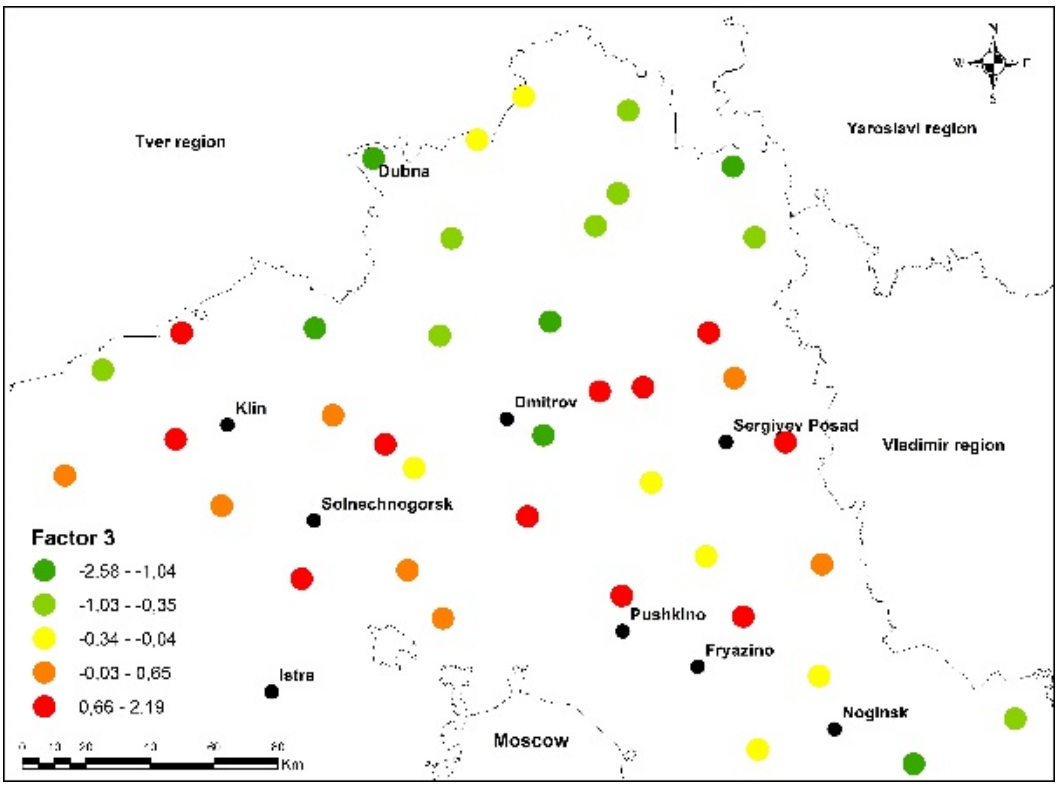

Figure 3. Maps showing the distribution of Factors 3.

Conclusion

Moss biomonitoring is suitable technique for detecting spatial trends in heavy metal deposition. Using neutron activation analysis in combination with atomic absorption spectrometry it was possible to determine 36 major and trace elements in the studied moss samples. According to contamination factor and geo-accumulation index Cr, Fe, Co, and W cause moderate or severe environment pollution. Moscow region is less polluted than Tula region, but more polluted than Tikhvin and Ivanovo regions. Present results showed no significant differences with respect to the previous, 2004 moss biomonitoring results. Industry, thermal power plants and transport could be considered main air pollution sources in Moscow region.

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Ivanovo region

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Background

Ivanovo region is situated at the center of the European part of Russia and has an area of 22 000 km^2. Ivanovo city is located 300 km North-East from Moscow. Moss biomonitoring in Ivanovo region has been started since 2010 within the framework of the International Cooperative Programme on Effects of Air Pollution on Natural Vegetation and Crops, ICP Vegetation. Samples of mosses *Pleurozium schreberi* and *Hylocomium splendens* were collected and prepared according ICP Vegetation moss manual. 40 moss samples were picked up in 2010. In 2015 the sampling grid was enlarged to 57 sampling sites. Two complementary analytical techniques were used: neutron activation analysis (NAA) at the reactor IBR-2 of FLNP JINR and atomic absorption spectrometry (AAS) at the ISUCT. A total of 40 elements (Na, Mg, Al, Cl, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Zn, As, Se, Br, Rb, Sr, Zr, Mo, Ag, In, Sb, I, Cs, Ba, La, Ce, Nd, Sm, Eu, Gd, Tb, Tm, Yb, Lu, Hf, Ta, W) was determined by NAA. To determine concentrations of Pb, Cd, and Cu AAS was used.

Metal concentrations in mosses

In 2015 the mean concentrations of the target elements in Ivanovo region mosses are the following (in mg kg^{-1}): Al - 3906, As – 0.72, Cd – 0.64, Cr – 8.25, Fe - 2184, Ni – 4.64, Co – 1.33, Sb – 0.23, Se – 0.21, V – 6.26, Ba – 92.6, Sr – 30.0, Mn – 588, and Zn – 64.7. The spatial distribution of some selected elements is depicted on Fig. 1.

It was established that in 2015 the mean concentrations of Al, Cr, Fe, V, and Co were increased in comparison with 2010 more than two times. The content of Ba, Sr, Se, Sb, and Mn is changed insufficiently. However, the analysis of the spatial distribution of anthropogenic elements is more interesting. In 2010 the main source of heavy metal deposition on the territory of Ivanovo region were the asphalt and metal processing plants near the town of Rodniki. In 2015 the situation is changed. Leading role of the heavy metal emission becomes play external sources: industrial objects of the Yaroslavl region as well as Volgorechensk power station. Northern-West part of Ivanovo region always undergoes the increased impact from neighboring regions, but recently the emission levels were grown due to development of the industrial sector of economy. This reason also describes appearance of “hotspot” near the city of Ivanovo. It should be noted that the concentration of the metals in mosses is decreased on a whole Southern-East part of Ivanovo region.

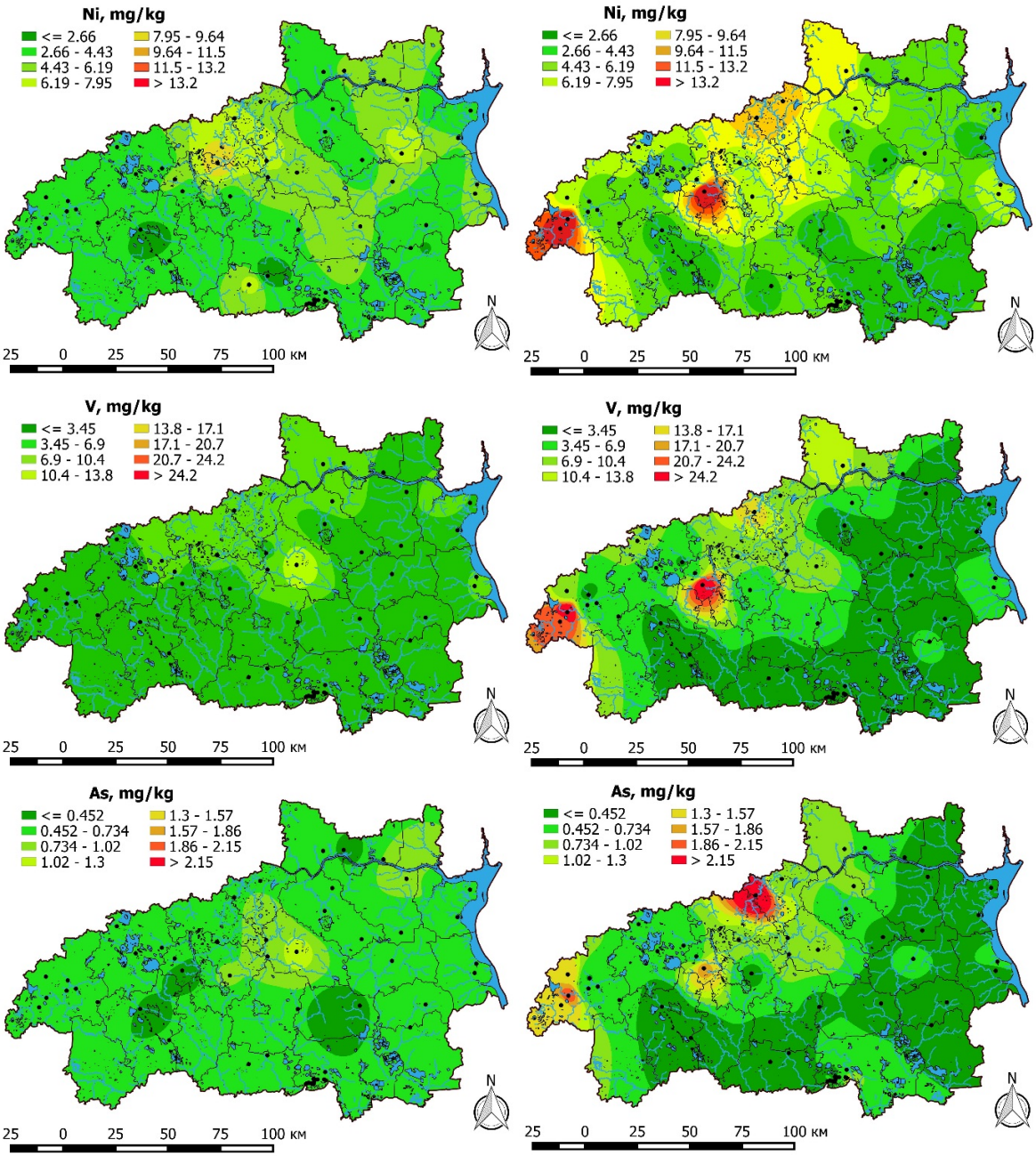

Figure 1. GIS distribution maps of Ni, V, and As in 2010 (left) and 2015 (right) in mosses sampled.

Further reading

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Ryazan' region

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Background

The air basin pollution is one of the main ecological problems of Central Russia. Central Russia is an industrially developed part of the country, home to 40% of the population, 76% of which live in urban areas. Ryazan region is one of the twelve regions here. The area of the region is thirty nine thousand six hundred square kilometers, which is close to the area of Switzerland (41.285 thousand km²). The population of Ryazan region is over one million and one hundred thousand people. The territory is unique from the point of view of its geographical position, which includes sub-taiga, broadleaf forest and forest-steppe zones.

In the last one hundred years the natural resources of Ryazan region have been abundantly used for industrialization of the area. Energy intensity and the presence of mineral resources base make Ryazan region attractive for Russian and foreign investors. Oil refining, woodworking, machine-building, metalworking, construction, roofing and finish materials production, electric power engineering, food and consumer goods industries, non-ferrous metals industry – these are the main spheres of industry and economic activities in Ryazan region. Ryazan Region is also one of the largest producers of electricity among the territorial entities of Central Russia, which, together with oil refining, cross-country gas pipelines and underground gas storages, allows the development of power-consuming industries. For such industries, biomonitoring of atmospheric fall-outs is required. All the necessary electric and thermal energy is produced by four large thermoelectric plants. Ryazan State District Power Station with the rated output power of three thousand and seventy megawatts is one of the largest thermoelectric plants in Europe. The threat to ecological safety of Ryazan district has occurred due to fast growth of concentration of industrial pollution agents in the atmosphere of Ryazan city, Mihailov and Skopin towns. Occasional peat-bog fires in north-eastern areas of the region and the echoes of Chernobyl accident in the south-west add to the negative effects. Ryazan region has become a participant of UNECE ICP Vegetation Programme for the first time. Sampling areas were distributed all over the region and include Ryazan city and twenty five townships around it. Sixty three samples of moss have been taken. Also, a sampling map has been made based on the studies of snow cover performed by scientists from Ryazan. Atmospheric fallouts in the region are controlled by the process of so-called "macroregional migration", which is strongly influenced by anthropogenic pollution.

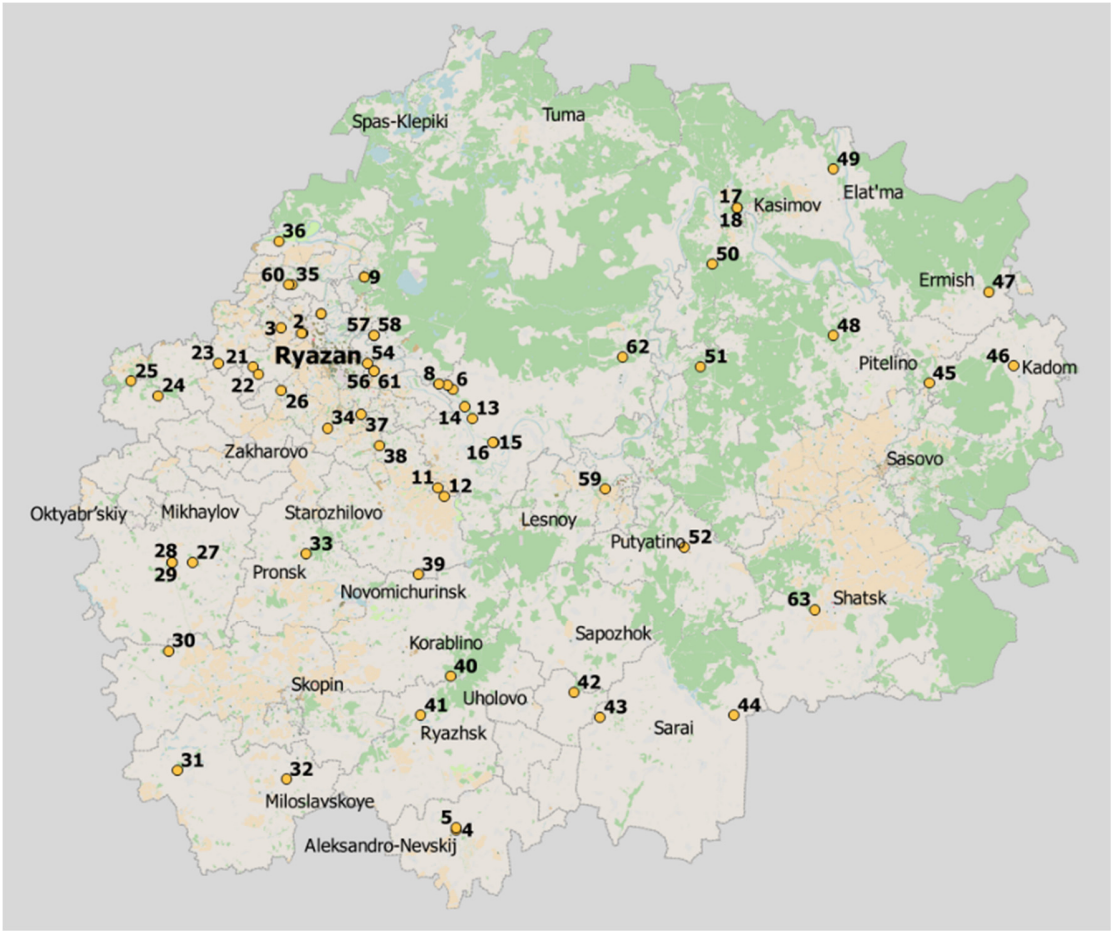

Figure 1. Sampling sites.

Below is the list of potential sources of man-made heavy metal pollution on the territory of Ryazan region:

1) Manganese, ferrum, chrome, nickel, zink found near Ryazan are supposedly produced by a joint-stock company “Ryazan Oil-Refining Company”. Its industrial facilities include five crude oil distillation units, a mild hydrocracker, a hydrogen production unit, a sulphuric acid alkylation unit, a catalytic fluid cracking unit, viscosity breaker, four catalytic reforming units, two distillate hydrotreatment units, a jet kerosene hydrotreating unit, isomerization unit and others.
2) Guardian Industries is one of the world’s largest producers of plate glass and special-purpose glass products for different industrial sectors. Potentially it could be a source of chrome, aluminium, plumbum, ferrum, manganese, nickel, cadmium.
3) Zink, plumbum, chrome, ferrum, manganese, aluminium and cadmium in the sampling points near Ryazan supposedly come from a closed joint-stock company «Splav», which owns a factory recycling lead and copper recoverable sources. First of all, there are run-down acid-storage batteries, and also lead, copper, brass and bronze scrap of all kinds.
4) The thermoelectric plant eighty kilometers southward of Ryazan (Ryazan State District Power Station) belongs to the five most powerful thermoelectric plants of Russia. The main fuels here are coal and natural gas, the back-up fuel is black oil. The sampling point forty kilometers away from the plant has shown high concentration of chrome, ferrum, vanadium, nickel.
5) Manganese, ferrum and aluminium in Sasovo township of Ryazan region are supposedly produced by a large machine-tool builder, joint-stock company «Sasta».

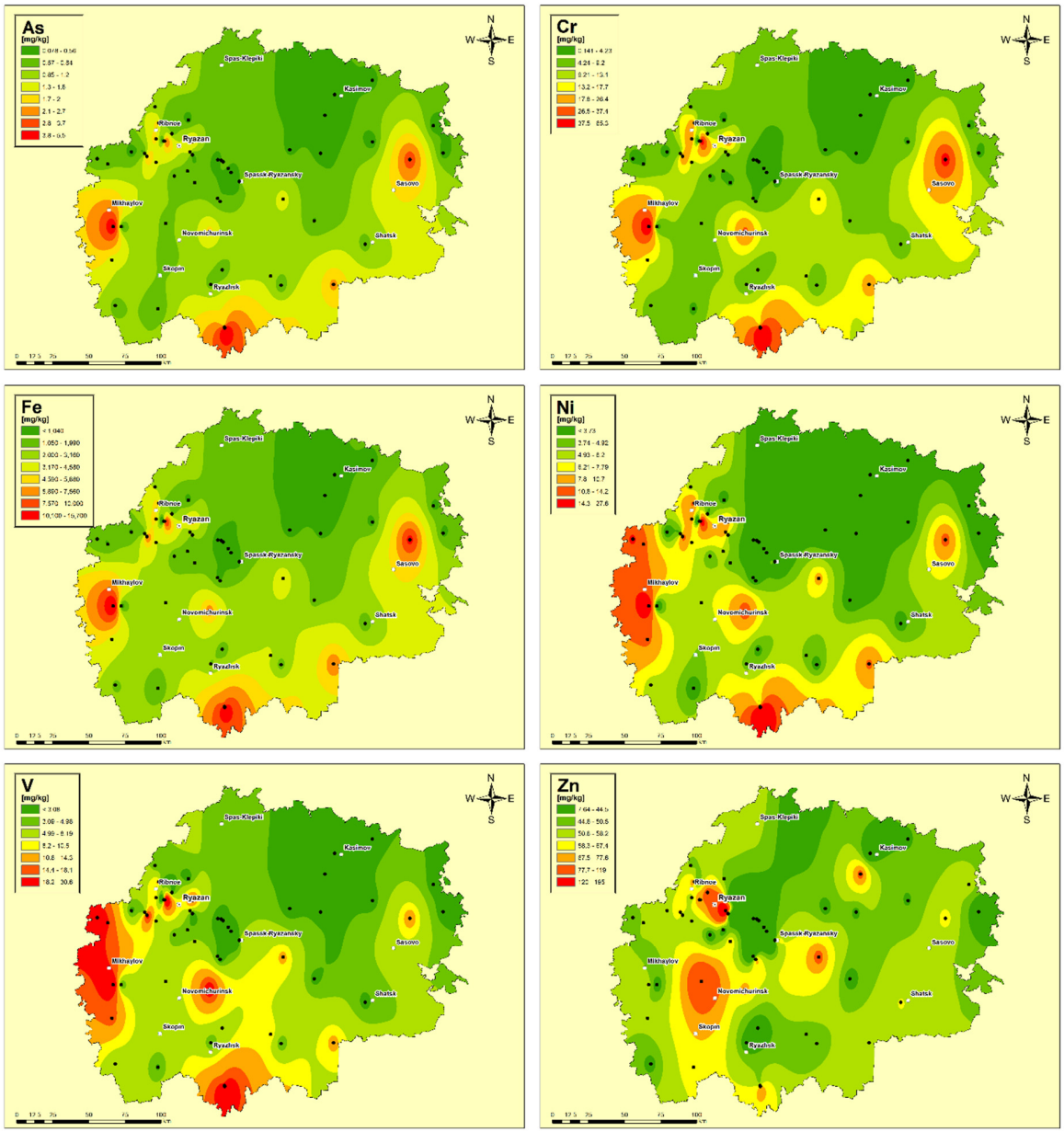

Figure 2. Distribution maps of As, Cr, Fe, No, V, Zn.

The areas with the highest concentrations of vanadium, aluminium and Manganese are Ryazan, Mikhailov, Rybnoe, Korablino, Starozhilovo, Alexandro-Nevskiy townships. The highest concentrations of chrome have been found in Ryazan, Mikhailov, Alexandro-Nevskiy and Shatskiy townships. This survey shows only a part of the interpretation of the data received from factor analysis. For example, the reason for high concentration of Manganese close to Oxkiy natural reserve (which is higher than five hundred and ninety-eight point two milligrams per gram) is yet to be found. It's interesting that concentration of heavy metals in mosses on the territory of Ryazan region is almost the same as in Moscow and Tula regions. Industrial output of Moscow region in 2016 was eight times higher than that of Ryazan region. Despite the huge difference in industrial output, the two regions have the same concentrations of heavy metals on their territories. The concentrations of most of the elements under study are higher on the territory of Ryazan region than on the territories of such countries as Serbia, Czech Republic, Romania, Latvia, Slovenia.

Tula region

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Background

Tula region is situated in the central part of the Eastern European Plain, it covers an area of 25.7 thousand km^2 and borders with Moscow, Ryazan, Lipetsk, Oryol and Kaluga regions. Regional environmental problems are caused, first of all, by clustering of 473 enterprises of chemical, metallurgy, defense, machine-building industry; fuel, energy and mining complex at a relatively small area, being the main sources of air pollution in the region. Moss biomonitoring in Tula Region of Russian Federation started in 1999/2000 by M.V. Frontasyeva and E.V. Ermakova (Ermakova et al., 2004) and continued by us in 2015-2016. Mosses collected in a regular grid (17 km x 17 km) started in July and finished in September of 2015-2016 from 91 monitoring sites in the forest, forest-steppe, steppe and marsh phytocoenosis of the Tula region (Fig.1). In several sampling points were selected and analyzed several moss species. Such species as: *Abietinella abietina, Atrichum undulatum, Rhytidiadelphus triquetrus, Brachythecium rutabulum, Brachythecium salebrosum, Eurhynchium angustirete, Plagiomnium ellipticum, Orthotrichum speciosum, Oxyrrhynchium hians, Rhytidiadelphus triquetrus* showed similar accumulative characteristics as the recommended ones or even surpass them. These species, as well as those recommended by Moss Manual 2015/2016, were selected for analysis. A total of 42 elements were determined by ENAA in Frank Laboratory of Neutron Physics, Joint Institute for Nuclear Research, Dubna, Russian Federation. The results of moss samples have been reported in several publications (Gorelova et al., 2016-2018) and included in the database http://moss.jinr.ru.

Metal concentrations in the air of region by moss-biomonitoring method

The concentration of trace elements in moss samples based on the mean values follows the trend Al>Fe>Ti>Mn>Ba>Zn>Sr>Zr>Cr>V>Ce>Br>Ni>Nd> La>I> Co>Th>Hf>As>Cd. CF - contamination factor (CF=MD element / background level) lies within 3-5 for such elements as Cd, Zn, Sr, Co, Mo, Cs, Nd, Eu, Yb; 5-7 for As, Fe, Ni, V, Al, Mn, U, Ba, Th, I; 7-10 for such elements as W, Tb, Sc, Cl, La. CF more than 10 for Ce, Sm, Ti, Zr, Hf and Tm. The level of contamination of region air compare with data for RF reserves can be classified as “slight pollution” (2-3.5) for W and Cl; as “average pollution” (3.5-8) for Cd, Cr, Fe, V, Al, Sr; as “high pollution” (8-27) for Mg, Sm, U, Tb, Th, Sc, La, Hf, Ta (Fig. 2).

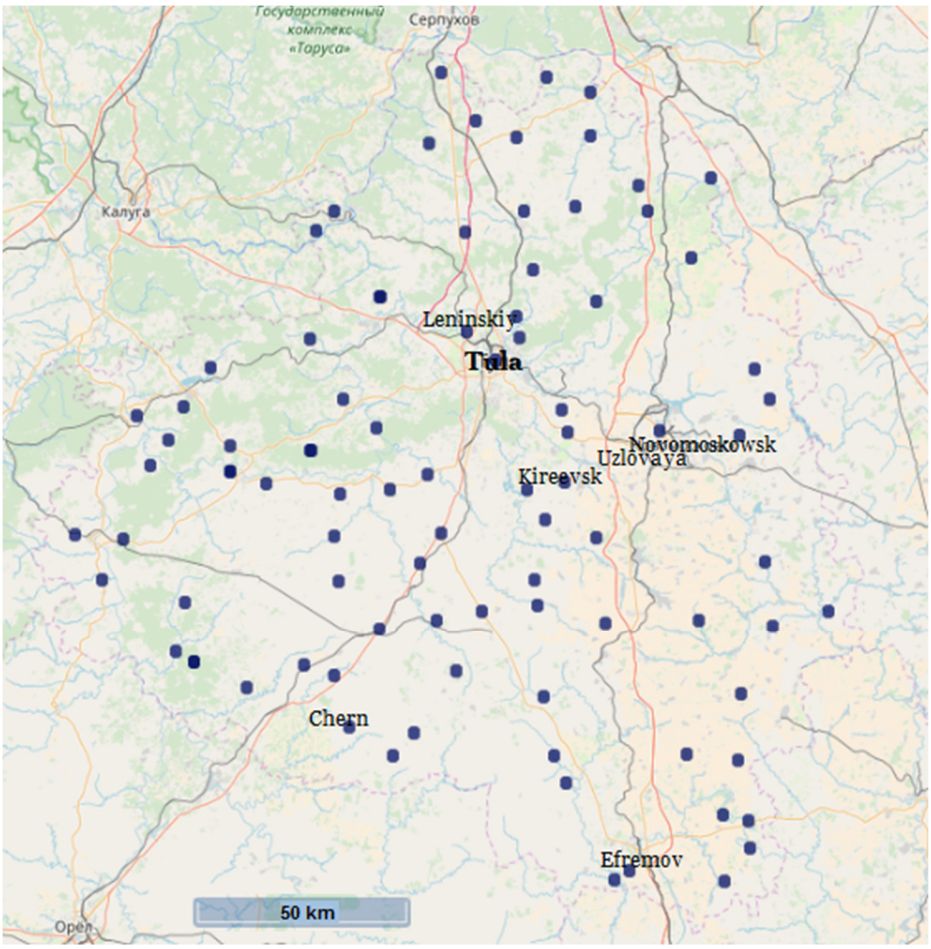

Figure 1. Sampling points of Moss biomonitoring in Tula region.

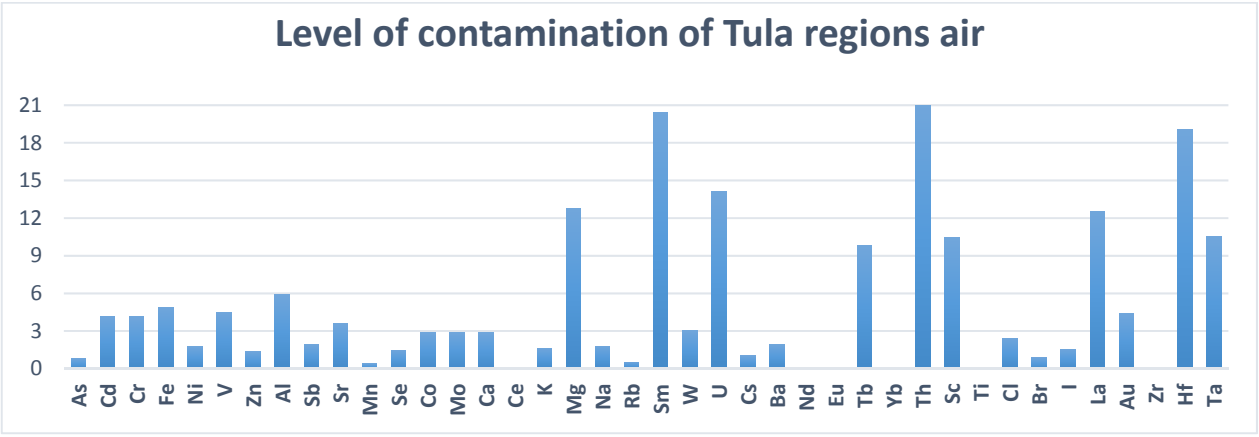

Figure 2. Level of contamination of Tula regions air compare the reserves of Russian Federation

Comparison of the data of elements concentration in the mosses of Tula region with the values for the European countries represented in the database 2015/2016 http://moss.jinr.ru shows a high level of content in the air of the region of such heavy metals and metalloids as:
V: values 4.8 times higher above the Republic of Belarus and 2 times higher above the Ukraine, in 1.6-10.5 times higher than European Union countries;
Cr: value in 1.7 times higher above the Ukraine, in 1.1-21 times higher than in Europe (excluding Albania, the Czech Republic and Greece);

Fe: value 4.8 times higher than for the Republic of Belarus mosses 3 times higher above the Ukraine, in 1.1-10.5 times above the European Union countries;
Zn: value exceed the data for Belarus Republic and for Ukraine by 37 %, and 1.2-2 times higher than in European Union countries (excluding Czech Republic);
As: value 3 times higher than the Republic of Belarus and 1.3-8.3 times higher than in European Union countries (excluding Czech Republic, Greece, Romania, Serbia);
Cd: values in the 1.2-6.4 times higher than in European countries (excluding Slovakia).
Results of the factor analysis revealed four factors:
Factor 1: Na, Mg, Al, Sc, Ti, Cr, Ni, Co, As, Rb, Zr, Ba, Cs, La, Ce, Nd, Sm, Eu, Tb, Yb, Hf, Ta, Th, U associate with soils, industrial pollution of soil and weathering processes.
Factor 2: V, Fe, Zn, Se, Mo - can be attributed to technogenic industrial pollution.
Factor 3: Ca, Cl, Br associate with physiological activity of mosses.
Factor 4: Sb, Tm, W associate with the extraction and processing of ores.

Temporal trends for Tula region for 10-15 years (Ermakova et all, 2004) shows increase of atmospheric pollution by such elements as Fe (12 %), Ba (17%), Cr (23 %), Co (28 %), As (13 %), Cd (32 %), Sr (18 %), Sm (15 %), Tb (12 %), Yb (45 %), Ta, (8 %) W (7 %), Th (15 %). The concentrations of such elements as Cl, Mn, V in atmospheric deposition decrease by 23 %. High content of As was found in the Kireyevsky and Uzlovsky districts of the region; Cd in Tula city (region center) (probably due to the influence of the vehicle emissions); Cr in the mosses of the Efremovskiy area, Fe in Tula and the Kireevskiy area, Ni in the Chernskiy and Efremovskiy areas, V in the Leninskiy area. The maximum content of Zn was observed inTula, the Kireevsky district and southern districts of the region. Mn deposition was revealed in the east of the region. Such a redistribution of toxic elements from the main sources of pollution with air masses can be associated with wind transfer in the southern direction, depending on the mobility of the elements.

Discussion and conclusions

The study of atmospheric pollution by passive biomonitoring in the industrial region of central Russia - Tula region revealed a tendency to increased pollution with such elements as: Fe, Ba, Cr, Co, As, Cd, Sr, Sm, Tb, and Yb in the past 10 years. Compared to the Moscow region the air of Tula region is contaminated with such elements as: Cr, Fe, V, Al, Sr, Ce, Sm, U, Tb, Th, Sc, Ti, Cl, La, Hf. These are the elements of technogenic origin, associated with the activity of the metallurgical, metalworking, coal mining enterprises in the region. Concentrations of V, Cr, Fe, Zn, As in atmospheric deposition for Tula region are 1.1-21 times higher than those for Republic Belarus, Ukraine and EU.

Acknowledgements: The study was supported by RFBR Grant 15-45-03252 - r_centre_a «*Biomonitoring of atmospheric pollution with industrial emissions of forest and forest-steppe ecosystems of Central Russia: Tula Region case study*» and RFBR Grant 19-29-05257 mk «*Technogenic soil pollution with toxic elements and possible methods for its elimination*».

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Serbia

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Background

Serbia participated in European moss survey, for the first time, in 2000, when the samples were collected only in northern part of the country (n=92), and analysed on the content of heavy metals by INAA (Frontasyeva et al., 2004). In 2005, the moss was collected through Serbia (n=193), and analysed to the content of heavy metals (using INAA) and radionuclides (Krmar et al., 2007). In 2010, the samples were collected but, unfortunately, have not analysed. Finally, in 2015/2016, over the whole territory of Serbia, the moss samples were collected (n=212) and analysed on the content of 27 elements by ICP-OES and ICP-MS techniques; prior the analyses, the samples were digested in microwave digester in solution of HNO_4+H_2O_2 (Aničić Urošević et al., 2018). In addition, natural and cosmogenic radionuclides were determined in the samples by low-background gamma spectroscopy (Krmar et al., 2016). In all mentioned sampling campaigns, only one moss species was collected – *Hypnum cupressiforme* Hedw.

Spatial patterns and temporal trends of element and radionuclide concentrations in mosses

Since 2000, the number of sampling sites is growing in Serbia with the time-span campaigns, and finally, in 2015, the whole territory of the state was included in the moss biomonitoring. Descriptive statistic of the element concentrations in the moss over the time intervals is presented in Table 1. In general, decreasing trend of the median element concentrations was observed in the moss through the years of investigation. Namely, considering 2000 vs. 2015, the median concentration of As, Cr, Cu, Fe, Ni, V, Zn decreased for more than 30%, while regarding 2005 vs. 2015, the median concentration of Cd, Pb, Sb fell extremely (≈70%). Note that different analytical techniques (INAA vs. ICP-OES/MS) were used for the elemental characterisation of the moss samples in the years of investigation.

Spatial distribution of the element concentrations in the moss across Serbia in 2015 highlighted the southern part of the country (Kosovo and Metohija) as the most loaded with the elements, especially As, Cd, Cr, Ni, Pb, Sb, V and Zn (Figure 1). This area is characterised by complex geological settings, followed by the mining, and the other accompanied activities. Besides, the highest concentrations of Cu found in the region of the copper-mining basin in the north-eastern part of Serbia.

Spatial distribution of natural radionuclides and ^{137}Cs were assessed in the moss samples collected in 2015 (Figure 2). Particular interest was on the spatial distribution of ^{7}Be, cosmogenic radionuclide, produced by cosmic radiation in lower stratosphere and upper troposphere. This radionuclide can be used as natural radiotracer in estimation of atmospheric transport paths. Higher concentrations of ^{137}Cs were found in the moss growing in forests of mountain regions than in agricultural areas. Spatial distribution of ^{7}Be was non-uniform across Serbia, and varied even for the order of magnitude.

Table 1. Heavy metal concentrations (μg g^{-1}) in moss *H. cupressiforme* in Serbia in 2000, 2005 and 2015 campaigns.

		Al	As	Cd	Cr	Cu	Fe	Ni	Pb	Sb	V	Zn	Ba	Cs
2015	Min	358	0.164	0.050	0.024	3.25	275	0.62	0.36	0.017	0.91	8.3	10.8	/
n=212	Max	11000	71.086	0.988	60.847	213.24	10119	90.61	459.68	2.195	21.49	115.2	147.7	/
	Median	**1021**	**0.732**	**0.182**	**3.647**	**8.75**	**1019**	**3.12**	**4.31**	**0.078**	**2.72**	**22.4**	**40.3**	**/**
2005	Min	1117	0.22	0.04	1	3.04	670	0.8	1.03	0.06	1.9	13	11	0.09
n=193	Max	31180	21.6	1.11	78.8	451	16100	23.8	248.6	1.37	32.7	259	438	6.77
	Median	**3946**	**1.41**	**0.26**	**6.44**	**11.1**	**2267**	**4.43**	**16.7**	**0.24**	**5.76**	**29**	**76**	**0.45**
2000	Min	1280	0.46	/	1.14	6.31	720	1.96	/	/	2.85	14	13.6	0.11
n=92	Max	22100	60.8	/	21.9	3140	9220	25.7	/	/	38.7	415	130	18.1
	Median	**5525**	**1.44**	/	**5.07**	**16.9**	**2360**	**5.65**	/	/	**9.26**	**32.6**	**34.2**	**0.477**

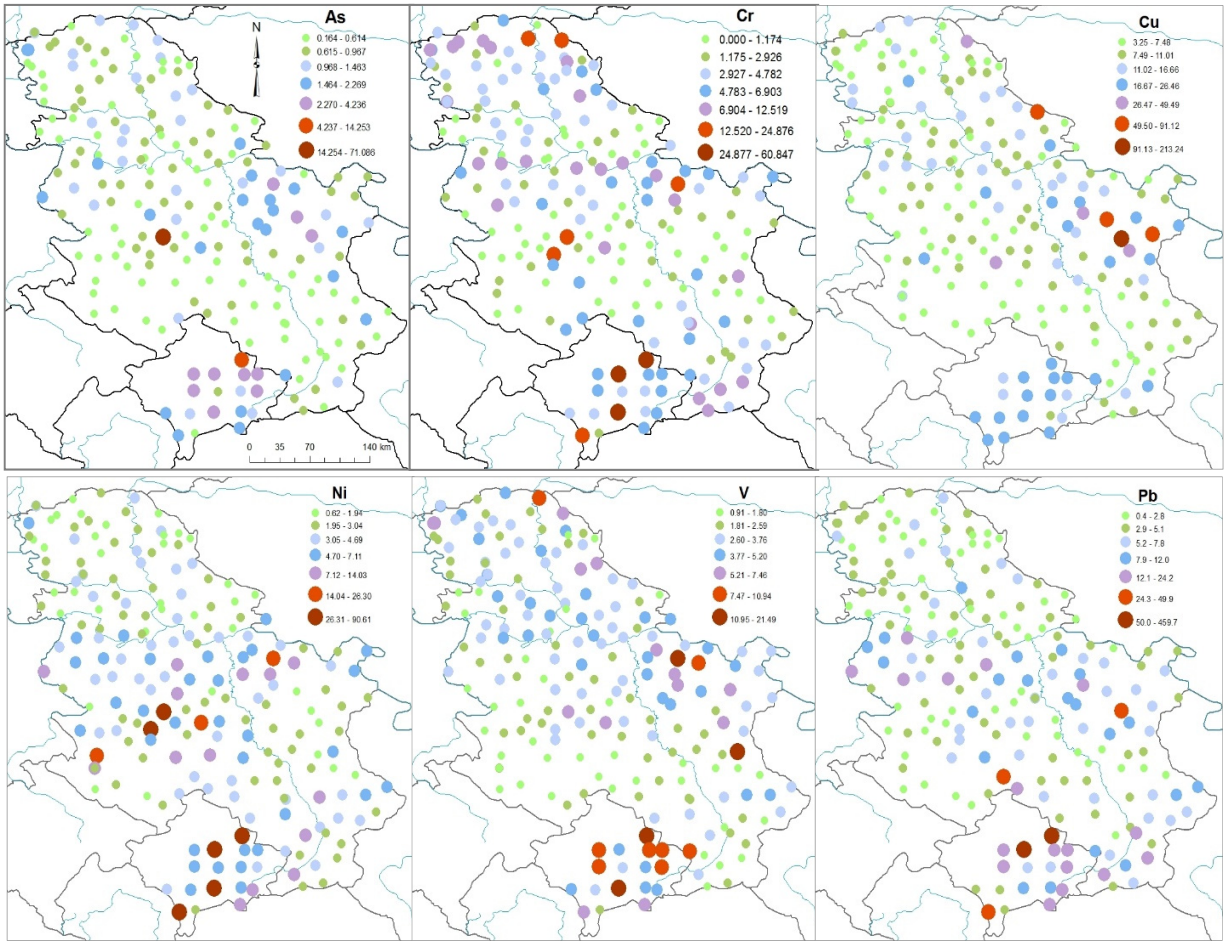

Figure 1. The mean element (As, Cr, Cu, Ni, V, Pb) concentration (μg g^{-1}) in moss *H. cupressiforme* across Serbia in 2015/2016.

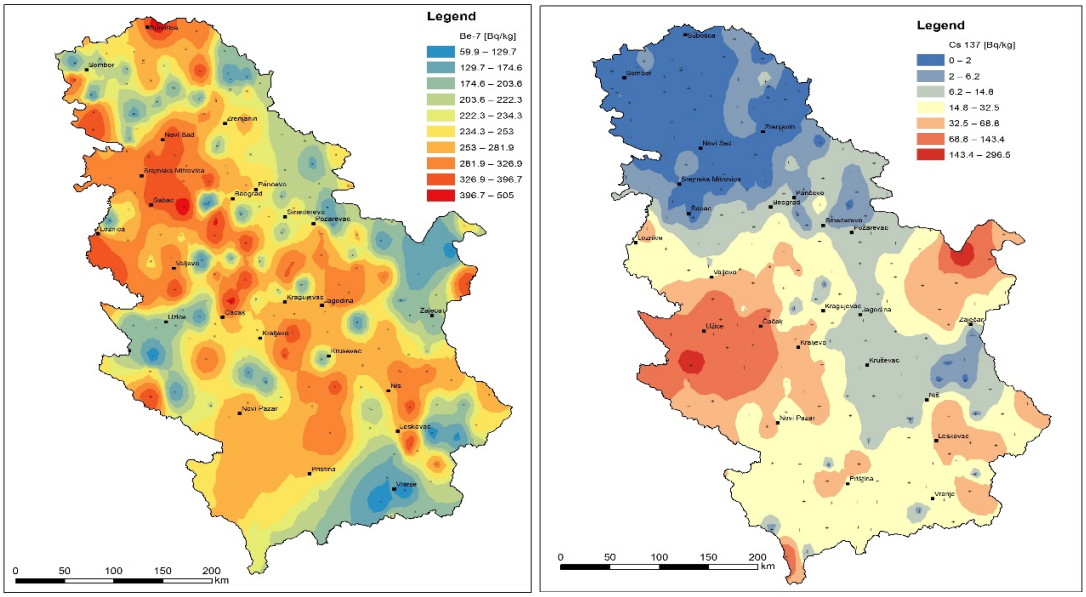

Figure 2. The content of radionuclides ^{7}Be and ^{137}Cs (Bq kg^{-1}) in moss *H. cupressiforme* across Serbia in 2015/2016.

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Slovakia

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The use of mosses as biomonitor of atmospheric deposition of heavy metals in Slovakia started more than 30 years ago in connection with the problems of the forest dying in Slovakia,1990s, within the framework of UNECE ICP Vegetation programme, systematic studies using moss were carried on in Slovakia (net 16x16 km), and the results were presented in the European Atlas *Atmospheric Heavy Metal Deposition in Europe – Estimations Based on Moss Analysis*, It is assumed that in the Slovakia (SK) a large gradient of the atmospheric deposition load of elements exists because part of the SK territory belongs to the most polluted areas in central Europe known as the 'Black Triangle II'. In the east of Slovakia (frontier with Poland and Ukraine) we are found out maximum concentration of 21 elements in the year 2015. In order to recognise the distribution of element deposition in the SK, the moss monitoring technique, also known as bryomonitoring, was applied to the whole territory in 1990, 1995, 1996, 1997, 2000, 2005, 2010 (Maňkovská et al, 2012) and 2015.

The moss samples (*Pleurozium schreberi, Hylocomium splendens* and *Dicranum* sp.) were collected on the same sites (ICP Forest) from of the year 1990. Mosses were analyzed in Chemical laboratory National Forest Centre Zvolen: N (NCS-FLASH 1112); S(LECO SC-132); Cu, Cd, Pb (AAS) - Certificat 315, No 172/2012/440/5; Norm ISO/IEC 17025:2005. Other elements were analyzed in JINR, Dubna, Russia. We continue study on Slovakia within the framework ICP vegetation (1990-2015). We determine on accumulated content of 51 elements in 2015.

We find out (median) in $mg.kg^{-1}$: Ag(0.058); Al(706); As(0.456); Au(0.0017); Ba(42,6); Br(3.02); Ca(3490); Cd(0.263); Ce(1.07); Cl(159); Co(0.329); Cr(2.78); Cs(0.192); Cu(9.11); Dy(0.340); Eu(0.053); Fe(673); Gd(0.163); Hf(0.091); I(0.73); In(0.014); K(8340); La(0.617); Lu(0.109); Mg(732); Mn(342); Mo(0.172); N(19750); Na(175); Nd(1.42); Ni(2.26); Pb(0.989); Rb(12.4); S(1695); Se(0.223); Sb(0.217); Sc(0.192); Sm(0.098); Sr(15.3); Ta(0.016); Tb(0.013); Th(0.165); Tm(0.037); Ti(48.5); U(0.074); V(1.50); W(0.250); Yb(0.087); Zn(43); Zr(6.87).

It is assumed that in the Slovakia (SK) a large gradient of the atmospheric deposition load of elements. The marginal hot spots were revealed in eastern part of Slovakia - near dumps of stone chips; Manufacture of basic metals and fabricated metal product; chemical and military products (Snina, Strážske, Stropkov); Volovské Mts, (Central Spiš); Kremnické and Štiavnické Mts. (nonferrous ores processing and aluminium factories). In comparison to the average Austrian and Czech values of heavy metal contents in moss, the Slovak atmospheric deposition loads of the elements were found to be higher on average.

Spatial trends of heavy metal concentrations in mosses were metal-specific, since 1990/2015 the metal concentration in mosses has declined for Cu, Cr, Fe, Ni, Pb, S and Zn, but is higher for Cd and Mn.

The observed temporal trends for the concentrations in mosses were similar to the trends reported for the modelled total deposition of study elements in Europe, The level of elements determined in bryophytes reflects the relative atmospheric deposition loads of the elements at the investigated sites, Factor analysis was applied to determine possible sources of trace element deposition in the Slovakian moss, In Slovakia we found in comparison with Norwegian limit values (Central Norway- as relatively the cleanest region) exceeded levels for Ag, Al, As, Au, Ba, Br, Ca, Ce, Cd, Cl, Co, Cr, Cs, Cu, Dy, Eu, Fe, Gd, Hf, Hg, I, In, K, La, Lu, Mg, Mn, Mo, N, Na, Nd, Ni, Pb, Rb, S, Sb, Sc, Se, Sm, Sr, Ta, Tb, Th, Ti, U, V, W, Yb, Zn and Zr, Concentrations of N in the 3-year old segments of

mosses (*Pleurozium schreberi, Hylocomium splendens* and *Dicranum* sp.) ranged from 0.85 to 3.96 %, median 2.0% (2015); from 1 to 2.85% (2010) and from 1.65 to 3.01% (2000). In comparison the year 2000 with 2015 we are find out decrease concentration N. Maximum attributes N we are find out on central Slovakia in surroundings chemical, metallurgy and automobile industry, glass production, sugar mill, atom electric generating station and agricultural production.

Correlation between elements
(Coefficient of correlation > 0.900)

Al	Ce, La, Fe, Hf, Ta, Tb, Th, Ti, U, V
Ce	La, Hf, Sc, Ta, Tb, Th, Ti, U, Yb
Co	Ce, Hf, La, Ta, Tb, Th, Ti
Cr	Ce, La, Hf, Sc, Tb, U
Fe	Al, Ce, La, Sc, Ta, Tb, Th, U, V
Hf	Al, Ce, La, Hf, Sc, Ta, Tb, Th, Ti, U, V, Yb
La	Hf, Ta
Na	U, Sc, Ta
Sm	La, Tb
Sc	La, Hf, Ta, Ti
Tb	La, Hf, Sc, Th, Yb
Th	Sc, La, Hf, Sc, Ta, Ti
Ti	La, Ta
U	La, Sc, Ta, Th
V	Al, Ce, La, Hf, Sc, Ta, Tb, Th, Ti, Yb
Yb	La, Sc, Ta

The rate of median values of element in Slovak vs. Norway mosses

Contamination factor CF			
1-2	2-5	5-10	>10
K, Na,S, Zn	Ag,Al,As,Au,Ba,Br,Ca,Ce,Cl,Co,Cr,Cs,Cu, Dy,Fe,Gd,Hf,Hg,La,Mg,Mo,N,Nd,Ni,Rb,Sb, Sc,Se,Sm,Sr,Ta, Th,U,V,W,Yb,Zr	Eu,I,Mn,Ti	Cd, Lu, Pb

I(geo) - geo-accumulation index, I(geo)=log2(CF/1,5			
>0,5	0,5 - 1	1-2	>2
Ag,Cu,Dy,K,Na,S,Zn,Zr	Al,Br,Ca,Cl,Co,Cs,Hf,Mg, Mo,N,Nd,Ni,Sc,Se,Sr,V,W	As,Au,Ba,Ce,Cr,Fe,Gd,Hg, La,Rb,Sb,Sm,Ta,Th,U	Cd,Eu,I,In,Lu, Mn,Pb,Tb,Ti

Affected areas in Slovakia in 2015

Name	Pollution	Elements with content CF >5*C (medians) **Maximal element value in Slovakia**
Central Spiš region (Volovské Mts,)	Industrial activity metallurgy, nonferrous ores and processing factories	Ag,Al,Au,Ba,Ce,Cd,Cl,Cr,Eu,Fe,Gd,Hf,**Hg**,I,In,La,Lu, Mn, Pb,Sb,Sc,Ta,Tb,Th,Ti,U,W,Yb,**Zn,**Zr
Region Košice - Prešov	Manufacture of basic metals and fabricated metal products	Ag,**Au**,Ce,Cd,Cl, Eu,Fe,Gd,Hg,I,In,Lu,Mn,Ta,Tb,Ti,U,
Snina -Stropkov-Strážske Sk, PL a U border **Black Triangle III)**	Manufacture of basic metals and fabricated metal product, chemical and military products.	Ag,**Al**,As,Au**, Ba**,**Br,CaCe**,Cd,**Cl**,**Co,Cr**,**Cs,**Eu**,Fe**, **Gd**,**Hf**,Hg,I,In,**La,**Lu,**Mg,**Mn**,Na**,**Ni,**Pb,**S**,**Sb**,**Sc,Sm Ta,Tb,Th,Ti,U,V,Yb, Zr**
Ružomberok -Svit	Pulp, paper products, chemical and fiber industry	Cd,Eu,Fe,Gd,In,Lu,Mn,Pb,Tb
Orava	Ferro-alloys plants, fabricated metal product	Ba,Ce,Cd,Eu,Fe,I,In,La,Lu,Mn,**Na**,**Nd,**Pb,Sb,Sm,Ta, Tb, Th,Ti
Detva -Brezno	Manufacture of basic metals and fabricated metal products	Au,Ba,Ce,Cd,Eu,I,In,Lu,Mn,Pb,Sr,Ta,Tb,Ti,Yb
Jelšava –Lučenec -Poltár	Magnesite plants, glass-ceramic production	As,**Br**,Cd,Eu,I,In,Lu,Pb,**Rb**,**Sb**,**Sc,**Tb
Kremnicko-Štiavnické Mts,	Non-ferrous ores and plants, old mining districts, Aluminium plant	As,Au,Ba,Ca,Ce,Cd,Eu,Fe,I,In,Lu,Mn,Pb,Tb,Ti
Upper Nitra and Martin	Thermal power stations, manufacture of machinery and equipment	**Na, Mg**, Al, Ca, Sc, Ti, V, Cr, Co, **Ni**, Se, Br, Zr, **Mo,** Ag, I, La, Sm, Tb, Hf, Ta**, W, Au**, Th, U, Zn, **Cd, Pb**, S, Hg
Orava, Kysuce, Border CZ, SK a PL **(Black Triangle II)**	Engineering and instrument industry, glass, tire and rubber industry	Al, **As,** Br ,Cl, Ca, Cd, Sc, Ti, V, Mn, Cr, Co, Ni, Se, Rb, Sr, Zr,Mo, I, Ce, La, Sm, Tb, Yb, Hf, W, Th, U, Cd, S, **Hg**
Anomalous zones		
Brezová pod Bradlom	Geogenic anomalous zones	**Na, Mg,Al, Sc, Ti, V**, Cr, Fe, Co, Ni, Zn, As, Se, **Br**, Rb, **Zr,** Mo**, I**, Ba, La, Ce, **Sm**, Tb, Yb, Hf, Ta, W, Th, **U**, S
Slanec	Output and crumbled of stone.	Na, Mg,Al, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, As, Se, Br, Rb, Sr,Zr, Mo, Ba, La, Ce, Sm, Tb, Yb**, Hf**, Ta, W, Th, U, S

Note: CF= contamination factor as the rates median value of element in Slovak mosses vs Norwegian mosses.

Spain

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Background

Data of heavy metals in mosses from La Rioja (north-central Spain) are available since 1995-96, when the first survey took place using samples of *Hypnum cupressiforme* collected in 5 stations. After that, several additional surveys have been conducted since 2006, using samples of the same species collected in 25 stations belonging to La Rioja and neighbouring provinces (Figure 1).

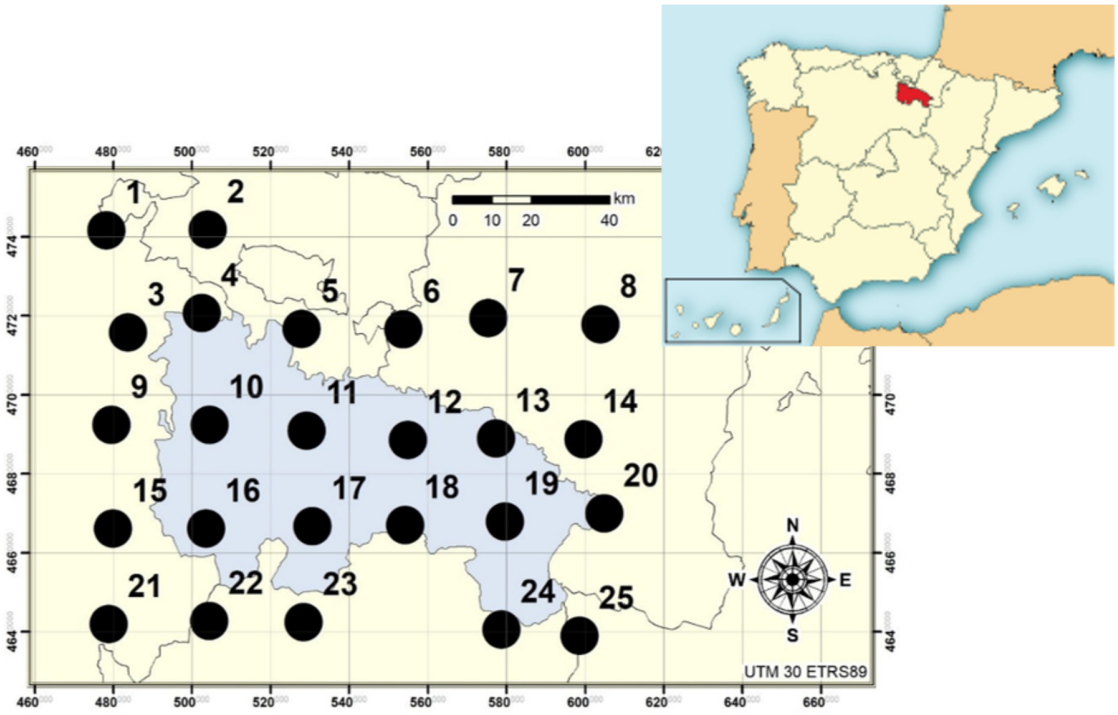

Figure 1. Situation of the 25 sampling points used in the 2016 moss survey in La Rioja and neighbouring provinces (north-central Spain).

Sampling stations are regularly distributed forming a grid of 25x25 km^2, with latitude (N) ranging between 41.9º and 42.8º, longitude (W) ranging between 1.8º and 3.3º, and altitude ranging between 311 and 1504 m. This design also allows to evaluate the microvariability of air quality. The five elements regulated by European Directives (As, Cd, Hg, Ni and Pb) were measured in the period 2006-2014, and results obtained in the 2010 survey were incorporated, for the first time, to the European moss survey. In 2010, nitrogen (N) and the nitrogen isotopic ratio ($\delta^{15}N$) were also measured and incorporated to the European survey.

In April 2016, a new survey was conducted using the same set of localities and the same species, but measuring a total of 39 elements by INAA in the Joint Institute for Nuclear Research (JINR) at Dubna (Russian Federation), under the coordination of Dr. Marina Frontasyeva: Al, As, Au, Ba, Br,

Ca, Ce, Cl, Co, Cr, Cs, Cu, Fe, Gd, Hf, I, K, La, Mg, Mn, Na, Ni, Rb, S, Sb, Sc, Se, Sm, Sr, Ta, Tb, Th, Ti, Tm, U, V, Yb, Zn and Zr. In addition, radionuclides in four composed samples were measured in JINR, and Cd and Pb (by AAS), and Hg and nitrogen (by elemental analysers), the nitrogen isotopic ratio ($\delta^{15}N$), and the 16 polycyclic aromatic hydrocarbons (PAHs) controlled by the U.S. Environmental Protection Agency (EPA) were measured in other laboratories. Given that in previous surveys, particularly in 2010, only As, Cd, Hg, Ni, Pb, N and $\delta^{15}N$ were measured, comparative data are available only for these variables (Table 1). The territory sampled mainly consists of rural and mountain areas, being noticeably free of heavy pollution sources and probably constituting a background territory for most pollutants. However, in its northern and eastern limits some gas-power central stations are located, together with an (apparently) inactive nuclear central station, a paper mill and some other industries. Our territory is also obviously exposed to long-range transboundary air pollution.

Heavy metal contents in moss

Among the 42 heavy metals measured, a summary of the data corresponding to the 12 metals most commonly used in previous European moss surveys (Al, As, Cd, Cr, Cu, Fe, Hg, Ni, Pb, Sb, V, and Zn) is shown in Table 1. Only the five metals previously analysed for La Rioja in the 2010 Moss Survey (As, Cd, Hg, Ni and Pb) can be temporally compared. As slightly increased from 2010 to 2016, but it must be taken into account that the 2016 analysis was carried out using INAA, which tends to give higher metal concentrations than the method used in 2010 (AAS). Both medians are higher than the European As median for 2010. Cd also increased from 2010 to 2016, but in both cases the medians are lower than the 2010 European median. Hg slightly decreased from 2010 to 2016, and both medians are lower than the 2010 European median. Ni and Pb showed a similar trend to Hg, but much stronger. For the remaining metals, Al and Cr showed higher medians in the 2016 survey in La Rioja than in the 2010 European survey, whereas Cu, Fe, Sb, V and Zn showed rather the contrary. No clear spatial pattern was identified in any of the metals analysed. The lack of a spatial pattern, and the usually modest metal contents found in La Rioja suggest that the presence of these metals in the moss material is due to pollution generated outside the territory sampled, in accordance with the relatively low industrialization and the absence of strong sources of heavy metals in La Rioja.

Table 1. Results of the 2016 moss survey conducted in 25 localities of La Rioja and neighbouring provinces (north-central Spain, see Fig. 1). Contents (minimum maximum, mean and median values, in mg kg^{-1}) of the 12 elements most commonly included in previous European moss surveys, together with nitrogen (N) percentages, nitrogen isotopic ratios ($\delta^{15}N$), and contents (ng g^{-1}) of the sum of the 16 EPA Polycyclic Aromatic Hydrocarbons (PAH), are shown. For comparison, median values obtained in the same locality set and in Europe in the 2010 moss survey, are also shown. NA, not available.

	Al	As	Cd	Cr	Cu	Fe	Hg	Ni	Pb	Sb	V	Zn	N %	δ^{15}N	PAH
Min	490	0.391	0.045	0.28	1.5	236	0.01	0.36	0.57	0.03	0.7	11.	0.6	-9.3	18.02
Max	202	1.450	0.773	3.41	12.	115	0.03	5.91	1.58	0.14	2.3	28.	1.2	-4.9	70.95
Mean	928	0.703	0.202	2.03	4.9	502	0.02	1.31	0.98	0.06	1.2	18.	0.8	-6.8	42.01
Median	834	0.621	0.120	1.92	3.9	428	0.02	1.16	0.97	0.07	1.1	18.	0.8	-7.0	39.42
Median 2010 (Rioja)	NA	0.544 *	0.069 *	NA	NA	NA	0.03 0	1.45*	2.43 *	NA	NA	NA	0.8	-7.4	NA
Median 2010 (Europe) **	762	0.21	0.20	1.82	6.5 3	538	0.05 3	1.94	3.57	0.10	1.7 2	31. 0	1.1 9	NA	172*** 171****

*Measured by graphite furnace atomic absorption spectrometry

**Based on Harmens *et al.* 2013, Heavy metals and nitrogen in mosses: spatial patterns in 2010/2011 and long-term temporal trends in Europe, CEH

***Mean value in rural areas of Spain in 2006-2007 (Foan *et al.* 2010, Atmospheric Environment 44: 3207-3214)

****Mean value in five European countries (Harmens *et al.* 2013, Air pollution and vegetation. ICP Vegetation Annual Report 2012/2013, CEH)

Nitrogen contents and $\delta^{15}N$ in moss

N showed a great temporal stability, with similar contents in 2016 with respect to those found in 2010 (Table 1). No clear spatial pattern was found, but N content showed a significant negative correlation with altitude. Thus, N content was higher in lower altitude stations with a remarkable agricultural inclination, and decreased towards higher altitudes. N contents in La Rioja in 2010 and 2016 were lower than those generally found in Europe in 2010. The ratio $\delta^{15}N$ in 2016 was also similar to that found in 2010. The relatively negative values found can be due to the mainly rural character of the territory, which is associated with reduced N forms originated in agricultural activities and a low deposition of oxidized forms of N.

PAH contents in moss

The sum of the 16 EPA PAHs in La Rioja was very low in comparison with other European territories (Table 1), showing little influence of this kind of pollutants. Nevertheless, the highest value was found in one locality affected by a severe forest fire, which supports the use of mosses as PAH biomonitors in such events.

Conclusions and recommendations

Clearly, mosses are good biomonitors of air quality and their use should be extended to wider regions, in order to increase the database available and the knowledge on their behavior in nature with respect to the different pollutants. Nowadays, there is currently no other inexpensive and easy technique to assess air quality from local pollution sources, to evaluate the effect of changes in legislation and to identify temporal trends in air pollution levels.

Switzerland

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Background

At the end of the 1980s small industries situated in Switzerland, with the main "hot spots" for ferrous metallurgy in Southern Switzerland, were an important source for heavy metal emissions. Further, 28 incineration plants were additional sources (especially for Cd). Hg was emitted by several crematoria and for Pb the major source was leaded petrol. Nowadays, all these plants have either been closed down or set up with filters. Leaded petrol was forbidden in Switzerland in 2000.
Switzerland has been participating in the European moss survey for heavy metals since 1990. Sites were reduced with no fundamental change in conclusion from 242 in 1990 to 73 in 2015. In addition, in 2010 and 2015 nitrogen has been analysed at 64 resp. 76 sites and in 2015 Persistent Organic Pollutants (POP) have been analysed at 22 sites as well. The sites are distributed across Switzerland, covering all geographical regions (J=Jura, P=Plateau, NA=Northern Alps, CA=Central Alps, SA=Southern Alps).

Heavy metal concentrations in mosses

Figure 1 shows the spatial distribution of the elements As, Cd, Cr, Ni, Pb and V in cumulative form. These elements were chosen because they are already toxic in small quantities and primarily the result from anthropogenic activities. The cumulative concentration of these heavy metals has decreased in moss since 1990. Between 2010 and 2015 however the decrease is only marginal. The highest heavy metal levels in 2015 were recorded in the southern Alps possibly caused by domestic emissions and transboundary long-range transport of pollutants from countries south of Switzerland. This effect could be observed since 1990. Further, one site in northern Switzerland showed elevated values for many elements in 2015.

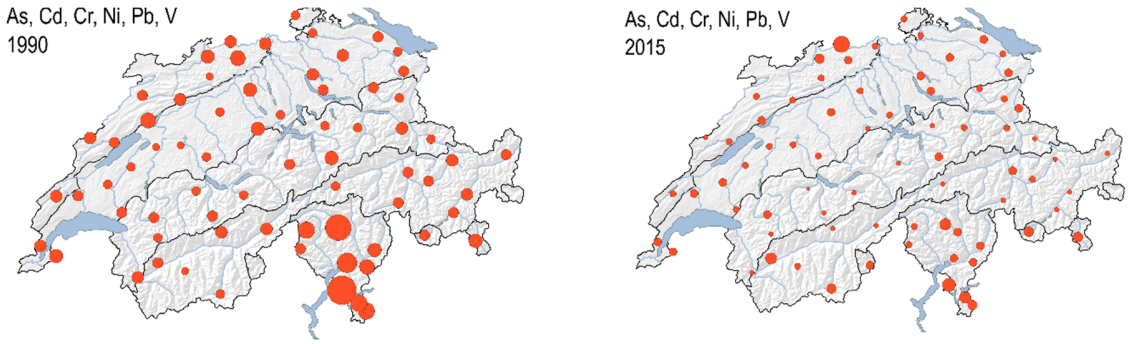

Figure 1. The spatial distribution of the summarised elements As, Cd, Cr, Ni, Pb and V normalised to their geometric mean in 1990 and 2015.

Figure 2 shows the temporal trends (normalized to 1990) of all metals measured in Swiss samples since 1990. Most of the considered elements have decreased since 1990, most remarkably for Pb (decrease of 88%). Only Ba, Cs, Cu, Se, Sr and U show no constant change over time. When the heavy metal concentrations in moss are compared to available emission data (Cd, Hg, Pb) we see that the trends follow the same pattern (Figure 3), however, the decrease is smaller in the moss, probably because of re-emission of already deposited heavy metals. The decrease from 1990 to 2015 of Hg in moss is only half of that of emission. A possible reason could be that Hg is volatile and therefore it remains longer in the atmospheric cycles.

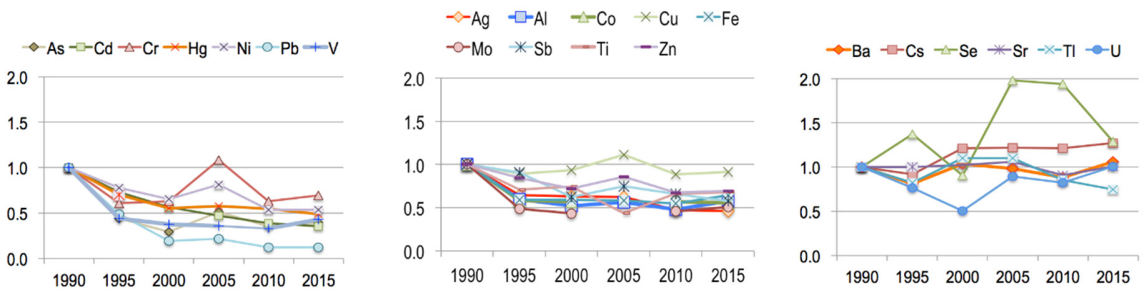

Figure 2. The Temporal trends of 20 elements, normalised to 1990.

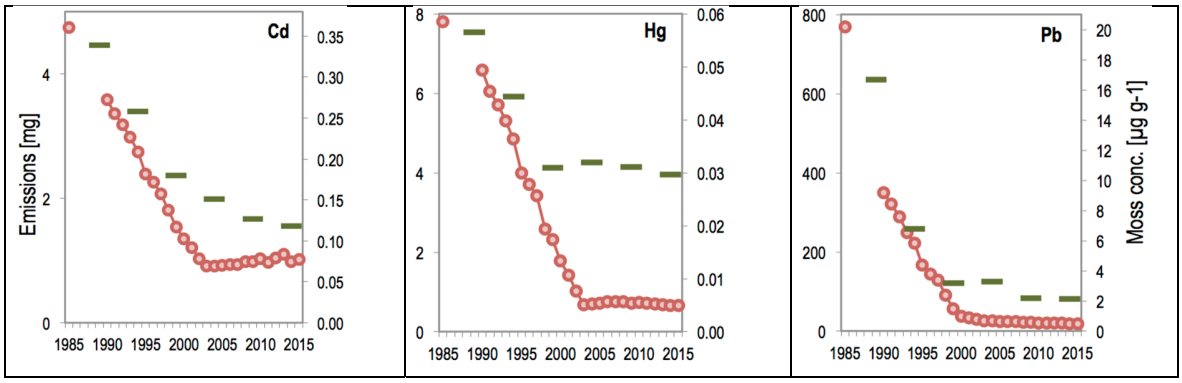

Figure 3. Cd, Hg and Pb concentrations in moss compared with the emission. Dots represent emissions, bars concentration in moss.

Nitrogen concentration in moss

Figure 4 shows the N concentration in moss in the 5 regions in Switzerland in 2010 and 2015. In accordance with the other analysed elements, the highest N level was found in southern Switzerland. A good correlation could be found when the N concentration in moss was compared with the total N input measured at nearby stations (Figure 5).

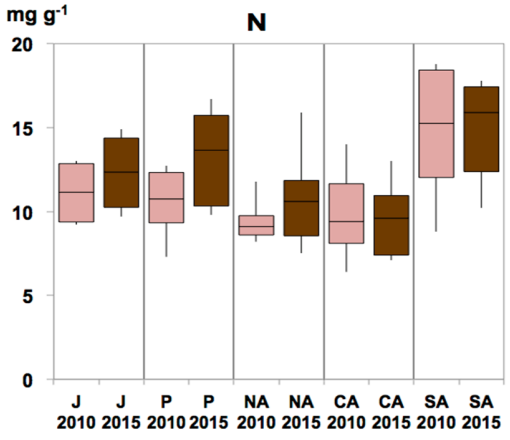

Figure 4. Boxplots of nitrogen concentration in moss in the 5 regions of Switzerland in 2010 and 2015 (only sites measured in both periods)

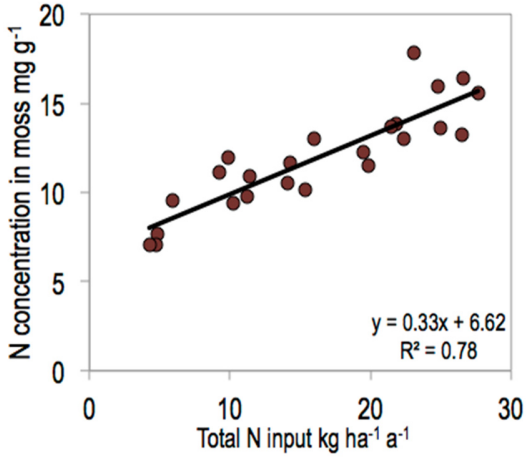

Figure 5. Nitrogen concentration in moss compared to total N input (gases: NH_3 NO_2, HNO_3; in aerosols and in precipitation: NH_4^+, NO_3^-) measured nearby.

Conclusions

The study showed that the relatively cheap moss method can be used to determine regional differences and temporal changes in the deposition of several elements. This enables the documentation of the effectiveness of emission-reduction measures.

Tajikistan

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Background

Many small industries located in Tajikistan are important sources of heavy metals emissions. Especially, aluminum, cement and antimony factories, as well as heat-electric central operating in coal combustion, are the main sources (especially for Al, Sb, and Pb). Currently, due to improper disposal of industrial waste and the filtration process, the spread of heavy metals has become one of the main factors of atmospheric pollution. Most of these enterprises are very close to the settlement and adversely affects the state of the inhabitants of a given region.

The Republic of Tajikistan for the first time took part in the European moss survey in 2016/2017 and for the first time participated in the meeting of the Task Force on ICP Vegetation in 2017. In May 2017, 29 moss samples were collected at 29 sampling sites distributed over the territory of Tajikistan (Figure 1). The most dominant and widespread moss species in Tajikistan are *Pleurozium schreberi* and *Hylocomium splendens*. The study was performed to assess air quality in the Central part of Tajikistan, to generate information necessary for better identification of pollution sources, and to create a database for future surveys.

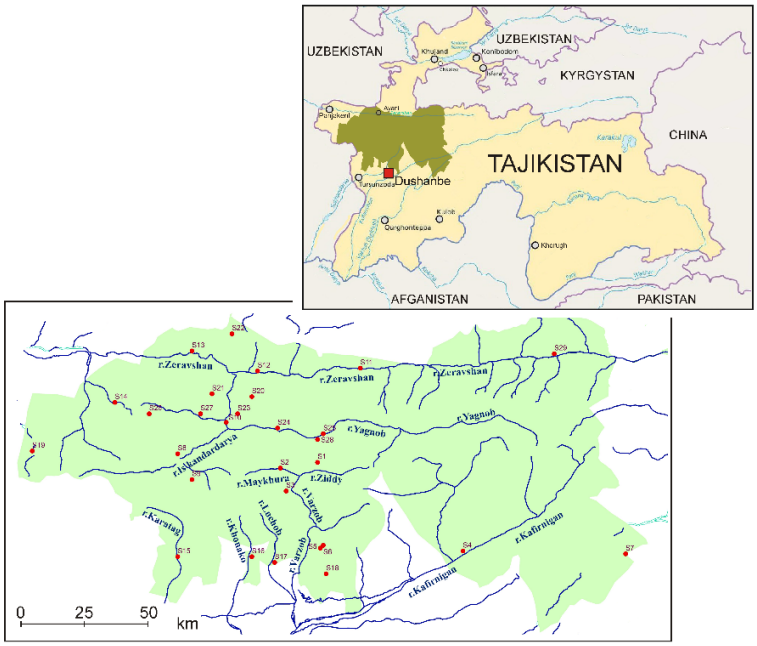

Figure 1. Sampling points in territory of Tajikistan.

Fluctuations in the level of pollution of the air basin occur to a large extent under the influence of atmospheric conditions that determine the transport and scattering of impurities. To assess this phenomenon, a characteristic called the potential for atmospheric pollution is used and determines the ability of the atmosphere to scatter or accumulate pollutants in a given area. In mountainous areas of Central Tajikistan, the wind regime depends, first of all, on orographic features, which in turn stimulate the potential for air pollution. In large cities, there is a significant amount of exhaust emissions from cars, which increase the flow of heavy metals into the atmosphere. Therefore, it is necessary to know the current state of the air environment, its potential capabilities and ways to overcome or reduce side effects.

Heavy metal concentrations in mosses

A total of 45 elements (Na, Mg, Al, Cl, K, Sc, Ca, Ti, Cr, V, Mn, Ni, Fe, Co, Zn, Pb, Cu, Se, As, Br, Sr, Rb, Zr, Mo, Cd, Sb, I, Ba, Cs, La, Ce, Nd, Eu, Gd, Sm, Tb, Yb, Tm, Hf, Ta, W, Th and U) were determined using the instrumental epithermal analysis of neutron activation and atomic absorption spectrometry. For example, a spatial picture of the content of arsenic, chromium, antimony, vanadium, nickel and lead in mosses are shown in Figure 2.

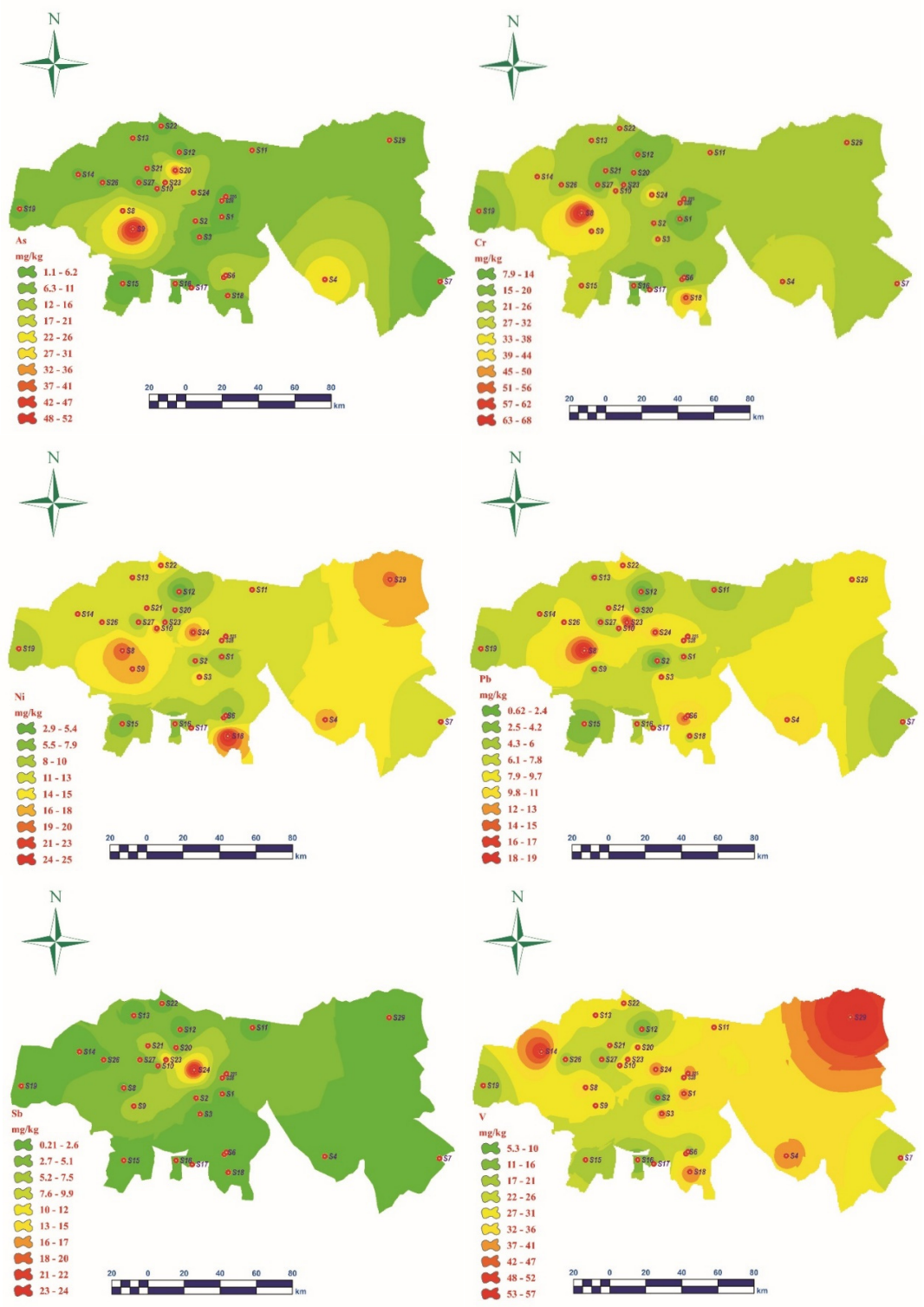

Figure 2. Interpolation maps (mg / kg) of more common main environmental pollutants in Central part of Tajikistan.

Discussion and conclusions

From the data obtained, it can be concluded that the main anthropogenic sources of heavy metals are heat-electric central transport and industrial activities. Three different indicators, the C_F pollution factor, the I_{geo} geocoding index and the pollution load index used to quantify the degree of pollution indicate moderate or severe industrial pollution located around the main industrial centers - the municipalities of Ziddi, Sioma, the gorge Odjuk river 1 and 2, Iskandarkul, Artuch, Harangoni Bolo, Anzob (Figure 3).

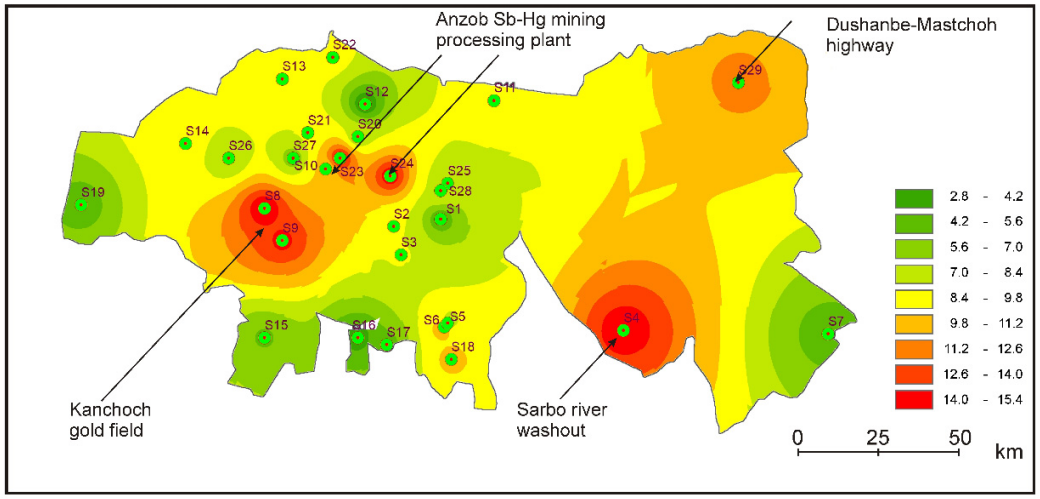

Figure 3 The spatial distribution of the Pollution Load Index (PLI) in investigated area.

The samples were examined on the basis of the Laboratory of the SNAAPI FLNP JINR in Dubna. The methodology of moss biomonitoring proved to be an effective method for studying the atmospheric deposition of heavy metals, as well as other trace elements and identification of pollution sources. The study showed that a relatively inexpensive method of moss can be used to determine regional differences and temporal changes in the deposition of several elements. This allows documenting the effectiveness of emission reduction measures. There is a need to continue the moss survey in all the territories of the Republic of Tajikistan.

Further reading

D. Abdusamadzoda Dj. A. Abdushukurov, O. Duliu, I. Zinicovscaia., N.S. Yushin M.V., Frontasyeva. Investigations of the Atmospheric Deposition of Major and Trace Elements in Western Tajikistan by Using the Hylocomium splendens Moss as Bioindicators. Archives of Environmental Contamination and Toxicology. doi.org/10.1007/s00244-019-00687-w

‘Mosses as biomonitors of air pollution: 2015/2016 survey on heavy metals, nitrogen and POPs in Europe and beyond’

Naturally-occurring mosses have been sampled across Europe and beyond to monitor the deposition of heavy metals, nitrogen and persistent organic pollutants (POPs) from the air. Since 1990, the moss survey has been repeated at five-yearly intervals for heavy metals. Since 2005 and 2010, nitrogen and POPs respectively were included too in some countries. In 2015/2016, mosses were collected at approximately 5,100 sites in 36 countries for heavy metals, 1,500 sites in 12 countries for nitrogen and at selected sites in eight countries for POPs. In 2015/16, participation in the moss survey has greatly increased in countries in Eastern Europe, Caucasus and Central Asia (EECCA region). The highest concentrations of heavy metals were often observed in South-Eastern Europe and the EECCA region, whereas the highest concentrations of nitrogen were found in parts of central Europe. In countries that have participated in at least four out of the six surveys, the concentration of lead and cadmium in mosses has declined the most (82% and 64% respectively since 1990) and the concentration of mercury has hardly changed (2% decline since 1995). The nitrogen concentration in mosses has hardly changed too since 2005 (2% decline).

This report is for scientists, policy makers and others with an interest in air pollution.

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ISBN: ISBN 978-5-9530-0508-1