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Mosses as biomonitors of air pollution: 2020/2021 survey on heavy metals, nitrogen and POPs in Europe and beyond

Felicity Hayes, Katrina Sharps and participants of the moss survey

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

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Report of the ICP Vegetation[1]

March 2025

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[1] 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.

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*References to Kosovo shall be understood to be in the context of Security Council resolution 1244 (1999).

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Executive Summary

Background

The European moss survey aims to monitor and understand the long-range transboundary air pollution of heavy metals, nitrogen and selected persistent organic pollutants (POPs). The survey uses carpet-forming, ectohydric mosses as biomonitors of atmospheric deposition as these obtain most elements and other compounds direct from precipitation and dry deposition and have very little uptake from the substrate that they grow on. The first survey at the European scale was conducted in 1990 and has been repeated every five years.

The European moss survey is currently coordinated by the UNECE ICP Vegetation[2] Programme Centre at the UK Centre for Ecology & Hydrology. The 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). Previously the European moss survey was established and coordinated by Lund University (Sweden) and Trondheim University (Norway) on behalf of the Nordic Council of Ministers.

The European moss survey has been used to demonstrate the effectiveness of some policies aimed to reduce emissions of selected heavy metals. It provides a complementary methodology to conventional precipitation analysis and allows spatial patterns and temporal trends to be evaluated.

Moss survey 2020

The 2020 moss survey analysed samples from 3433 sites across Europe and beyond. Sampling was extended to 2022 due to travel restrictions as a result of the Covid-19 pandemic. Thirty-two countries participated in the moss survey, with most countries reporting data on the ‘core’ metals of Al, As, Cd, Cr, Cu, Fe, Hg, Pb, Ni, Sb, V and Zn. Nitrogen concentration in the moss samples was reported by seventeen countries, and POPs data were reported by three countries. A few other countries collected moss samples, but it was not possible to analyse these in time for reporting.

Mosses were sampled according to a standardised protocol. Concentrations of the various metals, nitrogen and POPs were determined in growth segments representing the last two to three years’ growth. The most frequently sampled moss species were *Pleurozium schreberi* (36%), *Hypnum cupressiforme* (28%), *Hylocomium splendens* (12%) and *Pseudoscleropodium purum* (6%). A range of analytical techniques were used, and moss reference material was included in the analysis for quality assurance purposes.

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

Spatial patterns (2020) and temporal trends (1990-2020)

Heavy Metals

For many heavy metals the lowest concentrations were generally found in the north and west of Europe and higher concentrations in the south-east of the region. For some metals the influence of point sources within the region could be identified (e.g. antimony and cadmium), whereas others had either more dispersed sources within the region (e.g. lead), or more homogenous distribution (e.g. zinc) suggesting long-range transboundary sources from outside of the region.

Many (but not all) of the measured heavy metals have shown a decline in concentration within the moss tissue since 1990. In some cases, such as lead, this has mirrored the decline in emissions within the EU27 countries, however, in many cases the decline in concentration in moss tissue has been more modest (e.g. chromium and nickel). The reductions in metal concentration in moss tissue between 1990 and 2020 (based on all countries that participated in four or more surveys since 1990) were 83.2% for lead, 61.9% for cadmium, 51.0% for vanadium, 30.4% for nickel, 25.6% for copper, 20.1% for chromium, 18.1% for zinc, 15.0% for iron.

For arsenic and mercury there has been very little change. For arsenic there was an increase of 6% since 1995. For mercury the concentration in moss increased by 4.8%.

Aluminium and antimony concentrations in moss tissue have only been measured since 2005 and have shown a reduction of 36.4% and 41.5% respectively between 2005 and 2020.

Nitrogen

A small increase in nitrogen concentration in moss tissue of 3.1% was observed over the period 2005-2020. Highest concentrations of nitrogen in moss tissue were generally found in central Europe.

POPs

Occurrence of POPs in moss samples were only reported by Germany and Switzerland for the 2020 moss survey. Information is also given from Spain (Rioja region) from samples collected in 2018.

PAHs were found in moss samples from all the sites analysed. At many sites a wide range of different PAHs were found in the moss samples. Not all PAHs were found at all sites, and the relative proportions of the different PAHs was variable between sites. The most dominant PAHs in Germany were fluoranthene and pyrene. In Spain the most dominant PAHs were phenanthrene and fluorene. In Switzerland the most dominant PAHs were naphthalene and phenanthrene. It is apparent that the sum EPA 16 has decreased considerably in both Germany and Switzerland compared to those reported from the 2015 survey.

Microplastics were analysed for three countries and were found in the vast majority of sites analysed. The microplastics identified were from a range of types and potential sources and are an indication of the widespread prevalence of microplastics within the environment. Different techniques were used by the different participating countries, with corresponding differences in the limit of detection for particle sizes, and in the precision of determining the particle type. This means that although it is possible to identify larger trends and information, direct comparison of microplastic quantity in moss tissue between countries was not possible.

Note that a separate study used moss as a biomonitor for microplastics across the UNECE region and beyond, and this is covered in a separate report.

Conclusions and recommendations

Biomonitoring using moss continues to provide a suitable method to identify areas at risk from atmospheric deposition of heavy metals, nitrogen and POPs and to identify temporal trends. Concentrations of some metals in mosses have declined in line with reductions in emissions following successful implementation of policies. However, concentrations of other metals have not declined in line with emissions, sometimes due to additional sources outside of the UNECE region, or longevity of the metal in the atmosphere subsequent to release. Use of mosses within this survey have demonstrated the widespread occurrence of POPs and microplastics within the environment.

Introduction

Atmospheric deposition of metals and nitrogen and other contaminants such as POPs and microplastics could cause adverse impacts on ecosystems and human health. Within ecosystems atmospheric deposition of heavy metals contributes to the total metal load. Excess nitrogen deposition to ecosystems can result in reduced plant diversity and negative impacts on other species. POPs possess toxic characteristics, are persistent and can bioaccumulate, and can cause significant adverse human health and environmental effects on a wide variety of species.

Metals

In 1998, the first Protocol for the control of emissions of heavy metals was adopted in Aarhus, Denmark. 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, and potential health risks of these have been reviewed by the Joint World Health Organization/Convention Task Force on the Health Aspects of Air Pollution (Task Force on Health) (Task Force on Health, 2007).

The European Moss Survey forms part of the workplan of the UNECE Convention on Long-range transboundary Air Pollution (LRTAP) and is coordinated by the ICP Vegetation. The ICP Vegetation provides information for the review and possible revision of the Protocols of the LRTAP Convention. In recent decades, mosses have been applied successfully as biomonitors of heavy metal deposition across Europe (e.g. Harmens et al., 2007, 2008). 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).

Chemical analyses of moss specimens have been shown to provide a surrogate measure of the spatial patterns of element deposition, which can also be measured using deposition samplers that collect wet and dry deposition. The element concentrations found in mosses can complement the measured concentrations in atmospheric deposition (e.g. Harmens et al., 2010, 2015). Analysis of moss samples is easier and cheaper than conventional precipitation analysis, and therefore enables a high sampling density to be achieved. The biomonitoring can also be carried out over a large region. The information obtained can subsequently be used to enhance the spatial resolution of atmospheric deposition maps.

From the start (1990), 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) were also determined. For some metals, e.g. lead and cadmium, it has been shown that there is good agreement between European scale atmospheric deposition and the accumulation of cadmium and lead in mosses (Holy et al., 2010; Schröder et al., 2010), indicating that mosses are very effective biomonitors for these metals. For other metals e.g. mercury, the concentration in mosses was not closely related to modelled atmospheric deposition within Europe (Schröder et al., 2010). In some cases, this could indicate potential improvements to deposition models (Ilyin et al., 2007), particularly where there may be important local emission sources. Increased understanding of the processes influencing metal uptake by moss, including environmental factors could also be important.

Nitrogen

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). 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 where 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), although 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.

POPs

In 2010 the concentration of POPs in mosses was included as an option within the moss survey. It has previously been demonstrated that mosses are also suitable for monitoring spatial patterns of some POPs (Harmens et al., 2013, Wu et al., 2014). 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). PCBs have been found in vegetation and soil in Svalbard, far from any sources (Aslam et al., 2019). POP deposition can cause oxidative stress (Lui et al, 2009) and reduced biomass production (Sharma et al., 2020), and some specific types of POP have also been found to be carcinogenic and mutagenic (Shukla and Upreti, 2009).

Microplastics

Analysis for microplastics was included as an option within the moss survey in 2015. Microplastics have been found around the world, following widespread concerns about pollution by (macro) plastics. The impacts of microplastics on vegetation are unknown, and the consequences of potential airborne long-range transport and subsequent deposition are also unknown.

History of the survey

The heavy metals in mosses biomonitoring network was originally established in Sweden (Rühling and Skärby, 1979). This survey was expanded first to the Nordic countries, then beyond. The first moss survey at the European scale was conducted in 1990 and has been repeated every five years since then. The aim of the survey is to identify the main polluted areas for various metals and to 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.

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 history of the moss survey is summarised in Table 1.

Table 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 (ICP Vegetation, CEH Bangor, UK)
2015	Sixth European survey, 36 countries	Harry Harmens and Marina Frontasyeva (ICP Vegetation, CEH Bangor, UK and JINR, Russian Federation)
2020	Seventh European survey, 32 countries	Felicity Hayes (ICP Vegetation, UKCEH Bangor, UK)

Current survey

The 2020 moss survey analysed samples from 3252 sites across Europe and beyond. Sampling was extended to 2022 due to travel restrictions as a result of the Covid-19 pandemic. Thirty-two countries participated in the moss survey, with the majority of countries reporting data on the ‘core’ metals of Al, As, Cd, Cr, Cu, Fe, Hg, Pb, Ni, Sb, V and Zn. Some countries also reported moss concentrations for a variety of additional metals. Nitrogen concentration in the moss samples was reported by 17 countries, POPs data were reported by three countries and microplastics data were reported by three countries. Countries that contributed to the 2020 moss survey are summarised in Table 2. A few other countries collected moss samples, but it was not possible to analyse these in time for reporting.

Table 2: Countries and regions that submitted data for the 2020 moss survey

Note: all countries submitted data for heavy metals; $^{N,\ POPs\ and\ MP}$: countries that also submitted data for nitrogen, POPs and microplastics respectively.

SEE Europe	EECCA	Rest of Europe	
Albania	Armenia	Belgium ^{N}	Latvia ^{N}
Bulgaria	Belarus	Czechia ^{N}	Netherlands ^{N}
Greece	Georgia	Denmark-(Faroe Islands)	Norway
North Macedonia ^{N}	Moldova	Estonia ^{N}	Poland
Romania	*Kosovo ^{N}	France ^{N}	Slovakia ^{N}
Serbia	Russian Federation	Germany ^{N,POPs,MP}	Spain ^{N,POPs}
Slovenia ^{N}		Iceland	Sweden ^{N}
		Ireland ^{N}	Switzerland ^{N,POPs,MP}
		Italy ^{N}	United Kingdom $^{N,\ MP}$

* References to Kosovo shall be understood to be in the context of Security Council resolution 1244 (1999).
Note: Spain (Rioja region) sampling occurred in 2018
Note: Armenia collected moss samples, but it was not possible to complete the chemical analyses in time for the report.

1. Methodology for the 2020-21 survey

Field sampling

Field sampling of mosses occurred during the timeframe 2020-2022. Each participating country was responsible for their selection of sites and sampling of mosses, but all countries followed the guidelines of a common experimental protocol (Frontasyeva and Harmens, 2019). The protocol 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. Sampling occurred in a variety of habitats, but in forests or plantations samples were collected as far as possible in small open spaces to preclude any significant effect of canopy drip. At each site a sample was taken comprising a composite of about ten sub-samples. Sampling and sample handling were carried out using gloves and paper or plastic bags. 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 prior to chemical analysis.

Moss species

Pleurocarpous mosses were sampled, as these have very little uptake from the substrate and obtain most trace elements and nutrients directly from precipitation and dry deposition (Tyler, 1970). The moss species recommended for sampling where possible were *Hylocomium splendens, Pleurozium schreberi, Hypnum cupressiforme* and *Pseudoscleropodium purum,* however, where this was not possible alternative pleurocarpous species were collected.

Chemical analysis

For the determination of metal concentrations, sorted material (ca. last two to three years' growth) was dried at 40 °C (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 °C. For the determination of nitrogen, moss tissue was dried at 40 °C 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

Moss reference materials were included in the analyses. Moss reference materials M2 and M3, first prepared for the 1995/6 European moss survey (Steinnes et al., 1997), were used by the majority of laboratories. In addition, some laboratories used other certified reference materials for quality assurance. Where necessary, correction factors were applied to outlier datasets and in some cases severe outliers were excluded from further data processing.

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).

Draft maps were prepared and discussed with participants. Discussions with relevant participants occurred in particular when correction factors were being considered, and where large differences between concentrations in neighboring countries were observed.

Mapping

In the majority of cases where concentrations were below the detection limit of the analytical technique, these points were in the lowest concentration category (e.g. <250 mg kg^{-1} is the lowest category for Fe, and all techniques had a detection limit of 100 mg kg^{-1} or less). In cases where the detection limit was not in the lowest category, these points were plotted in grey as ‘below detection’. Note that in these cases the detection limit was high compared to some of the other techniques, so that the value of the points is ‘unknown’ rather than ‘low’.

Temporal trend analysis

Some countries have sampled mosses in different areas in different sampling campaigns. Hence, any changes in concentrations are confounded by a change in sampling strategy.

For trend analysis, countries were included if there were data from 4 or more of the moss surveys (with the exception of aluminium and antimony, which have been included in fewer surveys and the inclusion criteria was 3 and 2 or more survey years respectively). Analysis was based on median values per country.

Countries with data that were included in the trends analysis were Albania, Austria, Belarus, Belgium, Bulgaria, Czechia, Denmark (Faroe), Estonia, Finland, France, Germany, Iceland, Italy, Latvia, Lithuania, North Macedonia, Norway, Poland, Romania, Russian Federation, Serbia, Slovakia, Slovenia, Spain, Sweden, Switzerland, Ukraine, and United Kingdom.

2. Spatial patterns and temporal trends in Europe and beyond

Introduction

Of the 3433 samples analysed for content of heavy metals, the most frequently sampled species was *Pleurozium schreberi* (36%), followed by *Hypnum cupressiforme* (28%), *Hylocomium splendens* (12%) and *Pseudoscleropodium purum* (6%). The distribution of sampling sites and the moss species sampled is shown in Figure 3.1a.

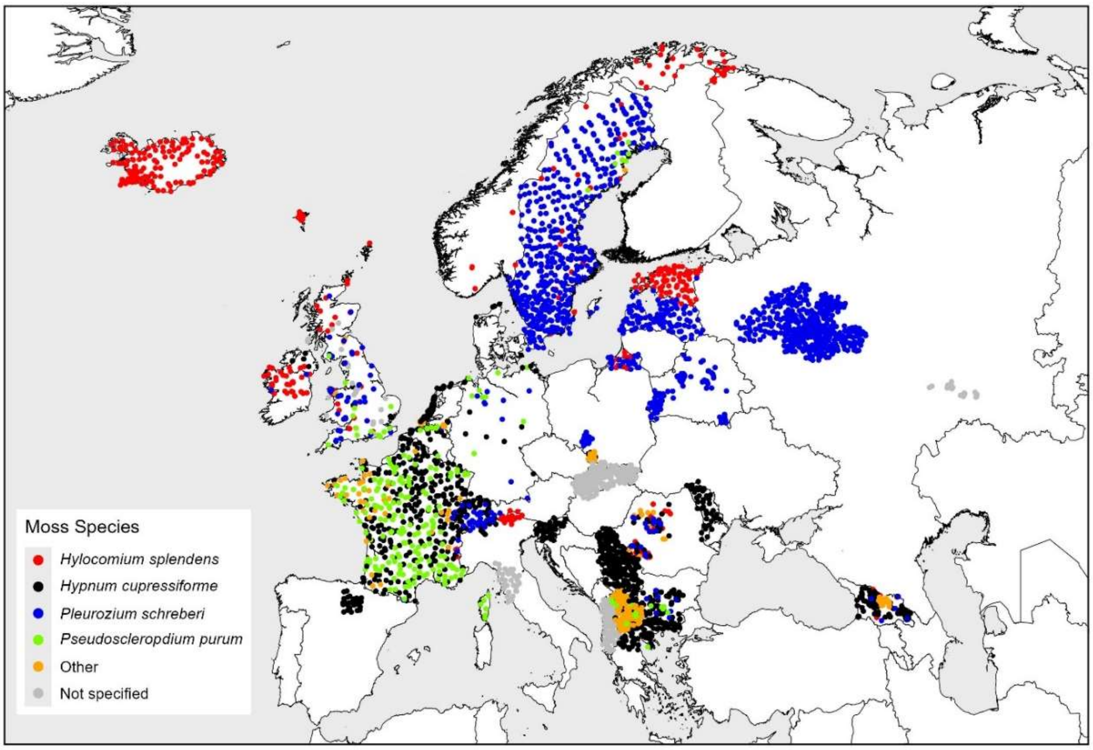
Nitrogen content was determined in 1865 moss samples, with the sampling locations and moss species shown in Figure 3.1b.

The 2020/2021 data on the concentration of each element in moss samples from each country are summarized in **Annex 3**. Some individual participants have investigated the impact of individual hotspot point sources on deposition and accumulation within moss tissue within their own country reports. The emphasis of this report is on Europe-wide spatial patterns and temporal trends. Elevated concentrations of metals within moss tissue can occur due to local sources within the region and also from long-range atmospheric transport of pollutants. There are some point source hotspots associated with mining and industrial processes. There are also some more diffuse sources, including those associated with domestic activities, agriculture and road transport. A few metals also have natural sources via geological processes.

In addition to changes in emission or deposition of metals between surveys, other factors can also contribute to temporal changes. In some cases, different sampling strategies are used in different years, which could involve changes in the number of sites sampled and/or the locations of sites. 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. However, by also including consideration of country-by-country trends in addition to the survey as a whole, increased confidence in the differences can be seen. In addition, comparisons between survey years are based on median values, which reduces the influence of extreme values (either very high or very low).

For the purposes of this survey, it has been assumed that metals are taken up by the moss in direct proportion to deposition rates and with no metal inhibition of growth rate due to toxicity impacts. At high concentrations some toxic metals may reduce moss growth, giving an overestimate of uptake. In addition, some metals are micronutrients and thus would be expected to be present in moss tissue at low concentrations even in ‘clean’ conditions. This effect is also apparent for nitrogen, which although has been shown to increase linearly with increasing nitrogen deposition (Harmens et al., 2014), is also an essential component of moss tissue.

Maps of concentrations of the various metals in moss samples are presented in the main report in a green-yellow-red colour scheme for consistency with previous reports, and are also presented in **Annex 6** in a purple-green-yellow colour scheme.



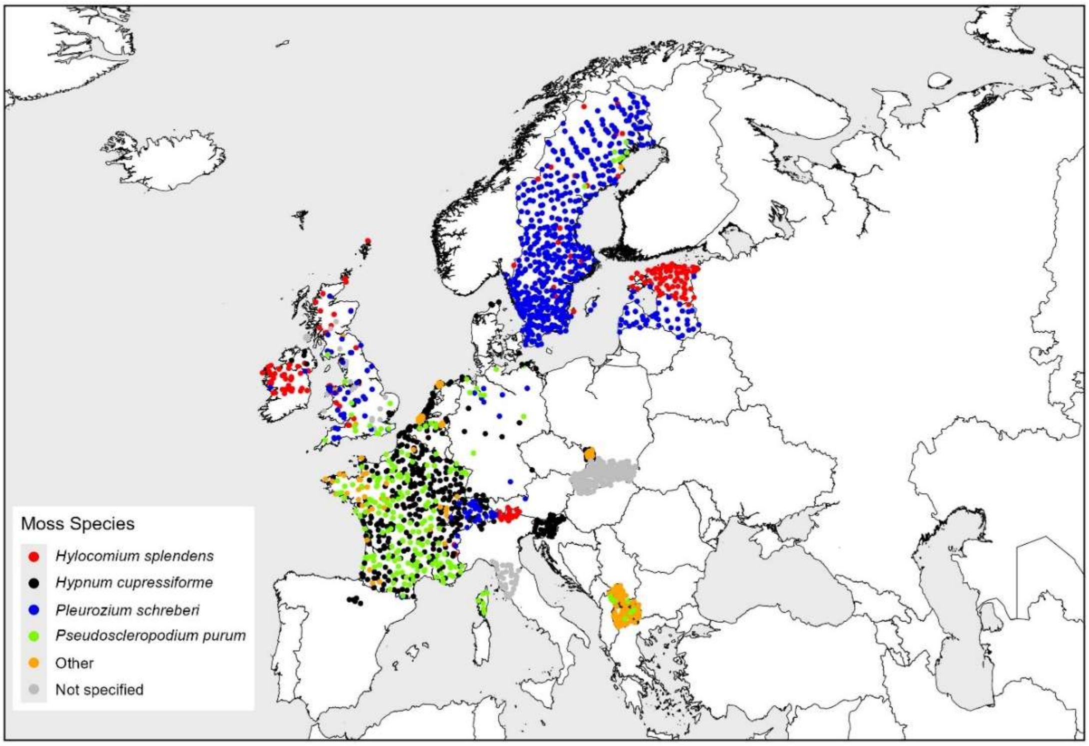


Figure 3.1: Sampling sites and moss species sampled for a) metals and b) nitrogen

Aluminium

Aluminium is present in high concentrations in the earth's crust, and accounts for 8.8% of the earth's crust by mass (Rauch and Pacyna, 2009). It is released to the environment by natural weathering of rocks. There are also large anthropogenic sources of aluminium. High levels in the environment can be caused by mining and processing of aluminium ores, or the production of aluminium metal, alloys and compounds. Small amounts of aluminium can also be released from coal-burning power stations.

Generally, there was a north-west to south-east gradient of aluminium content in moss, with higher concentrations in the south-east part of the region. Spatially, the concentrations of aluminium are similar within a close region, indicating a low impact of individual point sources within the region. The countries contributing to the survey that had the highest average concentrations of aluminium in mosses include Greece, Moldova, Georgia and North Macedonia.

There has been a large decline in concentration of aluminium in moss tissue since 2005. For only countries where data has been reported for three out of four of the survey years (11-15 countries depending on the year) where aluminium was included, this decline was 36.4%. When comparing all countries that reported data for both the 2015 and 2020 survey it is apparent that a large decline in aluminium concentration in moss tissue was apparent for almost all countries, the exceptions being Estonia and Germany, which already had low concentrations of aluminium in moss tissue.

A possible contributing reason is that a large proportion of global aluminium production has moved out of the UNECE region compared to previous years. In addition, implementation and improvements to abatement technologies in some of the aluminium processing plants have been shown to have a large potential reduction in aluminium emissions (Neto et al., 2009).

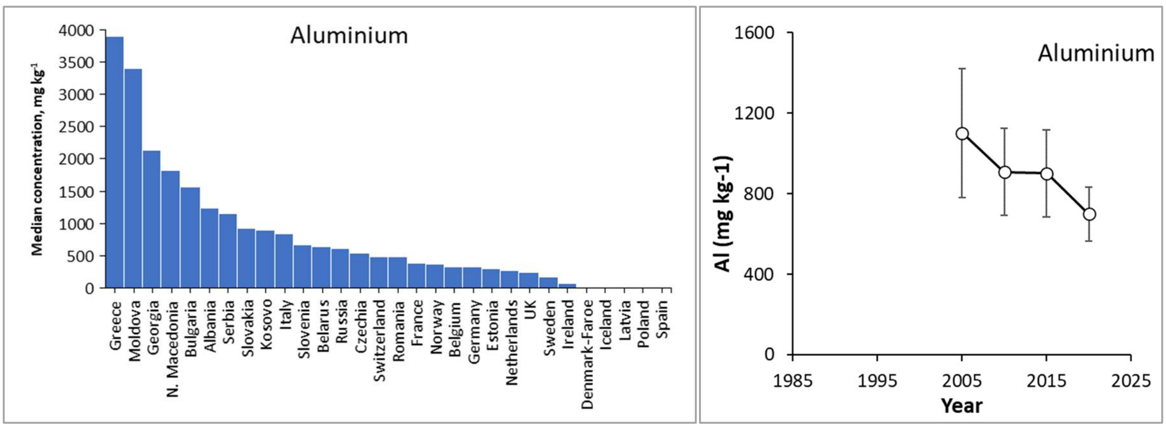


Figure 3.2: a) Median aluminium concentrations in mosses 2020 (note Denmark, Iceland, Latvia, Poland and Spain did not provide data for aluminium), and b) Average median aluminium concentrations in mosses for countries (n = 11-15, depending on year) that reported data between 2005 and 2020 for at least three survey years.

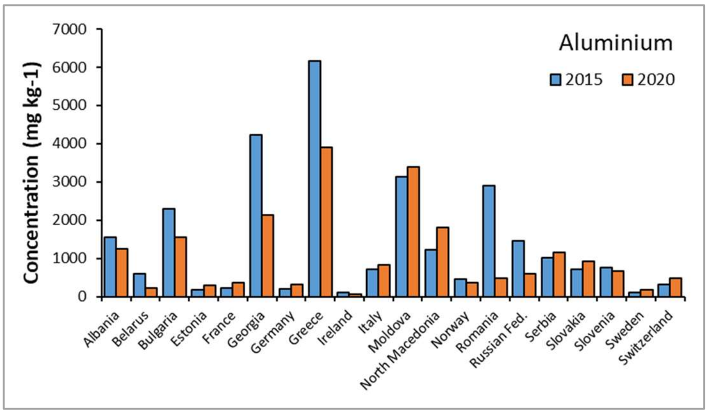


Figure 3.2c: Median aluminium concentrations in mosses in 2015 and 2020, for those countries that provided aluminium concentration data in both years

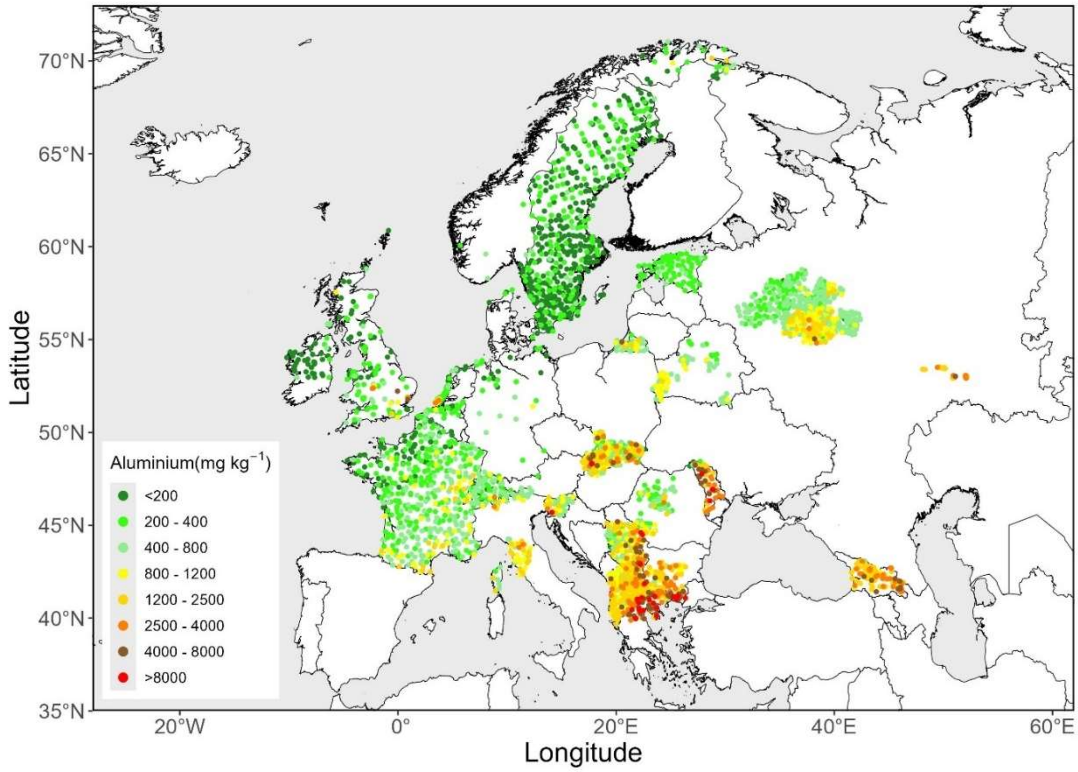


Figure 3.2d: Aluminium concentration in mosses 2020.

Antimony

Natural contributions to antimony deposition are negligible and are dominated by anthropogenic emissions. These have increased by 50% during the last three decades (Krachler et al., 2005). Most antimony is produced in Russia and China, with China accounting for 55% of global production in 2022. Mining and smelting can both cause the release of antimony to the air. Antimony is widely used as a component of flame retardants, as an alloy with lead, and in some plastics. Antimony can also be associated with road traffic, particularly from brake abrasion (Dousova et al., 2020) and studies have shown that antimony in plants growing in urban areas is almost exclusively related to vehicle traffic (Krachler et al., 2005).

The survey showed some hotspots of antimony concentration in mosses in Russian Federation and some parts of the Balkans that may be associated with industrial processes. There were also some indications of elevated concentrations in moss tissue in northern France and Netherlands (and possibly southern UK), and these might be associated with either road traffic or large conurbations. Although there was generally a trend towards increased concentrations in moss tissue in the south and east of the region compared to the north and west, this was not consistent, with many isolated hotspots and medium concentrations found in the south and west, together with many sites with low concentrations in the south and east. The countries contributing to the survey that had the highest average concentrations of antimony in mosses include Ireland, Estonia, Netherlands and Moldova, but note that there was a high detection limit for Ireland and this may have influenced the results.

Antimony has only been recently included in the moss survey, therefore, trends analysis was based on countries that had measured antimony concentration in moss in two or more surveys (9-14 countries, depending on the year). Overall, the decline in antimony concentration in moss tissue between 2005 and 2020 was 41.5%. Although initially there was a large decline in antimony concentration in moss between 2005 and 2010, this decline slowed and there has been no further decrease between the surveys in 2015 and 2020. Of the participating countries that measured antimony concentration in moss in both the 2015 and the 2020 survey, there was a mixed pattern of response with some countries showing an increase in the antimony concentration, whereas others showed a decrease.

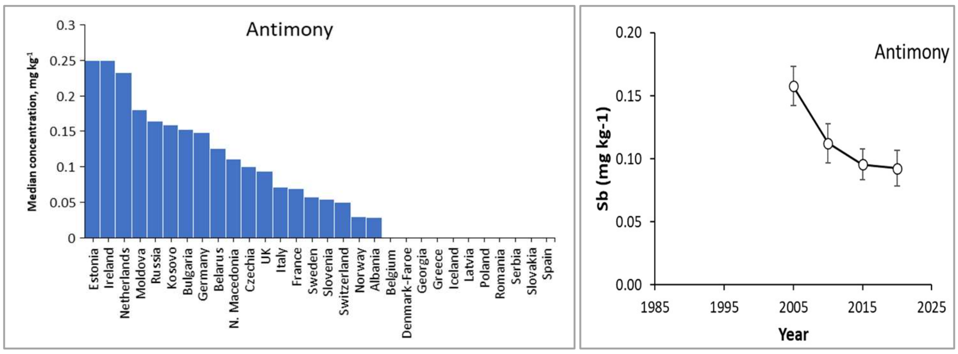


Figure 3.3: a) Median antimony concentrations in mosses 2020 (note not all countries provided data for antimony), b) Average median antimony concentrations in mosses for countries (n = 7-12, depending on year) that reported data for at least two survey years.

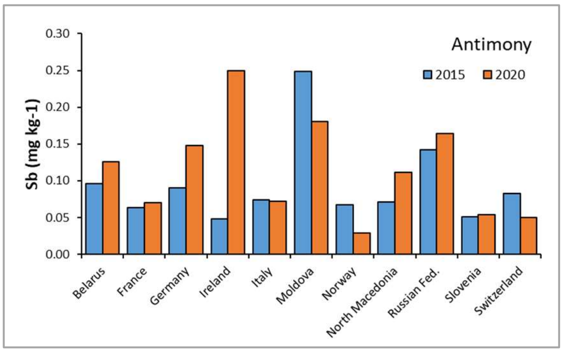


Figure 3.3c: Median antimony concentrations in mosses in 2015 and 2020, for those countries that provided antimony concentration data in both years.

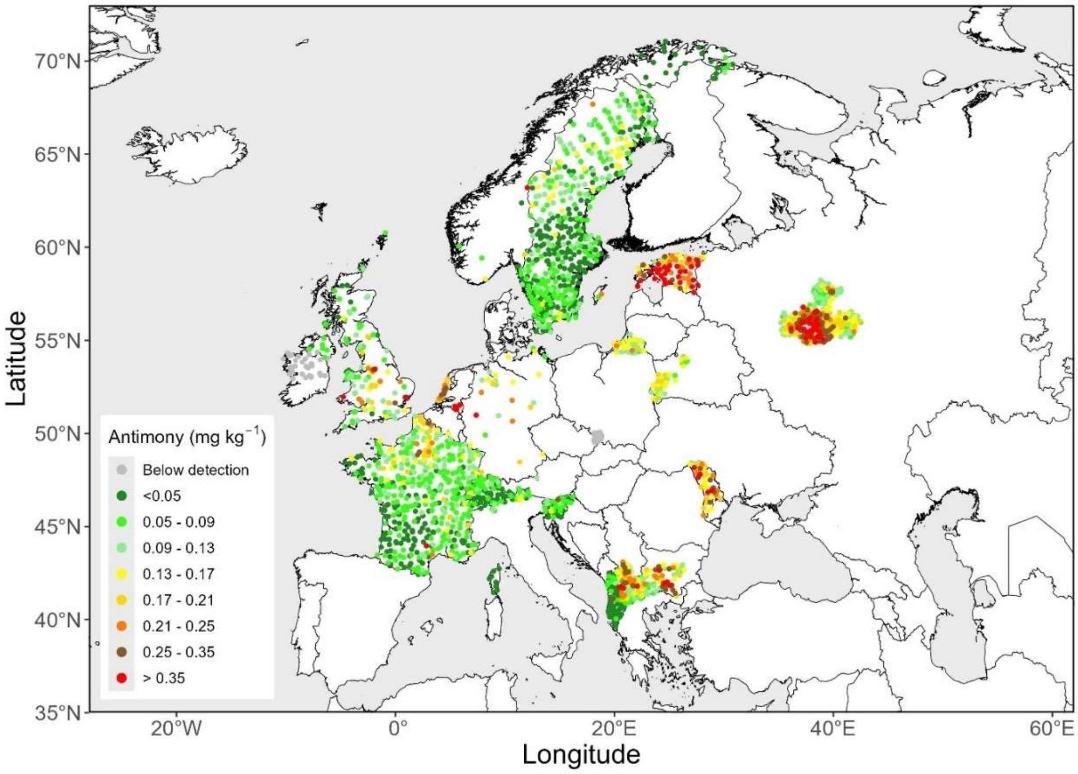


Figure 3.3d: Antimony concentration in mosses 2020.

Arsenic

Arsenic occurs naturally in some types of rock and can enter the environment via weathering. This means that arsenic can be naturally high in water in some parts of the region, such as Hungary. Anthropogenic sources of arsenic include from coal combustion (domestic and industrial) and the mining industry, including as a by-product of the smelting process for other metals. Arsenic can also be used as a wood preservative, although this is restricted within the EU. Previously (relating to moss surveys of the 1990's) there were some local sources from industries in the Kola peninsula (north-west Russian Federation). There were also emissions relating to metal smelting where filters were not present, although some filters have been introduced for industrial processes more recently. Currently, industrial processes in the Balkans are known to be high sources of arsenic in the region.

Although generally the concentration of arsenic in moss tissue is low for much of northern Europe and Scandinavia, concentrations are much higher in the south-east of the region, particularly the Balkans. Concentrations are also high in Slovakia and Moldova and in southern France there were medium concentrations. The countries contributing to the 2020 survey that had the highest average concentrations of arsenic in mosses include Serbia, Moldova, Bulgaria and Slovakia.

Analysis of trends for the whole dataset is based on countries where the concentration of arsenic in moss tissue has been measured in four or more surveys since 1995 (11 – 15 countries, depending on the year). This shows that the concentration of arsenic in moss tissue has remained fairly constant since 1995, the first time this was included by a sufficient number of countries to allow meaningful comparison, with an overall decrease of 1.4%. For those countries that measured arsenic concentration in moss tissue in both 2015 and 2020, concentrations were similar in both years, with some countries showing a slight increase in concentration of arsenic, while others showed a slight decrease. Larger decreases in concentration of arsenic were found for North Macedonia and Russian Federation.

For the EU27 countries, although there has been a large decline in emissions of 79.1% since 1990, this has not been matched to a corresponding decline in arsenic concentration in moss tissue. Based on countries of the EU27 that have measured arsenic concentration in moss in at least four surveys since 1995, there has been an increase of 6% since 1995, and an increase in arsenic concentration in moss tissue in 2020 compared to 2015. Many of the participating countries that are part of the EU27 showed a slight increase in concentration of arsenic in moss in 2020 compared to 2015, including Bulgaria, France, Ireland, Slovenia and Spain.

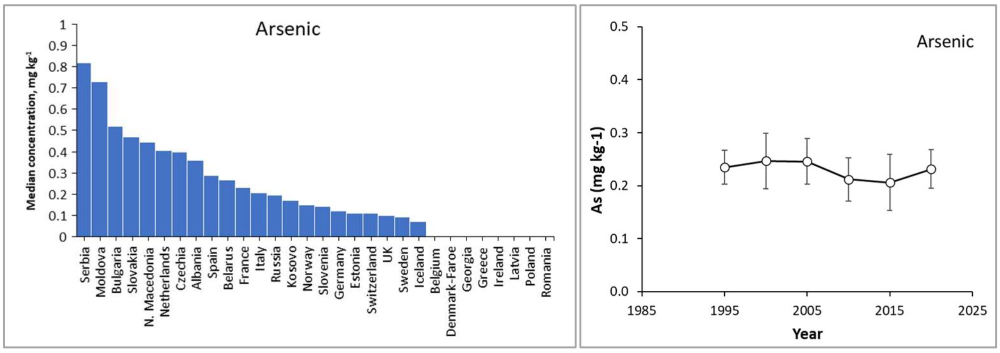


Figure 3.4: a) Median arsenic concentrations in mosses 2020 (note not all countries provided data for arsenic), b) Average median arsenic concentrations in mosses for countries (n = 11-15, depending on year) that reported data between 1995 and 2020 for at least four survey years.

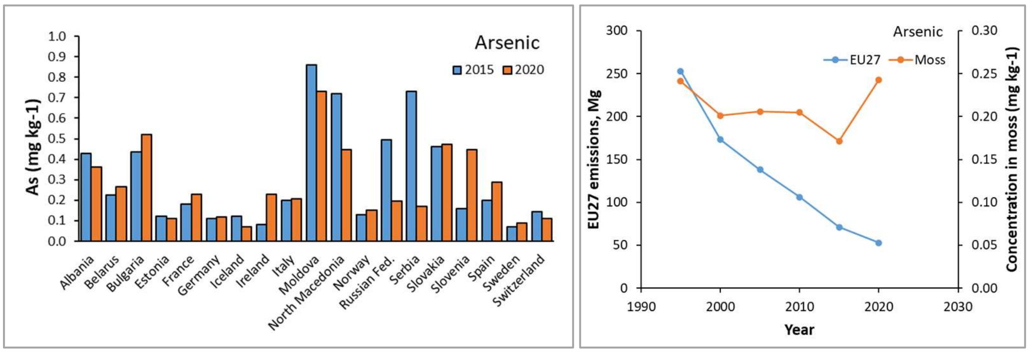


Figure 3.4: c) Median arsenic concentrations in mosses in 2015 and 2020, for those countries that provided arsenic concentration data in both years, d) Emissions of arsenic by all the EU27 Member states and average median arsenic concentration in mosses for the countries of the EU27 Member states that provided data (14 countries).

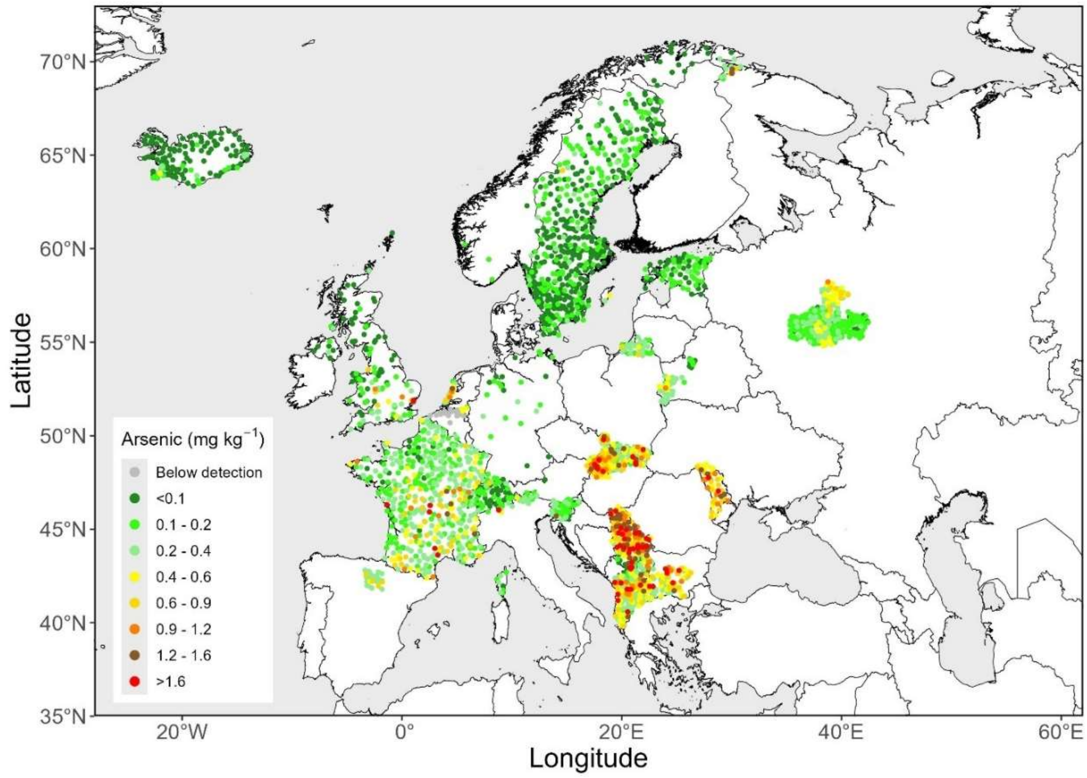


Figure 3.4e: Arsenic concentration in mosses 2020.

Cadmium

Cadmium emissions were previously dominated by industrial processes, with concentrations in mosses being locally elevated near sources such as smelters and waste incinerators. Following the widespread use of abatement technologies, more recently emissions were dominated by iron, steel and copper production, together with residential sources. Currently, sources include phosphate fertilisers.

Concentrations of cadmium in moss tissue are generally highest in the centre and south-east of the region. High concentrations in the south-east of the region are observed in Romania, Serbia, Greece, North Macedonia as well as in Kosovo. Czechia, Slovenia and Slovakia also show high concentrations. The 2020/21 survey shows some association with elevated concentrations of cadmium in moss tissue and regions of high traffic density or hotspots (presence of non-ferrous industries) in France and Belgium. For example, one site in Belgium is within the waste plume of a zinc smelter.

Analysis of trends for the whole dataset is based on countries where the concentration of cadmium in moss tissue has been measured in four or more surveys since 1990 (16-23 countries, depending on the year). This shows that there has been a steady decline in cadmium concentrations, with the decline levelling off in more recent years. The overall decrease in cadmium content in moss tissue between 1990 and 2020 was 61.9% for these countries. For those countries that measured the cadmium content in moss tissue in both 2015 and 2020 many countries show similar concentrations in both survey years. The exceptions were Belarus and Moldova, which both showed a large decline in cadmium content in 2020 compared to 2015.

Within the EU27 region, although emissions of cadmium have generally decreased in 2021 compared to those of 2005 there are some exceptions. Germany, Hungary and Poland have all had an increase in emissions of cadmium in 2021 compared to 2005 (EEA, 2023). The decline in concentration of cadmium in moss tissue in the EU27 countries shows a good match to the decline in emissions within the EU27 region. EU27 emissions declined by 66.3% and based on countries of the EU27 that have measured cadmium concentration in moss in at least four surveys since 1990, cadmium concentration in moss tissue declined by 60.5%.

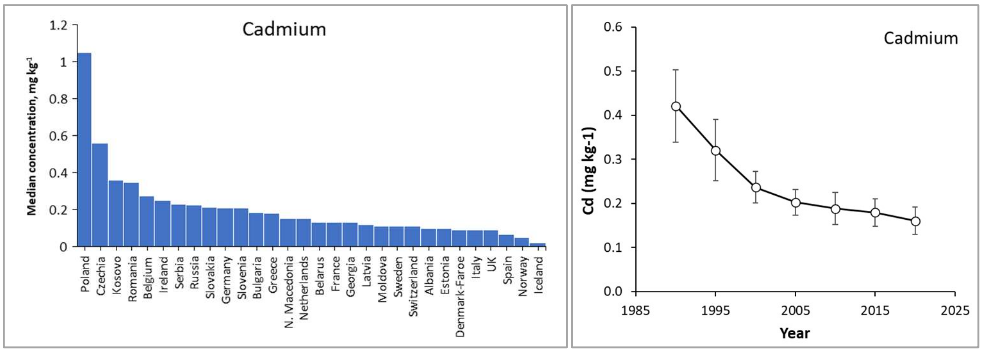


Figure 3.5: a) Median cadmium concentrations in mosses 2020, b) Average median cadmium concentrations in mosses for countries (n = 16-23, depending on year) that reported data between 1995 and 2020 for at least four survey years.

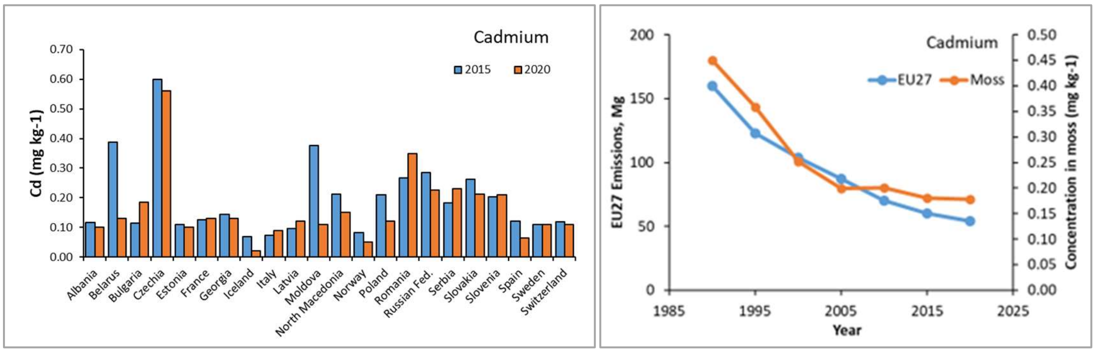


Figure 3.5: c) Median cadmium concentrations in mosses in 2015 and 2020, for those countries that provided cadmium concentration data in both years, b) Emissions of cadmium by all the EU27 Member states and average median cadmium concentration in mosses for the countries of the EU27 Member states that provided data (17 countries).

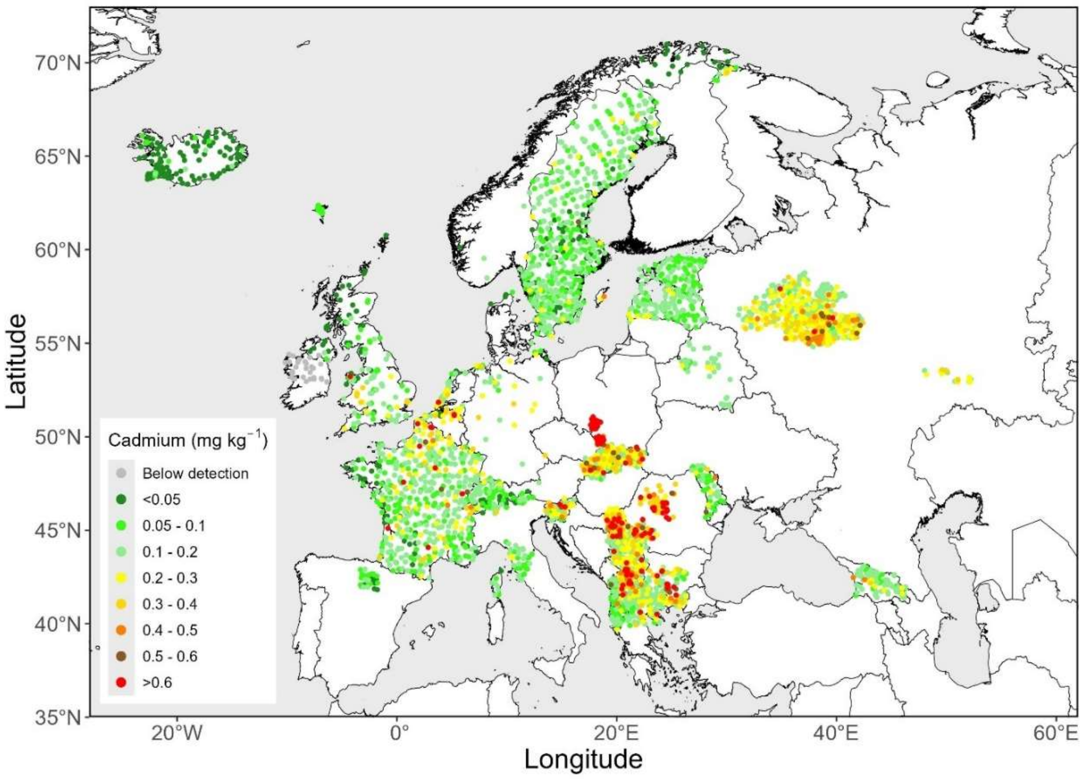


Figure 3.5e: Cadmium concentration in mosses 2020.

Chromium

Anthropogenic sources of chromium include from mining and metal works including the steel industry. Chromium is also released during coal combustion, waste incineration, and from local industries such as wood and paper processing. Increased use of particle scrubbers in industrial combustion processes have contributed to a decline in emissions over recent decades. Natural sources of chromium include from weathering of rocks and from volcanic activity.

Chromium concentrations in moss tissue are generally low in the north and west of the region, and moderate to high in the south-east of the region, although there are a few moderate hotspots in other places. The highest concentrations of chromium in moss tissue were found in Greece, North Macedonia, Albania and Moldova. Moderate concentrations of chromium in moss were also found in Iceland, compared to the other countries in the north and west of the region.

Analysis of trends for the whole dataset is based on countries where the concentration of chromium in moss tissue has been measured in four or more surveys since 1990 (16-24 countries, depending on the year). This showed that chromium concentrations in moss tissue declined slightly between 1990 and 2010 but increased between 2010 and 2020. Overall chromium concentrations in moss tissue have declined by 20.1% over the period 1990-2020. Further investigation of the subset of countries that measured chromium content in mosses in both 2015 and 2020 showed that for some countries there was a decline in chromium content, whereas others showed an increase.

Within the EU27 region emissions have declined by 70.6% since 1990. Based on countries of the EU27 that have measured chromium concentration in moss in at least four surveys since 1990, the corresponding decline in chromium concentrations within moss tissue was a more modest 37.2%.

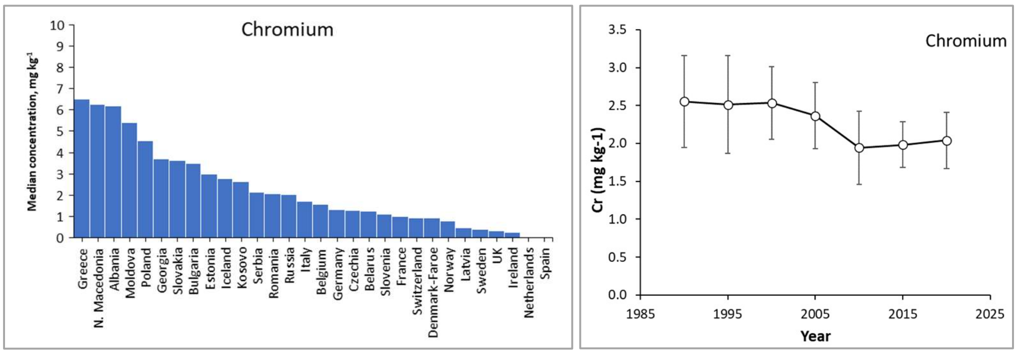


Figure 3.6: a) Median chromium concentrations in mosses 2020 (note Netherlands and Spain did not provide data for chromium), b) Average median chromium concentrations in mosses for countries (n = 16-24, depending on year) that reported data between 1995 and 2020 for at least four survey years.

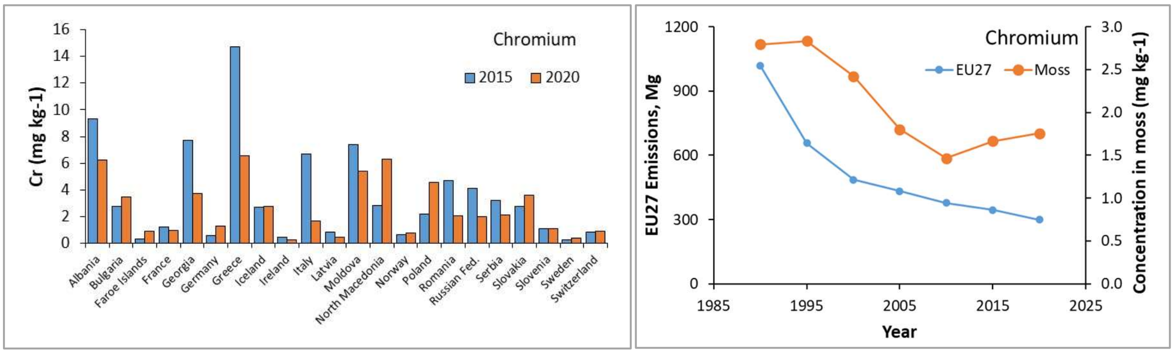


Figure 3.6: c) Median chromium concentrations in mosses in 2015 and 2020, for those countries that provided chromium concentration data in both years, d) Emissions of chromium by all the EU27 Member states and average median cadmium concentration in mosses for the countries of the EU27 Member states that provided data (17 countries).

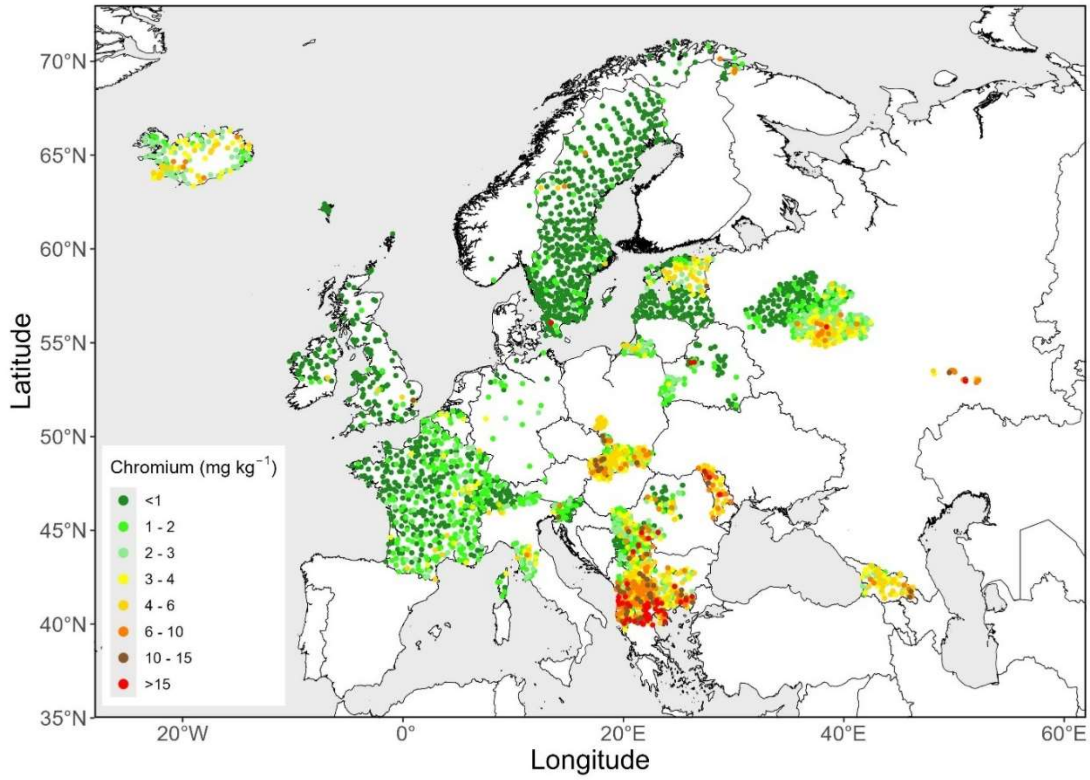


Figure 3.6e: Chromium concentration in mosses 2020.

Copper

Copper is an impurity found in nickel ore and can be associated with the process of nickel smelting in addition to copper smelting. Nickel and copper smelting both occurred in northern Scandinavia near to the town of Nikel (north-west Russian Federation, close to the Norway border) prior to the moss collection, which could account for the high concentrations of copper in moss in this region. There are also several large copper smelters in south-eastern Europe that may account for elevated concentrations in mosses in the SE.

Copper concentration in moss tissue across the region is generally low, with notable exceptions for the very north of Scandinavia and some parts of the Balkan region. The countries with the highest concentration of copper in moss tissue were Romania, Moldova, Czechia and Norway.

Analysis of trends for the whole dataset is based on countries where the concentration of copper in moss tissue has been measured in four or more surveys since 1990 (16-22 countries, depending on year). This shows that there has been a steady decline in copper concentrations in moss tissue since 1990, but the rate of decline has slowed and overall there has been no change since 2010. The overall decline in copper concentration from 1990 to 2020 was 25.6%. The lack of change since 2015 is reflected in further analysis of data from those countries that measured copper concentration in moss in both 2015 and 2020. This shows for the majority of countries either a very small increase or a very small decrease in copper concentration, with the exceptions being Albania (decrease) and Norway (increase). For Norway in particular this may reflect a different sampling strategy in 2020, with increased sampling near to the Kola Peninsula.

Within the EU27 region, emissions have declined by only 2.2% since 1990. Based on countries of the EU27 that have measured copper concentration in moss in at least four surveys since 1990, the corresponding decline in copper concentration within moss tissue was 28.8%.

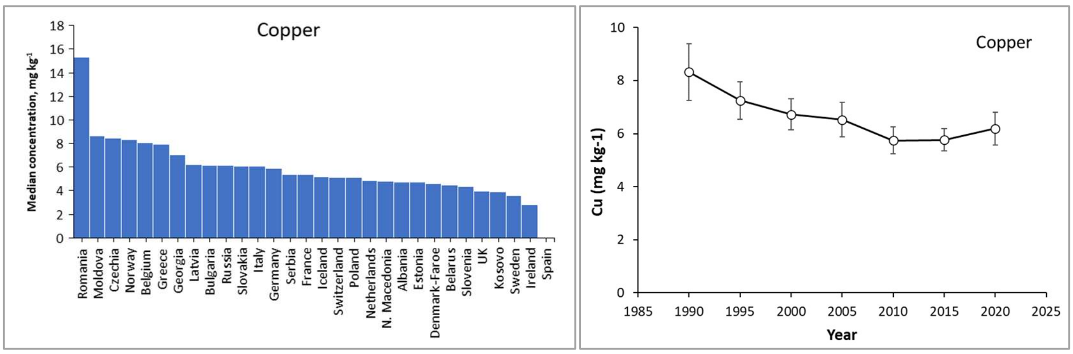


Figure 3.7: a) Median copper concentrations in mosses 2020 (note Spain did not provide data for copper), b) Average median copper concentrations in mosses for countries (n = 16-21, depending on year) that reported data between 1995 and 2020 for at least four survey years.

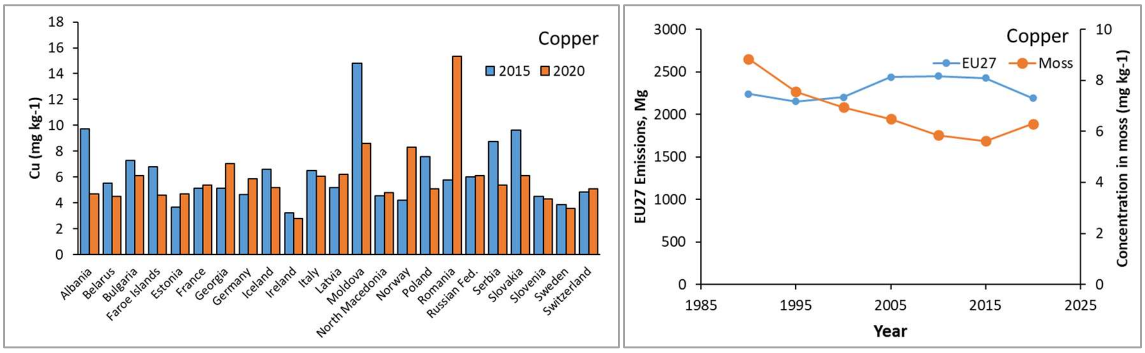


Figure 3.7c: Median copper concentrations in mosses in 2015 and 2020, for those countries that provided copper concentration data in both years, d) Emissions of copper by all the EU27 Member states and average median copper concentration in mosses for the countries of the EU27 Member states that provided data (20 countries).

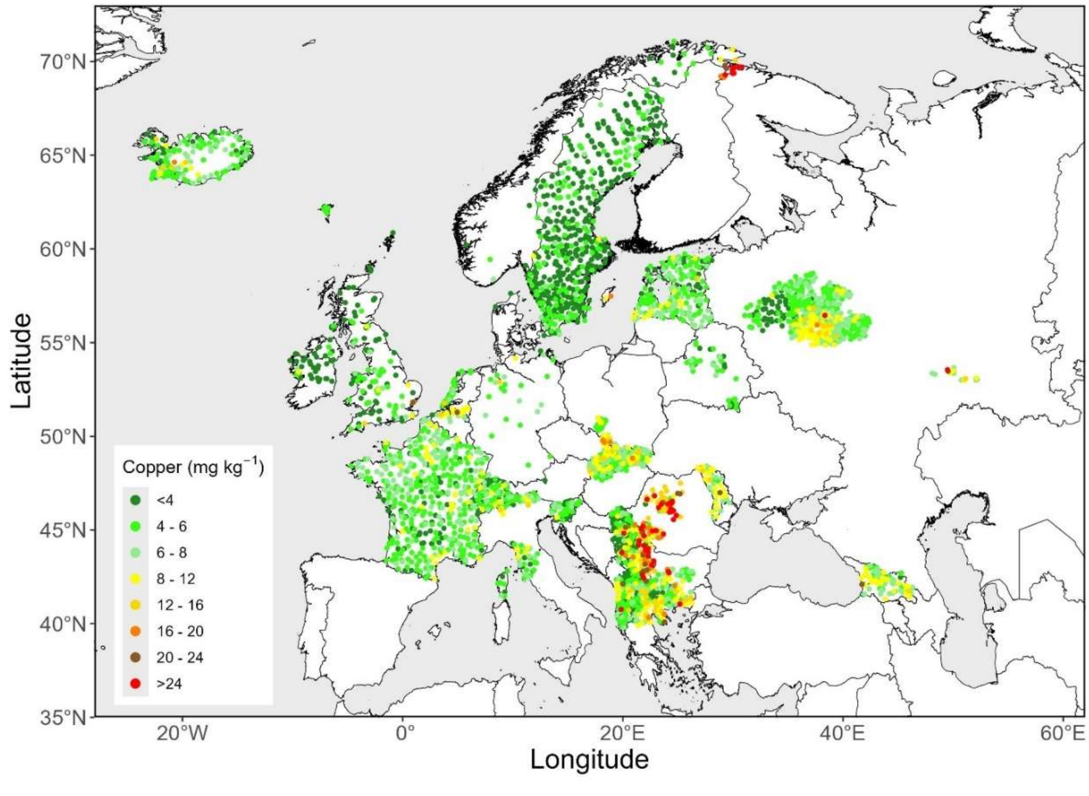


Figure 3.7e: Copper concentration in mosses 2020.

Iron

Iron is a commonly occurring element, found in igneous and sedimentary rock, and is an essential micronutrient. It is released to the environment through weathering of rocks. Iron was also released to the atmosphere following the eruption of the volcano Eyjafjallajökull in Iceland. Anthropogenic sources of iron include releases as a consequence of coal mining. Iron is also released from combustion of fossil fuels and biomass.

Iron concentrations in moss tissue are generally lower in the north and west of the region, and higher in the south-east. The exception is Iceland, which has moderate to high concentrations of iron in moss tissue across most of the country. The highest concentrations of iron in moss were found in Greece, Moldova, Georgia and Romania.

Analysis of trends for the whole dataset is based on countries where the concentration of iron in moss tissue has been measured in four or more surveys since 1990 (12-22 countries, depending on year). This shows only a small overall decrease since 1990, with a total decline of 15.0%. Concentrations of iron in moss have remained similar since 2005. The decline that was apparent between 2000 and 2015 was partially offset by the increase in iron concentration in moss between 2015 and 2020. Analysis of a subset of countries that measured iron concentration in moss in both 2015 and 2020 shows that concentrations were similar between the two years, and with the majority of countries showing a slight increase in iron concentration.

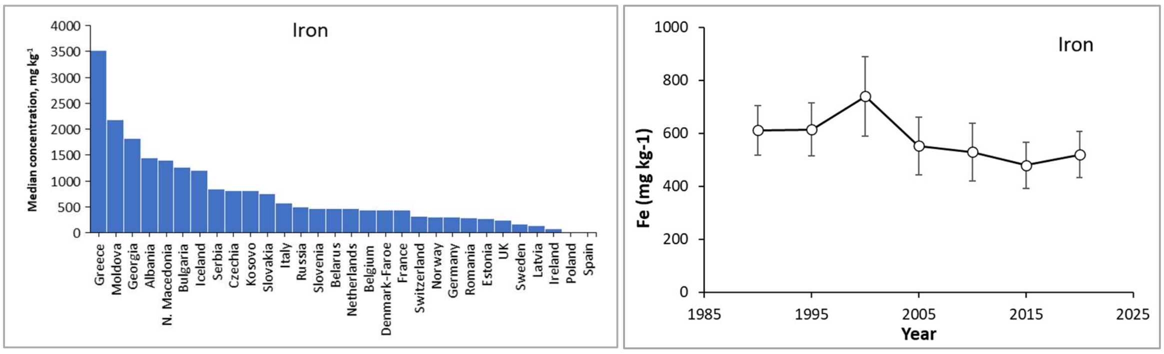


Figure 3.8: a) Median iron concentrations in mosses 2020 (note not all countries provided data for iron), b) Average median iron concentrations in mosses for countries (n = 12-22, depending on year) that reported data between 1995 and 2020 for at least four survey years.

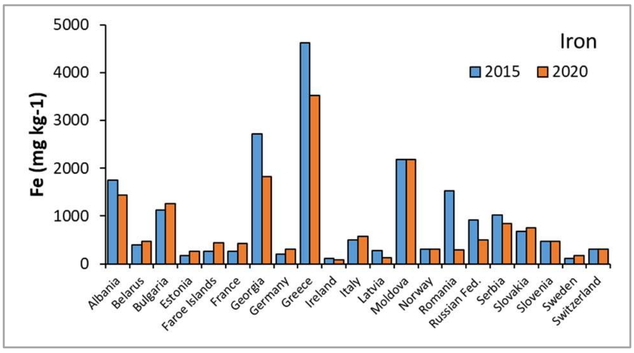


Figure 3.8c: Median iron concentrations in mosses in 2015 and 2020, for those countries that provided iron concentration data in both years.

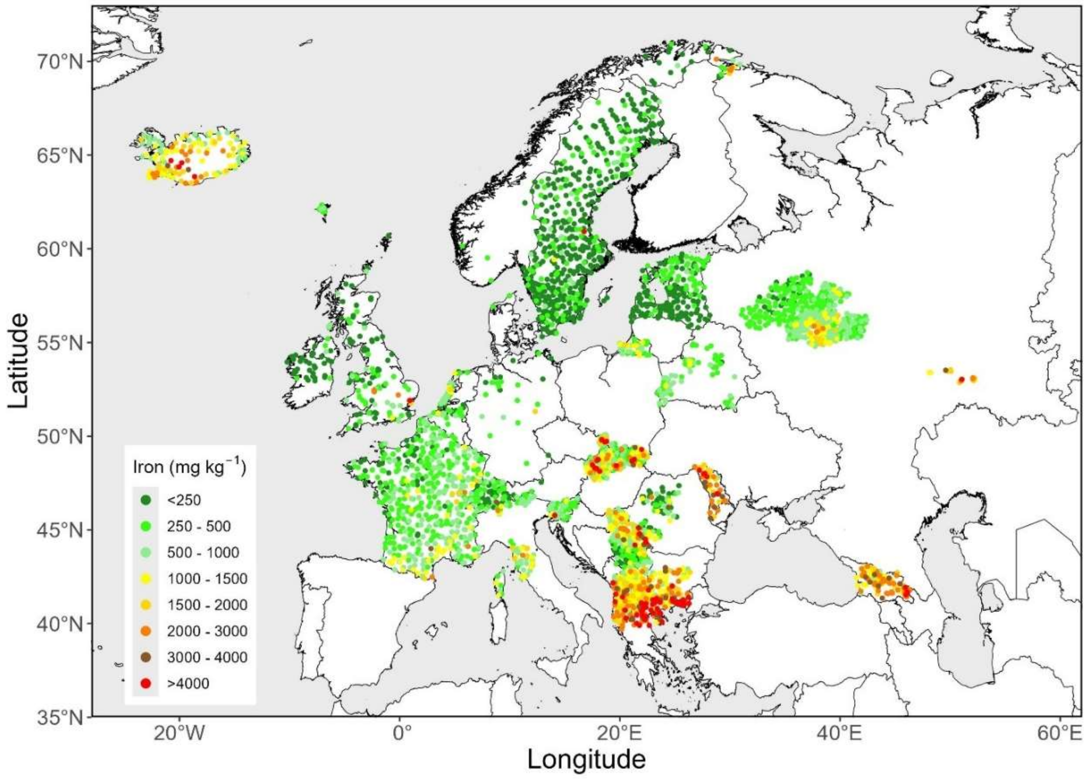


Figure 3.8d: Iron concentration in mosses 2020.

Lead

Historically the largest source of lead in the atmosphere was from anti-knock additions to petrol. Leaded petrol has been phased out across the region since the 1990's, however, this process took many years and leaded petrol was still in use in some parts of the south-east of the region until 2009. Lead emissions from tyre and brake wear remain. Iron and steel production also contribute to lead pollution to the atmosphere and these contributions have also been declining from a combination of decreasing production, and decreasing use of coal in the iron and steel production industry. Currently the major sources of lead pollution to the air within the EU are the manufacturing and extractive industry. Other sources that contribute to lead in the atmosphere include mining and smelters, waste incinerators, battery recycling and lead shot. Re-mobilisation of historical deposition as a result of re-suspension of road dust and topsoils are also thought to contribute to the persistence of airborne lead pollution (Resongles et al., 2021).

Lead concentrations in moss are generally low in the north and west of the region, and higher in the south and east. Overall, concentrations of lead in moss were highest in Poland, Belgium, Romania, as well as Kosovo. There are a few areas of medium concentrations that correspond to elevated population and traffic density. These include north-east France, Belgium and Netherlands.

Analysis of trends for the whole dataset is based on countries where the concentration of lead in moss tissue has been measured in four or more surveys since 1990 (17-22 countries, depending on year). This shows a large decline of 83.2% between 1990 and 2020, with the decline levelling off in recent years now that concentrations are very low. For the subset of countries that measured lead concentration in moss in both 2015 and 2020 there have been a mixture of small increases and small decreases in lead concentration.

The EU27 countries have generally shown a large decrease in emissions of lead in 2020 compared to 2005. The exceptions to this are Hungary and Lithuania, which have reported increases in emissions of lead of 3% and 10% respectively (EEA, 2023), although these were in comparison to low baseline levels. Overall, the emissions of lead for the EU27 countries reduced by 95.2% between 1990 and 2020. Based on countries of the EU27 that have measured lead concentration in moss in at least four surveys since 1990, the concentration of lead in moss tissue followed a very similar pattern and declined by 83.4%.

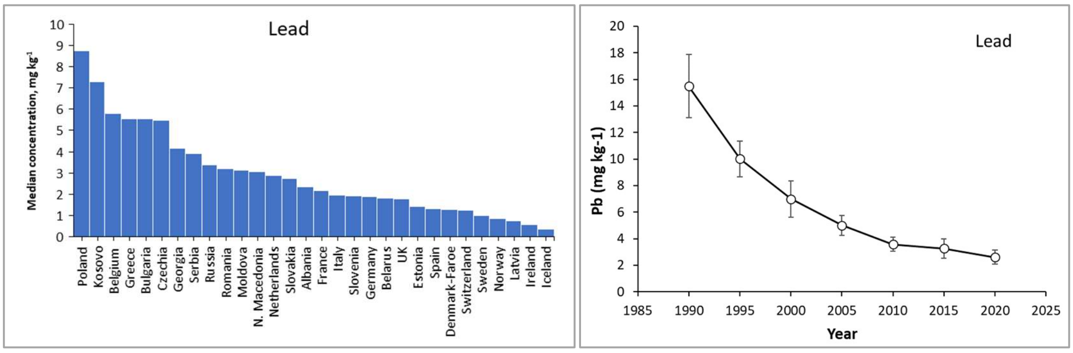


Figure 3.9: a) Median lead concentrations in mosses 2020, b) Average median lead concentrations in mosses for countries (n = 17-22, depending on year) that reported data between 1995 and 2020 for at least four survey years.

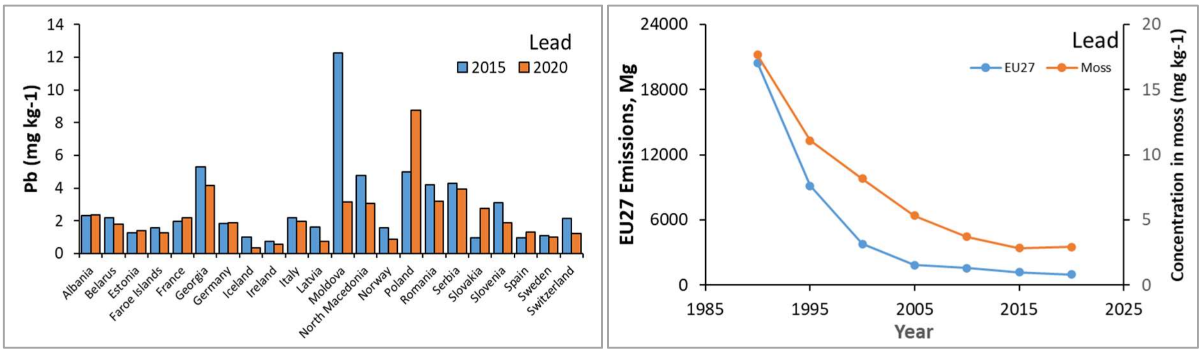


Figure 3.9: c) Median lead concentrations in mosses in 2015 and 2020, for those countries that provided lead concentration data in both years, d) Emissions of lead by all the EU27 Member states and average median lead concentration in mosses for the countries of the EU27 Member states that provided data (19 countries).

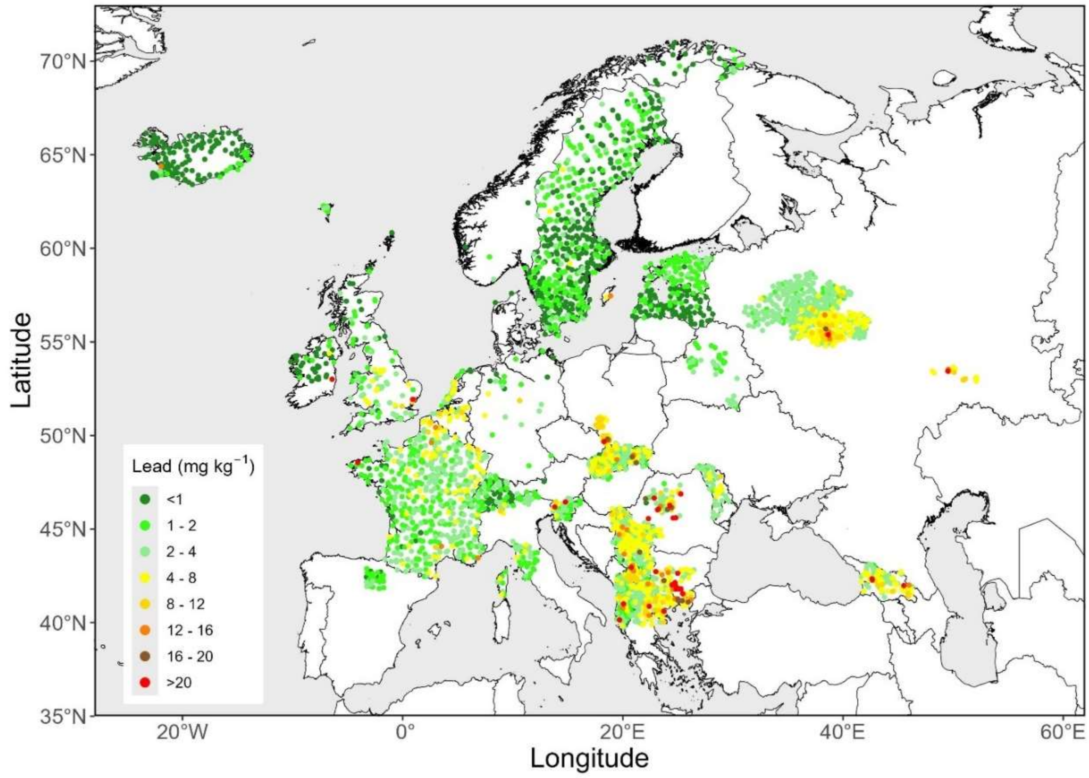


Figure 3.9e: Lead concentration in mosses 2020.

Mercury

Historically emissions of mercury within Europe and the UNECE region were high due to mercury mining and use of mercury in many industries. Legislation within Europe has led to a reduction in use in consumer products such as electrical equipment and within industries such as chlorine production. Globally emissions of mercury have been increasing due to activities such as coal burning and gold mining. It has been estimated that 50% of the mercury deposited in Europe originates from outside the region (EEA, 2018). Other sources of mercury to the atmosphere include vinyl chloride production (used to make PVC), dental fillings, batteries and lightbulbs.

Concentrations of mercury in mosses were generally homogenous across much of Europe. This is likely due to the longevity of mercury in the atmosphere and due to many source of mercury being outside of the UNECE region. Highest concentrations of mercury in mosses were found in Ireland, Germany, France and Kosovo.

Analysis of trends for the whole dataset is based on countries where the concentration of mercury in moss tissue has been measured in four or more surveys since 1995 (7-11 countries, depending on the year). This has shown that concentrations of mercury in moss have remained similar since it was first widely included in the survey in 1995, with overall the concentration of mercury in moss rising by 4.8%. Analysis of a subset of countries that measured mercury concentration in moss in both 2015 and 2020 shows that concentrations were similar between the two years.

For the majority of EU27 countries emissions of mercury have decreased in 2021 compared to 2005. Exceptions to this were Latvia and Estonia, with increased emissions of mercury in 2021 compared to 2005 of 9% and 19% respectively (EEA, 2023). Overall, the emissions of mercury for the EU27 countries reduced by 66.4% between 1995 and 2020. Based on countries of the EU27 that have measured mercury concentration in moss in at least four surveys since 1995, the concentration of mercury in moss tissue increased by 10.0%.

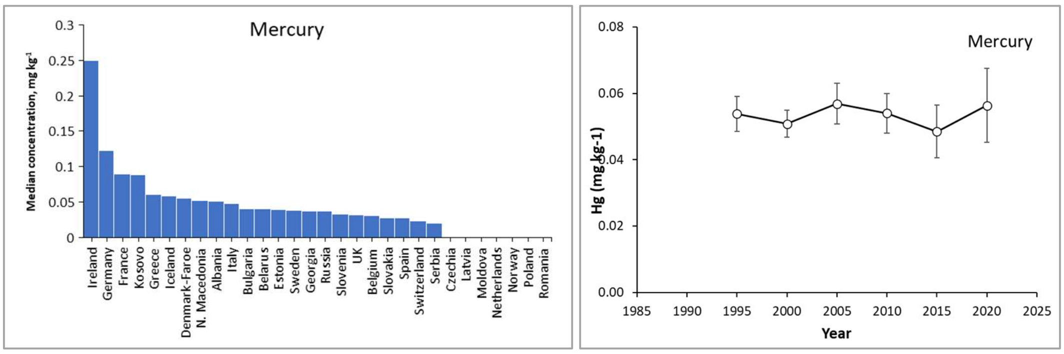
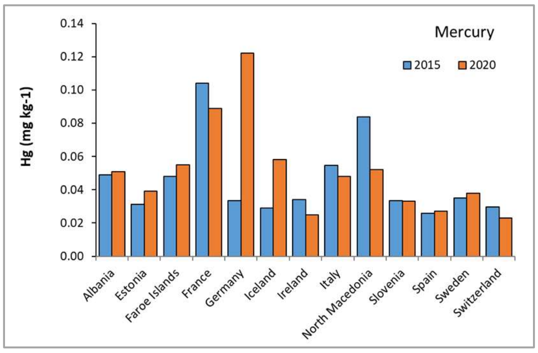


Figure 3.10: a) Median mercury concentrations in mosses 2020 (note not all countries provided data for mercury), b) Average median mercury concentrations in mosses for countries (n = 7-11, depending on year) that reported data between 1995 and 2020 for at least four survey years.



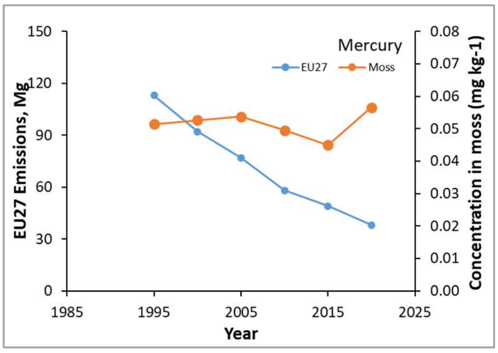


Figure 3.10: c) Median mercury concentrations in mosses in 2015 and 2020, for those countries that provided mercury concentration data in both years, d) Emissions of mercury by all the EU27 Member states and average median mercury concentration in mosses for the countries of the EU27 Member states that provided data (12 countries).

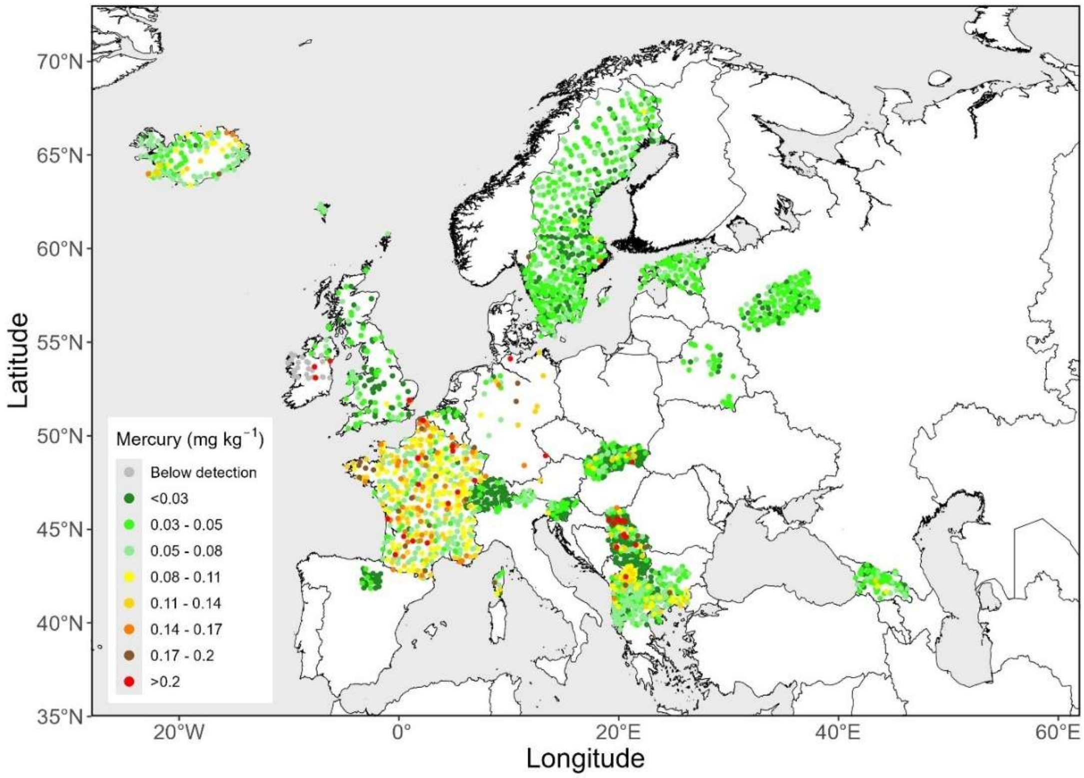


Figure 3.10e: Mercury concentration in mosses 2020.

Nickel

Concentrations of nickel in moss tissue are generally low in the north and west of the region, and slightly elevated in the centre and south-east. Iceland is an exception to this trend, with medium concentrations and some hotspots, which are likely due to volcanic origins of nickel. The highest concentrations in moss tissue were found in Albania, Greece, Norway and Georgia.

The hotspot in the north of Fennoscandia is due to very large nickel smelters located near to the town of Nikel in the Kola Peninsula and near to the border with Norway and Finland. Previously this has been identified as a serious pollution source in the region (Lukin et al., 2003). Closure of three nickel smelters was due to take place at the end of 2020, and the accumulation of nickel in moss samples near to here could have occurred in the years prior to these closures. There is also a hotspot of nickel concentration in mosses in Albania, likely associated with nickel mining and processing.

Analysis of trends for the whole dataset is based on countries where the concentration of nickel in moss tissue has been measured in four or more surveys since 1990 (17 – 23 countries depending on the year). This has shown that nickel concentration in mosses has been declining steadily since 1990 and the overall reduction in nickel content of mosses has reduced by 30.4%. Analysis of a subset of countries that measured nickel concentration in moss in both 2015 and 2020 shows that concentrations were similar between the two years.

Overall, the emissions of nickel for the EU27 countries reduced by 79.3% between 1995 and 2020. Based on countries of the EU27 that have measured nickel concentration in moss in at least four surveys since 1995, the concentration of nickel in moss tissue decreased by a more modest 42.2%.

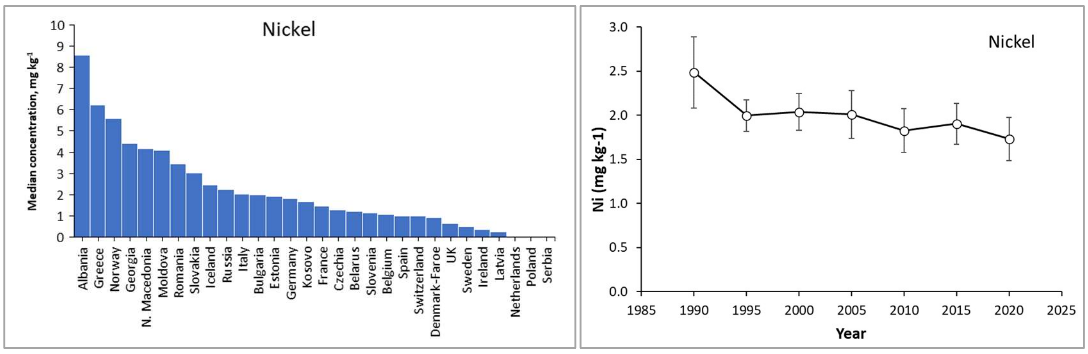
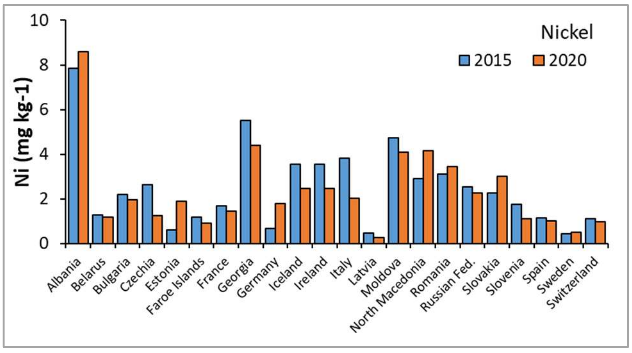


Figure 3.11: a) Median nickel concentrations in mosses 2020 (note Netherlands, Spain and Poland did not provide data for nickel), b) Average median nickel concentrations in mosses for countries (n = 17-23, depending on year) that reported data between 1995 and 2020 for at least four survey years.



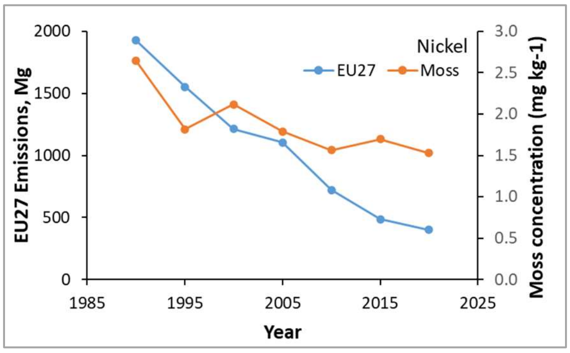


Figure 3.11 c) Median nickel concentrations in mosses in 2015 and 2020, for those countries that provided nickel concentration data in both years, d) Emissions of nickel by all the EU27 Member states and average median nickel concentration in mosses for the countries of the EU27 Member states that provided data (19 countries).

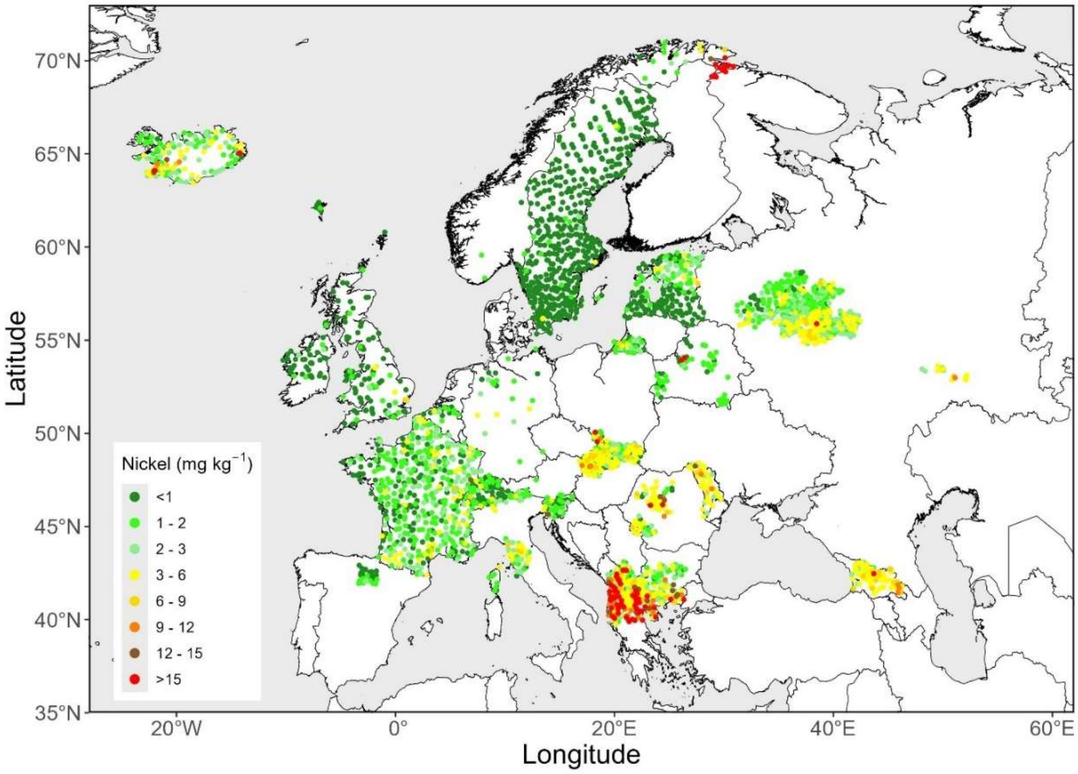


Figure 3.11e: Nickel concentration in mosses 2020.

Vanadium

Vanadium is mostly mined from China, South Africa and Russia. It is mainly used as an additive to steel and in titanium alloys. It is also present is coal and crude oil and previous studies have shown that within Europe most atmospheric vanadium, bound in aerosol particles, is associated with combustion processes involving heavy petroleum products (Moreno et al., 2010, Arienzo et al., 2021). The largest emission sources in 2005 were associated with the cities of Rotterdam, Antwerp and Hamburg (Visschedijk et al., 2013).

Vanadium concentrations in moss were generally lowest in the north and west of the region (with the exception of Iceland), and highest in the south-east. There were two hotspots on the coast of the Netherlands which might be associated with major ports. The countries with the highest concentration of vanadium in moss tissue were Romania, Greece, Moldova and Georgia.

Analysis of trends for the whole dataset is based on countries where the concentration of vanadium in moss tissue has been measured in four or more surveys since 1990 (13 – 21 countries depending on the year). This has shown that vanadium concentration in mosses has been declining steadily since 1990 and the overall reduction in vanadium content of mosses has reduced by 51.0%. Analysis of a subset of countries that measured vanadium concentration in moss in both 2015 and 2020 shows that concentrations were similar between the two years and with some countries showing a slight increase in concentration, while others showed a decrease. Between 2015 and 2020 there were particularly large decreases in concentration in moss tissue for Georgia and Iceland, and a notably large increase between 2015 and 2020 for Romania.

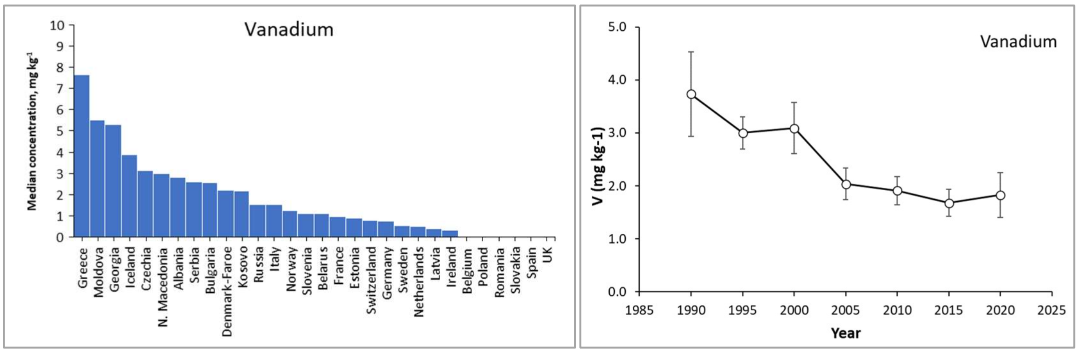


Figure 3.12: a) Median vanadium concentrations in mosses 2020 (note Slovakia, UK, Belgium, Romania, Spain and Poland did not provide data for vanadium), b) Average median vanadium concentrations in mosses for countries (n = 13-21, depending on year) that reported data between 1995 and 2020 for at least four survey years.

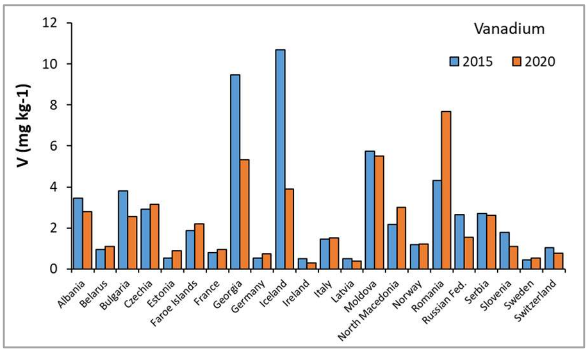


Figure 3.12c: Median vanadium concentrations in mosses in 2015 and 2020, for those countries that provided vanadium concentration data in both years.

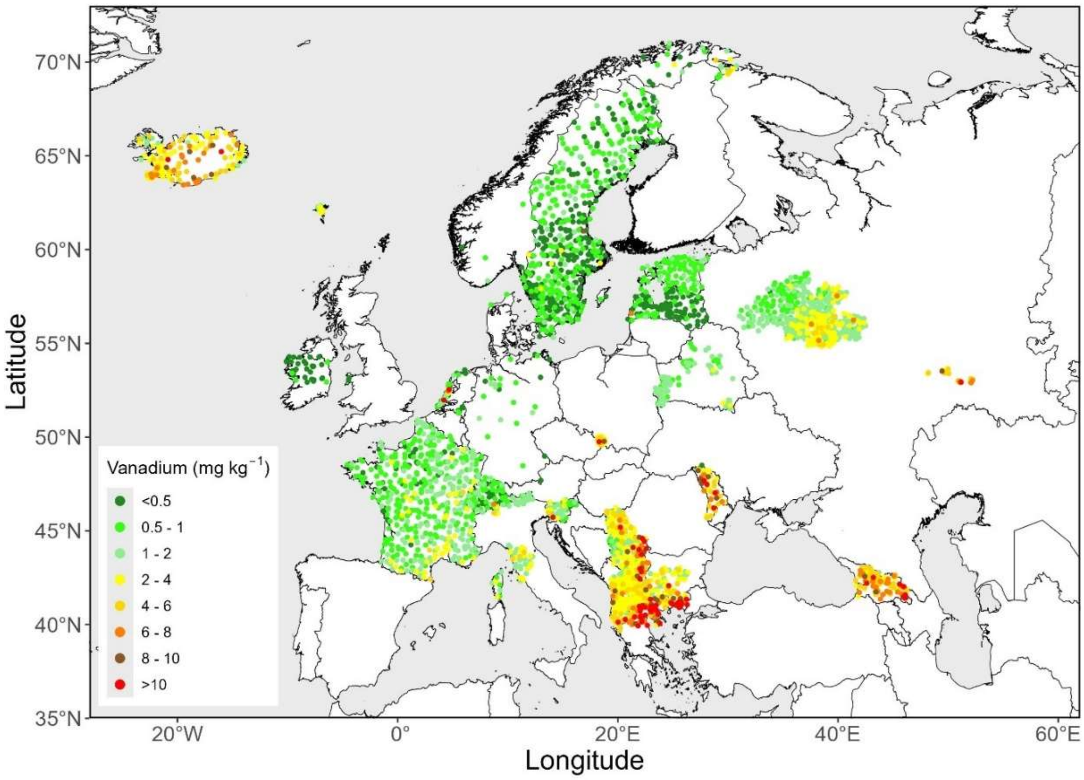


Figure 3.12d: Vanadium concentration in mosses 2020.

Zinc

Zinc is an essential trace element. It is normally found in association with other metals such as copper and lead. Zinc is most commonly used as an anti-corrosion agent and for galvanisation. It has also more recently been used as a lead replacement in some applications. Other industrial uses include as a pigment in paint, to protect rubber and plastic polymers from UV degradation and as a fire retardant to wood.

Zinc concentrations in moss are fairly homogenous across the region. There were a few hotspots in Belgium, the Balkans, and Russian Federation, for example, in Belgium this was associated with a zinc smelter. The countries with the highest concentrations of zinc in moss were Poland, Belgium, Russia and Moldova.

Analysis of trends is based on countries where the concentration of zinc in moss tissue has been measured in four or more surveys since 1990 (16 – 24 countries depending on the year). This showed that zinc concentration in mosses has been decreasing since 1990, although this decline has slowed in the most recent surveys. Overall zinc content of mosses has reduced by 18.1%. Analysis of a subset of countries that measured zinc concentration in moss in both 2015 and 2020 shows that concentrations were similar between the two years, with some countries showing a slight increase in concentration, while others showed a decrease.

Overall, the emissions of zinc for the EU27 countries reduced by 51.4% between 1995 and 2020. Based on countries of the EU27 that have measured zinc concentration in moss in at least four surveys since 1995, the concentration of zinc in moss tissue decreased by a more modest 17.6%. There was also an increase in zinc concentration in moss tissue for countries of the EU27 region in 2020 compared to 2015. This was largely influenced by results from Belgium, Germany and Poland, however, Belgium did not participate in the 2015 survey. Samples for Poland in 2020 were for a small area of the country, compared to a much wider area in 2015, so this large increase may not be reflective of the pattern for the whole country. The increase remains even if the particularly large increase in zinc for Poland is omitted from the analysis.

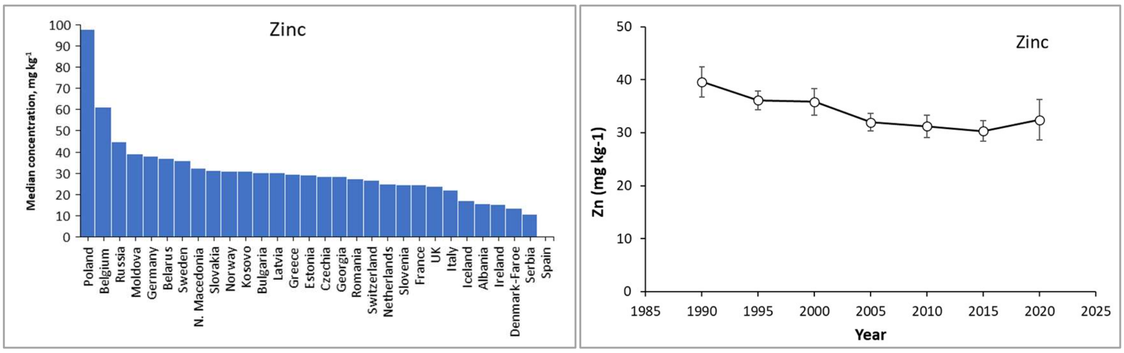


Figure 3.13: a) Median zinc concentrations in mosses 2020 (note Spain did not provide data for zinc), b) Average median zinc concentrations in mosses for countries (n = 16-24, depending on year) that reported data between 1995 and 2020 for at least four survey years.

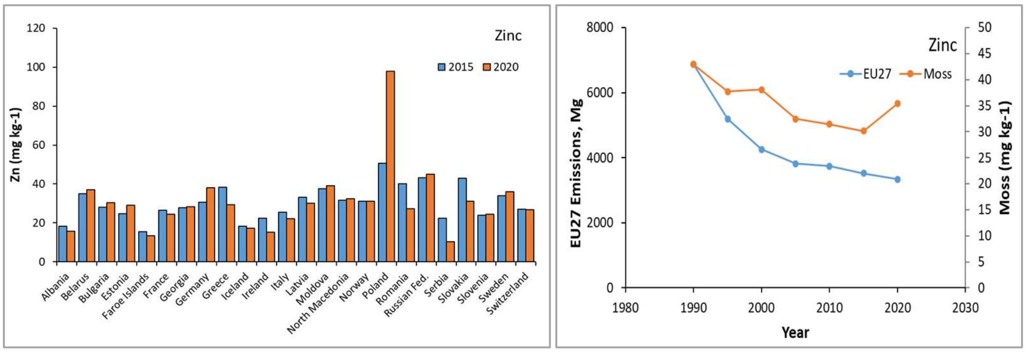


Figure 3.13: c) Median zinc concentrations in mosses in 2015 and 2020, for those countries that provided zinc concentration data in both years, d) Emissions of zinc by all the EU27 Member states and average median zinc concentration in mosses for the countries of the EU27 Member states that provided data (19 countries).

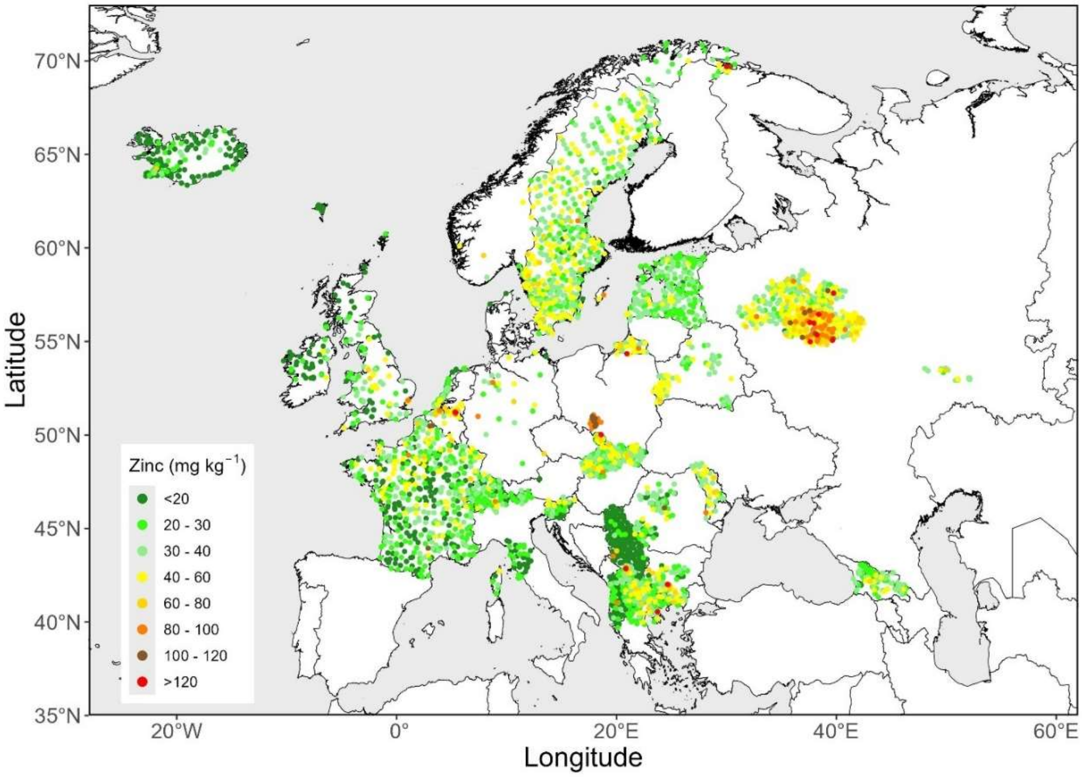


Figure 3.13e: Zinc concentration in mosses 2020.

Nitrogen

Anthropogenic sources of nitrogen to the atmosphere include oxidised nitrogen from combustion processes, and reduced nitrogen from agricultural activities. Although nitrogen is an essential nutrient, an excess deposition causes many detrimental impacts to ecosystems and critical loads for nitrogen are exceeded across much of Europe.

Nitrogen concentrations in moss show the highest concentrations in central Europe. The countries with the highest concentrations of nitrogen in moss were Czechia, Slovakia, Germany and Slovenia.

Analysis of trends for the whole dataset is based on countries where the concentration of nitrogen in moss tissue has been measured in three or more surveys since 2005 (10 – 13 countries depending on year). This has shown that nitrogen concentration in mosses has had a negligible change since 2005, and overall nitrogen content of mosses has increased by 3.3%. Analysis of a subset of countries that measured nitrogen concentration in moss in both 2015 and 2020 shows that concentrations were similar between the two years, with some countries showing a slight increase in concentration, while others showed a decrease.

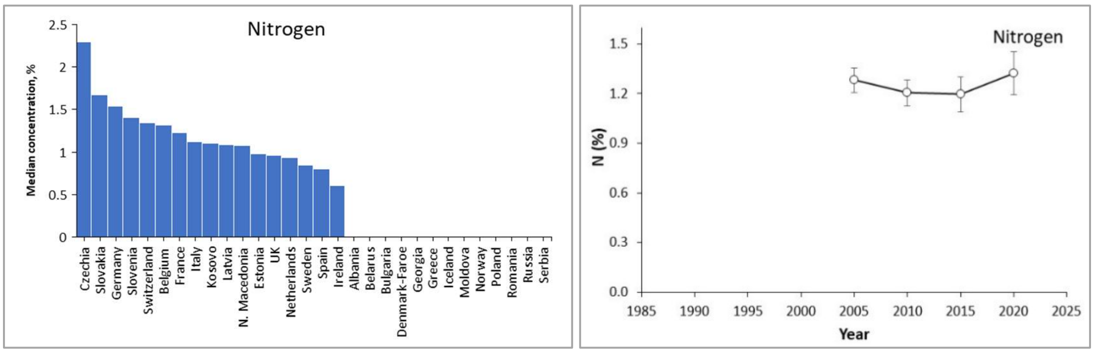


Figure 3.14: a) Median nitrogen concentrations in mosses 2020 (note not all countries provided data for nitrogen), b) Average median nitrogen concentrations in mosses for countries (n = 10-13, depending on year) that reported data between 2005 and 2020 for at least three survey years.

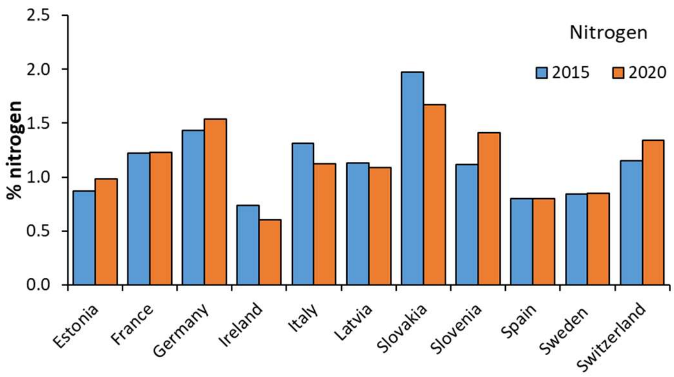


Figure 3.14c: Median nitrogen concentrations in mosses in 2015 and 2020, for those countries that provided nitrogen concentration data in both years.

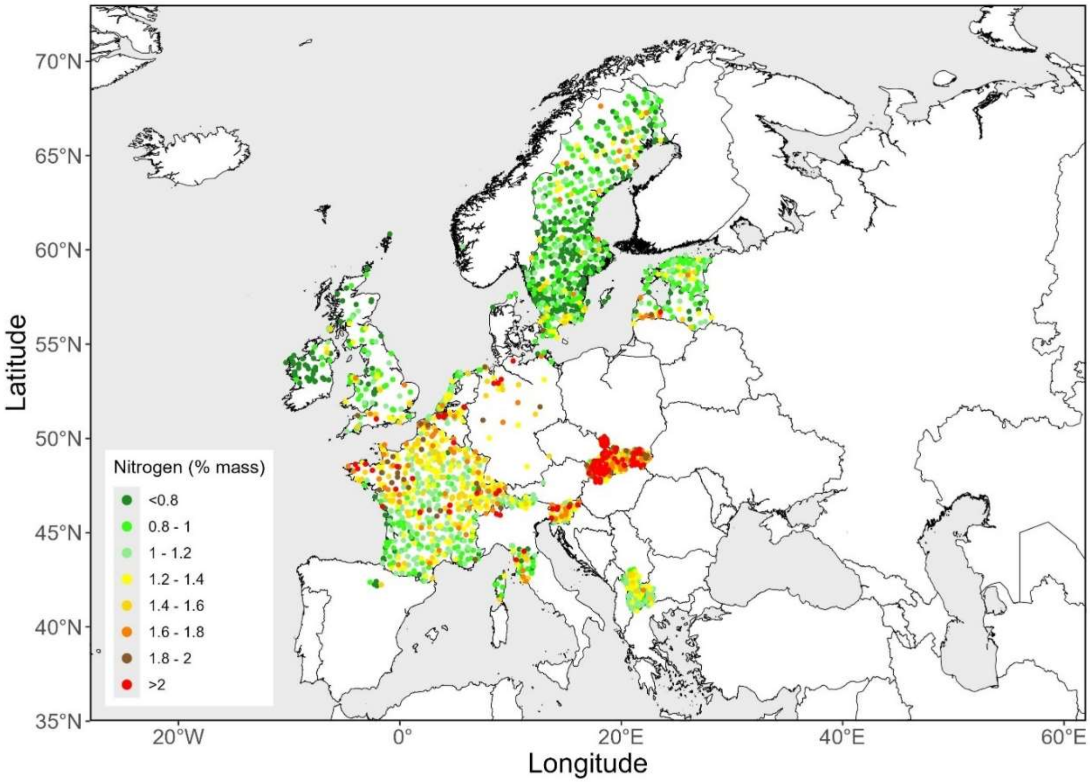
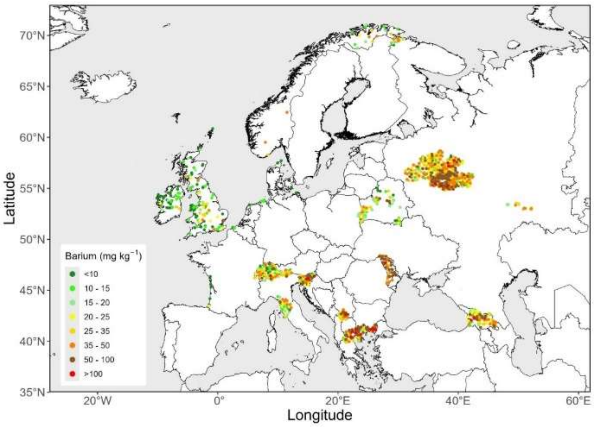
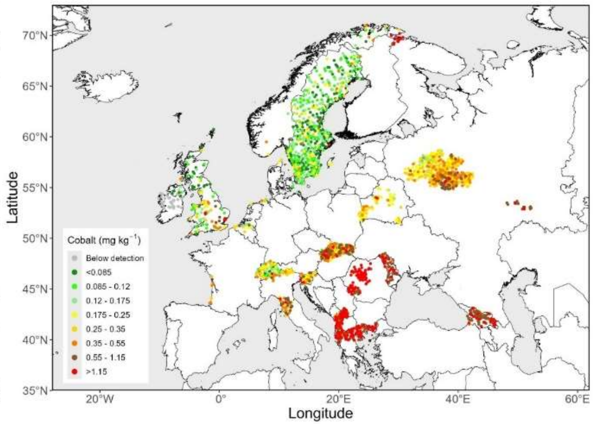


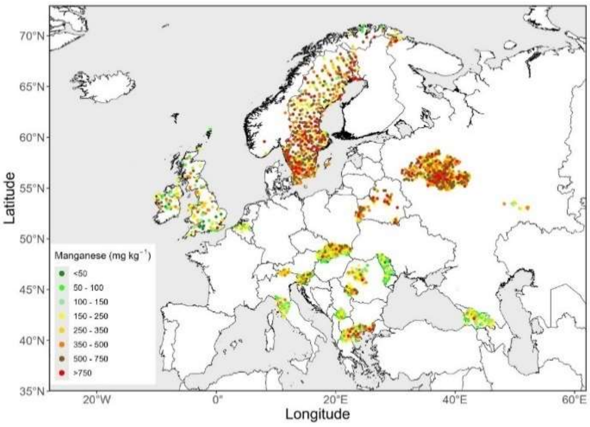
Figure 3.14d: Nitrogen concentration in mosses 2020.

Other metals (not core)

Note that these metals have not been subjected to the same intercalibration, as calibration information was not available for the standard moss. They have not been considered as part of any trend analysis or compared to emissions information. They have been included for information only.







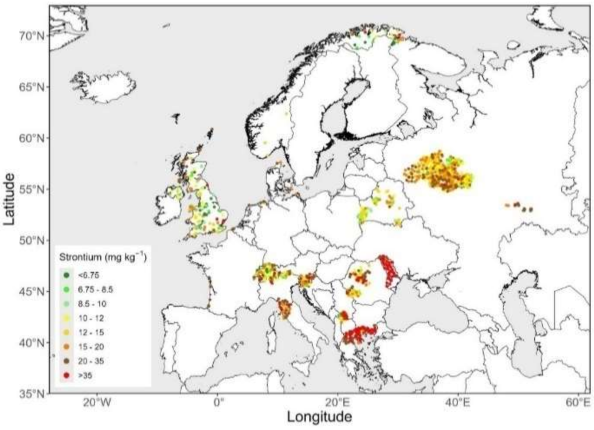


Figure 3.15: Barium concentration in mosses 2020.

Figure 3.16: Cobalt concentration in mosses 2020.

Figure 3.17: Manganese concentration in mosses 2020.

Figure 3.18: Strontium concentration in mosses 2020.

POPs

Occurrence of POPs in moss samples were only reported by Germany and Switzerland for the 2020 moss survey. Information is also given from Spain (Rioja region) from samples collected in 2018.

PAHs were found in the majority (but not all) of moss samples from the sites analysed. At many sites a wide range of different PAHs were found in the moss samples, and the relative proportions of the different PAHs was variable between sites. The most dominant PAHs in Germany were fluoranthene and pyrene. In Spain the most dominant PAHs were phenanthrene and fluorene. In Switzerland the most dominant PAHs were naphthalene and phenanthrene.

Germany has also reported other POPs including PFAS, HBCD, PBB, AFR, PBDE and PCDD/F. PBBs and PFAS were rarely found above quantification limits. PBDEs above the limit of quantification were found sporadically, with the exception of PentaBDE (BDE-99), which was found at all sites. AFRs above the limit of quantification were also found sporadically, with the most commonly found being syn-dechlorane Plus (syn-DP) and anti-dechlorane Plus (anti-DP), decabromodiphenylethane (DBDPE), pentabromotoluene (PBT), bis(2-ethyl-1-hexyl)tetrabromophthalate (BEHTBP) and 2,3-dibromopropyl-2,4,6-tribromophenyl ether.

No specific analytical techniques were recommended for analysis of POPs 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).

For these metrics, higher values were found in Germany than in Switzerland, and with the lowest values found in Spain (Table 3). The composition of POPs contributing to these metrics is indicated in Table 4.

POPs were only included in the moss survey as a pilot study in 2010, and more widely in 2015. Whilst it is not possible to determine trends based on very few countries, comparisons between 2015 and 2020 are shown in Figure 3.19. It is apparent that the sum PAH EPA 16, PAH 4 and Borneff 6 have increased in both Germany and Spain compared to those reported from the 2015 survey, whereas for Switzerland the values decreased for PAD EPA 16 and Borneff 6, whilst increasing for PAH 4. In Spain, but the number of sites sampled was comparatively low and the difference in sites sampled may account for some of the differences observed.

Table 3: Median values of PAHs (SUM EPA 16, SUM PAH 4 and SUM Borneff 6), PCBs (SUM PCB 7, SUM Dioxin-like PCBs) in mosses in the 2020 survey, sampled at selected sites in Europe. See annex 4 for further details.

	Germany	Spain	Switzerland
Number of sites	21	5	22
Median sum EPA 16, ng/g	278.2	61.6	79.5
Median sum PAH 4, ng/g	25.1	3.4	16.3
Median sum Borneff 6, ng/g	42.0	9.1	21.1
Median sum PCB 7, ng/g	0		0.28
Median sum Dioxin-like-PCB, ng/g	0		

Based on sum per site for POPs, excluding < LOD

Table 4: Composition of POPs contributing to the reported metrics of PAHs and PCBs.

	SUM EPA 16	SUM PAH 4	SUM Borneff 6	SUM PCB 7	SUM Dioxin-like PCBs
Compounds	Naphthalene	benzo[b]fluoranthene	Fluoranthene	PCB 28	PCB 77
	Acenaphthylene	benzo[k]fluoranthene	Benzo(b)fluoranthenes	PCB 52	PCB 81
	Acenaphthene	benzo[a]pyrene	Benzo(k)fluoranthenes	PCB 101	PCB 105
	Fluorene	indeno[123-cd]pyrene	Benzo(a)pyrene	PCB 118	PCB 114
	Phenanthrene		Indeno(1,2,3-cd)pyrene	PCB138	PCB 118
	Anthracene		Benzo(ghi)perylene	PCB153	PCB 123
	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				

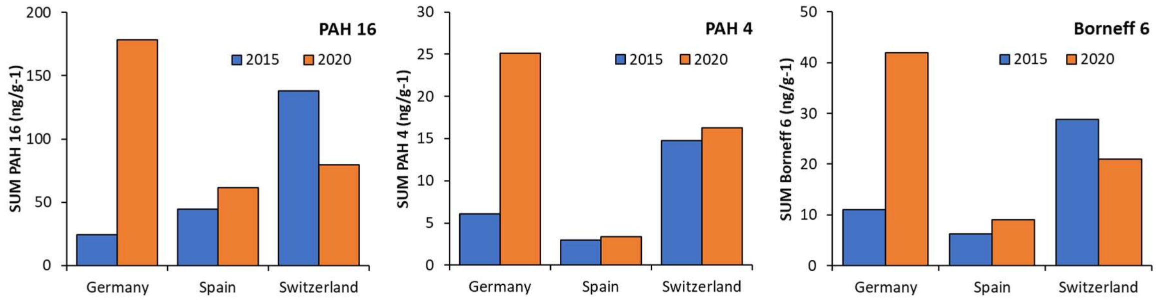


Figure 3.19: Median EPA PAH 16, PAH 4 and Borneff 6 concentrations in mosses in 2015 and 2020, for those countries that provided POPs concentration data in both years.

Microplastics

Some countries have also measured microplastic content of some samples from the main moss survey. These were Germany, Italy (Tuscany region) and UK. No standardised method was prescribed for the analysis of microplastics in moss tissue, as several methods are available and this was considered to be a pilot study. Different techniques were used by the different participating countries, with corresponding differences in the limit of detection for particle sizes, and in the precision of determining the particle type. This means that although it is possible to identify larger trends and information, direct comparison of microplastic quantity in moss tissue between countries is not possible. However, microplastics were found in the vast majority of sites analysed. These were from a range of types and potential sources and are an indication of the widespread prevalence of microplastics within the environment.

In Germany microplastics were found in all moss samples analysed (20 sites). The most common type of microplastic identified was polyethylene, followed by polyethylene terephthalate (PET). Styrene butadiene rubber was found at the majority of sites, and polystyrene and polypropylene were found at five and four sites respectively.

In Italy microplastics were found in all moss samples analysed (33 sites). The most common type of microplastic identified were fibres, followed by foams.

Microplastic content of moss samples was analysed from 52 sites across the United Kingdom. All except two sites monitored experienced some microplastic contamination above the limits of detection of the assessment. A diverse range of polymers were detected. The mean total number of microplastics >25 μm in size in moss across the UK was 4.5 MP/g with a maximum of 24.7 MP/g detected across the sampled locations. The most common polymer detected by particle number per gram of moss was polyurethane. The other major polymers detected were cellulose acetate, polyvinylchloride, ethylene vinyl acetate, polylactic acid, and polyethylene terephthalate.

Further details about microplastic content of each of these countries is given in the individual ‘country reports’. Microplastics content of mosses from a complementary survey using moss are considered in a separate report.

3. Discussion

Heavy metals

The concentrations of many metals in mosses have declined over much of Europe (and beyond) since 1990, although this is not consistent and some metals of concern including mercury and arsenic have shown little or no change. In many cases the decrease in concentration in moss tissue of metals such as cadmium, lead, chromium, nickel and zinc has been a result of a decline in emission and subsequent deposition. Some of the most polluting activities have ceased in some locations, for example closure of some mines and associated smelting processes. The phasing out of leaded petrol has had a marked impact on lead deposition. Other reductions in emissions of various metals have occurred as a result of abatement technologies Change of primary fuel source from coal to gas has also occurred in many parts of Europe.

Although the industrial emissions of many heavy metals within the EU have decreased over recent decades, this has been from very high levels compared to the natural deposition rate. It is likely that for many metals the concentration in mosses may not yet have returned to the levels that would be associated with very low emissions. For example, the concentrations of cadmium in Iceland and Norway are much lower than those for central and southern Europe.

Metals that have shown a large decline in concentration in moss tissue since 1990 (or later, depending on the start of measurement of a particular metal) include cadmium, lead, aluminium, vanadium and antimony (although the decline in concentration of antimony has slowed markedly during recent surveys). For cadmium and lead there is a good match between reductions in emissions and concentrations in moss tissue. There is not similar emissions data for aluminium, vanadium and antimony.

For chromium, nickel and zinc although there was a decline in concentration in moss tissue, this was not as much as the decline in emissions of these metals would suggest. By contrast, there was a decline in concentration of copper in moss tissue over the period 1990 to 2020 despite no reduction in reported emissions of copper over the same time period.

Some metals have shown little or no change in concentration in moss tissue over the survey period. For arsenic and mercury the concentrations in moss tissue remain high despite a reduction in EU emissions. Iron concentration in moss tissue also showed little change, but there was no comparative emissions data for iron.

Further changes in emissions and subsequent deposition are anticipated over the coming years and decades, but the potential consequences of these are uncertain. Although the extent of mining and smelting within Europe has drastically reduced over recent decades, global production for some metals including cadmium has remained stable. For other metals, e.g. zinc and copper, global production is still increasing. There have been shifts between countries for some activities, partly due to tightening of legislation in some regions. For example, the use of cadmium alloys in China has reduced and has been offset by increased use in India in some highly unregulated markets and activities (International Cadmium Association, 2021). The consequence of this for long-range transport and deposition is currently unknown. Anthropogenic emissions of metals from outside of the UNECE region may be one of the factors that contributes to the mis-match between decline in emissions, and the concentration of metal within moss tissue.

There is an increasing move towards electric powered vehicles. As part of this trend there is an increasing weight of domestic vehicles (both electric and their non-electric counterparts). There is evidence that heavier cars cause increased road wear and emissions of particles from tyres and brakes (Timmers et al., 2016). Other changes to the vehicle fleet include a transition away from asbestos in brakes towards increased use of antimony. Emissions from brake wear may change again if there is an increase in use of cars with regenerative braking systems, as these reduce brake wear (Hicks et al., 2023).

As many industrial processes become more regulated, it is possible that the influence of long-range transport of some metals will become increasingly important. In addition, the influence of disperse sources relating to population density and domestic activities may also influence airborne metal deposition. Due to a combination of increasing costs of clean fuel, together with social trends, there has been a recent increase in domestic wood burning as a fuel and this can be from a wide variety of sources that have markedly different emissions. In addition, there may be a mismatch in reported fuel sources by domestic users compared to the actual fuel source used, particularly when under economic pressures to reduce household expenditure.

Additional metals may need to be considered in future surveys, as there is anticipated to be increased use of some metals such as lithium, manganese and cobalt in batteries (together with nickel, which is already included in the survey) as part of the transition to renewable energy (Harpprecht et al., 2024).

The influence of re-suspension of previously deposited metals will likely form an increasingly large component of airborne metal deposition. Many countries banned leaded petrol by the 1980’s, and although 86 nations were still using leaded petrol in the early 2000’s, leaded petrol for cars and lorries has been eradicated completely since 2021 (UNEP, 2021). Elevated concentrations of some metals, including lead, can be found within 10 m of roads, and in the upper 10 cm of the topsoil (Resongles et al., 2021). However, a large proportion of these metals in topsoils are readily mobilised and can be redistributed if the roadside topsoils are disturbed. This may account for concentrations of some metals in mosses not declining to the extent anticipated following reductions in emissions.

Sampling for the current survey occurred around the time of the Covid-19 pandemic. During this time there were marked changes in emissions of many pollutants due to changes in industrial output and in road use. However, as the mosses take up metals and other pollutants over several years the effect on long-term trends may be small. For the vast majority of metals quantified, the trends do not show an anomaly for the current survey.

Nitrogen

The spatial pattern of nitrogen concentration in moss tissue shows the highest values in central Europe, and lower values in northern Europe. Not all participating countries measure and report on nitrogen concentration, therefore, the spatial pattern is slightly less clear than for the core metals.

Exceedance of critical loads for eutrophication caused by atmospheric nitrogen deposition shows that the critical loads were exceeded for much of Europe (with the notable exception of northern Scandinavia) in 2021 (European Environment Agency, 2023). The relationship between nitrogen concentrations in mosses and nitrogen deposition starts to show saturation between deposition rates of 15 - 20 kg ha^{-1} y^{-1} (Harmens et al., 2011, Harmens et al., 2014), which makes it difficult to assess the magnitude of risk in areas with medium to high nitrogen deposition. However, the moss technique still allows the identification of the areas potentially most at risk.

The concentration of nitrogen in moss tissue has remained similar since this was first included in the survey in 2005. Measurements of various forms of nitrogen as either concentration in the air or as deposition have generally shown a decrease since 1990. However, these decreases are lower for northern Europe than for southern Europe, and also lower for rural areas than for urban areas (de Vries et al., 2024). The nitrogen data from the moss survey is from rural areas and also mainly from northern and central Europe, which is where the reductions in emissions might be lower. Ammonia emissions have reduced less than the other forms of nitrogen (Aas et al., 2024). Comparisons between modelled and measured data have indicated that model predictions may overestimate the reductions in emissions for pollutants including oxidised nitrogen (Aas et al., 2024).

POPs

Only a limited number of countries submitted data on POPs concentrations in mosses, therefore, it is difficult to assess spatial trends across Europe. A wide variety of POPs were detected, and almost all moss samples contained at least one of the types of POPs investigated, with some samples containing a wide variety of PAHs.

PAHs found in moss samples included fluoranthene, fluorene, naphthalene, phenanthrene and pyrene, which are natural components of coal tar, crude oil, and fossil fuels, and as such are released during combustion processes, including from vehicles. Sources of these to the environment could also relate to other uses, for example, fluorene can be released during incomplete combustion of plastics. Naphthalene is a major component of creosote, and phenanthrene is used to make dyes, plastics, pesticides and explosives.

The highest emissions of PAHs are from Poland, and across the EU the commercial, institutional and households sector group is a very significant source of total PAH emissions (EEA, 2023). These have been reported to include from burning of hard coal and wood in the residential sector, and from field burning of agricultural residues. EU emissions of PAHs have decreased by approximately 50% between 1990 and 2020 (EEA, 2023), but increased between 2020 and 2021.

Microplastics

Moss has been used successfully to detect microplastics. The wide variety of microplastics found indicates that there are a wide range of sources. Although some of the microplastics found were associated with microplastic litter, this was not always the case. Some studies based on emissions have shown that airborne microplastics were present both upwind and downwind of an industrial composting facility (Zapata et al., 2024). It is currently unclear what impacts microplastics may have on moss tissue and other vegetation, however, microplastics have been shown to have detrimental impacts on a very wide range of fauna (Jeong et al., 2024).

4. 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 some metals e.g. cadmium and lead, the concentration within moss tissue continues to fall, with changes in-line with reductions in emissions. Some other metals have declined, but to a lesser extent than the decline in emissions, e.g. chromium, nickel and zinc. Several metals, including chromium, copper, iron and zinc show an increase in concentration in moss tissue compared to the previous survey, including in the EU27 countries.
- Arsenic and mercury show little or no change in concentrations in moss tissue despite reductions in emissions.
- Many metals show highest concentrations in moss tissue in the south-east of the region, which may be due to a slower uptake of abatement technologies and/or slower cessation of some polluting activities. Some metals, e.g. lead and cadmium continue to show elevated concentrations in mosses in regions with high population density, which may relate to high vehicular traffic.
- Nitrogen concentrations in moss tissue have increased slightly since 2005, indicating that there remains a high risk of adverse effects to ecosystems.
- POPs continue to be found in moss tissue, despite the reductions in emissions of POPS by the EU27 countries.
- When analysis included microplastics, these were found in almost all moss samples. The consequences of airborne deposition to vegetation and the wider terrestrial ecosystems are not currently known.

5. Recommendations

Due to the moss standard M2 no longer being available to purchase, there is a requirement for a new moss standard to be used to allow inter-laboratory comparisons and standardisation. The exchange of a few moss samples with neighbouring countries would also facilitate inter-country calibration. An extended range of standard moss material, or suitable alternative vegetation for use as a 'standard material' would be of benefit to allow the expansion of the moss survey further south and east, where the types of mosses present may be different to those more extensively used in the north of the region and that are comparatively well characterised.

It is recommended that sampling of moss material should occur from more countries, including those that have participated previously. This would allow further investigation of trends. The concentrations of some metals within moss tissue may be increasing, although this increase is comparatively small at present, it may reflect changing emissions due to large-scale changes in energy production and the vehicle fleet, which could both affect a wide geographical area and a large population.

Further statistical analysis would be recommended to identify hotspots of local emission sources vs long-range background concentrations. In addition, comparisons have been made to EU27 emissions, but this is only a subset of the countries of the survey. Extending the comparison to a wider geographic range of emissions would be beneficial. It would be useful to compare within UNECE emissions vs contributions to deposition from outside the UNECE region as this may explain some of the mismatch between emissions reductions and changes in metal concentration within moss tissue.

Further investigation of the contribution of re-suspension of previously deposited pollution is needed to establish the relative proportions of previously emitted vs newly emitted pollution to deposition and concentrations in moss tissue.

Nitrogen pollution continues to be a problem across much of Europe. Concentrations in moss tissue have remained the same or even increased over recent years. It is recommended that nitrogen content of moss tissue is measured on samples from all countries in order to better evaluate the spatial variation and temporal trends.

Quantification of POPs in moss tissue remains important due to the toxicity of these pollutants and adverse impacts on human health and the environment.

Further investigations of microplastic content are needed in order to identify sources, temporal trends and persistence within moss tissue.

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Annex 1 – Participants of the 2020 moss survey

Note: many others have contributed to sampling and analyses (their names are listed on page 4), but only main contributors are listed below.

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	Stefan Nickel	University of Vechta

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	Chrysoula Betsou	Aristotle University of Thessaloniki
	Evdoxia Tsakiri	Aristotle University of Thessaloniki
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	Magdalena Widmann	Environmental Agency of Bolzano
	Stefano Loppi	University of Siena
	Mehriban Jafarova	University of Siena
	Ilaria Bonini	University of Siena
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Latvia	Guntis Tabors	University of Latvia, Riga
Moldova	Inga Zinicovscaia	Horia Hulubei National Institute for R&D in Physics and Nuclear Engineering, Magurele, Romania; JINR Dubna
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	Katerina Bačeva Andonovska	Ss. Cyril and Methodius University, Skopje
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Annex 2 - Analytical techniques used in the 2020 moss survey

Location	Al	As	Cd	Cr	Cu	Fe	Hg	Ni	Pb	Sb	V	Zn	N
Albania	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	-
Belarus	INAA	INAA	ETAAS	-	ETAAS	INAA	-	INAA	ETAAS	INAA	INAA	INAA	-
Belgium	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	-	ICP-MS	ICP-MS	EA
Bulgaria	ICP-ES	ICP-ES	ICP-ES	ICP-ES	ICP-ES	ICP-ES	DMA	ICP-ES	ICP-ES	ICP-ES	ICP-ES	ICP-ES	-
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-MS	ICP-MS	ICP-MS	ICP-MS	ICP-ES	CVAFS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	Kjeldahl
France	ICP-ES	ICP-MS	ICP-MS	ICP-MS	ICP-ES	ICP-ES	CVAAS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-ES	EA
Georgia	ICP-ES	ICP-ES	ICP-ES	ICP-ES	ICP-ES	ICP-ES	DMA	ICP-ES	ICP-ES	ICP-ES	ICP-ES	ICP-ES	-
Germany	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	CVAAS	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	ICP-MS	DMA	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	EA
Italy	ICP-MS/ ICP-ES	ICP-MS	ICP-MS/ ICP-ES	ICP-MS/ ICP-ES	ICP-MS/ ICP-ES	ICP-MS/ ICP-ES	DMA	ICP-MS/ ICP-ES	ICP-MS /ICP-ES	ICP-MS	ICP-MS/ ICP-ES	ICP-MS/ ICP-ES	EA
Kosovo	ICP-ES	ICP-MS	ICP-MS	ICP-ES	ICP-ES	ICP-ES	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-ES	ICP-ES	Kjeldahl
Latvia	ICP-ES	ICP-ES	ICP-ES	ICP-ES	ICP-ES	ICP-ES	ICP-ES	ICP-ES	ICP-ES	-	ICP-ES	ICP-ES	EA
Netherlands	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	-	ICP-MS	ICP-MS	EA
North Macedonia	INAA	INAA	ICP-MS	INAA	ICP-MS	INAA	ICP-MS	INAA	ICP-MS	-	INAA	INAA	-
Norway	ICP- HRMS	ICP- HRMS	ICP- HRMS	ICP- HRMS	ICP- HRMS	ICP- HRMS	CVAFS	ICP- HRMS	ICP- HRMS	ICP- HRMS	ICP- HRMS	ICP- HRMS	-
Poland	INAA	ETAAS/ INAA	FAAS/ ETAAS/ INAA	FAAS/ INAA	FAAS/ INAA	FAAS/ INAA	DMA	FAAS/ ETAAS/ INAA	FAAS/ ETAAS/ INAA	INAA	ETAAS/ INAA	FAAS/ INAA	Kjeldahl
Republic of Moldova	INAA	INAA	ETAAS	INAA	ETAAS	INAA	-	INAA	ETAAS	INAA	INAA	INAA	-
Romania	ICP-MS	-	ICP-MS	ICP-MS	ICP-MS	ICP-MS	-	ICP-MS	ICP-MS	-	-	ICP-MS	-
Russian Federation	INAA	INAA	ETAAS/ INAA	INAA	ETAAS	INAA	-	INAA	ETAAS	INAA	INAA	INAA	-
Serbia	ICP-ES	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-ES	ICP-MS	ICP-ES	ICP-MS	ICP-MS	ICP-MS	ICP-ES	-
Slovakia	INAA	INAA	ETAAS	INAA	ETAAS	INAA	-	INAA		INAA	INAA	INAA	EA
Slovenia	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	DMA	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	EA
Spain		INAA	ICP-MS				DMA	INAA	ICP-MS				EA
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	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	EA
United Kingdom	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS		ICP-MS	EA

Abbreviations

CVAAS – Cold vapour atomic absorption spectrometry; CVAFS – Cold vapour atomic fluorescence spectrometry; EA – Elemental analysis; ETAAS – Electrothermal atomic absorption spectrometry; FASS – Flame 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 analyser; ICP-HRS – Inductively coupled plasma-high resolution mass spectrometry.

Annex 3. Metal (mg kg^{-1}) and nitrogen concentrations (mass %) in mosses in 2020

	As	Cd	Cr	Cu	Fe	Hg	Ni	Pb	V	Zn	Al	Sb	N (%)
Albania													
Number	75	75	75	75	75	75	75	75	75	75	75	75	
Min	0.2	0.0	1.3	2.9	589.0	0.0	1.6	0.9	1.3	7.7	602.4	0.0	
Max	3.2	0.9	159.2	29.3	7130.0	0.1	232.9	45.4	13.2	99.2	4965.1	0.4	
Mean	0.6	0.1	11.7	5.9	1800.9	0.1	17.9	3.7	3.5	18.5	1509.2	0.0	
Median	0.4	0.1	6.2	4.7	1444.0	0.1	8.6	2.3	2.8	15.7	1240.1	0.0	
90th percentile	1.1	0.2	17.9	8.8	2934.8	0.1	36.0	5.1	5.5	26.0	2373.2	0.1	
Belarus													
Number	52	51	86	51	86	34	68	51	86	86	86	52	
Min	0.0	0.0	0.5	3.0	199.0	0.0	0.6	1.0	0.5	13.0	223.0	0.0	
Max	1.0	0.2	21.5	7.2	1448.0	0.1	118.9	3.3	2.6	61.0	1720.0	0.2	
Mean	0.3	0.1	1.8	4.6	519.8	0.0	3.9	1.9	1.2	35.8	673.5	0.1	
Median	0.3	0.1	1.2	4.5	466.5	0.0	1.2	1.8	1.1	37.0	642.5	0.1	
90th percentile	0.5	0.2	2.3	6.1	745.0	0.1	1.9	2.8	1.7	52.0	995.0	0.2	
Belgium													
Number		18	18	18	18	18	18	18		18	18		18
Min		0.0	0.9	3.7	208.8	0.0	0.8	2.7		22.1	166.6		1.0
Max		0.8	4.0	22.2	1116.7	0.1	3.3	10.0		165.6	827.4		2.3
Mean		0.3	1.9	9.1	523.2	0.0	1.4	5.8		68.4	347.0		1.5
Median		0.3	1.6	8.1	440.4	0.0	1.1	5.8		61.3	329.4		1.3
90th percentile		0.6	3.2	11.6	836.8	0.1	2.2	8.5		112.7	442.2		2.2
Bulgaria													
Number	66	66	66	66	66	66	66	66	66	66	66	66	
Min	0.2	0.1	0.9	2.9	750.0	0.0	0.7	2.0	1.1	15.0	740.0	0.1	
Max	3.8	3.2	19.3	103.4	7400.0	0.2	13.9	210.4	12.5	160.0	7100.0	1.6	
Mean	0.7	0.3	4.2	8.8	1618.3	0.0	2.7	13.4	3.1	35.6	1947.1	0.2	
Median	0.5	0.2	3.5	6.1	1265.0	0.0	2.0	5.6	2.6	30.4	1560.0	0.2	
90th percentile	1.1	0.6	6.2	11.1	2735.0	0.1	4.2	22.8	5.0	57.5	3435.0	0.3	

	As	Cd	Cr	Cu	Fe	Hg	Ni	Pb	V	Zn	Al	Sb	N (%)
Czech Republic													
Number	41	41	41	41	41		41	41	41	41	41	41	41
Min	0.2	0.2	0.2	4.69	316.4		0.4	1.7	1.7	1.2	160.9	<0.1	1.2
Max	3.7	1.3	12.7	18.0	9188.0		51.0	42.9	12.2	126.0	4654.2	<0.1	3.9
Mean	0.6	0.6	2.3	9.1	1312.9		3.7	7.1	3.7	26.2	808.0	<0.1	2.3
Median	0.4	0.6	1.3	8.5	819.8		1.3	5.5	3.1	28.3	542.9	<0.1	2.3
90th percentile	0.7	0.9	6.1	12.2	1846.8		4.5	11.1	4.8	57.6	1772.5	<0.1	3.2
Denmark (Faroe Islands)													
Number		14	14	14	14	14	14	14	14	14			
Min		0.1	0.9	2.9	245.2	0.0	0.9	0.9	1.1	10.1			
Max		0.1	0.9	5.7	562.6	0.1	2.0	3.0	3.9	17.0			
Mean		0.1	0.9	4.4	408.2	0.1	1.0	1.5	2.3	13.5			
Median		0.1	0.9	4.6	437.3	0.1	0.9	1.3	2.2	13.4			
90th percentile		0.1	0.9	4.8	516.3	0.1	1.0	2.1	3.2	16.4			
Estonia													
Number	73	73	73	73	73	73	73	73	73	73	73	73	73
Min	0.0	0.1	0.8	3.0	190.0	0.0	0.6	1.0	0.7	20.0	210.0	0.1	0.8
Max	0.2	0.2	13.0	13.0	680.0	0.1	7.9	4.0	1.7	52.0	650.0	19.0	1.8
Mean	0.1	0.1	3.1	5.0	291.4	0.0	2.0	1.5	0.9	29.3	304.8	1.1	1.0
Median	0.1	0.1	3.0	4.7	270.0	0.0	1.9	1.4	0.9	29.0	290.0	0.3	1.0
90th percentile	0.2	0.1	5.3	7.0	394.0	0.1	3.0	1.9	1.1	35.8	378.0	1.8	1.3
France													
Number	443	443	443	443	443	443	443	443	443	443	443	443	443
Min	0.1	0.0	0.3	2.9	132.0	0.0	0.3	0.7	0.4	11.7	97.8	0.0	0.7
Max	3.4	1.3	5.4	11.4	3560.0	0.5	14.9	22.4	5.2	116.0	2300.0	0.7	2.5
Mean	0.3	0.2	1.2	5.7	544.8	0.1	1.7	2.8	1.2	28.4	463.3	0.1	1.3
Median	0.2	0.1	1.0	5.4	432.0	0.1	1.5	2.2	1.0	24.4	376.0	0.1	1.2
90th percentile	0.6	0.3	2.1	7.7	974.6	0.2	3.0	4.8	2.0	44.3	854.4	0.1	1.7
Georgia													
Number		95	95	95	95	95	95	95	95	95	95		
Min		0.1	1.6	3.8	561.0	0.0	1.6	1.6	1.9	14.2	674.4		
Max		0.5	13.7	22.1	6548.0	0.1	17.8	42.3	19.6	62.8	6708.4		

	As	Cd	Cr	Cu	Fe	Hg	Ni	Pb	V	Zn	Al	Sb	N (%)
Mean		0.1	4.1	7.6	1960.5	0.0	5.0	5.4	5.9	29.5	2361.4		
Median		0.1	3.7	7.1	1826.1	0.0	4.4	4.2	5.3	28.2	2131.0		
90th percentile		0.2	5.9	10.4	2979.6	0.1	7.7	7.8	8.7	40.5	3837.5		
Germany													
Number	26	26	26	26	26	26	26	26	26	26	26	26	26
Min	0.0	0.1	0.6	3.9	88.2	0.0	0.6	0.6	0.3	18.9	96.7	0.1	1.0
Max	0.3	0.4	4.7	14.5	1544.1	0.4	5.0	11.2	1.9	83.6	908.4	0.4	3.3
Mean	0.1	0.2	1.6	6.2	367.9	0.1	2.0	2.9	0.8	43.9	348.5	0.2	1.7
Median	0.1	0.2	1.3	5.9	308.1	0.1	1.8	1.9	0.7	38.1	325.2	0.1	1.5
90th percentile	0.2	0.3	2.9	7.8	532.5	0.2	3.8	6.7	1.3	71.0	595.5	0.2	2.2
Greece (North)													
Number		89	89	89	89	89	89	89	89	89	89		
Min		0.1	1.7	3.0	934.5	0.0	1.4	2.0	2.4	11.2	1367.0		
Max		0.8	151.2	25.0	24530.0	0.1	99.7	188.2	47.7	128.1	24820.0		
Mean		0.2	13.1	8.9	4811.8	0.1	12.3	8.9	10.7	33.0	5464.7		
Median		0.2	6.5	7.9	3519.0	0.1	6.2	5.6	7.7	29.4	3906.0		
90th percentile		0.4	28.6	14.0	10001.2	0.1	25.9	11.7	19.7	49.4	10670.0		
Iceland													
Number	144	125	144	144	144	144	144	144	144	144			
Min	0.0	0.0	1.2	2.7	415.5	0.0	0.8	0.1	1.4	7.3			
Max	0.5	0.2	9.9	17.3	5855.0	0.2	20.1	13.3	10.3	65.7			
Mean	0.1	0.0	3.2	5.6	1413.6	0.1	3.7	0.6	4.3	18.3			
Median	0.1	0.0	2.8	5.2	1203.9	0.1	2.5	0.4	3.9	17.2			
90th percentile	0.2	0.1	4.6	7.5	2322.3	0.1	8.2	1.2	6.9	27.0			
Ireland													
Number		32	32	32	32	32	32	32	32	32	32	32	34
Min		0.3	0.3	0.5	34.4	0.3	0.3	0.3	0.3	5.7	31.1	0.3	0.3
Max		0.3	4.1	8.8	354.0	2.2	2.1	90.0	0.9	41.6	517.0	0.3	1.0
Mean		0.3	0.5	3.0	108.1	0.4	0.5	3.4	0.3	16.5	101.0	0.3	0.6
Median		0.3	0.3	2.8	83.2	0.3	0.4	0.6	0.3	15.3	73.7	0.3	0.6
90th percentile		0.3	1.0	4.3	201.5	0.3	0.9	1.1	0.5	23.7	189.3	0.3	0.8

	As	Cd	Cr	Cu	Fe	Hg	Ni	Pb	V	Zn	Al	Sb	N (%)
Italy													
Number	24	57	57	57	57	24	57	57	57	57	57	24	57
Min	0.1	0.0	1.0	3.0	327.7	0.0	0.9	1.1	0.8	10.5	432.7	0.0	0.1
Max	0.4	0.2	8.6	13.1	2208.2	0.1	7.8	5.2	5.2	39.9	2711.2	0.2	2.1
Mean	0.2	0.1	2.2	6.3	783.6	0.0	2.4	2.2	1.9	21.7	1038.2	0.1	1.1
Median	0.2	0.1	1.7	6.1	576.2	0.0	2.0	1.9	1.5	22.2	831.9	0.1	1.1
90th percentile	0.3	0.2	3.5	9.4	1406.6	0.1	4.0	3.3	3.4	30.3	2003.8	0.1	1.5
Kosovo													
Number	45	45	45	45	45	45	45	45	45	45	45	45	45
Min	0.1	0.2	0.9	2.6	426.5	0.1	0.5	0.6	0.5	20.3	477.3	0.1	0.8
Max	6.9	2.1	10.1	8.1	2016.7	0.4	79.4	38.0	5.9	146.0	2740.0	0.3	1.5
Mean	0.5	0.5	3.1	3.9	924.0	0.1	4.4	6.6	2.4	35.7	1071.1	0.2	1.1
Median	0.2	0.4	2.6	3.9	818.3	0.1	1.7	7.3	2.2	30.8	887.5	0.2	1.1
90th percentile	0.5	0.8	5.3	4.6	1440.0	0.1	5.7	10.0	3.7	45.6	1880.1	0.2	1.4
Latvia													
Number		101	101	101	101		101	101	101	101			40
Min		0.1	0.3	3.3	75.2		0.0	0.4	0.2	19.6			0.5
Max		0.3	1.2	10.0	352.5		2.0	1.5	6.2	50.1			2.1
Mean		0.1	0.5	6.2	144.6		0.3	0.8	0.5	30.9			1.1
Median		0.1	0.4	6.2	135.1		0.3	0.8	0.4	30.1			1.1
90th percentile		0.2	0.6	8.1	199.5		0.5	1.0	0.6	38.9			1.7
Moldova													
Number	41	41	41	41	41		41	41	41	41	41	41	
Min	0.3	0.1	3.2	5.7	951.0		2.2	1.6	0.0	25.0	17.0	0.1	
Max	2.0	0.6	21.3	22.2	7810.0		14.3	8.8	18.8	86.0	11700.0	0.9	
Mean	0.8	0.1	7.1	8.8	2646.1		4.7	3.4	6.0	42.7	3718.0	0.2	
Median	0.7	0.1	5.4	8.6	2190.0		4.1	3.1	5.4	39.0	3400.0	0.2	
90th percentile	1.3	0.2	10.6	11.4	4100.0		7.5	4.9	9.4	60.0	6180.0	0.4	
Netherlands													
Number	28	90		70	70			70	70	95	115	28	136
Min	0.1	0.0		2.2	141.2			0.0	0.0	8.8	56.9	0.1	0.5
Max	1.5	4.4		13.2	1750.0			7.1	43.3	60.9	3121.4	0.5	1.9

	As	Cd	Cr	Cu	Fe	Hg	Ni	Pb	V	Zn	Al	Sb	N (%)
Mean	0.5	0.2		5.2	546.5			2.9	1.5	27.0	470.3	0.2	2.3
Median	0.4	0.2		4.9	464.3			2.9	0.5	24.9	263.8	0.2	1.0
90th percentile	0.8	0.3		8.4	930.0			4.7	1.8	43.7	1113.1	0.4	7.9
North Macedonia													
Number	72	72	72	72	72	72	72	72	72	72	72	72	72
Min	0.0	0.1	3.9	2.2	590.0	0.0	1.0	1.6	1.2	20.2	690.0	0.0	0.7
Max	2.3	0.5	13.3	15.0	4960.0	0.1	33.5	15.2	9.4	63.5	8100.0	0.6	1.7
Mean	0.6	0.2	7.0	5.7	1522.8	0.1	5.4	3.8	3.3	34.4	1981.8	0.1	1.1
Median	0.4	0.2	6.3	4.8	1395.0	0.1	4.2	3.1	3.0	32.3	1820.0	0.1	1.1
90th percentile	0.9	0.3	10.1	9.5	2244.0	0.1	8.1	6.0	5.4	48.9	2723.0	0.2	1.3
Norway													
Number	34	34	34	34	34		34	34	34	34	34	34	
Min	0.0	0.0	0.2	2.8	75.7		0.3	0.2	0.2	14.8	99.6	0.0	
Max	1.3	0.4	6.5	338.8	2219.8		539.0	3.8	5.8	124.0	1551.4	0.1	
Mean	0.3	0.1	1.8	49.9	642.0		81.6	1.2	1.6	39.1	447.2	0.0	
Median	0.2	0.1	0.8	8.3	308.6		5.6	0.9	1.2	31.1	361.7	0.0	
90th percentile	1.0	0.3	5.5	181.1	1888.5		313.3	2.8	3.2	59.2	979.4	0.1	
Poland													
Number		20	20	20				20		20			
Min		0.1	3.8	4.1				6.3		88.0			
Max		0.2	5.6	10.1				11.2		105.0			
Mean		0.1	4.7	6.1				8.5		98.2			
Median		0.1	4.6	5.1				8.8		98.0			
90th percentile		0.1	5.4	9.8				10.5		104.1			
Romania													
Number		82	82	82	82		82	82		82	82		
Min		0.1	0.0	1.0	0.0		0.0	0.5		2.6	245.7		
Max		4.6	23.5	200.7	4100.0		34.5	25.9		103.9	3858.8		
Mean		0.6	2.9	20.1	572.0		4.1	6.2		27.1	671.9		
Median		0.3	2.1	15.3	291.9		3.5	3.2		27.3	476.0		
90th percentile		1.1	6.3	29.3	1337.0		6.2	19.5		39.0	1206.4		

	As	Cd	Cr	Cu	Fe	Hg	Ni	Pb	V	Zn	Al	Sb	N (%)
Russian Federation													
Number	315	439	474	439	474	139	474	439	441	474	474	315	
Min	0.0	0.1	0.4	2.6	179.9	0.0	0.5	1.2	0.1	17.6	108.0	0.1	
Max	1.0	1.0	24.7	43.6	4630.0	0.1	18.5	31.4	12.8	243.0	5482.0	3.3	
Mean	0.3	0.3	3.2	8.5	784.5	0.1	2.9	5.7	2.4	55.4	984.8	0.2	
Median	0.2	0.2	2.0	6.1	497.0	0.1	2.3	3.4	1.5	45.0	603.0	0.2	
90th percentile	0.5	0.4	6.1	11.8	1447.4	0.1	5.0	9.2	0.4	86.1	1915.9	0.4	
Serbia													
Number	177	177	176	177	177	177		177	177	177	133		
Min	0.0	0.1	0.0	0.0	64.4	0.0		0.6	0.6	3.8	162.3		
Max	4.6	1.5	22.8	121.2	9912.6	1.4		18.2	21.8	86.6	12356.2		
Mean	1.0	0.3	3.0	10.1	1048.0	0.1		4.2	3.7	12.3	1850.9		
Median	0.8	0.2	2.1	5.4	848.0	0.0		3.9	2.6	10.4	1151.8		
90th percentile													
Slovakia													
Number	201	201	201	201	201	201	201	201		201	201		201
Min	0.0	0.0	0.5	3.3	168.8	0.0	0.2	0.6		17.4	138.9		0.9
Max	5.1	1.0	13.9	16.5	8460.0	0.3	10.2	16.8		84.9	9760.0		3.2
Mean	0.6	0.2	3.8	6.7	1153.0	0.0	3.0	3.6		33.0	1371.0		1.8
Median	0.5	0.2	3.6	6.1	761.0	0.0	3.0	2.7		31.1	918.0		1.7
90th percentile	1.1	0.4	6.2	9.7	2276.3	0.1	5.3	6.2		46.9	3050.0		
Slovenia													
Number	43	43	43	43	43	43	43	43	43	43	43	43	43
Min	0.1	0.1	0.6	2.7	192.0	0.0	0.5	0.8	0.5	11.0	308.6	0.0	0.9
Max	1.4	1.1	12.9	8.3	5654.0	0.1	12.5	67.5	12.9	58.2	8643.7	0.3	3.5
Mean	0.2	0.3	1.7	4.6	659.7	0.0	1.7	4.6	1.6	27.5	998.6	0.1	1.5
Median	0.1	0.2	1.1	4.3	470.0	0.0	1.1	1.9	1.1	24.4	668.7	0.1	1.4
90th percentile	0.3	0.4	2.4	7.0	906.0	0.0	2.9	4.9	2.4	46.4	1301.0	0.1	
Spain (Rioja)													
Number	25	25				25	25	25					5
Min	0.2	0.0				0.0	0.5	0.8					0.7
Max	0.9	0.1				0.0	2.9	3.4					1.5

	As	Cd	Cr	Cu	Fe	Hg	Ni	Pb	V	Zn	Al	Sb	N (%)
Mean	0.4	0.1				0.0	1.2	1.5					0.9
Median	0.3	0.1				0.0	1.0	1.3					0.8
90th percentile	0.7	0.1				0.0	1.8	2.4					
Sweden													
Number	496	496	496	496	496	496	496	496	496	496	496	496	496
Min	0.0	0.0	0.1	1.7	47.0	0.0	0.2	0.2	0.1	11.0	54.0	0.0	0.5
Max	0.7	0.6	45.0	20.0	5400.0	0.2	6.0	15.0	9.1	94.0	740.0	0.5	2.0
Mean	0.1	0.1	0.6	3.8	211.0	0.0	0.6	1.2	0.6	37.5	192.6	0.1	0.9
Median	0.1	0.1	0.4	3.6	170.0	0.0	0.5	1.0	0.5	36.0	170.0	0.1	0.8
90th percentile	0.2	0.2	0.9	5.2	330.0	0.1	0.8	1.9	1.0	52.0	300.0	0.1	1.3
Switzerland													
Number	73	73	73	73	73	73	73	73	73	73	73	73	55
Min	0.0	0.0	0.1	2.8	72.3	0.0	0.1	0.2	0.1	14.4	88.9	0.0	0.9
Max	4.3	0.3	5.9	12.3	3591.6	0.1	6.3	11.5	6.8	85.7	3290.6	0.1	2.4
Mean	0.2	0.1	1.2	5.6	422.2	0.0	1.4	1.7	1.0	28.8	607.2	0.1	1.4
Median	0.1	0.1	0.9	5.1	314.7	0.0	1.0	1.2	0.8	26.7	477.3	0.0	1.3
90th percentile	0.2	0.2	2.1	8.4	654.2	0.0	2.7	3.0	1.5	39.9	1022.8	0.1	1.9
United Kingdom													
Number	120	120	120	120	120	120	120	120		120	120	120	120
Min	0.0	0.0	0.0	1.7	83.6	0.0	0.0	0.4		10.2	89.5	0.0	0.6
Max	3.5	0.9	12.1	20.9	5878.3	0.3	7.3	32.9		89.4	7526.4	0.5	2.2
Mean	0.2	0.1	0.7	4.6	435.3	0.0	0.9	2.6		28.3	494.1	0.1	1.0
Median	0.1	0.1	0.3	3.9	246.8	0.0	0.6	1.8		23.8	236.5	0.1	1.0
90th percentile	0.3	0.2	1.3	7.0	691.8	0.1	1.8	5.5		44.9	730.7	0.2	1.4

Annex 4 - POPs concentrations in mosses in 2020

	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)
Germany					
Sampling points	21	21	21		21
Min	58.3	4.8	8.4		0
Max	1166.4	82	173.7		115
Mean	338.4	30.9	58.8		7
Median	178.2	25.1	42		0
90th percentile	643.4	71.7	120.2		13.6
Quantification frequency (%)	100	100	100		14
Spain					
Sampling points	5	5	5		
Min	42.5	2.4	7.6		
Max	78.4	16.3	24.4		
Mean	59.3	5.9	12		
Median	61.6	3.4	9.1		
90th percentile	74	11.5	18.9		
Quantification frequency (%)	100	100	100		
Switzerland					
Sampling points	22	22	22	22	
Min	50.3	7.3	11.3	0	
Max	202.3	76.5	92.5	9.5	
Mean	89.6	21.3	27.8	0.9	
Median	79.5	16.3	21.1	0.3	
90th percentile	140.6	36.0	50.2	2.1	
Quantification frequency (%)	100	100	100	91	

Annex 5. Country and (sub)Regional Reports

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

Albania

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Background

Since the 2009/2010 moss survey, Albania has been regularly participating in the ICP Vegetation programme. Moss samples, *Hypnum cupressiforme* moss species, which are widely grown in Albania, were collected on 2010, 2015, and 2021 moss surveys from respectively 64, 56, and 75 sampling sites evenly distributed throughout the territory of Albania. Moss samples were collected by following the ICP Vegetation Protocol and sampling strategy of the European Program on Biomonitoring of Heavy Metal (HM) atmospheric deposition. Induced coupled plasma mass spectrometry (ICPMS) method were applied for trace metal (Al, As, Cd, Co, Cu, Cr, Fe, Hg, Ni, Pb, Sb, V, and Zn) analysis.

Concentrations of toxic metals TMs) in mosses

To evaluate the spatiotemporal trend and related processes of hazardous chemicals in the air, the concentrations data of elements from moss surveys conducted in 2010, 2015, and 2021 was statistically analyzed using descriptive statistics, data transformation, multivariate analysis, and mapping. The sequence of the median concentrations of TMs in moss samples were Sb < Hg < Cd < As < Co < V < Pb < Cu < Cr < Ni < Zn < Al < Fe for three monitoring surveys of 2010, 2015, and 2015.

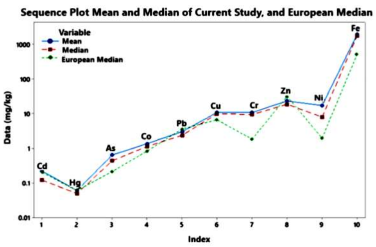

Fig. 1. Sequence plot of median and mean data of 2021 moss survey and European median data of 2015 moss survey

A satisfied agreement between the median concentrations of Co, Pb, Cu, and Zn in moss of 2021 and the data from the European moss surveys. Other elements, Cr, Ni, and Fe, are higher than the respective data from the European moss surveys.

According to the graph below, a decline is observed for the elements Cu, V, Pb, Fe, Al, and Cd, which is probably related to the isolation due to the pandemic in 2020-2021.

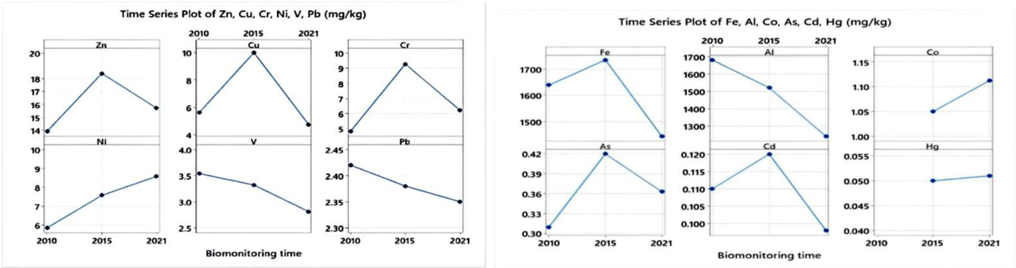

Fig. 2. Trend of median data of 2010, 2015, and 2021 moss survey in Albania

Factor analysis was applied to investigate the associations between the determined elements and to assess their probable sources. Factor analysis joined together the elements Al, V, and Fe, lithogenic elements, and As, Cu, and Hg at factor 1 (F1). It show the contributions of the local soil dust and anthropogenic particles trapped to the soil dust particles. F2 joined together the elements Cr, Ni, Co, and Fe, which are generated from geogenic, mining activity, and metallurgical industry in Albania.The last factor, F3, composed by high loadings of Zn, Pb, Sb, and Cd, which are predominantly derived from anthropogenic emission sources like traffic emissions, and long-range transport of pollutants.

Conclusion

Moss biomonitoring revealed that discrepancies in the amounts and chemistry of trace metals in Albanian atmospheric deposition were primarily caused by local emissions. Eastern Albania is subjected to high amounts of Co, Cr, Ni, and Fe resulting from local soil dust geochemistry and mining sector emissions. The higher concentrations of Cr, Ni, Co, and Fe are primarily due to metallurgical factories located in the country's center. Relatively high concentrations of Al, V, and Fe crustal elements and As, Co, Cu, Hg, Sb, and Zn anthropogenic elements in the western coastline are most likely linked to the dual emissions of re-suspended soil dust and human activities such as shipping, the oil and petrochemical industry, traffic emissions, and agricultural activity.

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Belarus

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Background Republic of Belarus is participating in the ICP Vegetation Moss Survey programme since 2005. This time 2020-2021/22 survey was conducted in different regions of Belarus taking into account results from the previous years of surveys. 86 sites were studied during this survey using *Pleurozium schreberi* (Figure 1). In 2020 the western part of the country was studied because in 2010 some «hot spots» were revealed there [1]. In 2021 samples were collected at the territory of Nalibokskaya Pushcha, one of the largest forests in the Republic of Belarus and throughout Eastern Europe, with a few samples sites at the Republican Landscape Reserve "Naliboksky". In 2022 study was made in the Polesie State Radiological and Ecological Reserve and in the Minsk region that is considered as the most anthropogenically affected [2].

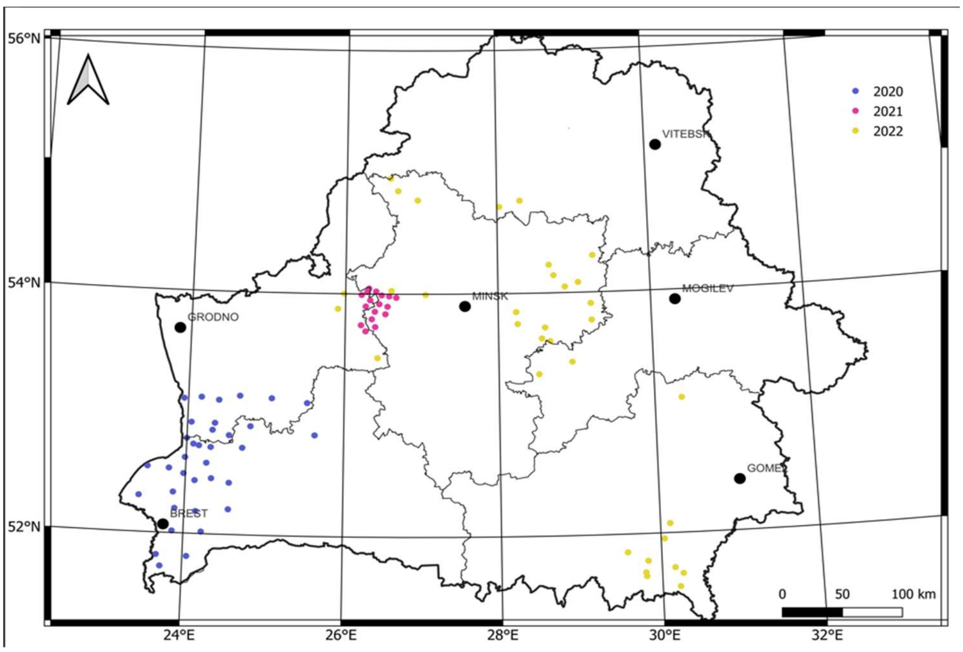

Figure 1. Distribution of the sampling sites

Results

To control transboundary transfer in 2020 samples were taken in the southwestern part of Belarus, in the forests of the Brest and Grodno region. A comparative analysis of the trace elements content showed differences in the accumulation of elements in these areas. We compared the median values of trace elements in mosses from the Brest region at the same sampling sites as in 2010 (Figure 2). The most significant decrease is observed for chromium. Other elements such as iron, cobalt, antimony varies slightly with a downward trend from 2010 to 2020.

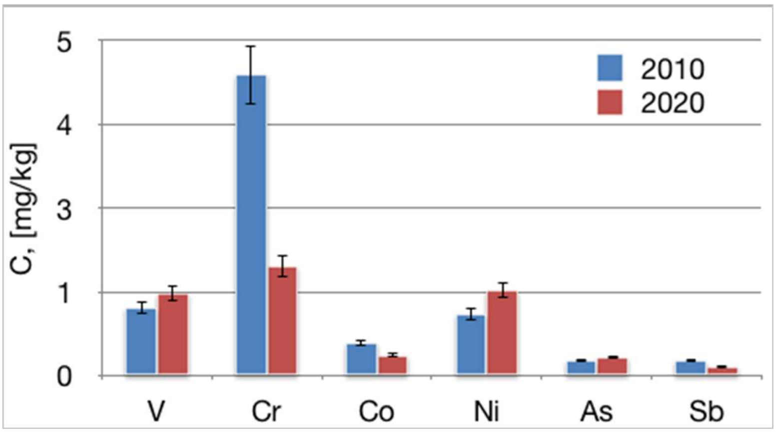

Fig. 2 Median elements concentration for the same sample sites in Brest region.

If we consider median concentration of heavy metals and trace elements from the different moss surveys the ecological situation in the Republic of Belarus is stable. For the most elements concentrations are at the same levels (Fig.3). Since 2005 significant decrease was observed only for the lead. It's declined in four times. And we noticed increase for arsenic in 2015 and 2020 in comparison with 2005 and 2010 moss surveys.

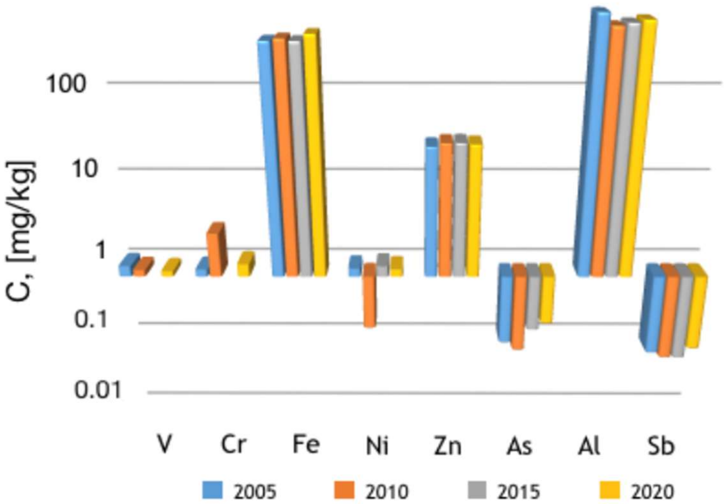

Fig. 3 Comparison of the median values for selected elements determined in 2005, 2010, 2015, and 2020 (log scale)

Despite the fact that median values for the most elements are kept at the same levels from survey to survey there are still some regions with the high anthropogenic influence, usually «hot spots» are revealed near cities with numerous plants. And during this moss survey it was decided to study not only pristine areas in order to establish background levels for the trace elements deposition, but also continue to monitor situation in the sites with high anthropogenic pollution. Comparison between median elemental concentration for Al, Co Cr, Cu, Ni, Pb, Co in different years of these survey didn't show significant differences (Figure 4). Only for As, Cd, Sb, V, and Zn in 2021 lower concentrations are observed. It could be explained b the sampling territory: all samples in 2021 were collected in the pristine area, primeval forest Nalibokskaya Pushcha.

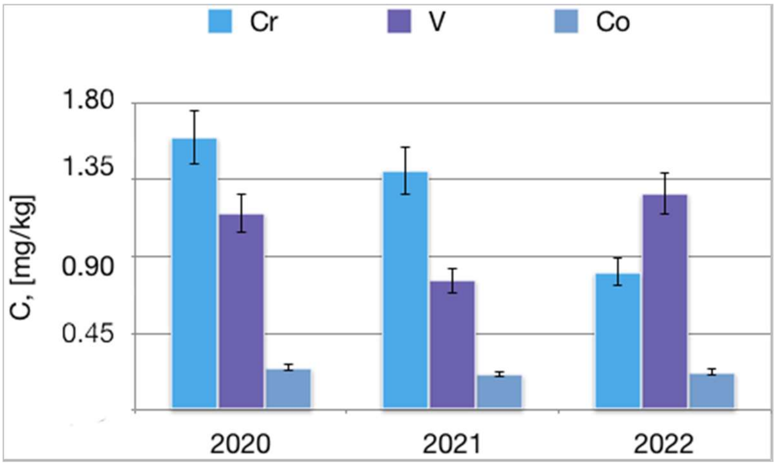

Fig. 4 Median concentration for some elements in mosses collected during moss survey 2020/2021-2022

Conclusion

Moss survey has been conducted repeatedly since 2005, providing information of temporal and spatial trends of metal deposition over Belarus [3,4,5]. This is an important and valuable supplement to the national monitoring programme of trace metals in precipitation.

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Bulgaria

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Background

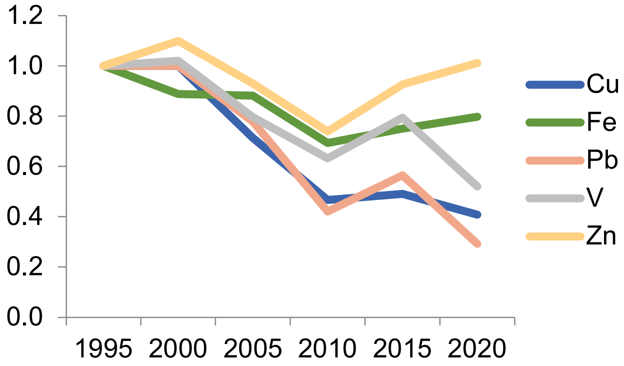
Since the 1995/96 moss survey, Bulgaria has been regularly participating in the ICP Vegetation programme. Despite the long-standing involvement, a uniform sampling net has not been implemented consistently to date. During the 32nd Task Force Meeting in Targovishte, Romania, a new, enhanced, and minimized sampling network plan, covering the entire territory of Bulgaria, was presented. However, for the most recent survey campaign, it had been decided to use for the last time the previously established sampling network. Thus, the northwest, north, and northeast parts of the country were not surveyed.

Neutron activation analysis and inductively coupled plasma atomic emission spectrometry were performed at JINR, Dubna, Russia, to determine the content of 39 elements. (NAA: Al, As, Ba, Br, Ca, Ce, Cl, Co, Cr, Cs, Fe, Hf, I, K, La, Mg, Mn, Mo, Na, Ni, Rb, Sb, Sc, Se, Sm, Sr, Ta, Tb, Th, Ti, U, V, W, Yb, and Zn; ICP-AES: Cd, Cu, Hg, and Pb). The predominant moss species is *Hypnum cupressiforme*, in the absence of which *Pleurozium schreberi* and *Pseudoscleropodium purum* were collected to obtain a total of 66 sampling sites.

Concentrations of heavy metals in mosses

To reveal associations between all determined elements, multivariate statistics (factor analysis) was employed. Five factors were ascertained, of which three were interpreted as anthropogenic. Factor 1 was characterized by crust elements and REEs ((Al (0.73), V (0.75), Fe (0.80), Na (0.73), Sc (0.77), Ti (0.87), La (0.83), Ce (0.85), Sm (0.84), Tb (0.80), Yb (0.86), Hf (0.86), Ta (0.73), Th (0.85)). Factor 2 contained elements related to coal fly ash (As (0.83), Se (0.90), Mo (0.88)). Factor 3 included the elements: Cu (0.88), Sr (0.90), Cs (0.74), and U (0.89) and the highest factor scores represented sites in regions with Cu-Ag mines and tailings. Factor 4 showed influence by marine aerosols: Hg (0.84), Br (0.87), I (0.86), and Cl (0.67). Factor 5, (Zn (0.82), Sb (0.78), and Cd (0.83), characterized sites located in a region where a non-ferrous metal plant operates.

The updated temporal trends for the metals reported to the Programme, except Hg and Sb, are shown in Fig. 1. Median values of the concentrations in each survey were normalized to the first available data for the country. A marked decrease in the concentrations of Pb and V was observed. The values were the lowest reported thus far, most probably due to the shutdown of a Pb-Zn smelting plant in 2011. The most recent results indicated that the concentrations of Cu, Fe, Ni, and Zn were rather similar to data from the preceding survey. In the case of Al, the decreased amount of atmospheric depositions could be explained by the less intensive traffic and road construction activities during the COVID-19 pandemic. The concentration of As was maximal in 2010/11, decreased in 2015/16, and increased again in 2020/22, which could be attributed to the operation activities in cement plants, fossil fuel power stations, and domestic heating. Most recently, the concentrations of Cr, Cd, and Sb also increased.



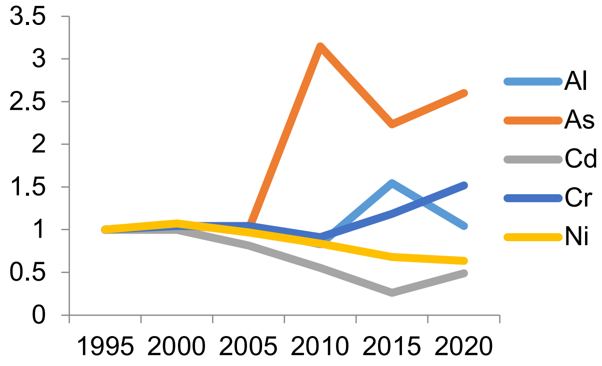


Fig. 1. Temporal trends - median values of concentrations normalized to values in the 1995/96 survey. It should be noted that due to the analytical methods applied for the quantification of Al, As, Cr, Fe, Ni, V, and Zn (ICP-AES until 2010/11, NAA since 2015/16), some differences in the results are anticipated.

Conclusion

An observation has been made that the number of local hotspots related to elements reported to the Programme has been decreasing gradually. This is due to the shutdown of facilities built during the planned economy era, as well as the utilization of contemporary environmental protection technologies. Current significant pollution emission sources in Bulgaria are contemporary and historical non-ferrous metal plants, coal mining and combustion for electricity production and domestic heating, vehicle emissions, road construction, and other industrial activities. In the preceding survey, sample sites located near the border with Greece, especially around the border crossing posts, were characterized by the highest concentrations of the elements Al, V, Ni, and Fe. The effect of the COVID-19 lockdowns could explain the “disappearance” of these hotspots in the most recent results.

Estonia

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Background and methods

This report outlines the Estonian submission to the ICP Vegetation 2021. There were 73 moss sampling sites throughout Estonia in 2021. Compared to previous monitoring time in 2015/2016 (n = 99), some places were changed and some were left out due to not matching the requirements for sampling sites, there was also one completely new monitoring site called Kaagvere.

Estonia has monitored heavy metals' deposition in mosses since 1989, an international survey has been conducted in every five years (1989/90; 1995; 2000/01; 2005/06; 2010/11; 2015/16 and 2021). Moss species used are *Pleurozium scherberi* and *Hylocomium splendens*. Estonia has analysed Cd, Cr, Cu, Fe, Ni, Pb, V and Zn starting since 1989. In 2005 nitrogen was added to the list of elements, in 2010 Al, As and Hg were also added to the list. 2021 was the first time Estonia also analysed Sb from mosses.

During the survey in 2021, slightly different methods were used for some elements than during previous surveys. As, Cd, Cr, Cu, Ni, Pb, Sb, V and Zn were analysed using ICP-MS. Total nitrogen was determined by Kjeldahl method, for Al and Fe ICP-OES was used and Hg was determined by fluorescence spectrometry.

Element concentrations in mosses

The results of moss survey in 2021 in Estonia can be seen on figure 1. Compared to previous monitoring results in 2015/16, in 2021 median concentrations of aluminium, iron, chromium, copper, nickel and vanadium have increased. The concentrations of mercury have increased slightly, from 0.031 mg/kg in 2015 to 0.039 mg/kg in 2021. No major declines were observed in median concentrations, hence cadmium, lead, zinc, arsenic and nitrogen stayed on the same level.

Looking back at the data from 1995 concentrations of most of the elements (Hg, As, Zn, Fe, Cd, Pb, V and N) have decreased or stayed around the same level. Concentrations of Al, Cr, Cu and Ni show a steady increase.

Raster maps to show the distribution of the elements' concentrations were generated using the Kriging algorithm (Figures 2-14).

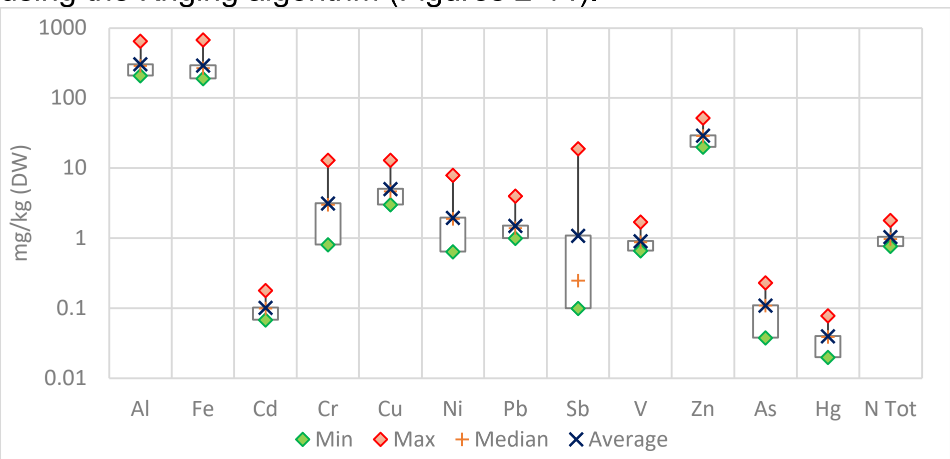

Figure 1. The Box Plot of data of the Estonian moss survey results in 2021.

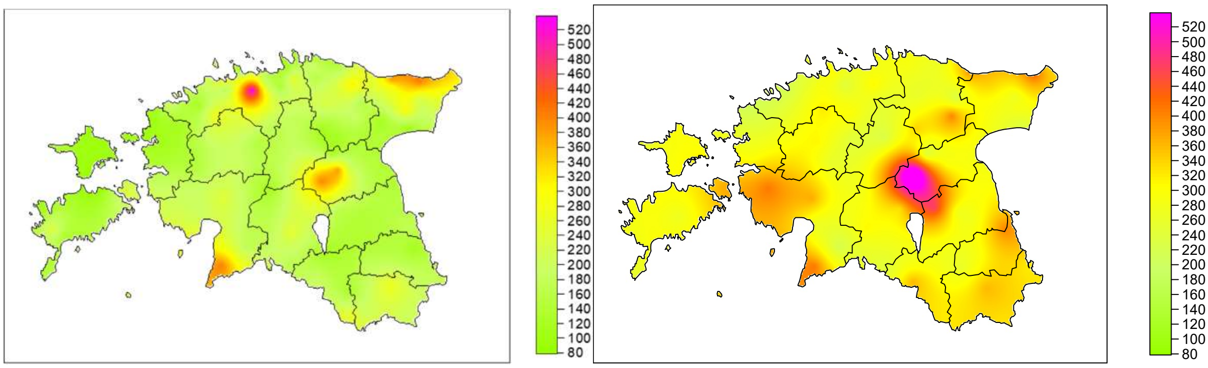

Figure 2. Distribution of Al concentrations (mg/kg) in mosses in Estonia in 2015 (left) and 2021 (right).

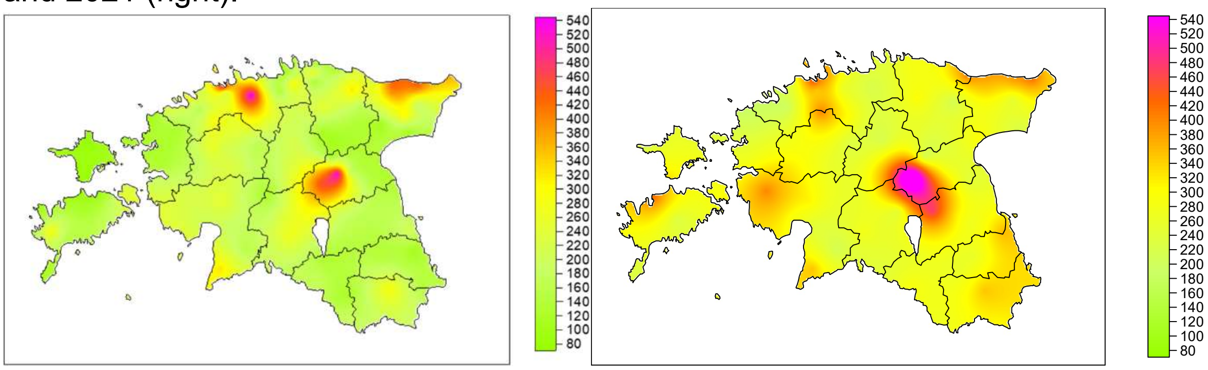

Figure 3. Distribution of Fe concentrations (mg/kg) in mosses in Estonia in 2015 (left) and 2021 (right).

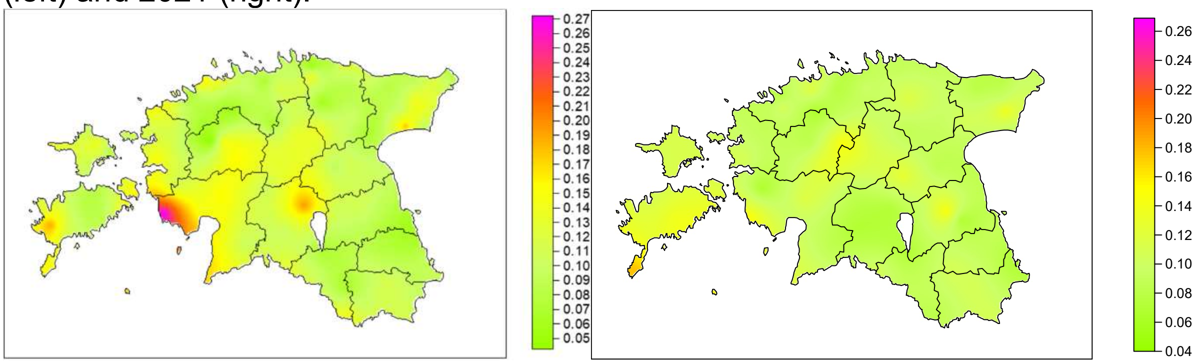

Figure 4. Distribution of Cd concentrations (mg/kg) in mosses in Estonia in 2015 (left) and 2021 (right).

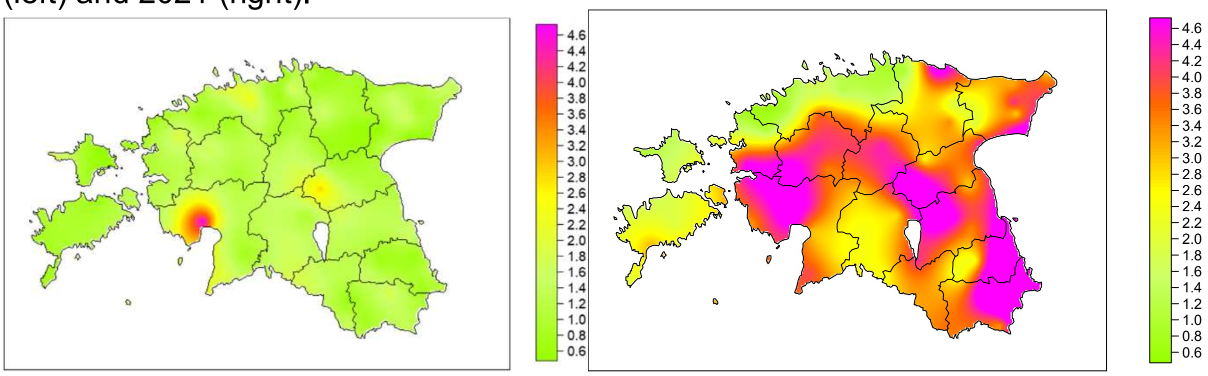

Figure 5. Distribution of Cr concentrations (mg/kg) in mosses in Estonia in 2015 (left) and 2021 (right).

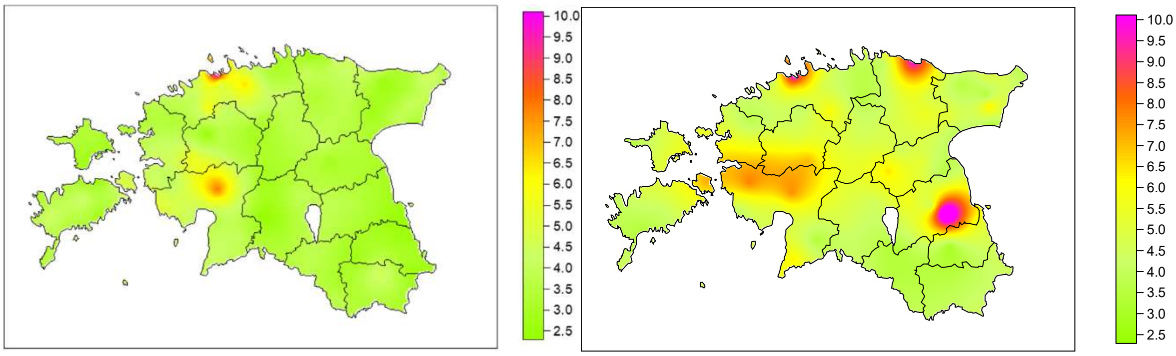

Figure 6. Distribution of Cu concentrations (mg/kg) in mosses in Estonia in 2015 (left) and 2021 (right).

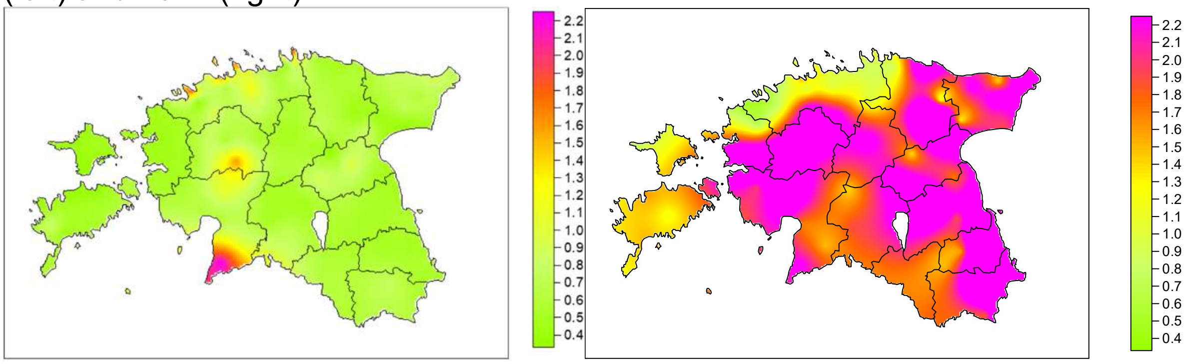

Figure 7. Distribution of Ni concentrations (mg/kg) in mosses in Estonia in 2015 (left) and 2021 (right).

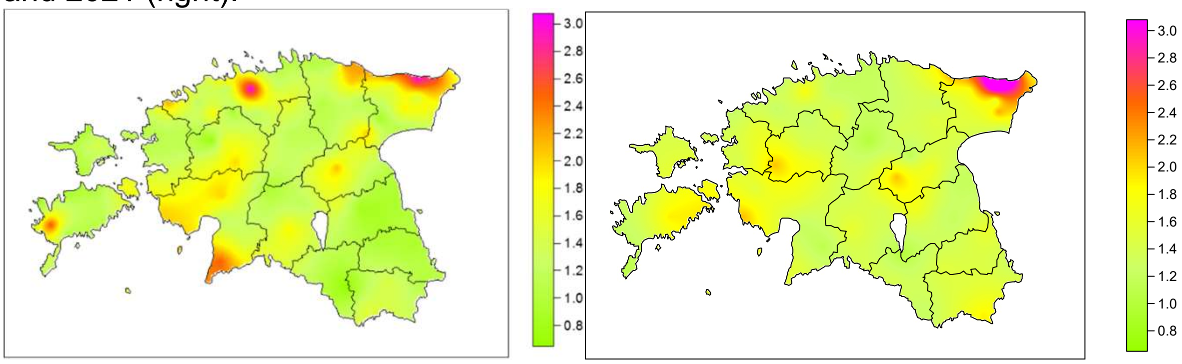

Figure 8. Distribution of Pb concentrations (mg/kg) in mosses in Estonia in 2015 (left) and 2021 (right).

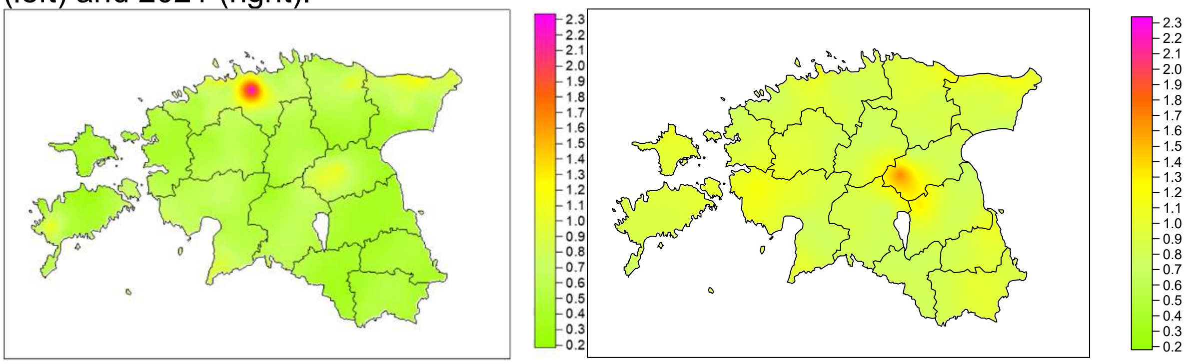

Figure 9. Distribution of V concentrations (mg/kg) in mosses in Estonia in 2015 (left) and 2021 (right).

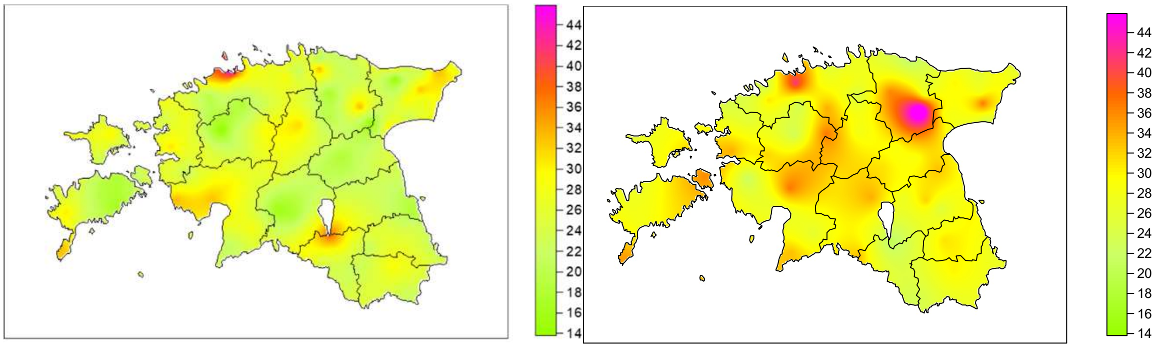

Figure 10. Distribution of Zn concentrations (mg/kg) in mosses in Estonia in 2015 (left) and 2021 (right).

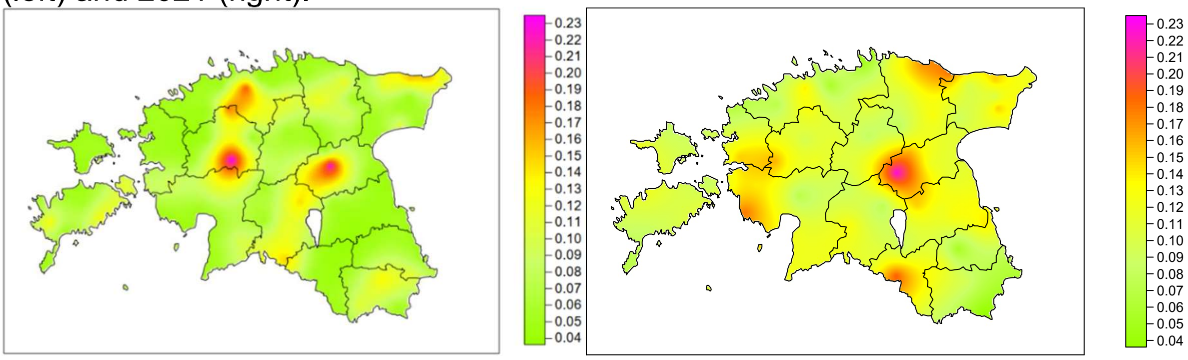

Figure 11. Distribution of As concentrations (mg/kg) in mosses in Estonia in 2015 (left) and 2021 (right).

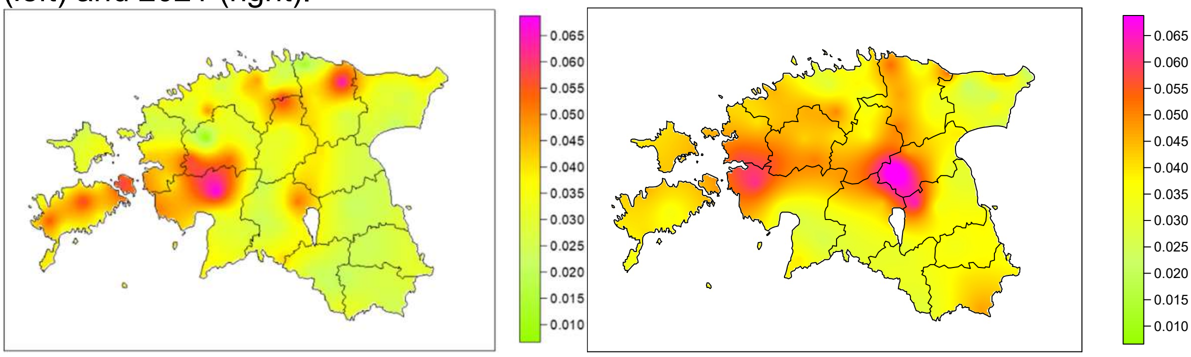

Figure 12. Distribution of Hg concentrations (mg/kg) in mosses in Estonia in 2015 (left) and 2021 (right).

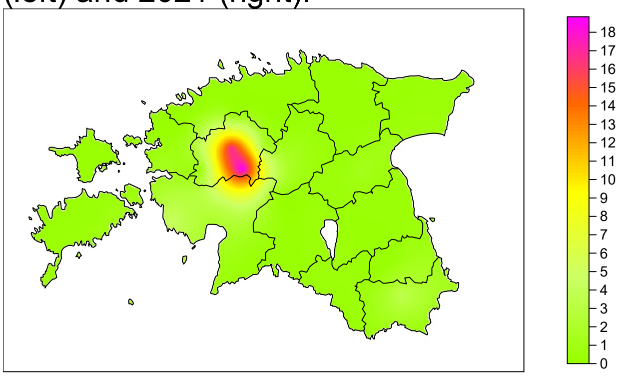

Figure 13. Distribution of Sb concentrations (mg/kg) in mosses in Estonia in 2021.

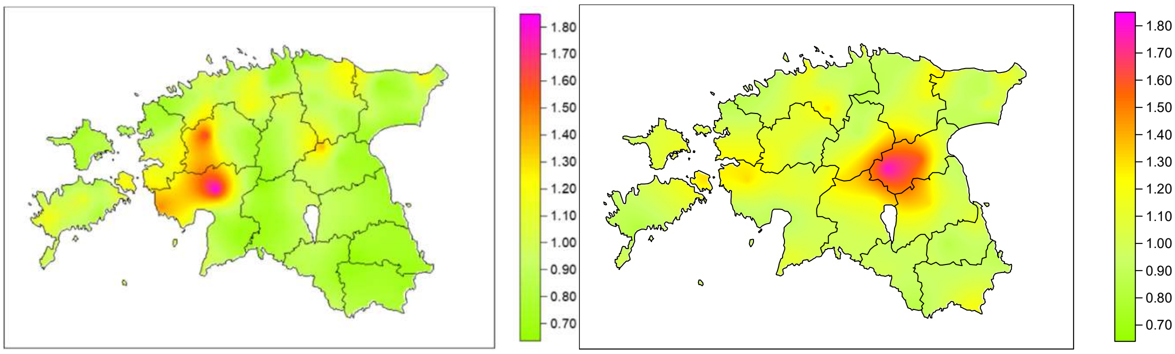

Figure 14. Distribution of total nitrogen concentrations (%) in mosses in Estonia in 2015 (left) and 2021 (right).

Discussion and conclusions

Some of the higher concentrations in North-East Estonia can be due to the chemical and oil shale industries in that area. The more contaminated area in Jõgevamaa central Estonia is possibly due to the heavy traffic and some industries.

Another reason for higher concentrations is probably due to different analyzing methods. To draw conclusions, analyzing with ICP-MS should be continued in Estonia in the future to see if any trends form.

France

Temporal trends in accumulated concentrations of chemical elements in French mosses between 2011 and 2021

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France has been participating to the European survey of heavy metal accumulation in mosses since 1996. In this document, we present the temporal variations observed over the last 3 surveys (2011, 2016, 2021).

Method

The number of sites sampled during French campaign is around 450. Field sampling follows recommendations of the moss monitoring manual with the exception of forest cover; mosses are always collected under the canopy. After sampling, moss sample is sent to the laboratory and the plant debris and other moss species are removed. The mono-specific samples are then dried at room temperature and grinded. An aliquot of approximately 1g is dried at 40°C for 48h before analysis. For all survey, the 13 elements required by ICP vegetation are analysed by the USRAVE laboratory in Bordeaux. Hg and N are analysed directly on moss powder using an AAS amalgamator and an elemental analyser. For the other elements wet ashing (HNO_3/H_2O_2) of moss sample is used. The metal determinations are performed using ICP-MS (As, Cd, Cr, Ni, Pb, Sb and V) and ICP-AES (Al, Cu, Fe and Zn). Standards are analysed for each survey and no temporal difference is observed in their value. For each element, the laboratory gives an analytical uncertainty, expressed as a percentage.

To follow the evolution of concentrations over time, we need to minimize influencing parameters other than atmospheric deposition. This is why we only compare samples collected (1) at a distance of less than one km, (2) under the same type of canopy (deciduous, coniferous or mixed) and (3) with the same moss species. Between 2011 and 2021, 291 sites correspond to these criteria.

Temporal trends over 2011-2021 period

To test temporal evolutions, the Wilcoxon signed ranks test and the sign test are used. For all our results, both tests give the same significant difference. Between 2011 and 2021, the concentration of all elements has changed significantly (Wilcoxon signed ranks test, $n = 291$, $p < 0.0001$): 4 elements (Al, As, Fe and Hg) have increased while 9 elements (Cd, Cr, Cu, N, Ni, Pb, Sb, V, Zn) have decreased (Table 1A). The percentages changes between the two surveys are presented Figure 1. Values range from - 94% for Hg to + 1127% for As. For each element, the number of sites (expressed as a percentage) showing an increase in concentration value is listed in table 1B. Percentage range from 10% (28 sites) for Sb to 73% (211 sites) for Al.

If we include the 2016 survey in the temporal trend, then the results are different. Only nickel gives consistent results between the two 5-year periods and the 10-year trend with a constant decrease. For all other elements, the variations observed over the periods 2011-2016 and 2016-2021 are not consistent (Table 1A). Only 2 elements (As, Cr) don't vary significantly (Wilcoxon signed ranks test, $n = 291$, $p > 0.05$) between 2011 and 2016 and 5 elements (Cd, N, Pb, Sb and Zn) for the period 2016-2021. Furthermore, only one element (Hg) shows a significant increase ($p < 0.0001$) over the period 2011-2016, whereas 5 elements (Al, As, Cu, Fe and V) show the same trend over the period 2016-2021.

Finally, it is interesting to note that the percentage of sites showing an increase is greater for the 2016-2021 period than for the 2011-2016 period for 12 elements (Table 1B).

The case of Cd and Pb

Mosses can accumulate elements in ionic or particulate form. Depending on the nature of the particles, it is more or less easy to solubilize them. To analyse siliceous particles, a hydrofluoric-acid-free digestion method is necessary. Since 2016, our samples have been analysed with both types of mineralisation (HNO_3/H_2O_2 and $HNO_3/H_2O_2/HF$). The concentrations of some elements are modified upon access to this particulate fraction. This is the case for terrigenous elements (for example Al) but also for some anthropogenic elements such as Cd and Pb.

For 9 elements (Al, As, Cr, Cu, Fe, Ni, Sb, V, Zn), HF mineralisation does not influence the results obtained with the Wilcoxon signed ranks test for the period 2016-2021 with HNO_3 digestion. For two elements (Cd, Pb), this change in digestion leads to different results, with a significant increase in concentration values between 2016 and 2021.

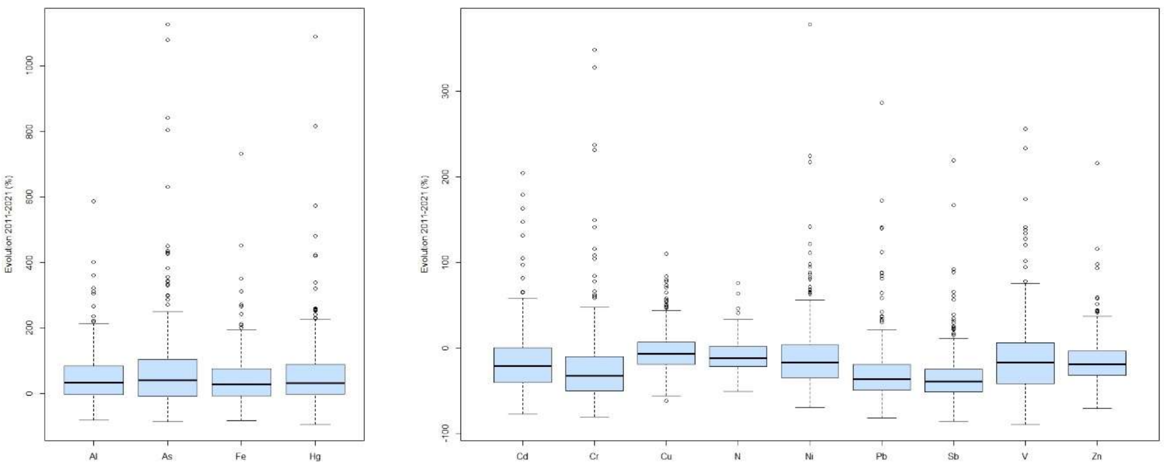

Figure 15. Distribution of the percentages changes for the period 2011-2021.

Table 1. A. *Summary of significant variations in element concentrations in moss collected in France as part of the BRAMM system for the period 2011/2021, 2011/2016 and 2016/2021 (n=291);* ***B.*** *Percentage of the number of sites showing an increase greater than the value of the analytical uncertainty calculated by the analysis laboratory for each period.*

1.A

Elements	2011-2021	2011-2016	2016-2021
Al	+	-	+
As	+	n.s	+
Cd	-	-	n.s
Cr	-	n.s	-
Cu	-	-	+
Fe	+	-	+
Hg	+	+	-
N	-	-	n.s
Ni	-	-	-
Pb	-	-	n.s
Sb	-	-	n.s
V	-	-	+
Zn	-	-	n.s

Sign-test ($p< 0.05$): n.s = non significatif ; **+** = significative increased ; **-** = significative decreased

1.B

Elements (analytical uncertainty)	Percent of sites with increase (%)		
	2011-2021	2011-2016	2016-2021
Al (15 %)	73	40	73
As (20 %)	70	55	59
Cd (20 %)	25	38	49
Cr (20 %)	21	46	38
Cu (20 %)	37	36	57
Fe (15 %)	71	39	70
Hg (10 %)	72	77	43
N (6 %)	26	35	50
Ni (20 %)	29	36	44
Pb (20 %)	11	26	55
Sb	10	24	52
V	27	27	60
Zn (10 %)	20	35	46

n total = 291 sites with same location, same biotope and same moss specie sampled

Conclusion

Over the 2011-2016 period, 10 of the 13 elements analysed showed a significant decrease. For the 2016-2021 period, only 3 elements showed a same pattern. Moreover, this period is characterized by a significant increase in Al, As, Cu, Fe, V contents on common sites but also by a few sites showing greater increases.

Current budgetary constraints are leading to a reduction in the number of elements monitored, based on the assumption that their concentrations decrease over time. Our results show that it is necessary to continue monitoring as many elements as possible.

Georgia

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Background

The first moss survey in Georgia was conducted between 2014 and 2017. In 2019/2023 the research was continued and 95 moss samples were collected. Of the original sampling locations, 33 sites either maintained their exact position or shifted less than 10 kilometers radius, allowing collection of the same moss species as in the first moss survey. The dominant species sampled was *Hypnum cupressiforme* Hedw., representing 70 samples. Secondary species included *Abietinella abietina* (Hedw.) M. Fleisch. (n = 14), *Pleurozium schreberi* (Brid.) Mitt. (n = 5) and *Hylocomium splendens* (Hedw.) Schimp. (n = 6). The altitude of sampling sites ranged from 2 to 2123 m above sea level. The sampling was carried out in accordance with the recommendations of the UNECE ICP Vegetation.

Concentrations of heavy metals in mosses

Elemental analysis was conducted using two complementary analytical techniques: inductively coupled plasma atomic emission spectroscopy (ICP-AES, PlasmaQuant PQ 9000 Elite, Analitik Jena, Jena, Germany) for determining content of Al, Cd, Cr, Cu, Pb, Fe, Ni, V, and Zn, while Hg content was separately analyzed using a direct mercury analyzer (DMA-80 evo, Milestone Srl, Sorisole, BG, Italy). A spatial representation of pollution distributions was generated using QGIS, utilizing the Pollution Load Index (PLI) to show variations in pollution levels across Georgia (Figure 1).

Discussion and conclusions

The comparison of the results of the 2014/2017 and 2019/2023 moss surveys in Georgia reveals complex temporal patterns. While many elements showed declining median contents over this period, specific metals displayed unique trends. Notably, Cd and Zn maintained consistent median values across both study periods, while Cu demonstrated an upward trend. Statistical analysis using the Mann-Whitney U test identified significant differences ($p < 0.05$) in the content of most elements, with the exception of Cd, Pb and Zn. Statistical analysis of moss samples from 33 unchanged sites also revealed significant temporal variations in elemental content between the 2014/2017 and 2019/2023 periods.

Based on Principal Component Analysis, the dataset reveals two distinct environmental signatures. The first principal component (PC1) explains 43.4% of the total variance and is characterized by strong loadings from metals of geogenic origin, specifically Al, Co, Cr, Fe, and V. Notably, samples 87, 89, 92, 94, and 90 contribute most significantly to PC1, corresponding to areas adjacent to agricultural lands. During dry seasons, these agricultural regions appear to generate atmospheric particulate matter through soil mobilization, which is subsequently dispersed over extensive areas due to the open nature of these spaces. The second principal component (PC2) accounts for 13.3% of the variation and is characterized by strong loadings of Cd, Hg, Mn, Pb, and Zn. These elements are predominantly associated with anthropogenic sources, specifically linked to areas with significant human activity including highways, urban development, and industrial activities.

These results highlight the importance of conducting regular moss surveys. The moss biomonitoring approach has proven quite effective in Georgia, revealing distinct patterns of atmospheric deposition and helping to identify specific sources of pollution.

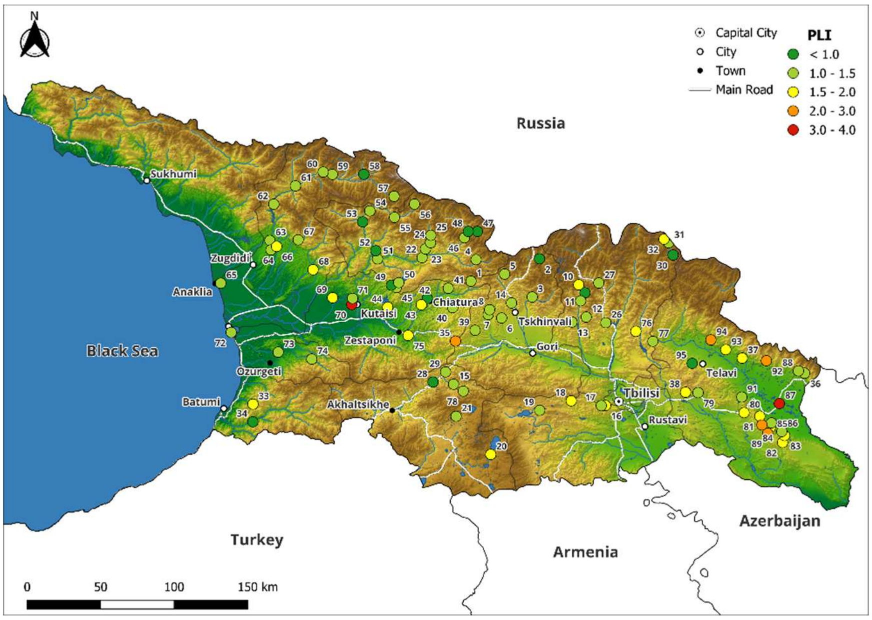

Figure1. Spatial distribution of the Pollution Load Index (PLI) across all sampling locations.

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Funding: Federal Environmental Agency, Germany
Project Number: 3720632010

After 1990, 1995, 2000, 2005 and 2015, Germany participated in the International Moss Monitoring 2020 (MM2020). The German contribution to MM2020 was financially supported by the Federal Environment Agency and included the determination of persistent organic pollutants (POPs) for the second time after 2015 and, for the first time, the measurement of microplastics (MP) in mosses. The measurement network used as a basis was reduced from 400 sites (MM2015) to 25 (MM2020). A transparent procedure based on statistical methods and decision modelling was developed for this purpose. Metals (M) and nitrogen (N) were measured without financial support.

Moss is generally suited as a bio-monitor for detecting the atmospheric deposition of POPs. MM2020 analyses principally confirmed concentration levels from the MM2015. The first temporal concentration variations were described. However, these cannot be generalized due to the low number of MM2015 sampling sites. Furthermore. the spatial distribution could be described in the MM2020, as well as a first estimation concerning different land uses.

Within the framework of the project, methods were developed to examine moss for MP using TED-GC-MS and Raman spectroscopy. In all 25 moss samples examined, microplastics in the range of 280 to 2,400 µg/g moss (dry matter) could be detected by TED-GC-MS. Polyethylene (PE) accounted for 82% of the total polymer load. By means of Raman spectroscopy, a particle size range from 10 to approximately 200 µm was tested for microplastic analysis of three samples. Depending on the sample, 24 to 295 particles per g of moss could be assigned to different polymers. Here, too, PE dominated with almost 50%. Moss could be proofed to be a suitable bio-monitor for detecting atmospheric deposition of MP. TED-GC-MS and Raman spectroscopy complement each other perfectly as analytical methods.

The measurements of M and N show - against the trend of published emission data - significant increases in M bioaccumulation and considerable element enrichment in forests compared to their surrounding areas. The corresponding enrichment factors should be taken into account in deposition modelling.

The determination of M (since 1990) and N (since 2005) was not funded in MM2020, since based on the emission register data, it was assumed that the trend of decreasing M emissions is transferred to bioaccumulation and that the same applies to N. Nevertheless, there are good reasons to continue recording M and N accumulation. Despite the publication of decreasing emissions, MM 2015 detected that the enrichment of M in mosses intermediately can increase in a statistically significant way, such as Cr, Sb and Zn between the years 2000 and 2005, or that it comes to a standstill (Al, As, Cd, Cu, Hg, Ni, V 2000-2005). And indeed, the measurements of M and N in MM2020 detected statistically significant increases in the accumulation of all recorded M in mosses and a statistically non-significant increase in N accumulation between 2015 and 2020 (Figure 1).

These findings demonstrate that the emission register data require control by exposure monitoring in the form of moss surveys as well as measurement and modelling of atmospheric deposition. The investigations of the canopy effect, also carried out in-house, suggest that the considerable, statistically significant increase in bioaccumulation of elements as a result of filtering through tree canopies, which can be up to 150% depending on the element and monitoring campaign, should be taken into account in deposition modelling and mapping in future.

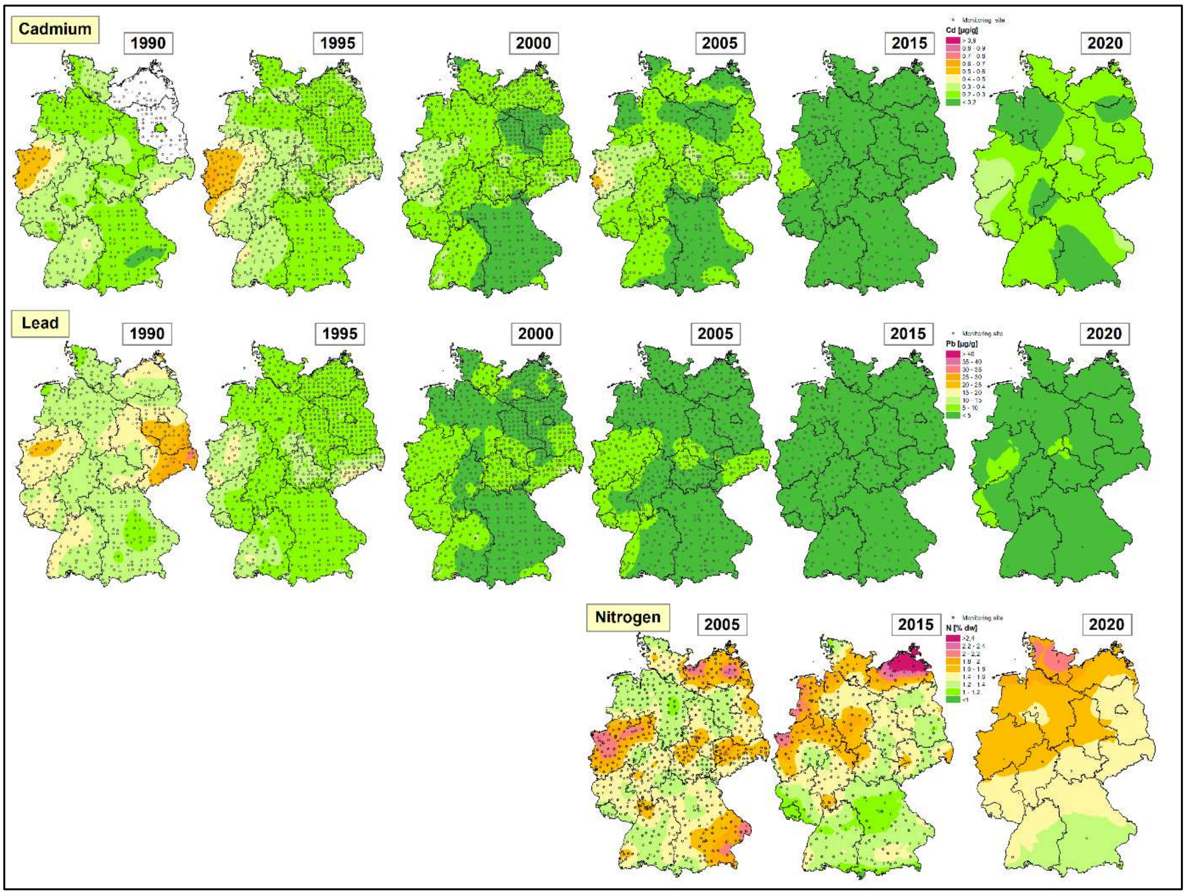

Figure 1. Spatio-temporal trends of Cd, Pb and N concentrations in moss (1990-2020)

Preliminary Final Report

Schröder W, Dreyer A, Nickel S, Völksen B, Wenzel M, Wolf C, Kube C, Türk J 2023. Pilot studies on the suitability of bioindication with mosses for detecting the atmospheric deposition of persistent organic pollutants and microplastics. Research and development project FKZ 3720632010 in the departmental research plan 2020 of the Federal Ministry for the Environment, Nature Conservation, Nuclear Safety and Consumer Protection. Commissioned by the Federal Environment Agency, Dessau. Volume 1: 1-138, Volume 2: 1-154 [in German]

Italy (province of Bolzano)

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Background

Since 1995 the province of Bolzano (South Tyrol) situated in the North of Italy has participated in the European monitoring of atmospheric heavy metal pollution. As in the previous years moss specimens of *Hylocomium splendens* were collected in 20 sample sites. The shoots of the last three year's growth were analyzed for the concentration of the following elements: arsenic (As), cadmium (Cd), chromium (Cr), iron (Fe), mercury (Hg), copper (Cu), nickel (Ni), lead (Pb), vanadium (V), zinc (Zn) and nitrogen (N).

Concentrations in mosses

The analysis of the monitoring in 2021 showed that the concentration of following measured air pollutants: iron, vanadium, lead, mercury, and nitrogen declined (Fig. 1 and Fig. 2). Additionally unusual higher concentration of chromium and nickel measured in the campaign of 2015/16 declined and returned to a similar range detected in the previous years (Fig. 3). The concentration of cadmium is in comparison to the previous 5 years remained stable. Whereas the concentrations of arsenic, copper and zinc showed a slight incline in comparison to the measurements of the year 2015/2016 (Fig. 4). Comparing although these values to the median European concentrations (Harmens *et al.* 2015) they remained still in the lower range. The slight increase in arsenic concentration could be led back to several events of Sahara dust (Harmens *et al.* 2015) in the beginning of 2021 (Francis *et al.* 2021).

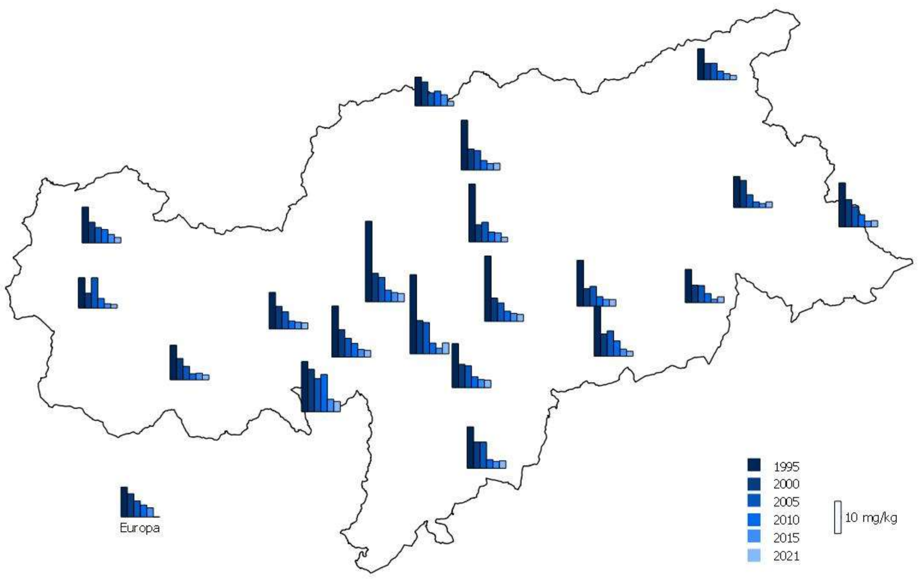

Figure 1. Lead (Pb) concentrations (mg/kg) at different sampling sites in South Tyrol from 1995 to 2021. The European mean of the respective year is shown in the lower left corner.

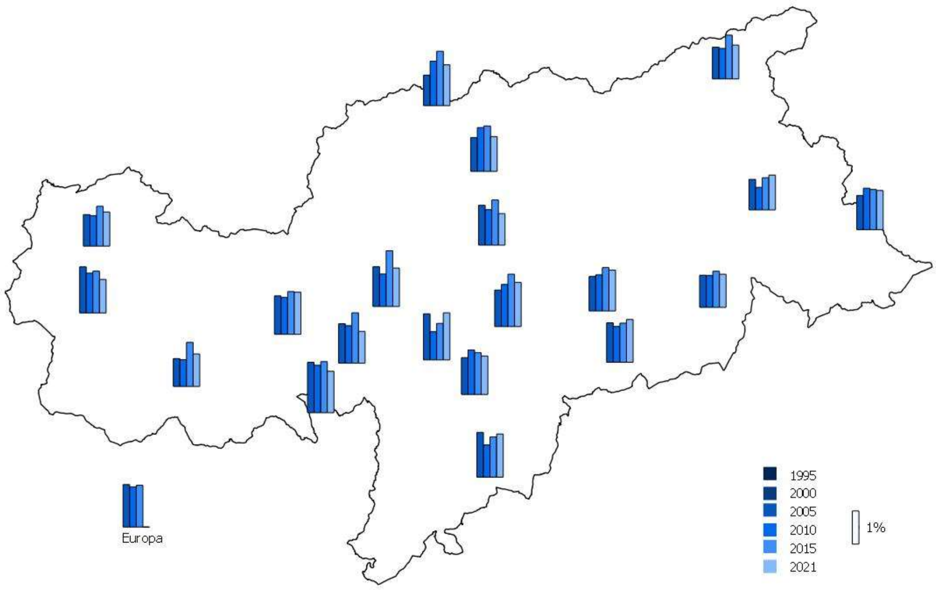

Figure 2. Nitrogen (N) concentrations (%) at different sampling sites in South Tyrol from 2005 to 2021. The European mean of the respective year is shown in the lower left corner.

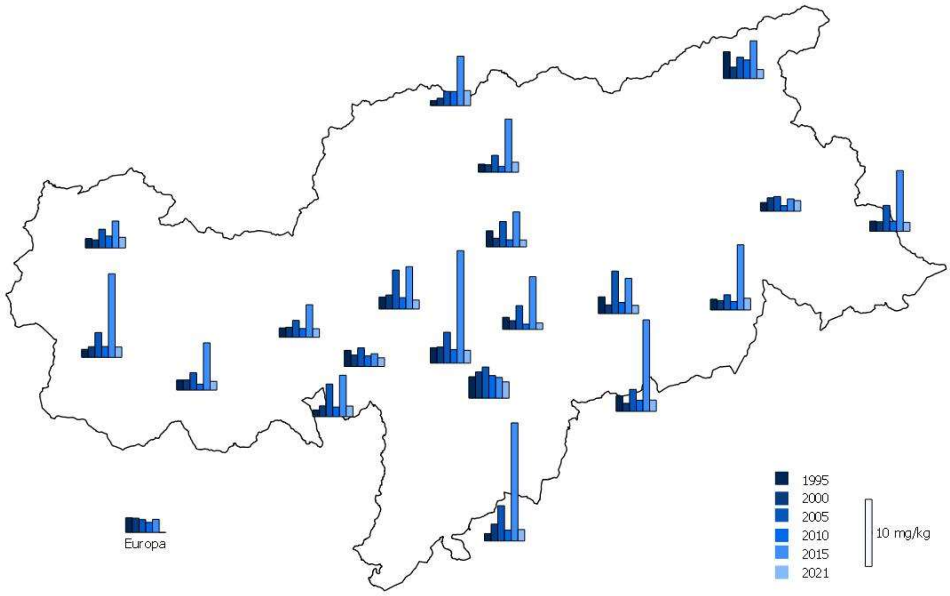

Figure 3. Chromium (Cr) concentrations (mg/kg) at different sampling sites in South Tyrol from 1995 to 2021. The European mean of the respective year is shown in the lower left corner.

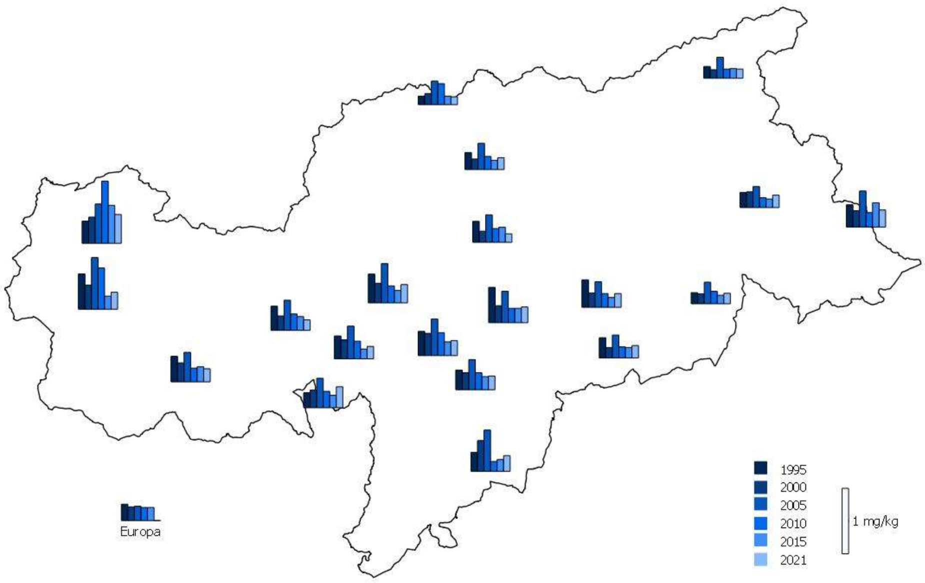

Figure 4. Arsenic (As) concentrations (mg/kg) at different sampling sites in South Tyrol from 1995 to 2021. The European mean of the respective year is shown in the lower left corner.

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Istituto Nazionale di Geofisica e Vulcanologia, Roma, Italy - Aldo Winkler (aldo.winkler@ingv.it)

Background:

This report summarizes the results of moss biomonitoring to assess the deposition of airborne potentially toxic elements (PTEs - Al, Ba, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, S, Sr, V, Zn), nitrogen (N) and microplastics (MPs) across the region of Tuscany, Central Italy (Fig. 1). In addition, the magnetic properties (susceptibility) and the physiological status of the samples (i.e. cell membrane integrity, chlorophyll content, photosynthetic efficiency) were also measured.

A total of seven moss species, namely *Hypnum cupressiforme* (64.0%), *Pseudoscleropodium purum* (13.4%), *Brachitecium rutabulum* (7.9%), *Eurynchium striatulum* (6.7%), *Homalothecium sericeum* (3.7%), *Eurynchium striatum* (3.0%), and *Isothecium alopecuroides* (1.2%), were collected from 33 remote sites, mostly selected following a regular grid of 50 x 50 km (Fig. 2), in agreement with the ICP Vegetation Moss Survey Protocol. The diversity of species was not a main factor affecting the results.

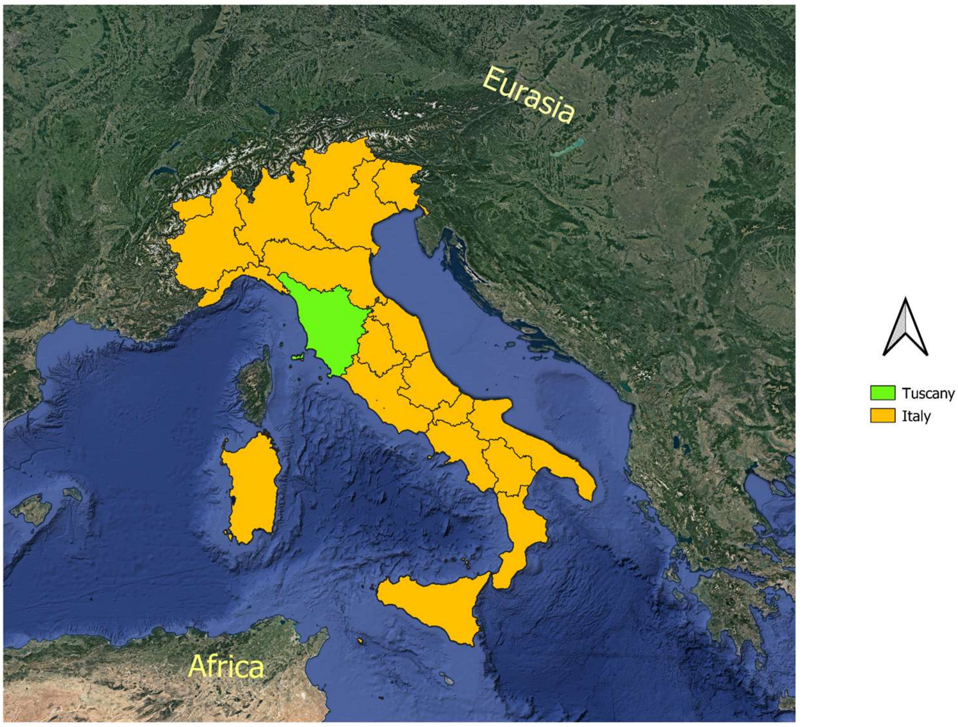

Figure 1. Italy with Tuscany region highlighted

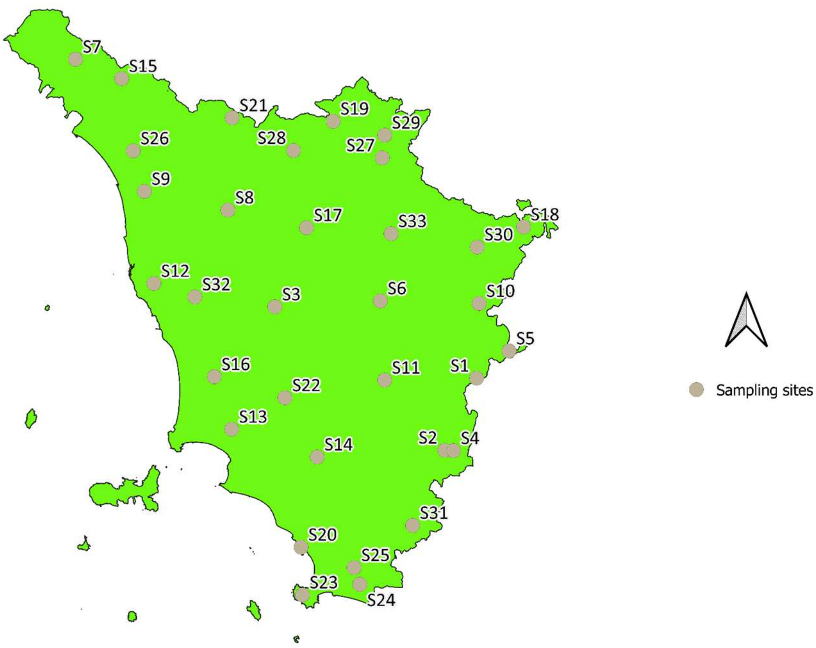

Figure 2. Tuscany with location of the 33 sampling sites

Results

The concentration of PTEs (mg/kg), nitrogen (%) and microplastics (nr/g) in moss samples, along with magnetic susceptibility (10^{-8} m^3/kg), cell membrane damage (%), chlorophyll content (mg/m^2) and photosynthetic efficiency of the moss samples, are summarized in the table below.

Conclusions

This study showed relatively high levels of soil-related elements (Al, Fe, Co, Cr, Ni, V) accumulated in moss samples, suggesting potential local geogenic contamination. Moderate concentrations of some anthropogenic elements (Cd, Cu, Pb, S, Zn) were also observed, which suggested long-range atmospheric transport from removed localities. The concentrations of N indicated an impact of agricultural practices, e.g. crop cultivation and livestock rearing, on the moss samples.

Fibers emerged as the predominant type of MPs, and this trend was further supported by the prevalence of PET as the primary polymer type. The overall count of accumulated MPs increased at sites in densely populated, and/or industrialized areas.

The magnetic properties of moss samples showed very low susceptibility values, confirming the role of soilborne elements and the modest contribution of airborne anthropogenic sources.

Physiological parameters indicated that the moss samples were healthy, suggesting that accumulated PTEs, N and MPs do not harm moss vitality.

	median	**IQR**	**min**	**max**	**90^{th} perc.**
Al	1053	912	335	5417	2457
Ba	20	18.8	7	130	49
Cd	0.11	0.07	0.04	0.52	0.19
Co	0.5	0.4	0.1	3.7	1.0
Cr	1.9	1.6	0.8	12.7	5.1
Cu	5.3	2.5	2.3	36.1	8.3
Fe	779	672.5	240	4560	1836
Mn	139	143.1	19	711	334
Ni	2.2	1.8	0.6	14.7	6.5
Pb	2.0	1.2	0.6	8.6	3.7

S	1096	254	633	1954	1471
Sr	24.6	11.3	10.3	70.4	36.9
V	1.9	1.7	0.7	11.3	4.3
Zn	16.4	10.2	8.6	36.9	27.8
N	1.1	0.6	0.1	2.1	1.6
Microplastics	6.4	4.1	2.2	12.9	9.4
Cell membrane damage	9.3	11.9	4.1	28.3	16.3
Chlorophyll content	427	115	117	833	567
Photosynthetic efficiency	0.665	0.081	0.125	0.844	0.735
Magnetic susceptibility	1.43	0.77	0.33	0.56	0.33

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 is a participant in the European moss surveying programme since 1990, and continued every 5 years, except in 2010 due to lack of funding. Bioimonitoring of atmospheric heavy metal distributions in Latvia has been conducted using moss in six national surveys: in 1990, using *Hylocomium splendens* collected in 81 plots, in 1995, 2000, 2005, 2015 and 2020 using *Pleurozium schreberi* in 101 plots. Change from one to other species was made because *P. schreberi* has wider distribution in Latvia. Mosses was sampled in each survey between August and October. The sites were located in pine forests. Each plot (50 × 50 m) was located at least 300 m from major highways and at least 1 km from stationary pollution sources and large cities. Concentrations of eight heavy metals (Cd, Cr, Cu, Fe, Ni, Pb, V, Zn) and nitrogen were analysed in *P. schreberi* moss to estimate atmospheric pollutions in the whole territory of Latvia.

Concentrations of heavy metals and nitrogen in mosses

In 2020 the median concentrations of heavy metals (mg kg^{-1}) and nitrogen (%) were as follows: V – 0.37, Cr – 0.44, Ni – 0.26, Cd – 0.20, Pb – 0.75, Zn – 30.10, Fe – 135.07, Cu – 6.22 (Table 1), and N – 1.09.

Table 1.

The median concentration (µg/g) of heavy metals (V, Cr, Ni, Cd, Pb, Zn, Fe, Cu) during the period 1990–2020 in Latvia.

	V	Cr	Ni	Cd	Pb	Zn	Fe	Cu
1990	3,19	1,45	1,40	0,31	11,15	42,00	465,52	6,02
1995	3,00	1,13	1,07	0,17	6,83	30,24	362,50	3,79
2000	1,80	0,95	1,00	0,16	2,90	31,00	134,00	5,10
2005	1,35	0,79	1,00	0,24	3,83	40,30	188,00	4,65
2015	0,49	0,33	0,48	0,10	1,26	33,13	133,02	5,17
2020	0,37	0,44	0,26	0,12	0,75	30,10	135,07	6,22

The strongest decrease in median concentration between 1990 and 2020 was for Pb (by 93%) followed by V (by 88%), and Ni (by 82%). Increased concentrations in the western part of Latvia are due to the long-range transboundary transport of pollution from Western Europe. Higher concentrations near the Lithuanian border are associated with pollution impact from Naujoji Akmene cement factory (Cd, Cr, Fe) and Mažeikiai oil refinery (Cd, Cu, V). The highest N concentrations in *P. schreberi* moss in 2020 were determined in the south-western part of Latvia (1.53-1.87%), the lowest N concentrations (< 0.95%) were determined in the northern part of Latvia. 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.

Discussion and conclusion

In Latvia from 1990 until 2020 concentration in mosses in all plots as a whole has declined for all heavy metals (Cd, Cr, Cu, Fe, Ni, Pb, V, Zn). The decrease of V and Ni concentrations in moss can be explained by the fact that many thermal power plants have a conversion of fuel sources from oil to natural gas (Nikodemus et al. 2004). 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). Despite an increased number of vehicles in the Latvia following the recovery of Latvia's independence, the reduction of Pb emissions was linked with improved of petrol and vehicle quality in Latvia (Nikodemus et al. 2004), and a reduction in cross-border pollution transfer from Europe (Tabors et al. 2017). 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). Overall, the loss of pollution point sources has been due to pollution abatement technology in the industry, energy production, and transport. This survey in 2020 confirmed the efficiency of moss biomonitoring.

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Background

The study of air pollution by heavy metals in the Republic of Macedonia using the moss biomonitoring technique was carried out for the first time in 2002 within the framework of the International Cooperation Programme of the United Nations Economic Commission for Europe on the effects of air pollution on natural vegetation and crops polluted with heavy metals in Europe (UNECE ICP Vegetation). The first moss biomonitoring study in Macedonia showed that the activities of mines and smelters are the main sources of emissions of potentially toxic elements (PTEs) (Barandovski et al. 2008). The results of the second moss survey in 2005, the third survey in 2010, and the fourth in 2015 confirmed the results of the first survey (Barandovski et al., 2012, 2013, 2015, 2020; Stafilov et al., 2018, 2020). In the period from August to October 2020, moss samples were collected at the same 72 sites with a dense network of 17x17 km^2. Samples of the terrestrial mosses *Homalothecium lutescens* and *Hypnum cupressiforme* were used for the moss survey in all surveys. The moss samples collected in 2020 were analyzed for 46 elements using neutron activation analysis (NAA), inductively coupled plasma–mass spectrometry (ICP-MS), and the Kjeldal method for the determination of nitrogen.

It was concluded that the main emission sources are found in the vicinity of 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 as fuel. The results of the previous surveys in 2005, 2010 and 2015 confirmed the results of the first survey and provided information on temporal deposition trends (Barandovski et al., 2012, 2013, 2015, Stafilov et al., 2018, 2020). The survey conducted in 2020 showed that air pollution with PTEs in Macedonia decreased slightly compared to the results of previous surveys. This is mainly due to the fact that despite the operation of all mining and smelting facilities with the same capacity during this five-year period, government regulations for the installation of waste/gas cleaning systems and additional regulations to reduce pollution were introduced. Nevertheless, the fact remains that the highest anthropogenic air pollution with potentially toxic elements is still caused by the operation of ferronickel in Kavadarci (with Ni and Cr) in the southern part, lead and zinc mines in Probištip, Makedonska Kamenica and Kriva Palanka in the eastern part, and the former Pb-Zn smelter in Veles and the steel plant in Skopje (with Cd, Pb and Zn).

Material and methods

To determine the content of the different elements in the mosses collected in 2020, NAA and ICP-MS techniques were used. The ICP-MS analyses were performed at the accredited laboratory ACME Ltd. from Vancouver, Canada, NAA was performed at the Joint Institute for Nuclear Research, Frank Laboratory of Neutron Physics, Department of Neutron Activation Analysis in Dubna, Russia, while nitrogen was determined at the Tobacco Research Institute, Prilep, Macedonia. Using all of these techniques, the content of 46 elements was determined (Ag, Al, As, B, Ba, Br, Ca, Cd, Ce, Cl, Co, Cr, Cs, Cu, Fe, Ga, Hf, Hg, I, K, La, Mg, Mn, Mo, N, Na, Ni, Mo, P, Pb, Rb, S, Sb, Sc, Se, Sm, Sr, Ta, Tb, Th, Ti, U, V, W, Yb, and Zn).

Results and discussion

From the obtained results, almost all potentially toxic elements (As, Cd, Co, Cr, Cu, Hg, Ni, Pb and Zn) showed elevated levels in the moss samples collected in 2002 and 2005, while their levels slightly decreased in the samples collected in 2010, 2015 and 2020. The elevated mean and median levels observed in 2002-2005 were for Cd and Pb, probably due to the reactivation of lead and zinc mining in eastern Macedonia, which deposited large amounts of flotation residues in the landfills. However, the Cd and Pb contents in the previous surveys from 2010 to 2020 show declining values, which is due to the closure of the Pb-Zn smelter in Veles, the reduced use of leaded gasoline for cars, and the cultivation of some of the tailing's piles. Similarly, the higher Ni content in the 2005 samples (5.8 mg/kg) is due to the capacity expansion of the ferronickel smelter near the town of Kavadarci, while these levels are significantly reduced in 2020 (5.4 mg/kg) due to the reconstruction of the dust filters.

Factor analysis is a set of statistical-mathematical procedures and a methodological basis used in the analysis of relationships between simultaneously occurring variables. Six factors were identified with a 80.4% variability in the identified elements: F1 (Al, Fe, La, Ti, U, Ga, Co), F2 (B, Ca, Hg), F3 (Ag, Pb), F4 (Ba, Sr), F5 (Cr, Mo, Ni), F6 (Cd, Sb, Zn). Factor analysis revealed two geogenic associations (F1 and F4); two anthropogenic associations (F3 and F6) and two mixed geogenic and anthropogenic associations (F2 and F5).

Table 1. Average and median values for the reported elements (in mg/kg)

	Average					Median				
Year	2002	2005	2010	2015	2020	2002	2005	2010	2015	2020
Al	5100	4900	2800	2300	2000	3800	3600	2400	2000	1800
As	1.2	0.84	0.59	0.71	0.56	0.80	0.68	0.48	0.72	0.44
Cd	0.29	0.42	0.29	0.25	0.18	0.16	0.29	0.22	0.21	0.15
Cr	14	11	8.5	7.1	5.7	7.9	6.8	6.5	5.7	4.8
Cu	28	7.4	4.0	4.7	7.0	24	6.7	3.5	4.6	6.3
Fe	3400	2800	2100	1700	1500	2400	2200	1900	1600	1400
Hg	0.068	0.080	0.11	0.085	0.054	0.056	0.068	0.093	0.084	0.052
Ni	3.8	9.1	6.8	7.7	5.4	2.5	5.8	4.3	4.4	4.2
Pb	7.5	9.7	5.4	5.3	3.8	6.0	7.6	4.6	4.8	3.1
Sb	0.26	0.18	0.10	0.13	0.15	0.20	0.15	0.089	0.11	0.11
V	9.6	8.4	4.4	3.7	3.3	6.9	6.4	3.8	3.3	3.0
Zn	46	41	32	33	34	39	36	29	32	32

The higher Hg content (Fig. 1) in air was found to be of both anthropogenic and geogenic origin. Anthropogenic origin is observed in central and eastern Macedonia due to soil pollution near the town of Veles and the presence of a slag deposit from the former operation of the Pb-Zn smelter in Veles (Stafilov et al., 2010), as well as flotation waste dumps from the mines of Zletovo, Sasa and Toranica in the east of the country. The influence of the thermoelectric power plant near Bitola can also be seen in the dust emissions, which contain Hg due to the use of large amounts of lignite. The high accumulation of Hg in moss samples collected near the capital Skopje is partly related to the mercury-contaminated areas of the former organic chemistry factory in Skopje, where a sodium chloride electrolysis plant with mercury electrodes operated from 1964 to 1995. In the northwestern part of the country, the main source of pollution in the village of Jegunovce in the Tetovo region and in the city of Skopje is the smelting plant for steel and ferrosilicon production using scrap metal.

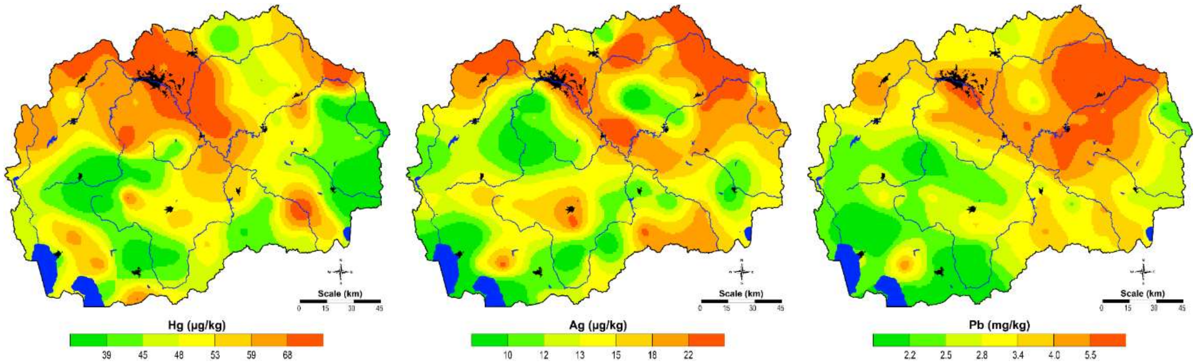

Figure 1. Spatial distribution of the content of Hg, Ag, Pb

From the maps of spatial distribution of Ag and Pb (Fig. 1), it is evident that higher contents of these elements are found in the moss samples collected in the central and northeastern part of the country (near Skopje, Veles, Tetovo, Probištip, Makedonska Kamenica and Kriva Palanka). The increased Ag and Pb content in moss samples from these regions is directly related to dust from the surface of mining flotation residues and slag deposits from the iron and steel industry and ferrosilicon industry. The association of Cr and Ni also represents a geogenic and anthropogenic association. High contents of these elements (Fig. 1) are found in the central region of the country, in the Paleogene and Neogene basins such as the Vardar zone, which are of geogenic origin (Stafilov & Šajn, 2016) and are due to pollution from the ferronickel smelter, especially in the Kavadarci region, where high contents of these elements occur as a result of the work of the ferronickel smelter, which processes ores enriched with these elements.

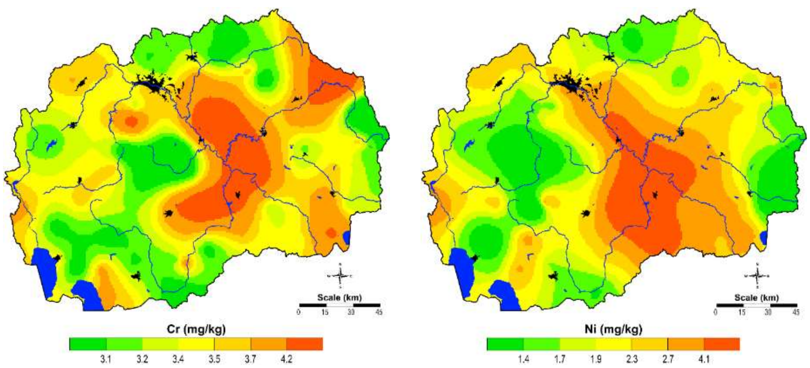

Figure 2. Spatial distribution of the content of the Cr and Ni

The spatial distribution of this compound of Cd, Sb, and Zn is shown in Figure 3. The highest values for these elements were found in the central and eastern regions of the country. In Eastern Macedonia, the highest values for these elements were found in moss samples from the vicinity of mines with flotation plants (Zletovo, Sasa and Toranica). In addition, high levels of Zn were found in moss samples collected in the vicinity of the town of Kavadarci, which can also be attributed to air pollution from the ferronickel smelter. The highest values of Cd and Zn in the central region were found in the regions of Veles and Skopje, which can be attributed to the urban and industrial activities (steel smelter) and to the slag deposit from the former Pb-Zn-Cd smelter in Veles.

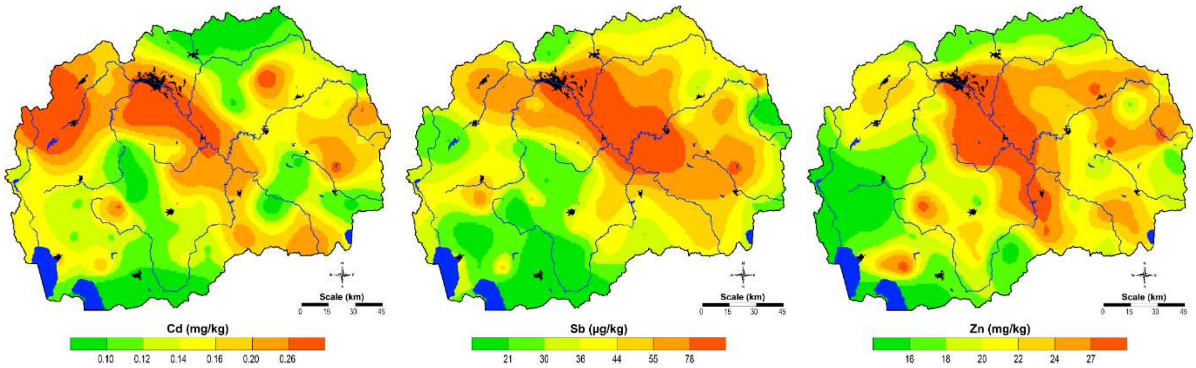

Figure 3. Spatial distribution of the content of Cd, Sb and Zn

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Republic of Moldova

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Background

For the first time, the Republic of Moldova joined the ICP Vegetation program in the 2015/2016 moss survey, when samples were collected throughout the country. Based on the obtained data, the cities of Chisinau and Balti were determined to experience particular environmental stress [1]. The purpose of the second survey performed in 2020 was to (i) to determine current concentrations of elements in the Republic of Moldova; (ii) to compare the results of the two moss surveys; (iii) to verify the pollution sources identified in the first national survey performed in 2015.

Sampling and elemental analysis

In April 2020, Hypnum cupressiforme moss samples were collected at 41 sampling sites evenly distributed over the territory of Moldova (Figure 3). The samples were collected at the same 33 locations as in 2015 and 8 new sampling sites were added, which cover the South part of the country. A total of 35 elements (Na, Mg, Al, Cl, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Cu, Cd, Ni, Zn, As, Br, Se, Rb, Sr, Sb, Cs, Ba, La, Ce, Sm, Eu, Tb, Pb, Hf, Ta, Th, and U) were determined by instrumental epithermal neutron activation analysis and atomic absorption spectrometry. To discover associations of chemical elements and decrease the number of variables for the obtained data factor analysis was used. The ArcGIS software (Esri, Redlands, CA, USA) was used to build maps showing the spatial distributions of elements using the radial basis functions method.

Results and discussion

The values obtained for 11 elements, reported to ICP vegetation, in 2020 were compared with data from the previous sampling campaign (Fig. 1). According to the Wilcoxon test, significant differences ($p < 0.05$) between the median values were revealed for more than half of the elements, namely Cr, As, Sb, Cd, Pb, and Cu. At the same time, it should be mentioned that the mean values for all elements were lower in 2020, except Zn, the content of which slightly increased in 2020. The most significant decrease was observed for Pb and Cd. The median concentrations of these metals were reduced by 75% and 66%, respectively. The concentrations of Cu declined by 43% and of V and Cr by 31% for both elements. The content of Al, Fe, Ni, As, and Sb decreased by less than 30%, while the content of Zn increased by 8.9% [2].

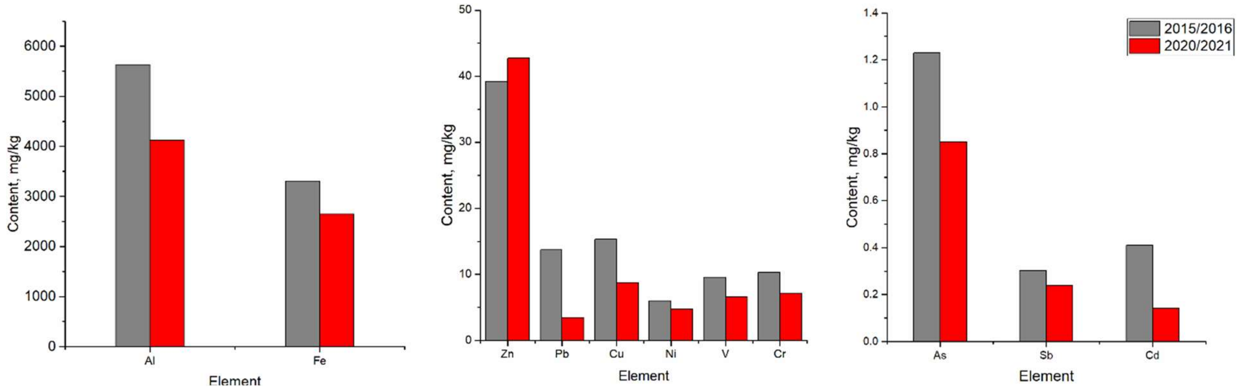

Figure1. Comparison of the results from the 2020/2022 survey with values from the 2015/2016 moss survey [2].

Factor analysis was applied to provide a multivariate view of the distribution of the elements and to reveal the origin of pollution sources for the elements of interest. Four factors were identified, including 84% of the variability of the treated elements (Fig. 2).

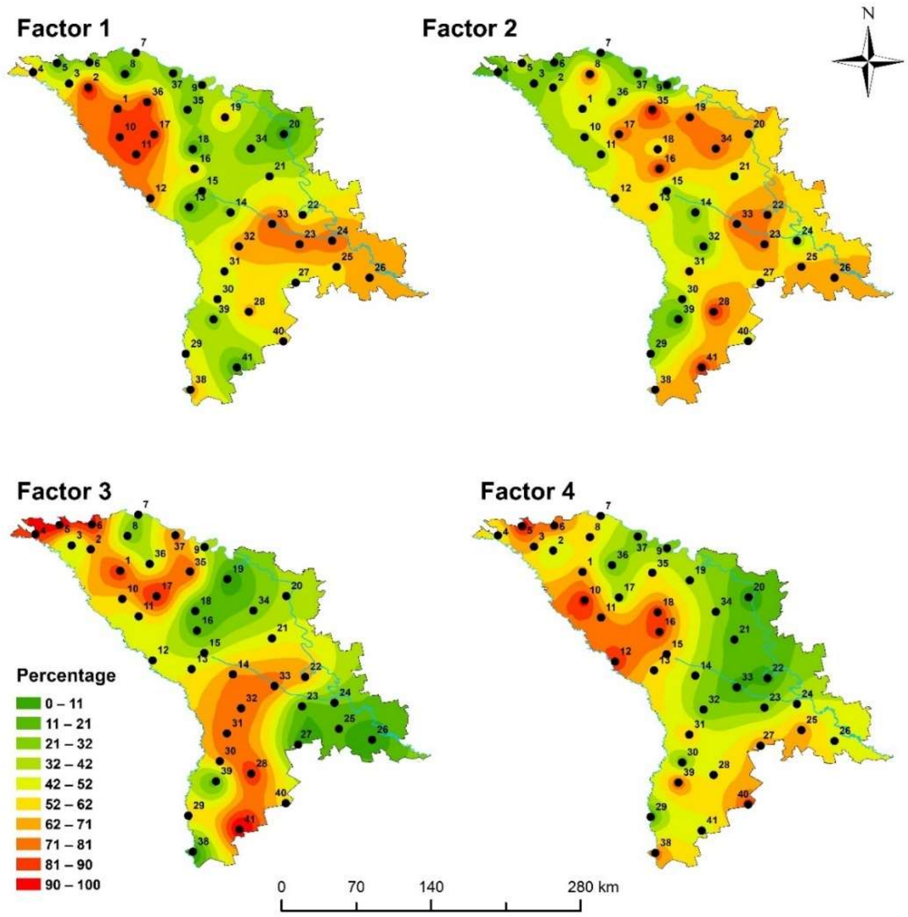

Figure 2. Map showing spatial distributions of Factors 1–4. (Note: Black dots on the map are the sampling sites) [3].

Factor 1 (Na-Al-Sc-Ti-Cr-Fe-Co-Ni-As-Rb-Sb-Cs-Th-U) is the strongest factor representing 47% of the total variability. The presence of Al, Sc, Ti, and Th in this group confirms the terrigenous origin of these elements. Since Moldova is characterized by a dry climate with a low amount of precipitation, moss contamination with windblown dust and mineral particles takes place due to soil erosion. At the same time, elements such as Cr, Ni, and As can have an anthropogenic origin. The highest values of the factor scores in the Balti and Chisinau areas confirm this assumption. With factor 2 (contribution 14%) are associated the elements Mg, Ca, and Sr. The main source of these elements may be mining activities. Factor 3 is the third strongest factor, with 12% of the total variability and associated elements Cl, K, Br, and Cu, suggesting inputs by agricultural activities. Factor 4 (Zn-Sb-Cd-Pb) is anthropogenic and represents 11% of the total variability of the dataset. It includes elements that are considered indicators of emission from fossil fuel combustion processes, including vehicle exhaust [3].

Conclusions

During the second moss survey study in Moldova, the mass fractions of 35 elements were determined using NAA and AAS. The mass fractions of the determined elements varied in a wide range and the highest concentrations were determined in urban areas, mainly in Chisinau and Balti. Comparison of the obtained data with the results of the 2015 moss survey showed a significant decrease in Cr, As, Sb, Cd, Pb, and Cu content.

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Russian Federation - Kaliningrad region

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Background

Kaliningrad region is the westernmost territory of Russia, located on the southeastern coast of the Baltic Sea. The region borders Poland to the south and Lithuania to the north and east. A humid continental climate, with cold, cloudy winters and mild summers with frequent showers and thunderstorms, with huge temperature differences between July and January [1], as well as westerly winds and Baltic Sea marine aerosol dominate the climate in the region and determine the atmospheric transport and deposition of trace elements.

The first joint expedition of scientists of Kaliningrad State University and representatives of the European project ICP-vegetation took place in 1994. About 30 samples of mosses were taken, in which the content of Cu, Pb, Cd, V, Ni, Cr, Fe and Zn was determined by atomic absorption spectroscopy at the University of Lund, Sweden [2].

The regional monitoring network had more than 100 sampling sites in 2000 year. Later, the network was significantly adjusted. Currently, the network consists of 33 sampling sites, which is 2.5 moss samples/1000 km^2. Mosses were sampled in plots of 50 by 50 m, using the recommended method. The total sample volume is approximately one liter, although less is allowed in case of low moss coverage of the plot. Two species of mosses were used in the study: *P. schreberi, H. splendens.*

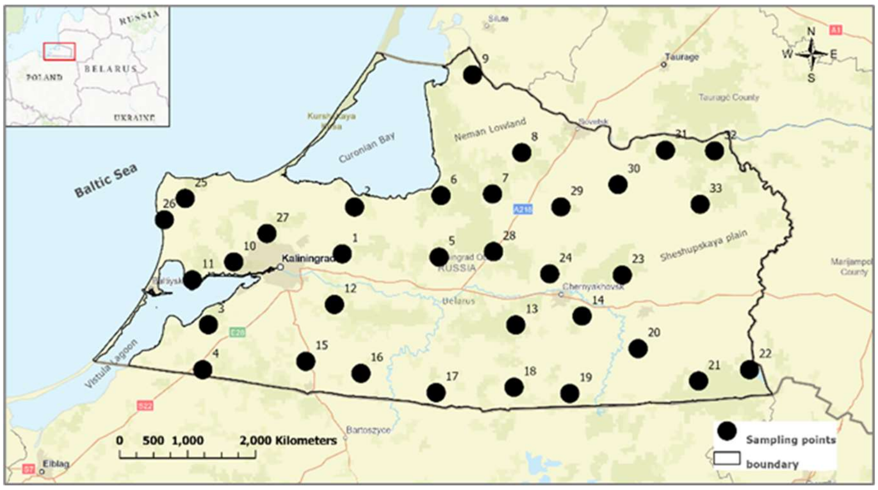

Figure 16. Map of the study area.

Results and conclusion

In 2015, 2020 the content of 33 elements (K, Na, Rb, Cs, Mg, Ca, Sr, Ba, Cl, Br, I, Al, Sc, Ti, V, Cr, Mn, W, La, Ce, Sm, Tb, Yb, Hf, Ta, Th, U, As, Sb, Se, Zn, Fe, Co, Ni, Mo) were determined by epithermal neutron activation analysis (ENAA) at the IBR-2 pulsed fast reactor FLNP JINR Dubna, Russia [3].

In most cases, some increase in the accumulation of metal pollutants by mosses is obvious. While the overall trend of heavy metals increased from 2015 to 2020, the amount of arsenic in mosses decreased. The content of such elements as W, Sb, and other elements, not shown on the diagram in mosses, remains practically unchanged (within the margin of error).

The diagrams of the concentration (median) of some metals for the period from 2015 to 2020 are presented in the figure 2.

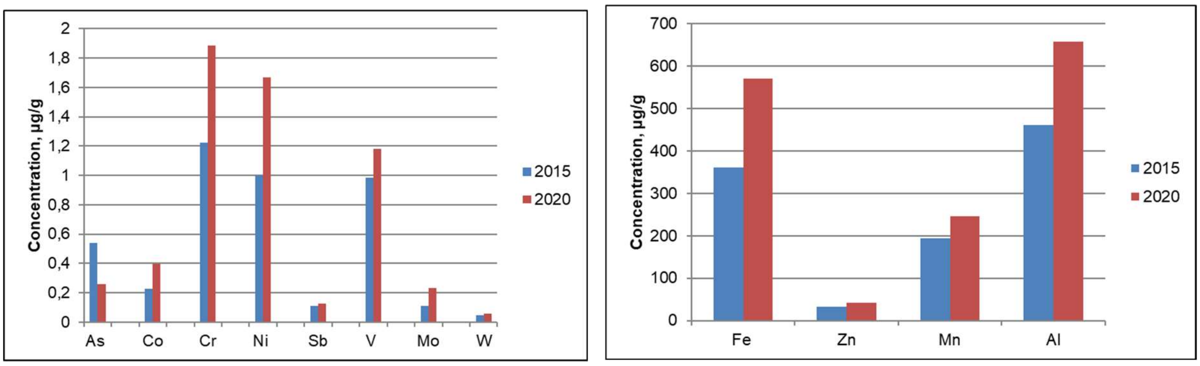

Figure 2. Temporal trend of concentration (µg/g) of 12 metals in mosses collected in Kaliningrad region in 2015 and 2020.

The spatial interpolation was conducted using The Empirical Bayesian kriging regression prediction (EBKRP) interpolation available in the ArcGIS® Geostatistical Analyst toolbar. The distribution of elements on the territory of the region is mainly related to the peculiarities of wind transport, as the south-western transport prevails, so there is a tendency to stretch the distribution areas towards the continent.

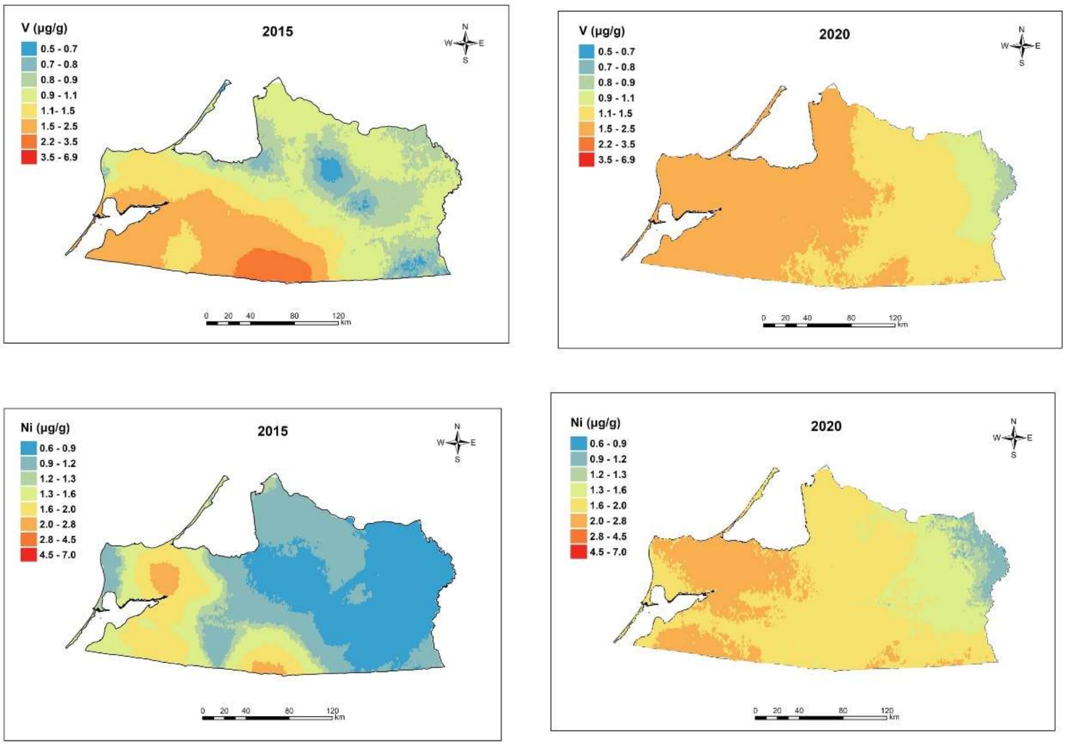

Figure 3. Spatial distribution of vanadium and nickel in Kaliningrad region in 2015, 2020.

For the region of strong cyclonic activity, with a high frequency of westerly air-mass trajectories, atmospheric transport is of great importance. In winter, the western and south-western directions of atmospheric transport prevail, while the summer mainly enjoys the north-western and southern wind currents. Western and southern cyclones causing rainy weather contribute to the deposition of pollutants into the region’s territory. Airborne transport with deposition plays a dominant role.

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Serbia

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Background

Serbia has participated in European moss survey – 2020. In this campaign, a moss species – *Hypnum cupressiforme* Hedw. was collected over the territory of country at 182 sampling sites. The samples were collected following all procedures described in Moss sampling manual 2020. After that, the moss samples were analysed to the content of 21 macro and microelements, and 18 rare earth elements by inductively coupled plasma optical emission spectrometry (ICP-OES) and inductively coupled plasma mass spectrometry (ICP-MS).

Spatial patterns and temporal trends of element concentrations in moss

Descriptive statistic of the selected element concentrations in the moss over the 5-year 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. Considering 2020 vs. 2000, the median concentration decreased from 40 to 80% depends on the element, specifically: Al (80.6%), As (45%), Cr (58.6%), Cu (68.7%), Fe (66.2%), V (72.7%), Zn (68.1%); and Pb (76.6%) compared to 2005. The only element which concentrations remains the same through the time is Cd. Comparing the result of two last campaigns (2020 vs. 2015), in which the same analytical conditions and techniques were used, the median concentrations of the elements also follow a decreasing pattern for Cr (41.6), Cu (39.4%), Fe (21.7%), Pb (9.5%) and Zn (53.6%) while stay about the same level for As and V. The spatial distribution of the potentially toxic element concentrations in the moss across Serbia in 2020 is presented in Figure 1.

Table 1. Element concentrations (μg g^{-1}) in moss *H. cupressiforme* in Serbia in 2000, 2005, 2015 and 2020 campaigns.

		Al	As	Cd	Cr	Cu	Fe	Ni	Pb	Sb	V	Zn
2020	Min	0.86	0.011	0.008	0.0014	0.002	0.2	/	0.002	/	0.0083	3.8
n=182	Max	12356	4.601	1.508	22.769	121.2	9913	/	18.2	/	21.78	86.6
	Median	**1069**	**0.793**	**0.223**	**2.1112**	**5.3**	**798**	/	**3.9**	/	**2.53**	**10.4**
2015	Min	358	0.164	0.050	0.024	3.25	275	0.62	0.36	0.017	0.91	8.3
n=212	Max	11000	71.086	0.988	60.847	213.24	10119	90.61	459.68	2.195	21.49	115.2
	Median	**1021**	**0.732**	**0.182**	**3.647**	**8.75**	**1019**	**3.12**	**4.31**	**0.078**	**2.72**	**22.4**
2005	Min	1117	0.22	0.04	1	3.04	670	0.8	1.03	0.06	1.9	13
n=193	Max	31180	21.6	1.11	78.8	451	16100	23.8	248.6	1.37	32.7	259
	Median	**3946**	**1.41**	**0.26**	**6.44**	**11.1**	**2267**	**4.43**	**16.7**	**0.24**	**5.76**	**29**
2000	Min	1280	0.46	/	1.14	6.31	720	1.96	/	/	2.85	14
n=92	Max	22100	60.8	/	21.9	3140	9220	25.7	/	/	38.7	415
	Median	**5525**	**1.44**	/	**5.07**	**16.9**	**2360**	**5.65**	/	/	**9.26**	**32.6**

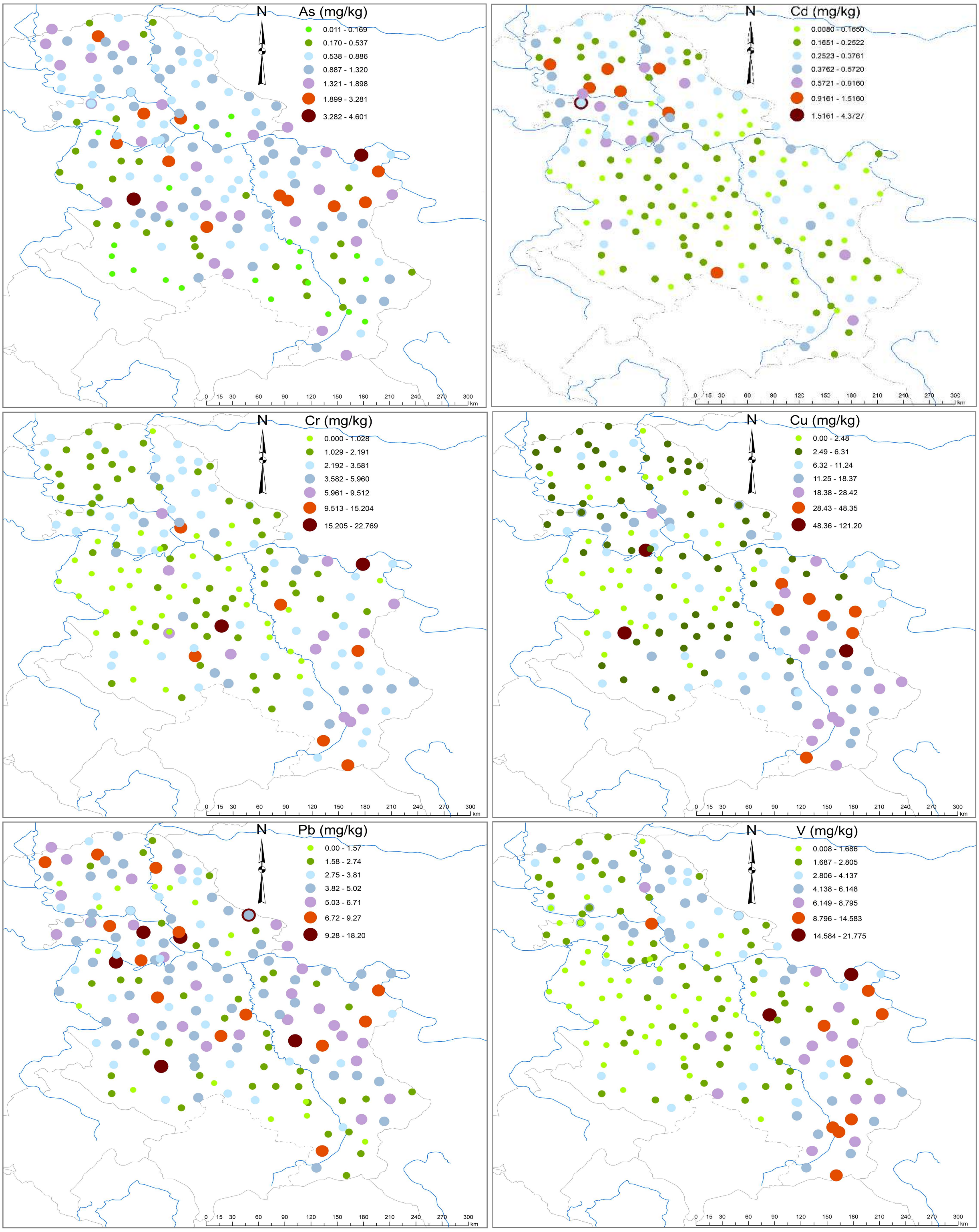

Figure 1. The mean element (As, Cd, Cr, Cu, V, Pb) concentration (μg g^{-1}) in moss *H. cupressiforme* across Serbia in 2020.

Slovakia

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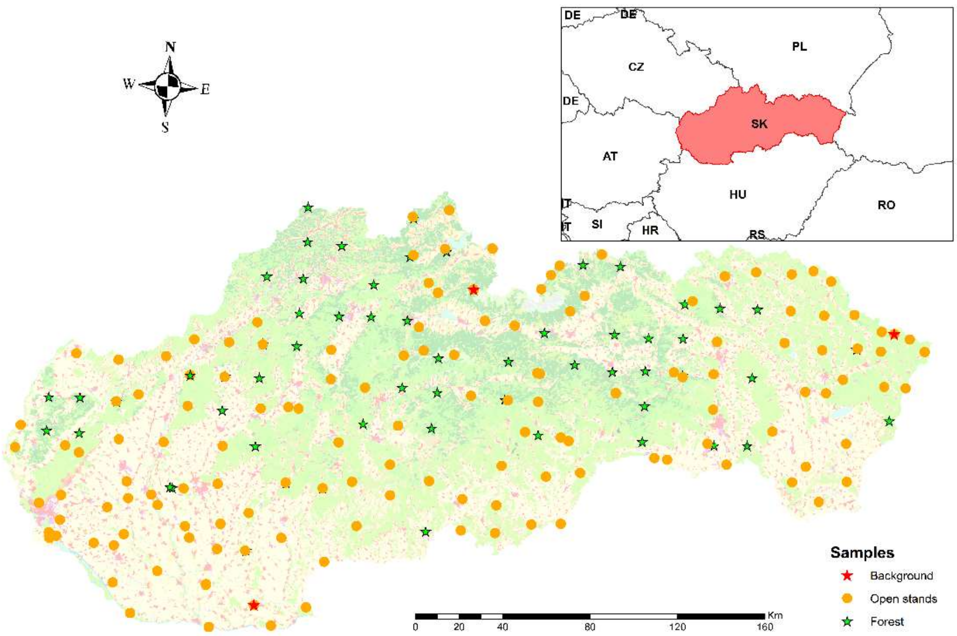
Background

The Slovak Republic is an inland country located in the central Europe. The total area of the country is 49 035 km^2 of which lowlands (below 300 m) cover 40 %, low mountains (301 – 800 m) 45%, middle mountains (801 – 1,500 m) 14% and high mountains (above 1,500 m) 1% (Michaeli, 2015). Forests cover 41.1 % and agricultural areas cover 48.4 % of Slovakia (Statistical Office of SR). The georelief of the country is very heterogenous.

Environmental studies using bryophytes (mosses) for biomonitoring of changes in atmospheric deposition of heavy metals in Slovakia started in 1990. The basic grid of monitoring sites was arranged according to a national forest monitoring program (ICP Forest Slovakia) in a 16x16 kilometer grid. Until the last survey, only forest sites were studied. In the 2020-2023 survey, new sampling sites were added to (1) cover the whole territory of the country, (2) comply with location requirements, and (3) monitor the vicinity of main pollution sources. Finally, we collected and analysed moss samples from 201 sites: 142 open sites and 59 forest sites (Map 1). Sampling sites cover localities with high potential of heavy metal exposure as well as background localities. Predominant moss species were from the genus *Pleurozium, Hylocomium, Hypnum* and *Dicranum*.



Map 1: Map of Slovakia with moss sampling sites:
green star – forest site, orange dot – open site, red star – background site

Methods

Moss samples were collected according to a standardized protocol (Frontasyeva et al., 2020). Only pleurocarpous moss species were collected. In the 2020-2023 survey, 142 new sampling sites were added. From open sites were selected background localities. A distance filter was applied and finally 3 background sites were selected. Not one, but three ones to provide stronger statistical representation. The background localities are presumably the less affected by human activities. None of the selected areas are completely “pure” nowadays and no prior data from these sites exist.

Collected mosses were analysed by EA-TCD (N, C, S), AES-ICP (Al, P, Ca, Mg, K, Na, Fe, Mn, Zn, B, Cu), AES-ICP-U (As, Cr, Co, Cd, Ni, Pb) and by AAS-AMA (Hg) techniques in a laboratory of the National Forestry Centre in Zvolen, Slovakia.

Pollution load index (PLI), developed by Tomlinson et al. (1980) and Cabrera et al. (1999), can directly reflect the contribution of selected metals to environmental pollution and their variation or trend in time and space. Two different PLIs have been proposed by Tomlinson et al. (1980), namely, zone PLI (PLIzone) and site PLI (PLIsite). According to Zhang et al. (2011) the PLI values were divided into multiple levels as follows:
PI1 = (PLI> 0-1) No pollution
PI2 = (PI1>1-2) Moderate to no pollution;
PI3 = (PI1>2-3) Moderate pollution;
PI4 = (PI1>3-4) Moderate to high pollution;
PI5 = (PI1>4-5) High pollution
PI6 = (PI1>5) Extreme pollution.

Results

Forest sites and trends

Since 1990 were monitored following heavy metals on the ICP Forest sites: Al, As, Cd, Cr, Cu, Fe, Hg, Ni, Pb, Zn. The results of statistical analysis for these element concentrations in moss samples are presented in Figure 1.

Comparing the median values from 1990, respectively from 2000 for Al and 1995 for Hg, to median values from 2020-2023 survey the metal concentration in moss samples follow the declining trend: Pb (89.87%) > Cd (86.32%) > Zn (80.81%) > Al (78.59%) > Hg (70.80%) > Fe (63.45%) > Cu (60.10%) > Cr (50.48%) > As (38.17%) > Ni (17.82%).

Comparing lead concentrations from 1990 to 2020/23 survey a prominent decline is seen from max 359.00 $mg.kg^{-1}$ in 1990 to max 16.27 $mg.kg^{-1}$ in 2020/23. The median value dropped from 40.85 $mg.kg^{-1}$ to 4.14 $mg.kg^{-1}$. Cadmium concentration declined from max 5.70 $mg.kg^{-1}$ in 1990 to max 0.65 $mg.kg^{-1}$ with median values declined from 1.36 $mg.kg^{-1}$ to 0.19 $mg.kg^{-1}$. Zinc concentration declined from max 353.00 $mg.kg^{-1}$ in 1990 to 61.24 $mg.kg^{-1}$ in 2020/23 and median value declined from 162.50 $mg.kg^{-1}$ in 1990 to current 31.18 $mg.kg^{-1}$. Aluminium has been measured in mosses since 2000 and declined from max 17.4K $mg.kg^{-1}$ to 2470.00 $mg.kg^{-1}$ and median from 9760.00 $mg.kg^{-1}$ to 529.02 $mg.kg^{-1}$. Chromium max concentration declined from 30.60 $mg.kg^{-1}$

in 1990 to 13.90 mg.kg^{-1} and median values from 3.55 mg.kg^{-1} to 1.76 mg.kg^{-1}. Concentration of iron and nickel did not have the stable decline trend. The max concentration of iron in 2020/23 is higher (8460.00 mg.kg^{-1}) than in 1990 (5778.00 mg.kg^{-1}), but the median value is lower (568.18 mg.kg^{-1}) in 2020/23 than in 1990 (1554.50 mg.kg^{-1}). Similar trend is for nickel. Max in current survey is higher (10.20 mg.kg^{-1}) than in 1990 (6.30 mg.kg^{-1}) with total max in 2005 (59.72 mg.kg^{-1}). The current median value is 1.40 mg.kg^{-1}. Arsenic concentrations were measured in 2000, 2015 and 2020/23 surveys. The median values proved the declining trend from 0.71 mg.kg^{-1} to 0.44 mg.kg^{-1}.

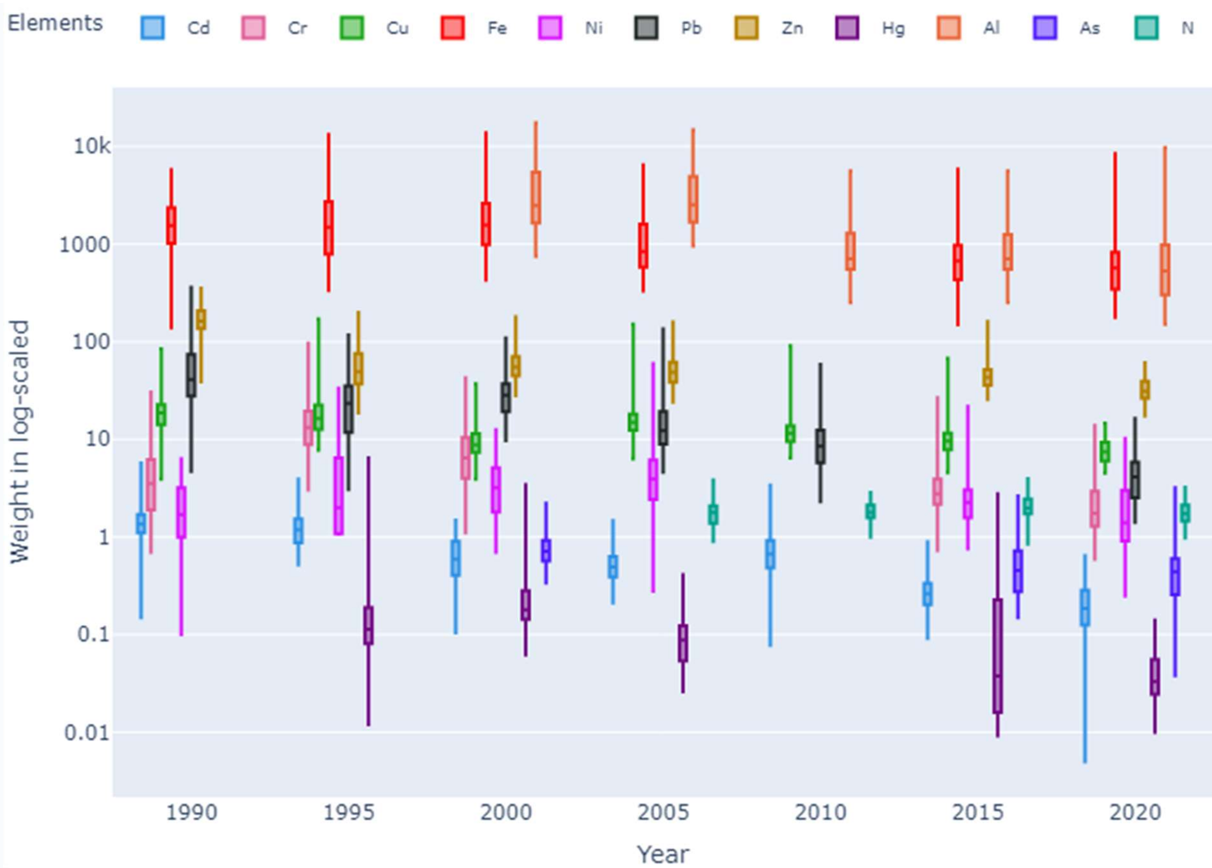


Figure 1: Boxplot showing the natural logarithm of all measured element concentrations

According to Frontasyeva et al. (2020) Slovakia, along with Czech Republic and France, had the highest levels of mercury in mosses in 2015 survey. The maximum concentration of Hg in Slovakia in 2015 survey was 2,76 mg.kg^{-1} and in 2020/23 survey 0,14 mg.kg^{-1} with median 0,03 mg.kg^{-1}. Since 1995 mercury concentrations in moss samples in Slovakia have declining trend (70.80%). Also copper concentrations in mosses belonged among the highest, despite of declining trend from maximum 171.21 mg.kg^{-1} in 1995 to current maximum 14.63 mg.kg^{-1} and median 7,422 mg.kg^{-1}.

In Slovakia, there were always reported high nitrogen concentrations in mosses. Nitrogen is an essential macronutrient. According to Harmens et al. (2011) and Schröder et al. (2010) there is a natural background concentration of nitrogen in mosses about 0.5%. In Slovakia the nitrogen concentration in mosses has been monitored since 2005 and the median values were from 1.74 to 1.79 %. The nitrogen concentration in mosses are stable.

Open sites and background sites

In the last survey 2020/23, 142 new sampling sites were added to comply with the manual requirements and to include background localities. To select new sampling sites distance from towns, villages, roads, railways, agricultural fields etc. were taken into consideration. The results are presented in a figure 2, where is a comparison of open sites to background sites.

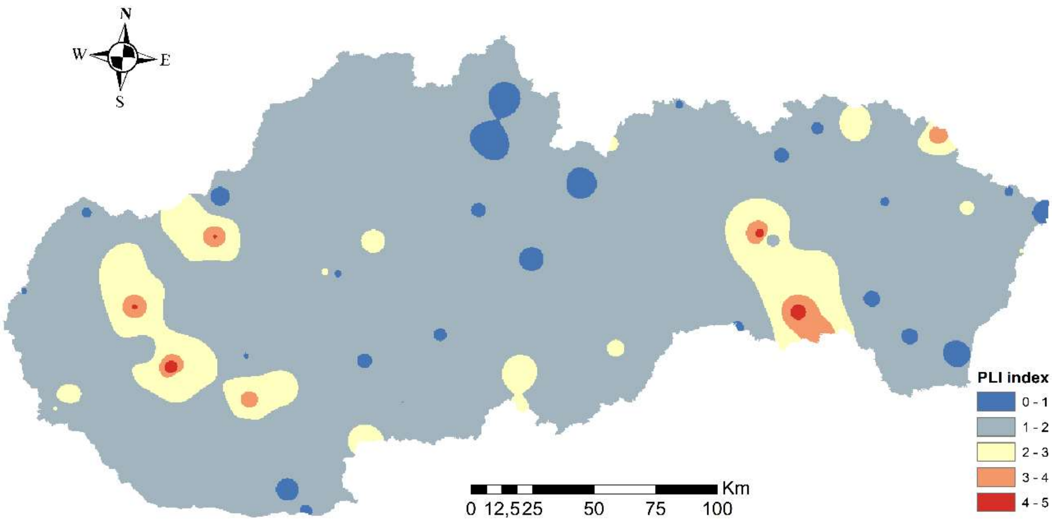
Figure 2: Boxplots comparing element concentrations in background and open sites.

The median concentrations of measured elements in mosses from open sites comparing to background sites are following: aluminium (1150.55 $mg.kg^{-1}$ / 465.24 $mg.kg^{-1}$) – iron (863.46 $mg.kg^{-1}$ / 302.87 $mg.kg^{-1}$) – zinc (31.10 $mg.kg^{-1}$ / 18.11 $mg.kg^{-1}$) – copper (5.80 $mg.kg^{-1}$ / 3.91 $mg.kg^{-1}$) – chromium (4.23 $mg.kg^{-1}$ / 0.87 $mg.kg^{-1}$) – nickel (3.28 $mg.kg^{-1}$ / 1.20 $mg.kg^{-1}$) – lead (2.42 $mg.kg^{-1}$ / 1.99 $mg.kg^{-1}$) – arsenic (0.49 $mg.kg^{-1}$ / 0.33 $mg.kg^{-1}$) – cadmium (0.22 $mg.kg^{-1}$ / 0.15 $mg.kg^{-1}$) – mercury (0.024 $mg.kg^{-1}$ / 0.015 $mg.kg^{-1}$). The median nitrogen concentration for open sites was 1.67 % and for background localities 1.35 %. The minimum measured nitrogen concentration was 0.94 % that is still too high comparing to natural background concentration of nitrogen (0.50 %).

Conclusion and discussion

Since 1990, the metal concentration in mosses in the ICP Forest sites has declined the most for lead (89.87%), cadmium (86.32%), zinc (80.81%), aluminium (78.59%), mercury (70.80%), iron (63.45%), copper (60.10%), chromium (50.48%), arsenic (38.17%), and nickel (17.82%). The nitrogen concentration in mosses are stable (1.74 - 1.79 %), but too high above its natural background concentration in mosses (approx. 0.50%).

Mosses from open sites were collected and analysed within the survey 2020/23 for the first time. Comparing the median values of the open sites versus background localities revealed that the highest difference is for chromium (79.41 %), following with iron (64.93 %) – nickel (63.29 %) – aluminium (59.56 %) – zinc (41.78 %) – mercury (37.50 %) – arsenic (33.61 %) – cadmium (32.74 %) – copper (32.61 %) – lead (17.83 %). The difference between the median value for open sites to the median value for background sites was 19.41 %.



Map 2: Spatial distribution map of the Pollution Load Index (PLI) in Slovakia

According to the Pollution Load Index (PLI), Slovakia generally experiences moderate to no pollution (PLI = 1.45). There are several hotspots with moderate to high pollution levels (Map 2). In the eastern part of the country, the highest PLI is in the Košice region - a centre of metallurgy and steel production with many related companies. The next highly polluted area is the Spiš – Gemer region where mining activities started in the 14th century. There are many pits for nonferrous ores, mainly magnesite, limestone with associated processing factories and a copper refined factory. In the western part of the country, the highest PLI is in the area of a large and important fertilizer producer. Next high PLI is in the Trnava region with dominant glass fibre production and automotive industry.

For protection of the environment and human health, monitoring of heavy meals and trace elements at atmospheric deposition via bryophytes should continue also in the next international moss survey.

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Spain (La Rioja)

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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 between 2006 and 2018, using samples of the same species collected in 25 stations belonging to La Rioja and neighbouring provinces (Figure 1, Table 1). 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. The five elements regulated by European Directives (As, Cd, Hg, Ni and Pb) were measured in the period 2006-2018, and the 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 (δ^{15}N) were also measured and incorporated to the European survey. In 2016, different variables were incorporated to the 2015-16 ICP-Vegetation report:

42 elements, together with radionuclides, mostly in collaboration with the Joint Institute for Nuclear Research at Dubna (Russian Federation), under the coordination of Dr. Marina Frontasyeva. Nitrogen and the nitrogen isotopic ratio δ^{15}N. The 16 polycyclic aromatic hydrocarbons controlled by the U.S. Environmental Protection Agency (EPA).

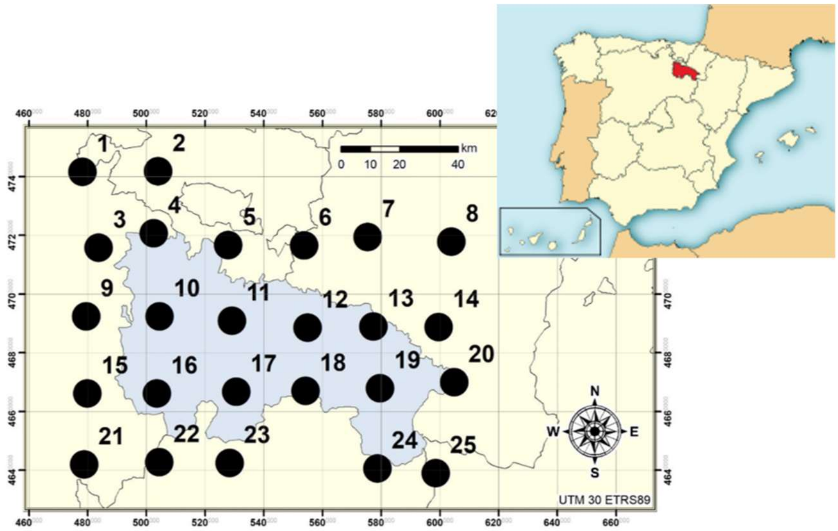

Figure 1. Situation of the 25 sampling points used in the 2018 moss survey in La Rioja and neighbouring provinces (north-central Spain).

In 2018 we performed our last survey, which was not further continued due to lack of funding. For five elements (As, Cd, Hg, Ni, and Pb), the 2018 survey was conducted using the same set of localities as in previous surveys, whereas we used only five localities (11, 12, 13, 19, and 20) for N, $\delta^{15}N$, and 18 PAHs.

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.

Results

Results are shown in Tables 2-4. As, Ni, and Pb contents slightly increased in 2018 in relation with previous surveys, whereas Cd decreased and Hg remained stable. N, $\delta^{15}N$, and PAHs showed similar values to other previous surveys, showing that the pollution due to these agents is very low or inexistent in our territory.

Table 1. Location of the 25 sampling points used for the 2018 survey in La Rioja and neighbouring provinces (northern Spain). UTM locations are referred to European Datum 1950 (ED 50).

Sampling point	UTM 30T (X,Y)*		Nearest locality and province
1	478.17	4741.76	Las Viadas (Burgos)
2	504.00	4741.98	Escota (Álava)
3	483.69	4715.93	Vallarta de Bureba (Burgos)
4	502.44	4720.85	Galbárruli (La Rioja)
5	527.87	4716.75	Pipaón (Álava)
6	553.74	4716.63	Azuelo (Navarra)
7	575.37	4719.48	Ázqueta (Navarra)
8	603.92	4717.92	Artajona (Navarra)
9	479.50	4692.46	Puras de Villafranca (Burgos)
10	504.46	4692.46	Santurdejo (La Rioja)
11	529.16	4691.02	Santa Coloma (La Rioja)
12	554.90	4688.62	Ribafrecha (La Rioja)
13	577.37	4689.06	Pradejón (La Rioja)
14	599.58	4688.82	Peralta (Navarra)
15	479.85	4666.26	Barbadillo del Pez (Burgos)
16	503.57	4666.27	Mansilla de la Sierra (La Rioja)
17	530.91	4666.76	Aldeanueva de Cameros (La Rioja)
18	555.42	4670.47	Zarzosa (La Rioja)
19	579.60	4668.00	Villarroya (La Rioja)
20	604.88	4670.09	Alfaro (La Rioja)
21	478.83	4642.06	Cabezón de la Sierra (Burgos)
22	504.40	4642.77	Duruelo de la Sierra (Soria)
23	528.38	4642.56	El Royo (Soria)
24	578.68	4640.63	Castilruiz (Soria)
25	598.57	4639.07	Torrellas (Zaragoza)

Table 2. Results of the 2018 survey in the 25 localities studied (see Table 1).

	As (ng g^{-1})	Cd (ng g^{-1})	Hg (ng g^{-1})	Ni (µg g^{-1})	Pb (µg g^{-1})
1	234	64	30	0.6	1.11
2	288	109	39	0.7	0.97
3	624	63	24	1.0	1.03
4	353	59	27	0.8	1.22
5	262	65	21	0.7	1.15
6	235	84	23	0.7	1.13
7	281	59	24	1.0	0.99
8	262	51	22	0.8	1.01
9	218	54	18	0.5	0.84
10	241	104	31	1.0	1.19
11	293	115	30	1.4	1.79
12	217	43	22	0.7	0.97
13	315	44	22	0.9	1.39
14	390	47	25	0.9	1.10
15	250	74	40	1.6	3.27
16	437	49	19	1.3	2.11
17	889	92	41	2.1	3.39
18	235	64	29	1.8	1.67
19	276	43	22	0.9	1.32
20	887	71	29	1.8	1.70
21	335	74	25	1.6	2.62
22	395	103	29	1.4	1.86
23	269	105	33	2.9	1.52
24	766	34	28	1.4	1.40
25	349	40	30	1.2	1.57
Min	217	34	18	0.5	0.84
Max	889	115	41	3.0	3.40
Median	288	64	27	1.0	1.32
Mean	372	68	27	1.2	1.53

Table 3. N contents and $\delta^{15}N$ values.

	N (%)	$\delta^{15}N$ (‰)
11	0.9	-7.2
12	0.8	-7.0
13	0.8	-6.5
19	0.7	-7.1
20	1.5	-4.4

Table 4. Contents (ng g^{-1}) of 18 PAHs in five localities (11, 12, 13, 19, and 20) in 2018. No value means that the content was below the limit of quantification. The sum of the 16 PAHs considered by EPA (*) is shown.

	11	12	13	19	20
Naphthalene*	-	-	-	-	-
Acenaphthylene*	-	-	-	-	-
Acenaphthene*	5.3	7.4	7.5	5.7	9.8
Fluorene*	9.2	13	11.4	10	14.8
Phenanthrene*	13.9	20	18.3	12.4	22.7
Anthracene*	-	-	1.6	1.4	1.2
Fluoranthene*	5	5.9	8.1	3.7	4.8
Pyrene*	8.5	10.8	10.8	4.4	6.7
Rethene	1.2	1.1	0.8	1.9	1.5
Benzo(a)anthracene*	-	-	-	-	0.3
Chrysene*	1.6	1.3	4.4	1	1.2
Benzo(b+j)fluoranthene*	2.4	1.1	9	0.9	1.6
Benzo(k)fluoranthene*	-	-	2.2	-	0.7
Benzo(e)pyrene	1.7	0.9	4.9	0.9	1.2
Benzo(a)pyrene*	0.8	0.7	4.2	0.9	1.2
Dibenzo(a.h)anthracene*	-	-	-	-	-
Indeno(1.2.3-cd)pyrene*	0.2	0.6	0.9	1.1	0.9
Benzo(ghi)perylene*	-	0.8	-	1	1.4
EPA sum	49	63	83	43	69

Switzerland

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Background

Until the end of 1980s, small industries situated in Switzerland, particularly those involved in ferrous metallurgy in Southern Switzerland, were significant sources for heavy metal emissions. Additionally, 28 incineration plants contributed to these emissions (especially for Cd) and Hg was emitted by several crematoria. Leaded petrol was the primary source for Pb. However, today, all these facilities have either been closed or equipped with filters and leaded petrol was banned in Switzerland in 2000. Switzerland has been participating in all the sampling periods of the European moss survey for heavy metals since 1990. In 2015 the number of sites was reduced to 73 from the original 242 sites in 1990. This change, however, did not result in any fundamental changes in conclusions drawn from the results. In 2020, these 73 sites were again sampled for heavy metals, and in addition, nitrogen and Persistent Organic Pollutants (POP) were analysed at 55 and 22 sites, respectively. Due to the different geographical regions and the corresponding differences for example in weather conditions, elevation, population densities and likelihood for transboundary pollution, the Swiss sampling sites are covering all geographical regions (J=Jura, P=Plateau, NA=Northern Alps, CA=Central Alps, SA=Southern Alps).

Heavy metal concentrations in mosses

Figure 2 shows the temporal trends (normalized to 1990) of all metals measured in Swiss samples 2020. Many of the considered elements have decreased since 1990, most remarkably Pb (decrease of 93%). Ba, Cs, Cu, Se, Sr and U show no constant change over time and Al, Co Mo and Fe seem to stagnate since 1995. When comparing the heavy metal concentrations for Cd, Hg and Pb in moss with the available emission data the data sets follow the same pattern (Figure 3). However, the decrease in moss is less pronounced, probably because of re-emission of already deposited heavy metals as well as transboundary pollution.

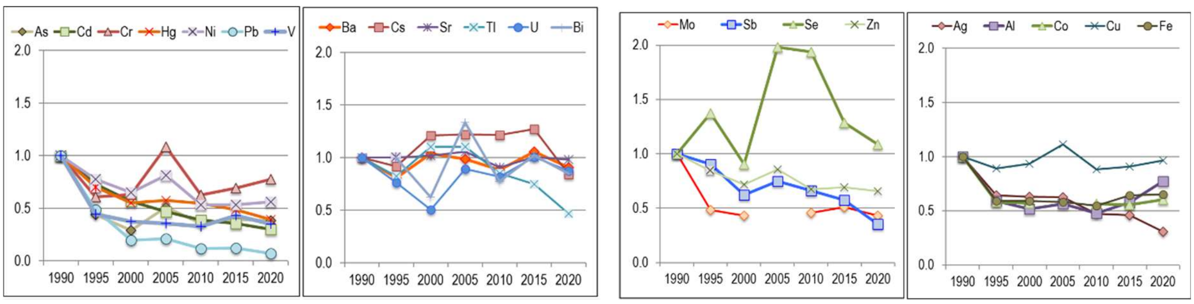

Figure 2. The Temporal trends of 22 elements, normalised to 1990

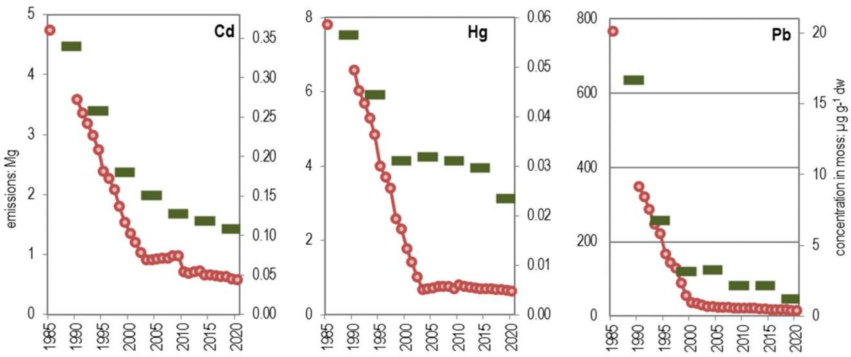

Figure 3. Cd, Hg and Pb concentrations in moss compared with the emission.

Red dots represent emissions, concentration in moss are indicated with green bars.

Nitrogen concentration in moss

Figure 4 shows the nitrogen concentration in moss in the 5 regions in Switzerland in 2010 -2020. In accordance with the other analysed elements, the highest nitrogen level was found in southern Switzerland. A good correlation could be found when the nitrogen concentration in moss is compared with the bulk deposition of nitrogen measured at nearby sampling stations (Figure 5).

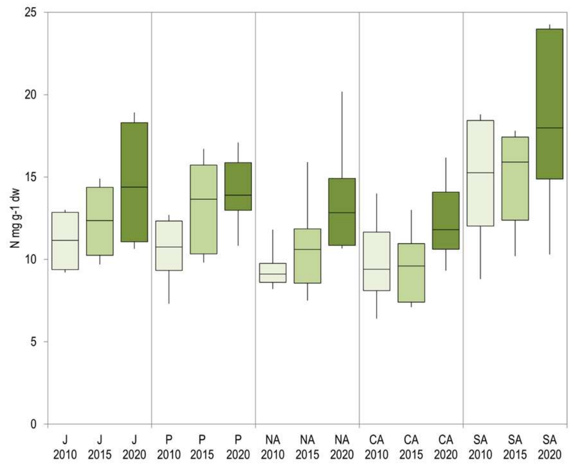

Figure 4. Boxplots of nitrogen concentration in moss in the 5 regions of Switzerland in 2010-2020 (only sites measured in all three periods)

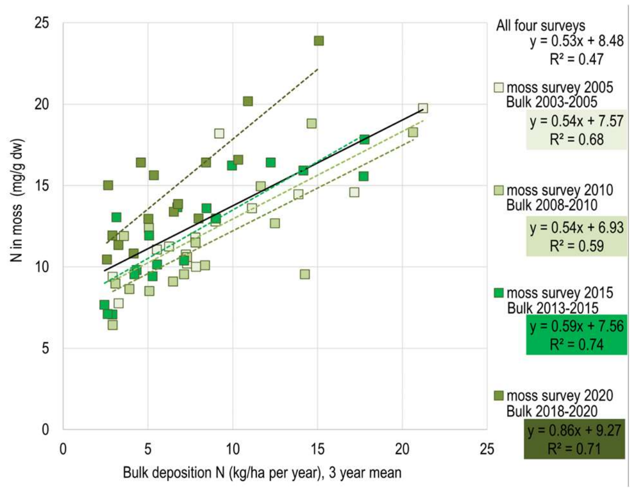

Figure 5. Nitrogen concentration in moss compared to bulk deposition of nitrogen

Persistent organic pollutants

Most of the PAH were below limit of quantification (LOQ) but above limit of determination (LOD). A summary of all the results for PAH concentrations in moss is shown in Figure 6 (>LOD). The results indicate, that a) the PAH deposition varies between sampling sites and b) the concentration in moss has decreased over time at most of the sites but not to the same extent at each site. Phenanthrene was above LOQ at all sampling sites and was together with naphthalene the most dominant PAH. The distribution of the different PAH varies between the sampling sites.

The concentrations for the different PCB congeners were mostly below LOQ or even LOD.

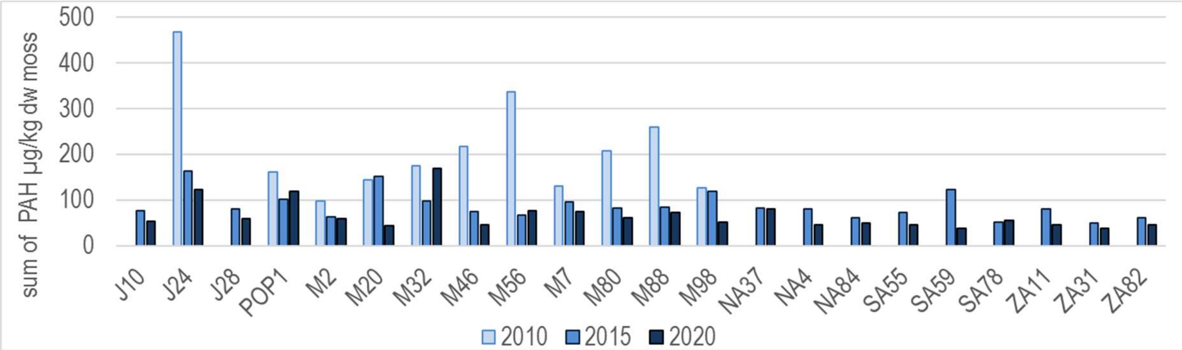

Figure 6. Sum of all measured PAH for each sampling site in each period measured.

Conclusions

The study once again demonstrates that the relatively inexpensive moss method is a suitable tool for assessing regional variations and temporal changes in the deposition of various pollutants, including heavy metals, POPs and nitrogen. This method allows for monitoring human impacts on the environment and documenting the effectiveness of emission-reduction measures over time.

United Kingdom

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Methods

Moss samples were collected from 124 sites across the UK and analysed for content of metals, nitrogen and microplastics. Moss material was dried at 30°C. Acid-digestion of milled samples was performed in a microwave oven. The metal concentrations were determined by Inductively Coupled Plasma Mass Spectrometry (ICP-MS).

A novel technique was developed for analysis of microplastics from moss samples. Moss samples of 10 g were flushed at high flow rate, with a downstream stainless steel 5 µm filter onto which displaced microplastics were captured. The material captured on the stainless-steel filter was then further cleaned through oxidation by Fenton's reactions before deposition on silver filters for analysis. Analysis of the extracted microplastics used µ-FTIR spectrometry using a pixel size of 25 µm.

Automated spectral matching of the raw data was performed using the Purency Microplastics Finder software to identify 21 common polymers: polypropylene, polyethylene, polyvinylchloride, polyurethane, polyethylene terephthalate, polystyrene, acrylonitrile butadiene styrene, polyamide, polycarbonate, poly(methyl methacrylate), polyoxymethylene, cellulose acetate, ethylene-vinyl-acetate copolymer, ethylene vinyl alcohol, polyacrylonitrile, polybutylene terephthalate, polyether ether ketone, polyphenylsulfone, polysulfone, silicone and polylactic acid.

Results

The focus was on rural sites in order to assess the input from long-range sources. For the metals that will contribute to the 7th European moss survey, hotspots were rare but were most frequently associated with Manchester (an urban site) and Wivenhoe, Essex (which may also have some urban influences). More widespread elevations in concentration in mosses were found for cadmium and zinc, and to a lesser extent, copper.

Although median concentrations of many metals in mosses have declined or stabilised over the UK as a whole since the last UK moss survey in 2005, there are possible increases in median concentration in mosses for the metals cadmium, zinc and copper. It is possible that these may be associated with vehicle use including lubricants and brake and tyre wear (copper and zinc), in addition to domestic wood burning (cadmium), although this is currently unconfirmed. There are no signs that nitrogen concentration of mosses has declined since previous surveys, despite a decline in emissions to the air from NO_x and NH_Y.

Microplastic content of moss samples was analysed from 52 sites across the United Kingdom. All except two sites monitored experienced some microplastic (MP) contamination above the limits of detection of the assessment. A diverse range of polymers were detected, with the highest concentrations and diversity concentrated in the more north-westerly regions. The mean total number of microplastics >25 µm in size in moss across the UK was 4.5 MP/g with a maximum of 24.7 MP/g detected across the sampled locations. The most common polymer detected by particle number per gram of moss was polyurethane. This was detected in 87% of samples, with a mean concentration of 1.7 particles of polyurethane per gram moss. This polymer has very wide-ranging applications, from its use in clothing to its application as a coating and binder, from flexible foams used in construction, to insulation in home furnishings and appliances. Possible sources to the outdoor environment should be explored to know whether this polymer has diverse and numerous local sources. The other major polymers detected were cellulose acetate, polyvinylchloride, ethylene vinyl acetate, polylactic acid, and polyethylene terephthalate. Common polymers associated with packaging and macroplastic litter such as polyethylene and polypropylene were less commonly detected above limits of detection in these samples. The major microplastics found were different to those found in UK rivers e.g. the Thames.

Note that a few samples will be omitted from the submission to the 7th European Moss Survey as they do not meet the rural criteria, however, these samples were used for UK specific analysis.

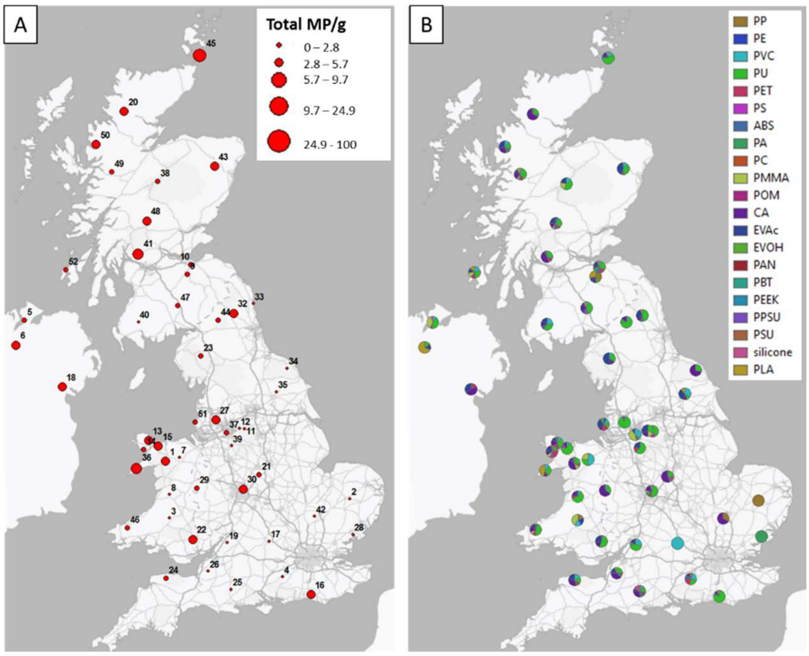
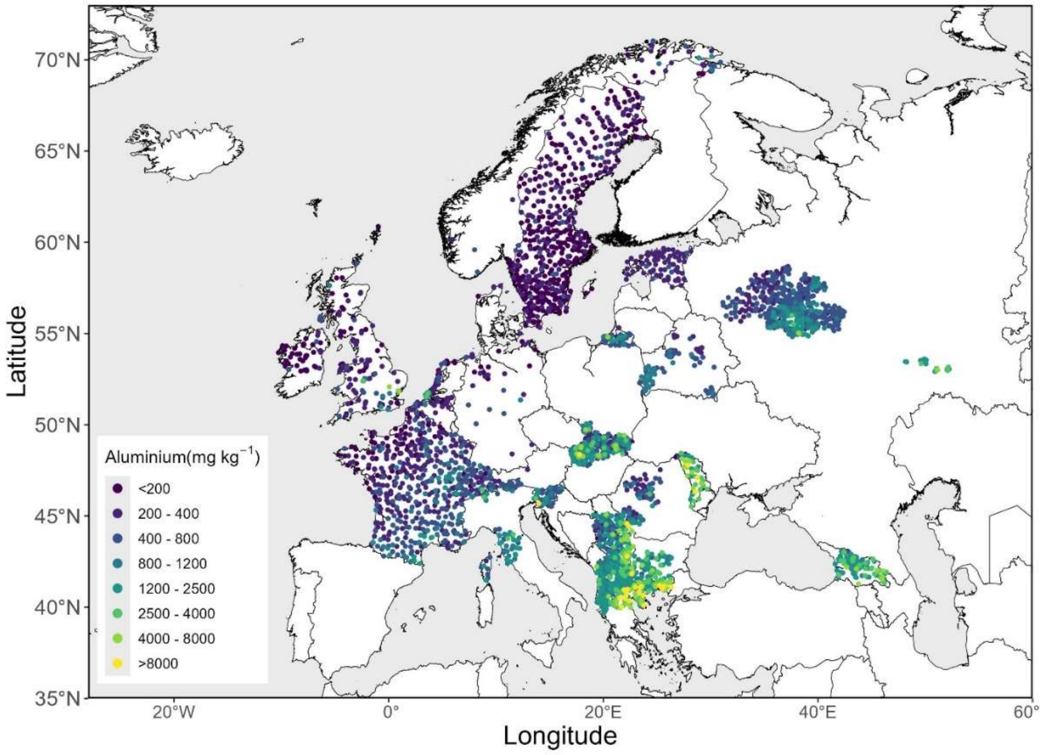


Figure 1: Microplastics in moss samples from the UK showing a) total microplastic (MP) abundance in mosses across the United Kingdom. Each red datapoint on the map represents moss from a single sampling location. The size of each data point indicates the total abundance of microplastics per gram of moss from 0 – 100 MP/g. b) Pie charts of the proportional contribution of different polymers to the overall microplastic contamination in moss at each sampling location.

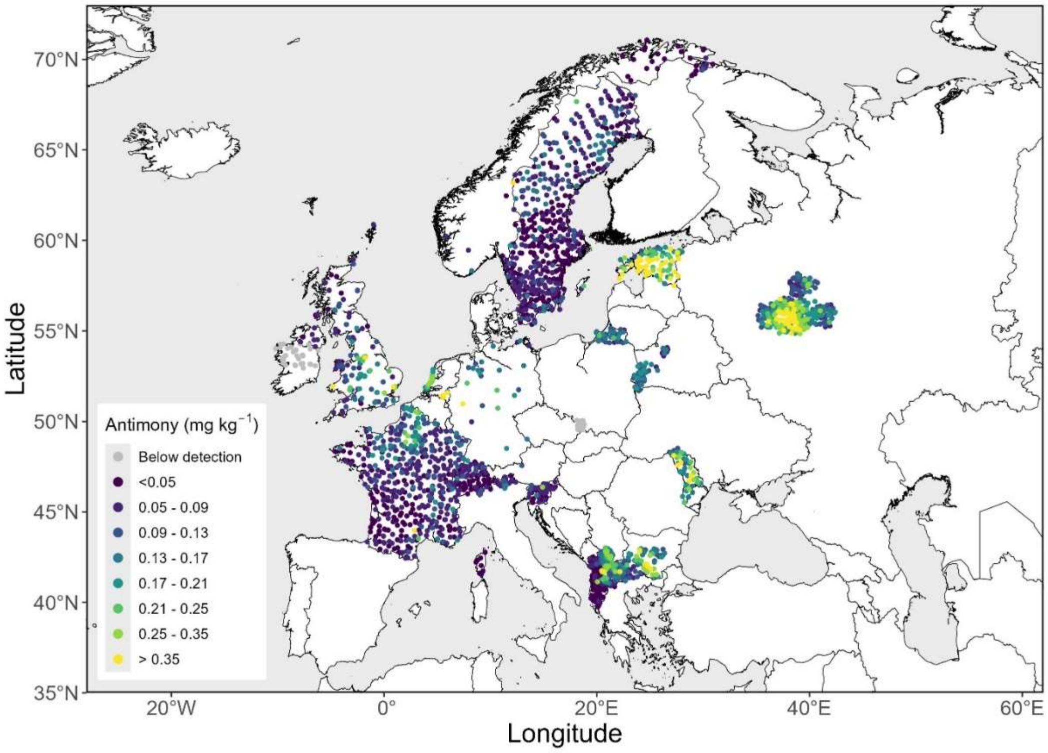
Table 1: Element concentrations for metals (μg / g) and nitrogen (%) in moss in the UK survey.

	Al	Cr	Fe	Ni	Cu	Zn	As	Cd	Sb	Pb	Hg	N
min	90	0.0	84	0.0	1.7	10.2	0.0	0.0	0.0	0.4	0.00	0.6
max	7526	12.1	5878	7.3	21.6	89.4	3.5	1.0	1.1	34.0	0.51	2.2
median	241	0.3	249	0.7	4.0	24.0	0.1	0.1	0.1	1.8	0.03	1.0
mean	531	0.8	471	1.0	4.8	29.3	0.2	0.1	0.1	3.3	0.04	1.0

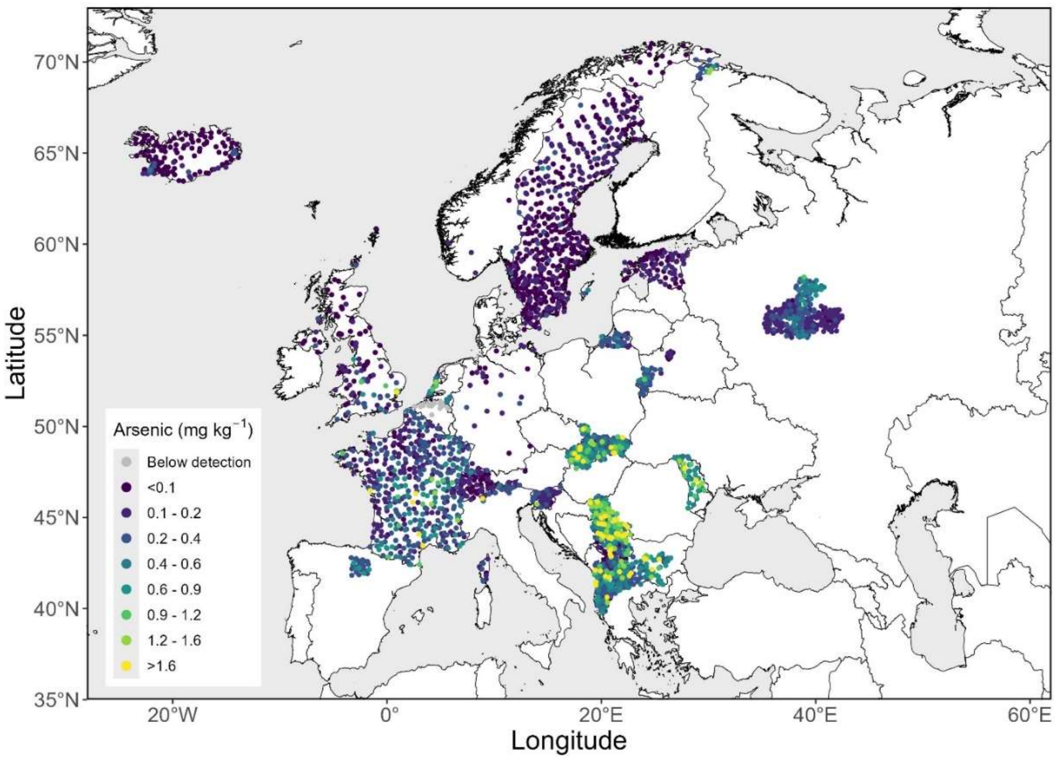
Annex 6 – Maps of concentrations of metals and nitrogen in mosses, in an alternative colour scheme



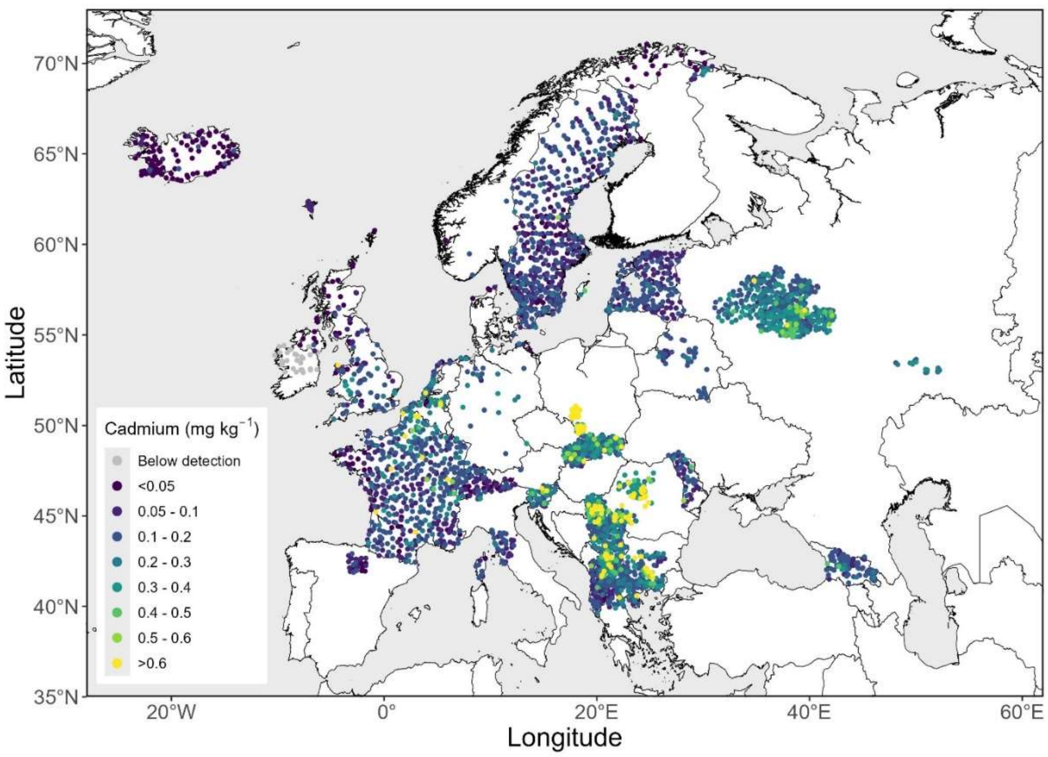
Aluminium concentration in mosses 2020.



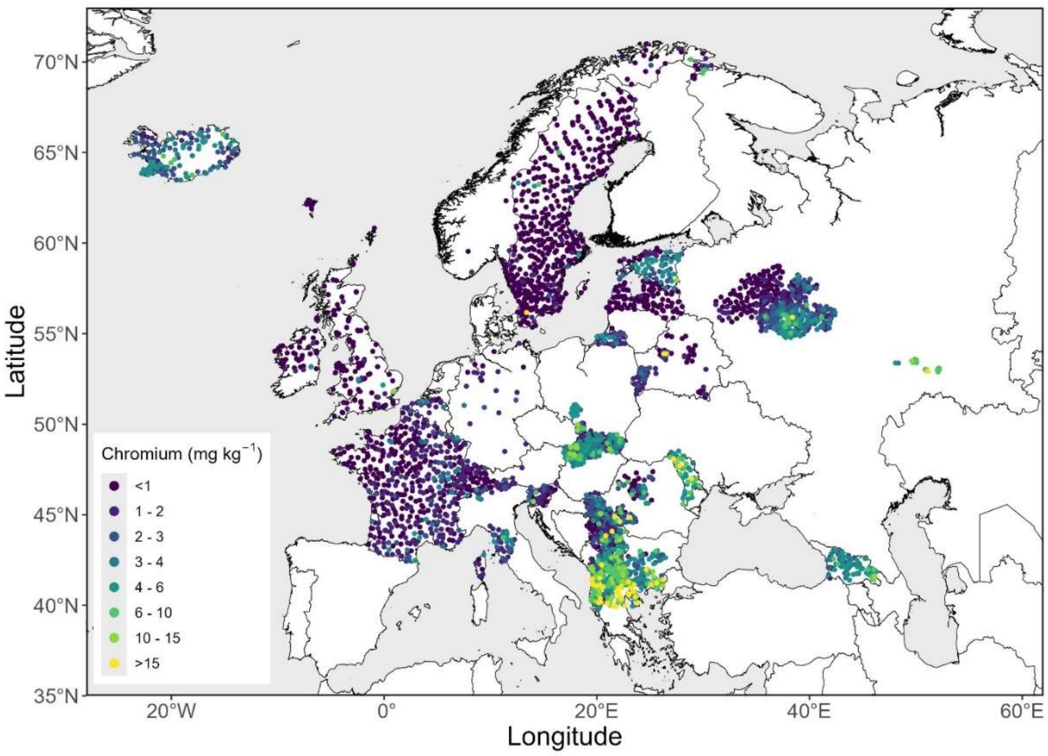
Antimony concentration in mosses 2020



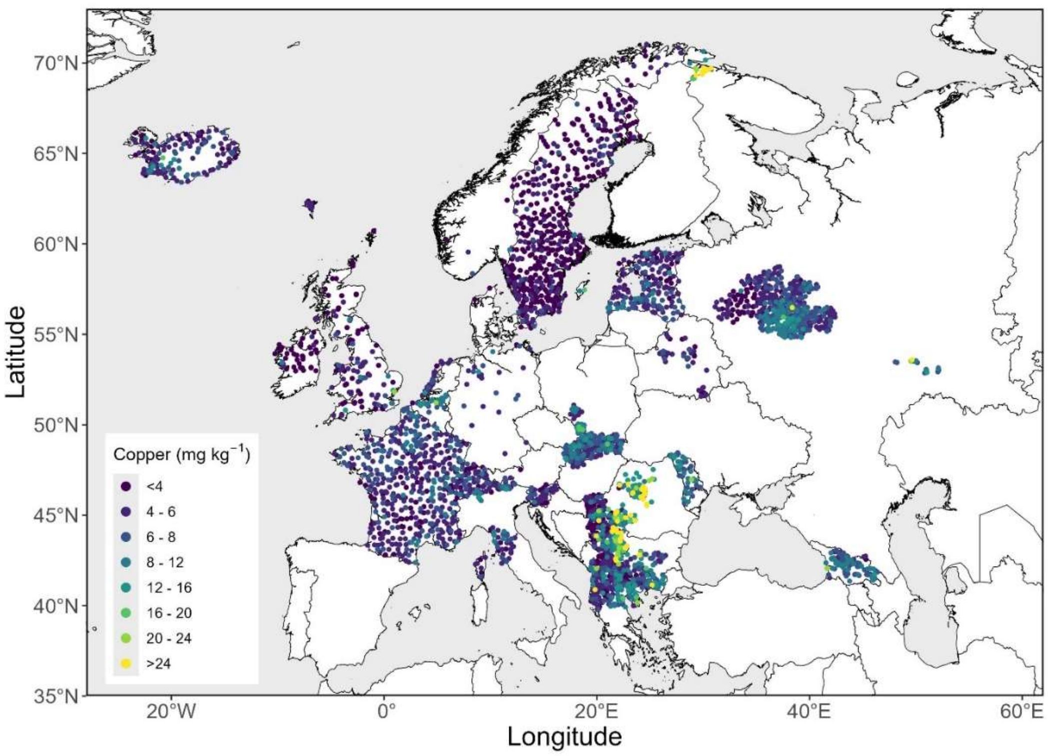
Arsenic concentration in mosses 2020



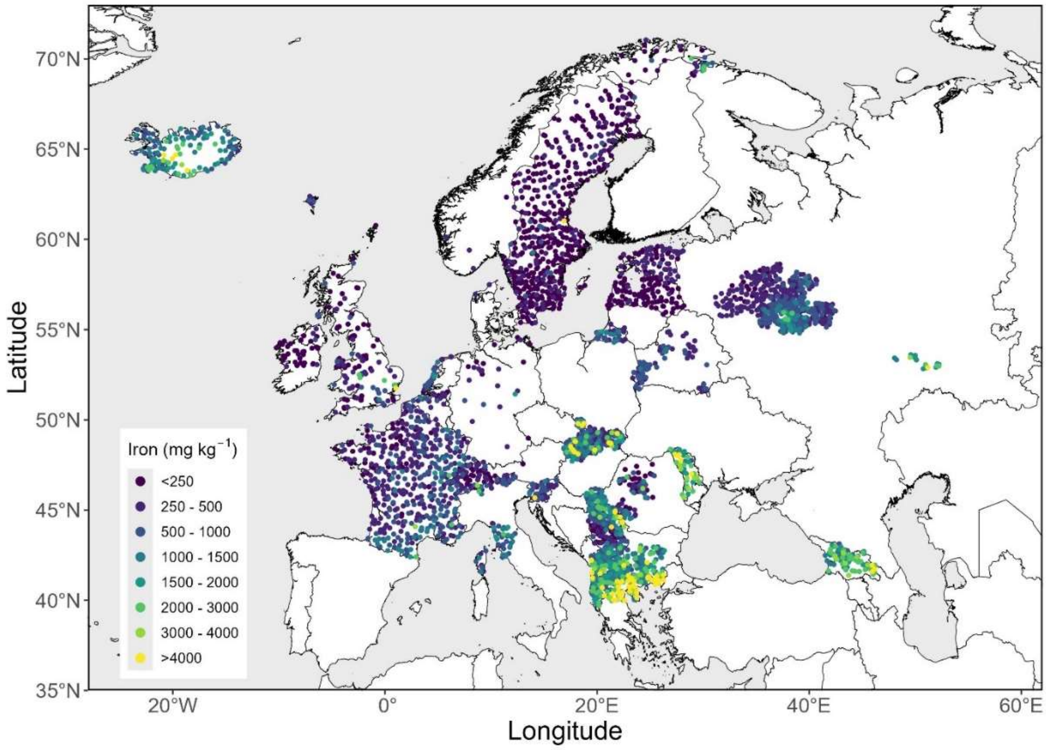
Cadmium concentration in mosses 2020



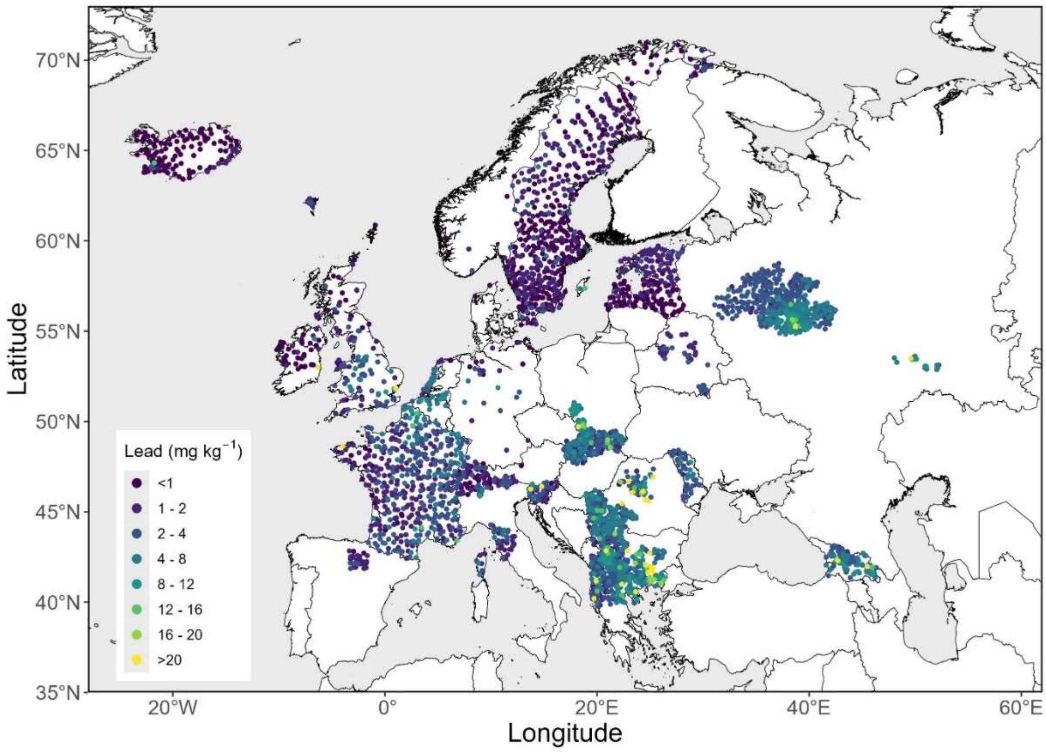
Chromium concentration in mosses 2020



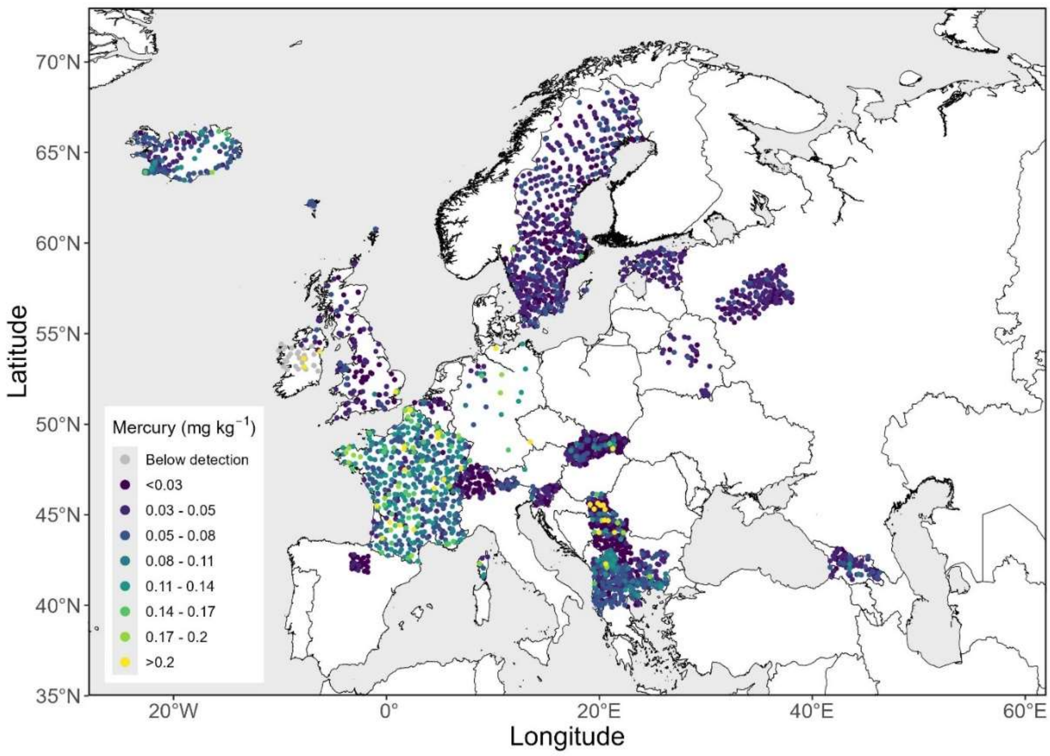
Copper concentration in mosses 2020



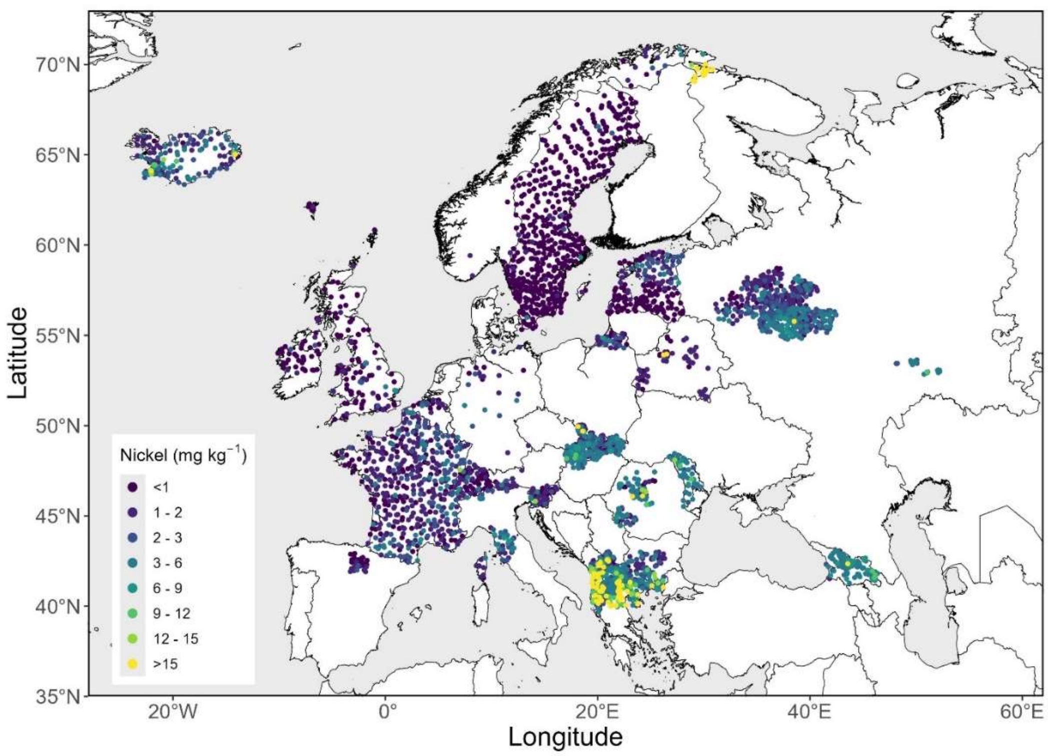
Iron concentration in mosses 2020



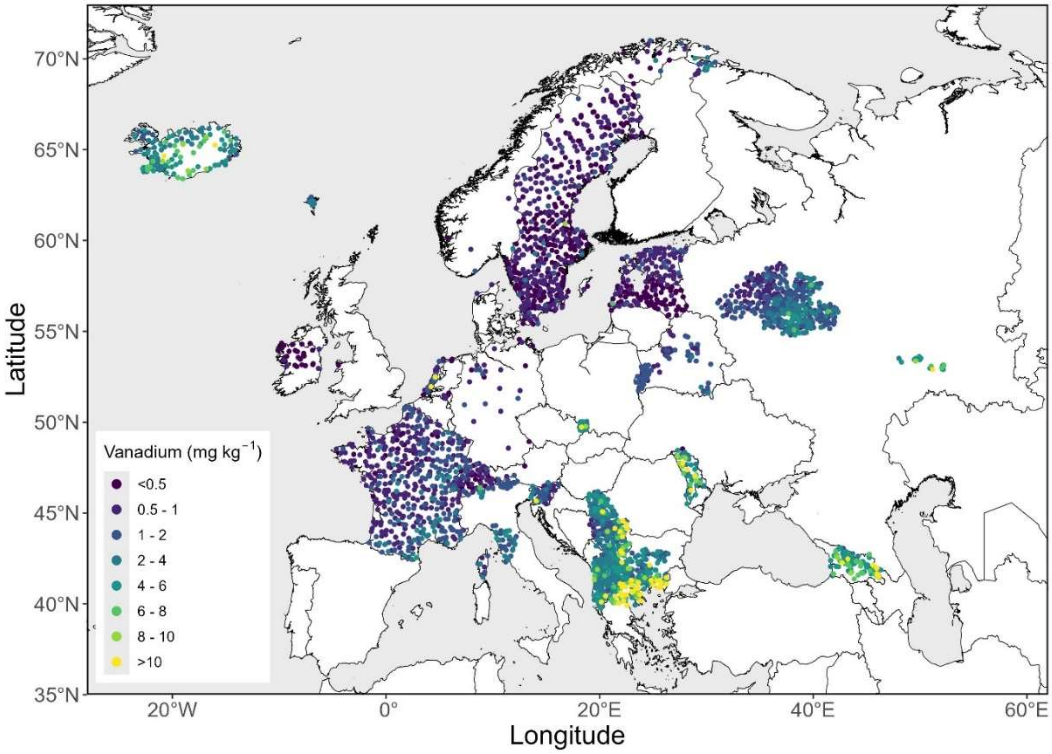
Lead concentration in mosses 2020



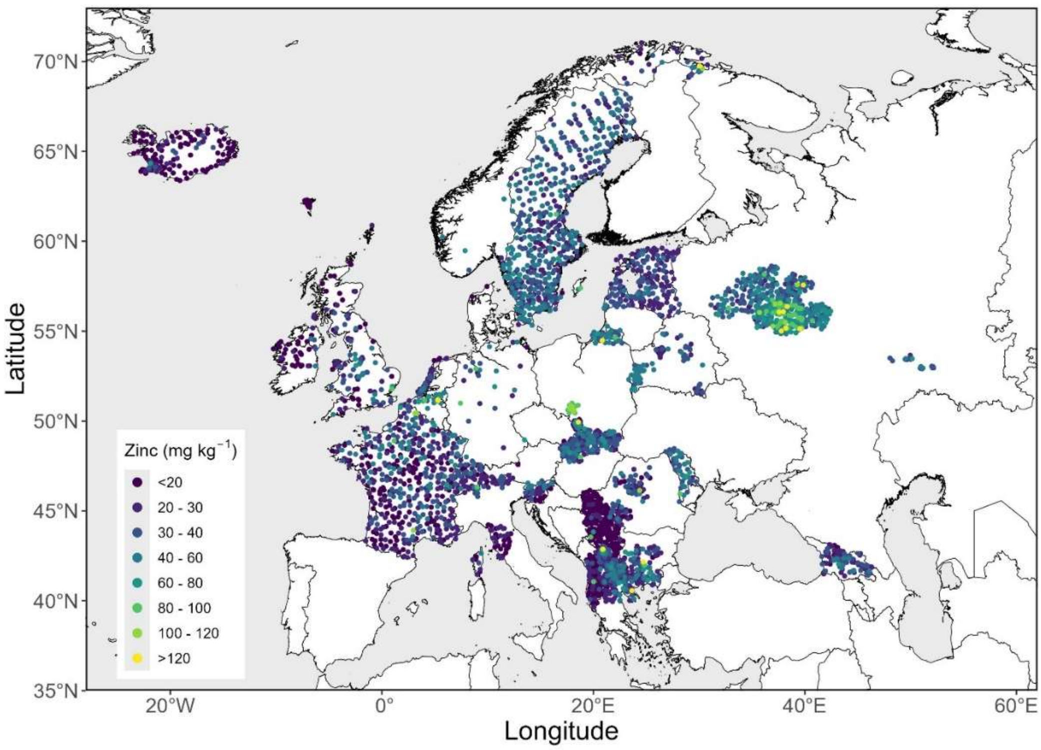
Mercury concentration in mosses 2020



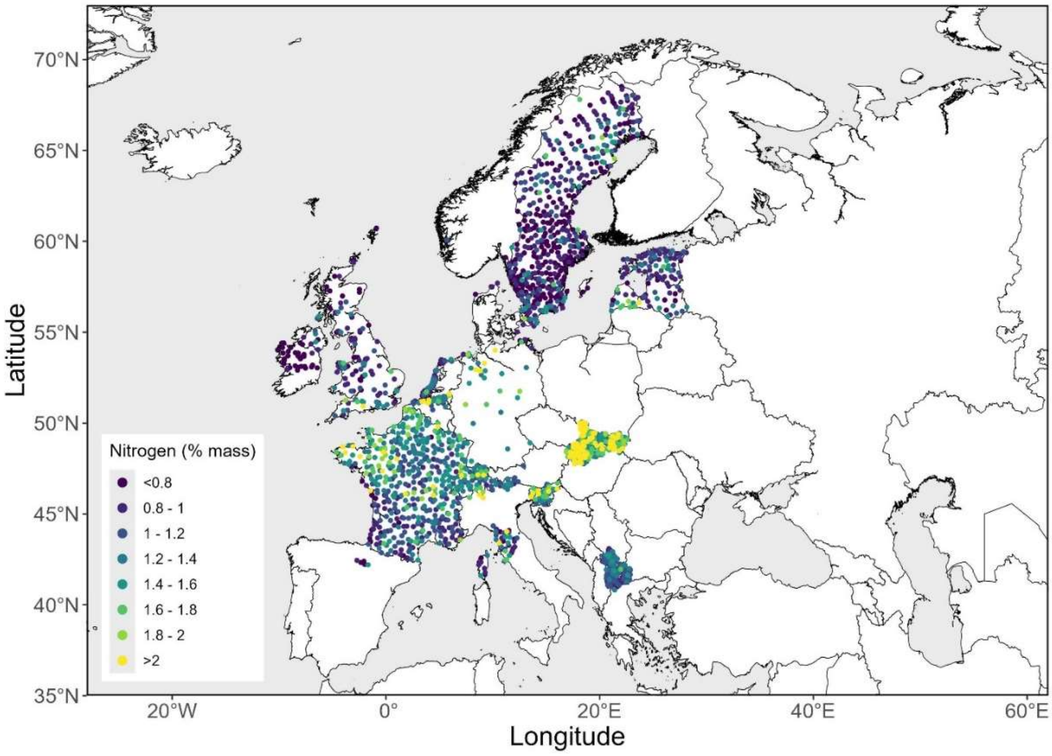
Nickel concentration in mosses 2020



Vanadium concentration in mosses 2020



Zinc concentration in mosses 2020



Nitrogen concentration in mosses 2020

UK Centre for Ecology & Hydrology

45 YEARS 1979-2024 AIR CONVENTION

Mosses as biomonitors of air pollution: 2020/2021 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 at five-yearly intervals since 1990. In 2020/21 mosses were collected from >3000 sites from 32 countries. For some metals, e.g. lead, there has been a decrease in concentration in moss tissue since 1990 that has mirrored the decline in emissions within the EU27 countries, however, in many cases the decline in concentration in moss tissue has been more modest e.g. chromium and nickel. Some metals remain a cause for concern. For arsenic there has been an increase of 6.0% in moss tissue since 1995, and for mercury the concentration in moss increased by 4.8%. A small increase in nitrogen concentration in moss tissue of 3.1% was observed over the period 2005-2020. Highest concentrations of nitrogen in moss tissue were generally found in central Europe.

For Further Information Please Contact:
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Working Group on Effects
of the
Convention on Long-range Transboundary Air Pollution