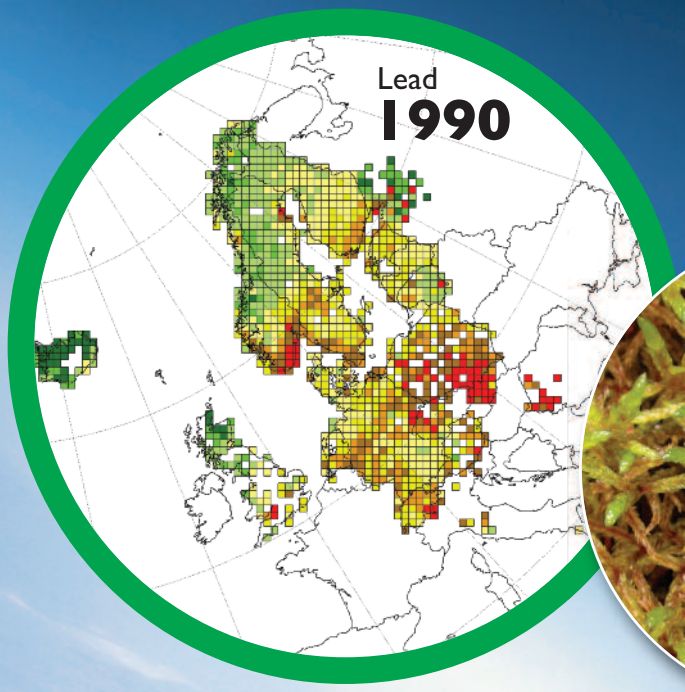
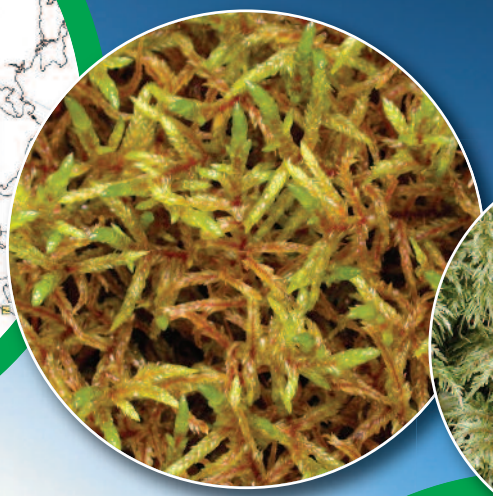
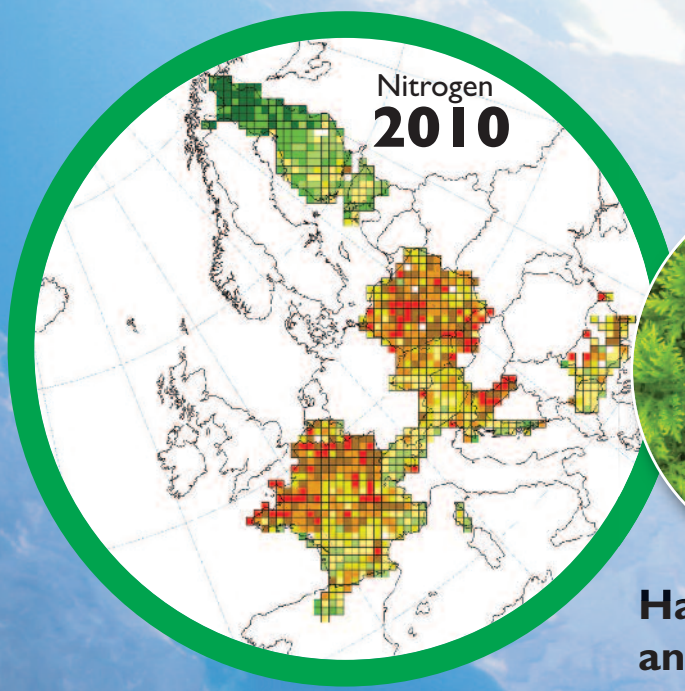
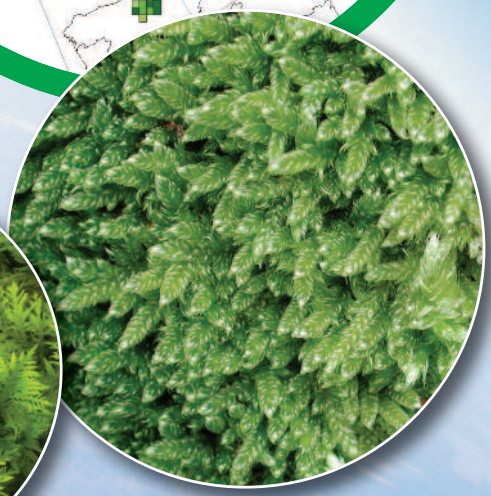




Heavy metals and nitrogen in mosses: spatial patterns in 2010/2011 and long-term temporal trends in Europe





Harry Harmens, David Norris, Gina Mills and the participants of the moss survey

ICP Vegetation Programme Coordination Centre

Centre for Ecology & Hydrology
NATURAL ENVIRONMENT RESEARCH COUNCIL

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

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Heavy metals and nitrogen in mosses: spatial patterns in 2010/2011 and long-term temporal trends in Europe

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ICP Vegetation Programme Coordination Centre

Centre for Ecology and Hydrology
Environment Centre Wales
Deiniol Road, Bangor
Gwynedd, LL57 2UW
United Kingdom

Tel: + 44 (0) 1248 374500
Fax: + 44 (0) 1248 362133
Email: hh@ceh.ec.uk
http://icpvegetation.ceh.ac.uk

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Contents

Executive summary

Background

The heavy metals in mosses biomonitoring network was originally established in 1980 as a Swedish initiative and has since then been repeated at five-yearly intervals. The first moss survey at the European scale was conducted in 1990 and since then the number of participating countries has greatly expanded. Twenty five European countries and over 4,500 sites were involved in the 2010/11 survey. In 2005, nitrogen was included for the first time, and 15 countries reported on nitrogen concentrations in mosses, collected at ca. 2,400 sites in 2010/11. In addition, six countries determined the concentration of selected persistent organic pollutants (POPs), particularly polycyclic aromatic hydrocarbons (PAHs), at a selected number of sites (data not reported here). During 2001, responsibility for the coordination of the survey was handed over to the ICP Vegetation[1] Programme Coordination Centre at the Centre for Ecology and Hydrology (CEH) Bangor, UK. The UNECE ICP Vegetation was established in the late 1980s to consider the science for quantifying the impacts of air pollutants on vegetation. It reports to the Working Group on Effects (WGE) of the Convention on Long-range Transboundary Air Pollution (LTRAP). The WGE monitors, models and reviews the effects of atmospheric pollutants on different components of the environment and health.

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

Methodology for the 2010/11 survey

As in previous surveys, moss samples were collected according to a standardised protocol and the elemental concentrations were determined in the last two to three years' growth segments using a range of analytical techniques. *Pleurozium schreberi* was the most frequently sampled species (ca. 42%), followed by *Hylocomium splendens* (23.5% and 15.3% for heavy metals and nitrogen respectively) or *Hypnum cupressiforme* (19.6% and 26.9% respectively), *Pseudoscleropodium purum* (ca. 8%) and other species (ca. 7 - 9%). For quality assurance purposes moss reference material was included in the analyses and where necessary, correction factors were applied to outliers and in some cases, severe outliers were excluded from further data processing. The reported data were checked for anomalies and the format standardised before European maps were produced for 2010/11, including maps showing the relative changes since the 2005 survey. The maps display the mean element concentration per 50 x 50 km^2 EMEP[2] grid cell.

Spatial patterns in 2010/11 and temporal trends (1990 – 2010) in Europe

Heavy metals

The decline in emission and subsequent deposition of heavy metals across Europe in recent decades has resulted in a decrease in the heavy metal concentration in mosses since 1990, with the decline continuing since the previous moss survey in 2005 (Table 1). In general, the decline in metal concentrations in mosses was higher between 1990 and 1995 (or 2000) than in later years. The metal concentration in mosses has declined the most for lead, due to the abolishment of leaded petrol, and

[1] The International Cooperative Programme on Effects of Air Pollution on Natural Vegetation and Crops
[2] Cooperative Programme for Monitoring and Evaluation of Long-range Transmission of Air Pollutants in Europe

the least for copper. For cadmium, lead and mercury, the temporal trends in concentrations in mosses are in good agreement with trends reported for atmospheric deposition modelled by EMEP. Between 1990 and 2010, the average cadmium and lead concentration in mosses has declined by 51% and 77% respectively, whereas the average modelled cadmium and lead deposition in the EMEP domain has declined by 51% and 74% respectively (Figure 1). Between 1995 and 2010, the average mercury concentration in mosses has declined by 23%, whereas the average modelled mercury deposition in the EMEP domain has declined by 27%. For other metals, the decline in concentrations in mosses also follows the decline in reported emissions since 1990, with the lowest decline being reported for copper for both variables. However, on a national or regional scale within countries deviations from the general European trend were found sometimes, i.e. temporal trends were country or region-specific, with no changes or even increases being observed between survey years. Therefore, even in times of generally decreasing metal deposition across Europe, temporal trends can be different for different geographical scales.

Table 1. Decline in the average median heavy metal and nitrogen concentrations in mosses since the start of the European moss survey in 1990 and since the previous survey in 2005.

Element	Decline since 1990* (%)	Decline since 2005 (%)	Element	Decline since 1990* (%)	Decline since 2005 (%)
Aluminium	n.a.	28	Lead	77	36
Antimony	n.a.	23	Mercury	23*	20
Arsenic	26*	25	Nickel	33	12
Cadmium	51	7	Vanadium	57	27
Chromium	43	23	Zinc	34	7
Copper	11	6			
Iron	52	15	Nitrogen	n.a.	5

* Decline since 1995 for arsenic and mercury as only a few countries have reported concentrations in mosses for these metals in 1990; n.a. = not available.

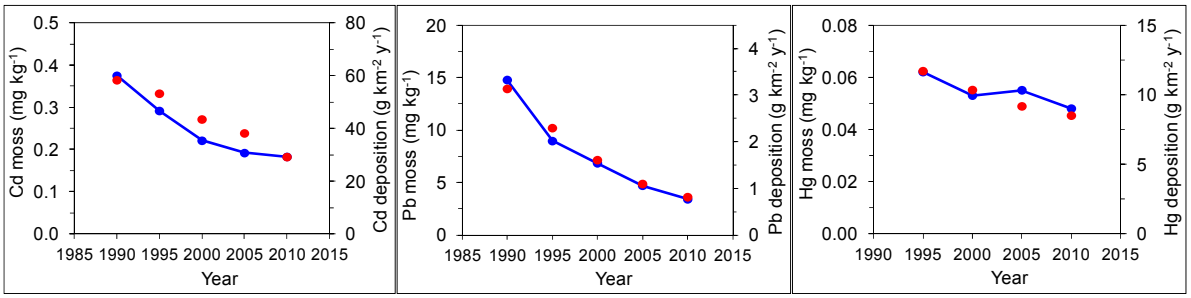

Figure 1. Temporal trend of cadmium (Cd), lead (Pb) and mercury (Hg) concentration in mosses compared to the trend of EMEP-modelled deposition for these heavy metal (red dots).

As in previous surveys, the lowest concentrations of heavy metals in mosses were generally found in northern Europe, although higher concentrations were reported near local sources. Low to intermediate heavy metal concentrations in mosses were generally observed in western and central Europe. The highest concentrations were often found in (south-)eastern Europe, with localised lower concentrations being observed. The spatial pattern of mercury concentrations in mosses was more homogeneous across Europe due its more hemispheric origin. For zinc, the spatial distribution of concentrations in mosses was also more homogenous across Europe than for other metals.

Nitrogen

The spatial pattern of the nitrogen concentration in mosses in 2010/11 was similar to the spatial pattern in 2005, with lower values being observed for Finland than the rest of Europe (Figure 2). Generally, high concentrations of nitrogen were found in western and central Europe. The small decline (5%) in the average median nitrogen concentration in mosses (Table 1) is in agreement with the 7% decline reported by EMEP for modelled total nitrogen deposition in the EU27 since 2005. Previous analysis of the relationship between nitrogen concentration in mosses and EMEP-modelled

total nitrogen deposition showed considerable scatter with saturation occurring at a total nitrogen deposition rate of ca. 15 kg N ha^{-1} y^{-1} (Figure 2). However, in some countries a linear relationship has been observed between the total nitrogen concentration in mosses and measured bulk nitrogen deposition at the site level. Although these relationships needs to be analysed further using the 2010/11 moss and modelled or measured deposition data, we do expect these relationships to be similar as in 2005 (see country report from Switzerland).

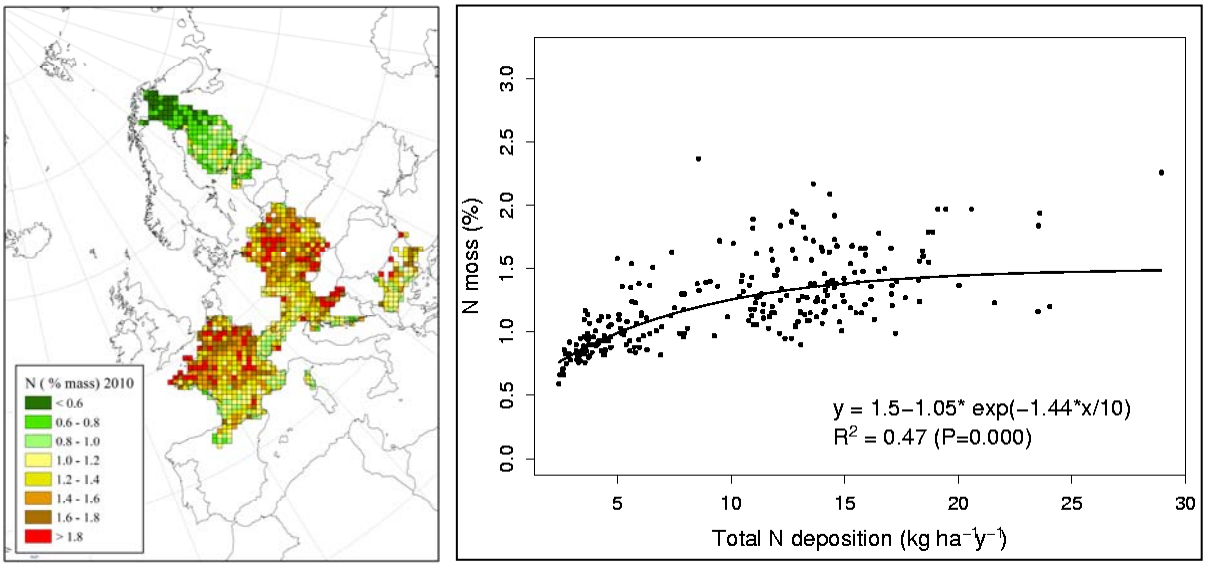

Figure 2. Mean nitrogen concentration in mosses per EMEP grid cell in 2010 (left) and the relationship between nitrogen concentration in mosses and EMEP-modelled total nitrogen deposition in 2005 (right; Harmens et al., 2011).

Conclusions

- Moss biomonitoring provides 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 the priority metals cadmium, lead and mercury and for nitrogen the decline in average median concentrations in mosses across Europe is in agreement with that reported for modelled atmospheric deposition.
- Despite the general European decline in concentrations in mosses between 2005 and 2010 (and also since 1990), country and region-specific temporal trends were observed.
- Despite the apparent success of the implementation of air pollution abatement techniques in large areas of Europe, further measures are required in (south)-eastern Europe to reduce the relative high emissions of heavy metals. For nitrogen, more stringent air pollution abatement strategies are required across Europe to reduce the area at risk from adverse effects of high atmospheric nitrogen deposition.

Recommendations

As ecosystems and human health are still predicted to be at risk from adverse effects of heavy metals and nitrogen in the future, the moss survey should be continued to monitor any future trends in heavy metal and nitrogen deposition in Europe, with the next survey anticipated for 2015/16. Further stimulation of the participation in (south)-eastern European countries for both heavy metals and nitrogen is especially encouraged. In addition, more countries are encouraged to report on the nitrogen concentration in mosses in the future. An extension of the moss survey into Asia would also be welcome. It is recommended to use the newly available data for 2010/11 to further assess the performance of the EMEP models, particularly the model that estimates the atmospheric deposition of the priority heavy metals cadmium, lead and mercury. For nitrogen we recommend to investigate in further detail the relationship between measured total nitrogen deposition and the total nitrogen concentration in mosses at the site level.

1 Introduction

Background

Since 1979, the Convention on Long-range Transboundary Air Pollution (LRTAP) has addressed major air pollution problems in the UNECE (United Nations Economic Commission for Europe) region through scientific collaboration and policy negotiation. The Convention has been extended by eight protocols that identify specific measures to be taken by countries to cut their emissions of air pollutants. The 1998 Aarhus Protocol on heavy metals targets three harmful heavy metals: cadmium (Cd), lead (Pb) and mercury (Hg). The 1999 Gothenburg Protocol was the first Protocol dealing with multi-pollutants and aims to abate acidification, eutrophication (nitrogen enrichment) and ground-level ozone. Within the Convention, the European Monitoring and Evaluation Programme (EMEP) i) collects emission data from Parties, ii) measures air and precipitation quality, and iii) models atmospheric transport and deposition of air pollutants. Deposition of the heavy metals cadmium, lead and mercury is modelled using the EMEP atmospheric transport model MSCE-HM (Ilyin and Travnikov, 2005) and deposition of nitrogen is calculated using the EMEP Unified Eulerian chemical transport model (Simpson et al., 2012). The calculation of deposition of air pollutants is based on official emission data reported by the countries. The output of the models is validated each year against measurement data collected at EMEP measurement stations (Fagerli et al., 2012; Travnikov et al., 2012). However, the number of EMEP measurement stations is limited across Europe and EMEP stations are generally under-represented in southern and eastern Europe. Nevertheless, the number of monitoring sites measuring cadmium, lead and mercury has increased from 44 in 1990 to 66 in 2010 (Travnikov et al., 2012), and number of sites measuring acidifying and eutrophying pollutants and photo-oxidants has increased in recent years in western Mediterranean areas (Aas et al., 2010).

Within the Convention, the Working Group on Effects (WGE) monitors and models the impacts of air pollutants on human health and the environment, including materials. Furthermore, the WGE makes predictions on the impacts of air pollutants in the future based on various emission abatement strategies, also taking into account climate change scenarios. The ICP Vegetation (International Cooperative Programme on Effects of Air Pollution on Natural Vegetation and Crops) reports to the WGE on the deposition of air pollutants to and their impacts on vegetation (Harmens et al., 2012b). Since 2000, the ICP Vegetation has been coordinating the European moss survey (Harmens et al., 2010; 2011). The survey has been repeated at five-yearly intervals since 1990 and the latest survey was conducted in 2010/11: 25 countries reported on heavy metal concentrations in mosses, collected at ca. 4,500 sites across Europe, and 15 countries reported on nitrogen concentrations in mosses, collected at ca. 2,400 sites (Table 1).

Table 1.1. Countries (regions) that submitted data for the 2010/11 European moss survey.

Albania	**Finland**	Russian Federation[1]
Austria	**France**	**Slovakia**
Belarus	Iceland	**Slovenia**
Belgium	**Italy (Bolzano)**	**Spain**[2]
Bulgaria	Kosovo	Sweden
Croatia	**Macedonia**	**Switzerland**
Czech Republic	Norway	Ukraine (Donetsk)
Denmark (Faroe Islands)	**Poland**	
Estonia	Romania	

[1] Ivanova, Kostromskaya and Tikhvin-Leningradskaya region; [2] Galicia, Navarra and Rioja region. Countries in bold submitted data on heavy metals and nitrogen, the other countries submitted only data on metals.

In addition, a pilot study was conducted in six countries on the application of mosses as biomonitors of persistent organic pollutants (POPs), particularly polycyclic aromatic hydrocarbons (PAHs; Harmens et al., 2013). The results of the pilot study on POPs will be reported in the annual ICP

Vegetation report for 2012/13. Since 1990, the European moss survey provides data on concentrations of ten metals (arsenic, cadmium, chromium, copper, iron, lead, mercury, nickel, vanadium and zinc) in naturally growing mosses. Since 2005, data on aluminium, antimony and nitrogen were also included. Some countries determined the concentration of additional elements in mosses, but these are not included in this report.

Mosses as biomonitors of atmospheric deposition

Heavy metals

The heavy metals in mosses biomonitoring network was originally established as a Swedish initiative (Rühling and Skärby, 1979). The idea of using mosses to measure atmospheric heavy metal deposition is based on the fact that carpet forming, ectohydric mosses obtain most trace elements and nutrients directly from precipitation and dry deposition; there is little uptake of metals from the substrate. The technique of moss analysis provides a time-integrated measure of heavy metal deposition from the atmosphere to terrestrial systems. It is easier and cheaper than conventional precipitation analysis as it avoids the need for deploying large numbers of precipitation collectors with an associated long-term programme of routine sample collection and analysis. In recent decades, mosses have been applied successfully as biomonitors of heavy metal deposition (e.g. Harmens et al., 2007, 2008b, 2010; Zechmeister et al., 2003) across Europe. Heavy metal concentrations in mosses provide a complementary, time-integrated measure of the spatial patterns and temporal trends of heavy metal deposition from the atmosphere to terrestrial systems, at least for the metals cadmium and lead (Aboal et al., 2010). It has been shown that at the European scale atmospheric deposition is the main factor determining the accumulation of cadmium and lead in mosses (Holy et al., 2010; Schröder et al., 2010b). Compared to the EMEP monitoring network, the moss survey has the following main advantages: i) the density of the moss monitoring network is much higher and ii) their spatial distribution is wider, including parts of southern and eastern Europe. Although the heavy metal concentration in mosses provides no direct quantitative measurement of deposition, this information has been derived in some countries by using regression or correlation approaches relating the results from moss surveys to deposition data (e.g. Berg and Steinnes, 1997; Berg et al., 2003; Schröder and Pesch, 2010; Thöni et al., 2011). However, Bouquete et al. (2011) recommended that the results of moss biomonitoring studies should be regarded as qualitative or semi-qualitative, rather than attempting to provide absolute data, which may not be temporally representative, and may have a high degree of uncertainty associated with them, at least in Spain.

Nitrogen

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. 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. At the European scale, the relationship between site-specific nitrogen concentrations in mosses and modelled nitrogen deposition per EMEP 50 km x 50 km grid starts to show saturation at deposition rates of ca. 15 kg ha^{-1} y^{-1} (Harmens et al., 2011). Detailed statistical analysis of the European moss data revealed that the total nitrogen concentration in mosses is significantly and best correlated with EMEP modelled air concentrations and atmospheric nitrogen deposition rates in comparison to other predictors that might contribute to the spatial variation of nitrogen concentrations in mosses (Schröder et al., 2010a). Factors potentially affecting the relationship between nitrogen deposition and its concentration in mosses were discussed in further detail by Harmens et al. (2011).

Persistent organic pollutants (POPs)

Worldwide there is concern about the continuing release of persistent organic pollutants (POPs) into the environment. Examples in the literature show that mosses are suitable organisms to monitor spatial patterns and temporal trends of atmospheric concentrations or deposition of POPs (Harmens et al., 2013). These examples include polycyclic aromatic hydrocarbons (PAHs), polychlorobiphenyls (PCBs), dioxins and furans (PCDD/Fs), and polybrominated diphenyl ethers (PBDEs). So far, the

majority of studies report on PAHs concentrations in mosses and relative few studies have been conducted on other POPs. Many studies have focused on spatial patterns around pollution sources or the concentration in mosses in remote areas such as the polar regions, as an indication of long-range transport of POPs. Very few studies have determined temporal trends or have directly related the concentrations in mosses with measured atmospheric concentrations and/or deposition fluxes.

Sources and effects of heavy metals and nitrogen

Heavy metals

Heavy metals are emitted mainly as a results of various combustion processes and industrial activities like metals works and smelters. The contribution of various sources to emissions of heavy metals across Europe has changed in recent decades (EEA, 2012; Travnikov et al., 2012). The most important emission sectors include:

- Metals industry (Al, As, Cd, Cr, Cu, Fe, Pb, Zn);
- Other manufacturing industries and construction (As, Cd, Cr, Hg, Ni, Pb);
- Electricity and heat production (Cd, Hg, Ni);
- Road transportation (Cu and Sb from brake wear, Pb, V, Zn from tires);
- Petroleum refining (Ni, V);
- Phosphate fertilisers in agricultural areas (Cd).

Whereas road transport (76%) was the key source of lead deposition in 1990, the phasing out of leaded petrol has reduced the contribution of road transport to 11% in 2010. Stationary combustion in industry (29%) and metal production (26%) were the key sources of lead deposition in 2010 (Travnikov et al., 2012). The sector contribution to cadmium deposition has changed less dramatically. In 1990, metal production (23%), stationary combustion in industry (22%) and non-industrial combustion (20%) were the major sources. In 2010, these sectors contributed 12%, 17% and 33% respectively to cadmium deposition. No substantial changes in the key sources of mercury deposition occurred between 1990 and 2010 in the EMEP countries. Combustion of fossil fuels for public electricity and heat production made up 35% and 40% of total mercury deposition in 1990 and 2010, respectively. Other key sectors include stationary combustion in industry, non-industrial combustion and metal production. Emissions from waste incineration have changed the most, with its relative contribution to mercury deposition declining from 6% in 1990 to 3% in 2010. Further details on changes in key emission sources since 1990 for cadmium, lead and mercury and the key emission sources in 2010 in the EU27 were reported by the EEA (2012).

As well as polluting the air, heavy metals are deposited on terrestrial or water surfaces and subsequently build up in soils or sediments. Heavy metals are persistent in the environment and may bioaccumulate in food chains. The heavy metals cadmium, lead and mercury were targeted in the 1998 Aarhus Protocol as the environment and human health are most at risk from adverse effects of these metals (Task Force on Health, 2007; VROM, 2007). Further details on the toxic effects of heavy metals on human health and the environment were summarised by the Task Force on Health (2007) and Harmens et al. (2008a). Atmospheric deposition of metals has a direct effect on the contamination of crops used for animal and human consumption. In particular, leafy vegetables and fodder crops can accumulate heavy metals (e.g. De Temmerman et al., 2004; De Temmerman et al., 2009). Washing leafy vegetables before consumption reduces the risk of exposure by humans considerably (Harmens et al., 2005). Despite reductions in the averaged modelled deposition of lead (74%), cadmium (51%) and mercury (36%) in EMEP countries between 1990 and 2010, human health and the environment continue to be at risk in many countries, particularly in large parts of eastern Europe (Travnikov et al., 2012). In 2010, the exceedance of critical loads for lead and mercury was widespread across Europe for human health and ecotoxicological effects. However, the critical loads for cadmium was only exceeded in a small area, mostly in the Russian Federation (Slootweg et al., 2010).

Nitrogen

Nitrogen oxides are emitted during fuel combustion, for example from industry and road transport. The vast majority of ammonia emissions (ca. 94% in Europe) come from the agricultural sector, in connection with activities such as manure storage, slurry spreading and the use of synthetic nitrogenous fertilisers (EEA, 2012). Nitrogen oxides and ammonia contribute both to acid deposition and nitrogen enrichment of soil and water. Nitrogen dioxide is associated with adverse affects on health: high concentrations cause inflammation of the airways and reduced lung function. Nitrogen oxides also contribute to the formation of secondary particulate matter and ground-level ozone with associated climate effects. Although nitrogen has benefits for food, fibre and industrial production, it is a severe threat to water, air and soil quality, to terrestrial biodiversity and the greenhouse gas balance (Sutton et al., 2011). For a more detailed description of sources and effects of nitrogen pollution, we refer to Sutton et al. (2011).

Aims and structure of this report

The main aims of this study are:

- To summarise, in the form of maps and figures:
  - i) Spatial patterns of heavy metal and nitrogen concentrations in mosses in 2010/11 and changes in these patterns since the 2005/6 survey;
  - ii) Temporal trends since 1990, with an emphasis on changes since 2005/6;
- To identify main polluted areas in 2010/11.

In the following chapters, the methodology for the 2010/11 moss survey is described (Chapter 2), followed by a summary of spatial patterns and temporal trends, including maps based on the 50 x 50 km^2 EMEP grid (Chapter 3). In Chapter 4 the results are discussed, conclusions are drawn and recommendations for the future are made. As an annex to this report, 13 countries have summarised in more detail the results of the 2010/11 moss survey in their country, with some of them also reporting on temporal trends (Annex 4).

For heavy metals, spatial patterns in other European moss surveys (1990, 1995, 2000 and 2005) were reported in more detail previously (Rühling, 1994; Rühling and Steinnes, 1998; Buse et al., 2003; Harmens et al, 2008a, 2010). Further details on temporal trends between 1990 and 2005 can be found in Harmens et al. (2008a, 2010). For nitrogen, details on the spatial patterns in 2005 were reported by Harmens et al. (2011). A more detailed description of spatial and temporal trends in heavy metal and nitrogen concentrations in mosses and changes in local emission sources at the national level has been provided elsewhere by the participants in national reports or published papers.

2 Methodology for the 2010/11 survey

Moss species

As in previous surveys, the carpet-forming mosses *Pleurozium schreberi* and *Hylocomium splendens* were the preferred species for analysis. Where necessary, other species were collected, *Hypnum cupressiforme* and *Pseudoscleropodium purum* being the next choice. Because the mosses were collected in a range of habitats and climatic conditions, it was necessary to collect a range of moss species (Figure 2.1). *Pleurozium schreberi* (Brid.) Mitt was the most frequently sampled species, accounting for ca. 42% of the samples for both heavy metals and nitrogen, followed by *Hylocomium splendens* (Hedw.) (23.5% and 15.3% for heavy metals and nitrogen respectively) or *Hypnum cupressiforme* Hedw. (19.6% and 26.9% respectively), and *Pseudoscleropodium purum* (Hedw.) (7.7% and 7.5% respectively). Other moss species constituted 7.1% and 8.7% of the mosses sampled for heavy metals and nitrogen respectively.

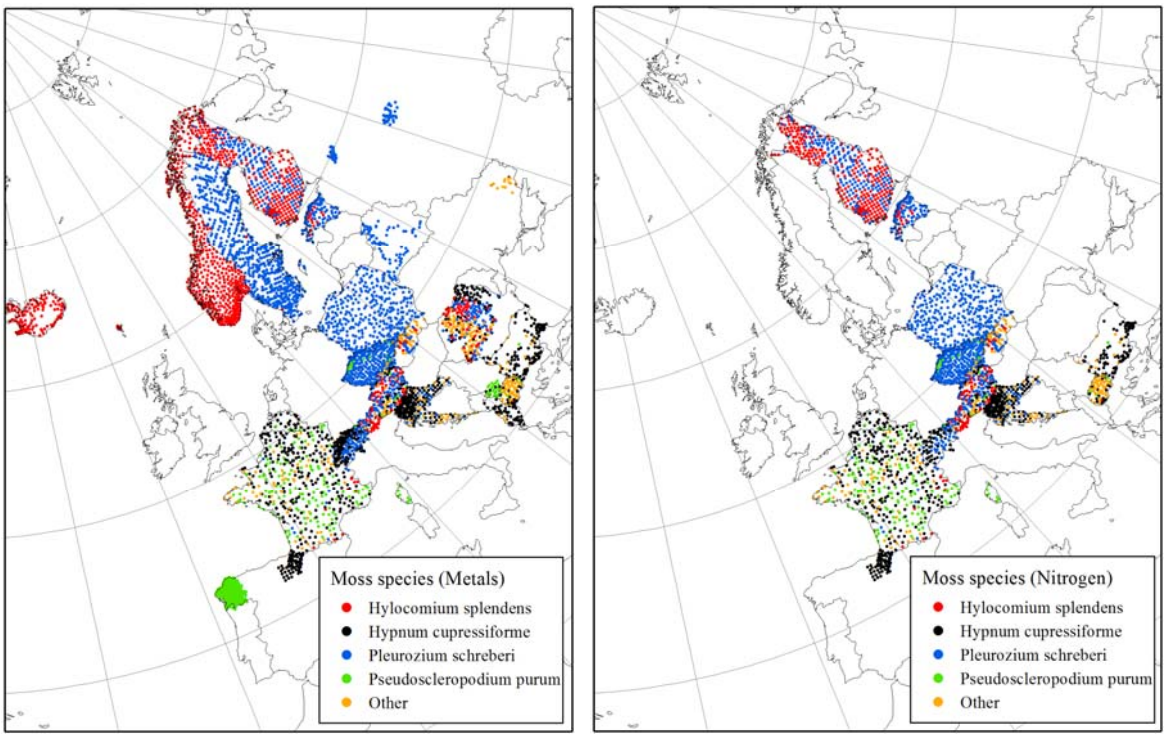

Figure 2.1. Sites where mosses were sampled for heavy metals (left) and nitrogen analysis (right).

Field sampling

The distribution of the sampling sites throughout Europe can be seen in Figure 2.1. Moss sampling was according to the guidelines set out in the experimental protocol for the 2010/11 survey (ICP Vegetation, 2010). The procedure was similar to that used in previous European moss surveys. Each sampling site was located at least 300 m from main roads and populated areas and at least 100 m from any road or single house. In forests or plantations, samples were collected as far as possible in small open spaces to preclude any significant effect of canopy drip. Sampling and sample handling were carried out using plastic gloves and bags. Each sample was a composite of about five sub-samples. Dead material and litter were removed from the samples and only the last two to three years' growth segments were used for the analyses. Samples were refrigerated, frozen or dried at room temperature and stored under those conditions until chemical analysis.

Chemical analysis

For the determination of metal concentrations, sorted material (ca. last two to three years' growth) was dried at 40°C (room temperature for Hg) and either dissolved 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). For further data processing, values below the quantification limit were set at the quantification limit.

Quality control

A quality control exercise was conducted for assessing the analytical performance of the participating laboratories. Moss reference material M2 and M3, first prepared for the 1995/6 European moss survey (Steinnes et al., 1997), were distributed amongst the laboratories. In addition, some laboratories used other certified reference material for quality assurance. For determination of the elemental concentrations in the reference material, laboratories followed the same analytical procedure as used for the collected moss samples. Generally, data obtained indicated acceptable agreement between laboratories. However, outliers were identified for some laboratories for selected metals (not for nitrogen). This was the case when the values were outside the range of two standard deviations (as determined for the 2010/11 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).

In 2010/11, the mean values of M2 and M3 were generally in good agreement with the recommended values and ranged from 85% (for arsenic; followed by 93% for vanadium) to 105% (antimony) for M2, the reference material with high metal concentrations, and from 92% (chromium) to 113% (arsenic) for M3, the reference material with background metal concentrations. For nitrogen the mean values of M2 and M3 were 101% and 102% of the recommended value respectively. The accuracy of data received by the Programme Coordination Centre was assessed by inspecting them for extremes and by sending summarised data and the relevant draft maps to individual contributors for checking and approval before incorporating the final data into the maps, figures and tables in this report. Summary data for each country are presented in Annex 3.

Mapping

The maps were produced using ArcMAP, part of ArcGIS, an integrated geographical information system (GIS) and were based on the EMEP 50 x 50 km^2 grid, which display the mean elemental concentration for each cell (Harmens et al., 2010, 2011). For convenience we refer to the 1990/1, 1995/6, 2000/1, 2005/6 and 2010/11 European moss surveys as 1990, 1995, 2000, 2005 and 2010 surveys from here onwards. The concentration ranges used in the maps are the same as those used by Harmens et al. (2010, 2011) to allow comparison of the 2010 results with those for previous years.

3 Spatial patterns and temporal trends in Europe

Introduction

The 2010 data on the concentration of each element in moss samples from each country are summarised in Annex 3. Extreme values are often for single hot spots. The emphasis of this chapter is on Europe-wide spatial patterns and temporal trends. The temporal trends for cadmium, lead and mercury are compared with temporal trends in modelled deposition as reported by EMEP (Travnikov et al., 2012). For some of the other metals, the temporal trends are compared with temporal trends in emissions as reported by the European Environment Agency (EEA, 2012). One should bear in mind that changes with time for emissions in Europe are not necessarily of a similar magnitude as trends in deposition due to the contribution of long-range transport outside Europe to deposition of elements in Europe and the contribution of wind-blown dust to deposition, representing historic deposition of heavy metals. Many contributors to the survey have reported national trends in greater detail elsewhere, including local emission sources of the pollutants and the relationship between concentration in mosses and measured or modelled atmospheric deposition (see also Annex 4). Elevated concentrations of heavy metals in mosses sampled in a particular region can arise in several ways; hot spots can be associated with either contemporary or historical industrial and mining activities, or with large conurbations, whereas widespread effects can be due to widespread sources, particularly vehicle emissions along major roads or geological sources, or to long-range transport of pollution. Important sources for elevated concentrations of nitrogen in mosses are combustion of fossil fuel and agricultural activities. Elements such as copper, iron, zinc (micronutrients) and nitrogen (macronutrient) are essential for moss growth and development and are therefore to some extent recycled from dying tissues to new growth. Therefore, these nutrients have a baseline concentration in moss tissue.

The element concentrations in mosses per EMEP grid cell are shown in the maps for 2010. In addition, relative changes in the concentrations since 2005 are also shown in a separate map, but only for those grid cells for which mean values were available for both 2005 and 2010. One should bear in mind that the relative values in 2010, expressed as a percentage of the values in 2005, can sometimes be high when the absolute values are close to the quantification limit of the applied analytical technique, as the uncertainty associated with such very low values is relatively high. Bar charts show the medium value per country from the highest to the lowest one in 2010; for comparison, the median values for 2005 are also included, but only for those countries that submitted data for 2010. Figures for the temporal trends of average median values for Europe since 1990 (1995 for arsenic and mercury) are shown as well, using only the data for those countries that participated in at least four (three for arsenic and mercury) out of the five (four) surveys. This allowed the inclusion of data from more countries compared to temporal trend analyses based only on countries that participated in all survey years. When comparing changes since 2005 or earlier years, one should bear in mind that many countries have not consistently sampled mosses from the same sites each year and/or might have changed the sampling density or strategy between years. In addition, the application of different analytical techniques and/or improvements in the performance of analytical instruments might have contributed to the variation in element concentrations in mosses between years.

Arsenic

As in 2005, arsenic concentrations in mosses were generally low in northern Europe (Figure 3.1 and 3.2). However, arsenic concentrations in mosses have changed in these areas since 2005, with both increases and decreases being observed. In Sweden, the median value was higher in 2010 due to a higher limit of quantification than in 2005, hence the considerable presence of red and brown areas indicated on the map expressing the 2010 data as a percentage of the 2005 data. High levels of arsenic were observed in south-eastern Europe (Macedonia, Romania and Bulgaria). Considerable reductions in the median arsenic concentration were found in Belgium (76%), Italy-Bolzano (52%), France (51%) and Slovenia (41%). The median arsenic concentration has increased in Spain since 2005, primarily due to an increase of the concentration in mosses sampled in Galicia (as a decline

was observed in Navarra). In Spain, the highest arsenic values were found in mosses in Rioja. The general decline in France strongly reduced the cross-border gradient that was reported in 2005 between France and Switzerland. For the 17 countries reporting arsenic data in both 2005 and 2010, the average median value has declined by 25% from 0.27 to 0.21 mg kg^{-1}. Since 1995, the average median arsenic concentration has declined by 26% (Figure 3.2), which is similar to the 30% decline in arsenic emissions in the EU (EEA, 2012). Based on the data for the four countries that reported arsenic in 1990 and 2010, the decline in arsenic concentrations in mosses was 75%, similar to the 64% decline in arsenic emissions in the EU since 1990 (EEA, 2012). Hence, the biggest reductions in arsenic concentrations in mosses occurred between 1990 and 1995.

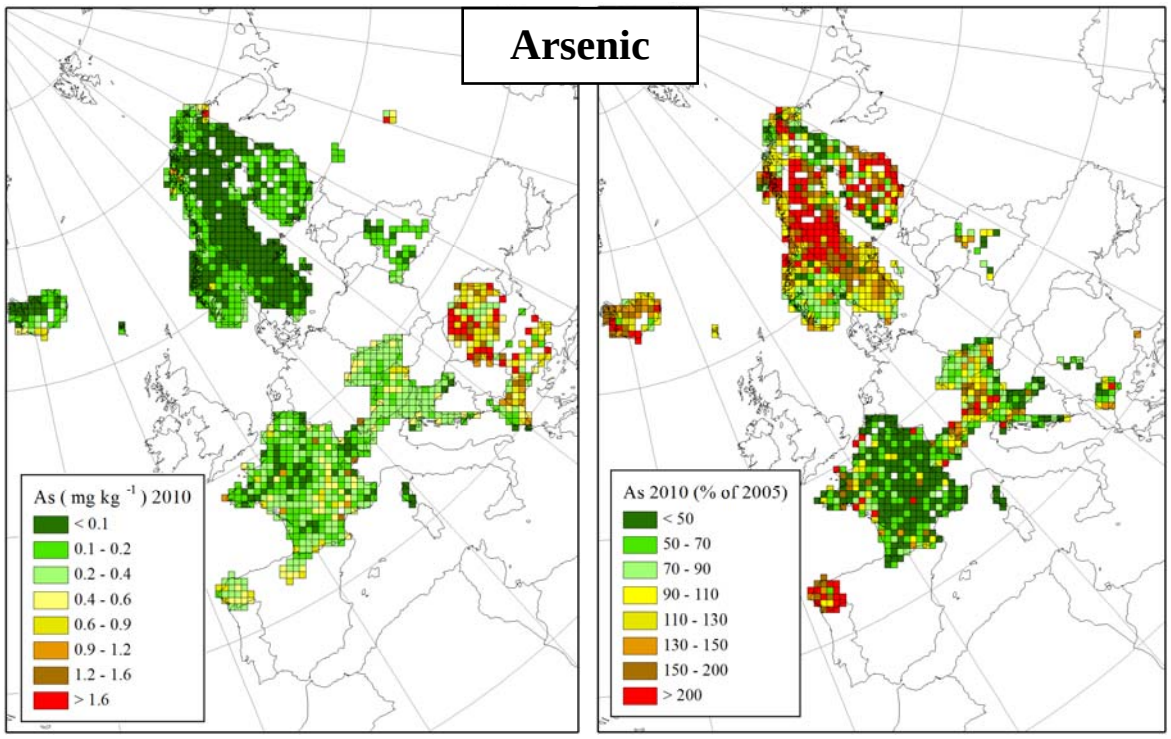

Figure 3.1. Mean arsenic concentration in mosses per EMEP grid cell in 2010 (left) and expressed as percentage of the values in 2005 (right); values below 100% represent a decline, values above 100% represent an increase since 2005.

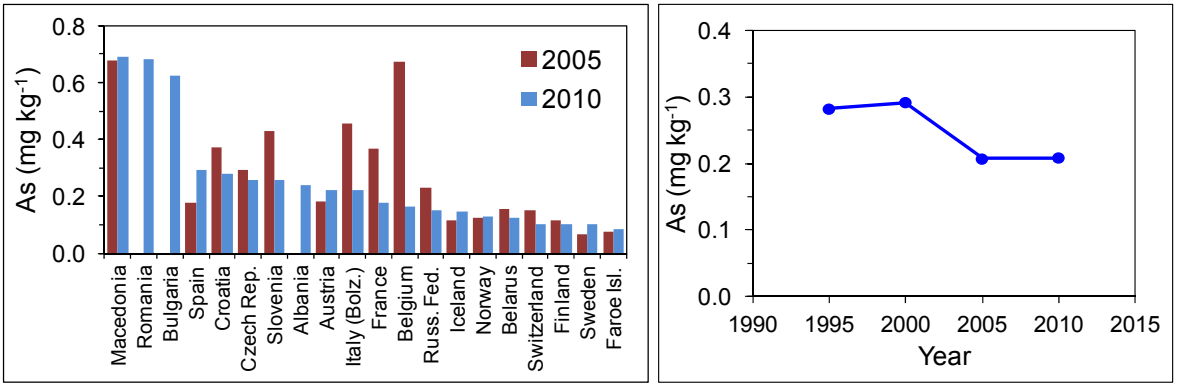

Figure 3.2. Median arsenic concentrations in 2005 and 2010 (left) and average median arsenic concentration in mosses for countries (n = 14-16, depending on year) that reported arsenic data for at least three survey years since 1995 (right).

Cadmium

As in 2005, cadmium concentrations in mosses were generally low in northern Europe (Figure 3.3 and 3.4). The cadmium levels were lowest in north-west Scandinavia, Iceland, and western parts of France. However, in France the median value has increased since 2005. This is likely due to the

higher uncertainty and potential underestimation of the cadmium concentrations in mosses in 2005, particularly in areas with low cadmium concentrations in mosses (Harmens et al., 2008a). Relatively low median values were also observed in Albania, Kosovo and the Russian Federation. Very high levels of cadmium were observed in Romania, followed by Slovakia, Croatia, Ukraine and Belgium. However, in Belgium the median value has declined by 38% since 2005. Whereas a decline has also been found in other countries, several countries reported an increase of the median value since 2005. Hence, for the 21 countries reporting cadmium data in both 2005 and 2010, the average median value has declined by only 7% from 0.21 to 0.20 mg kg^{-1}. In Spain, an increase in the cadmium concentrations in mosses in 2010 compared to 2005 was observed in both Galicia and Navarra. Since 1990, the average median cadmium concentration has declined by 51% (Figure 3.4), which is the same as the decline in modelled deposition (Ilia Ilyin, pers. comm.; Travnikov et al., 2012). The decline in cadmium concentrations in mosses has slowed down since 2000.

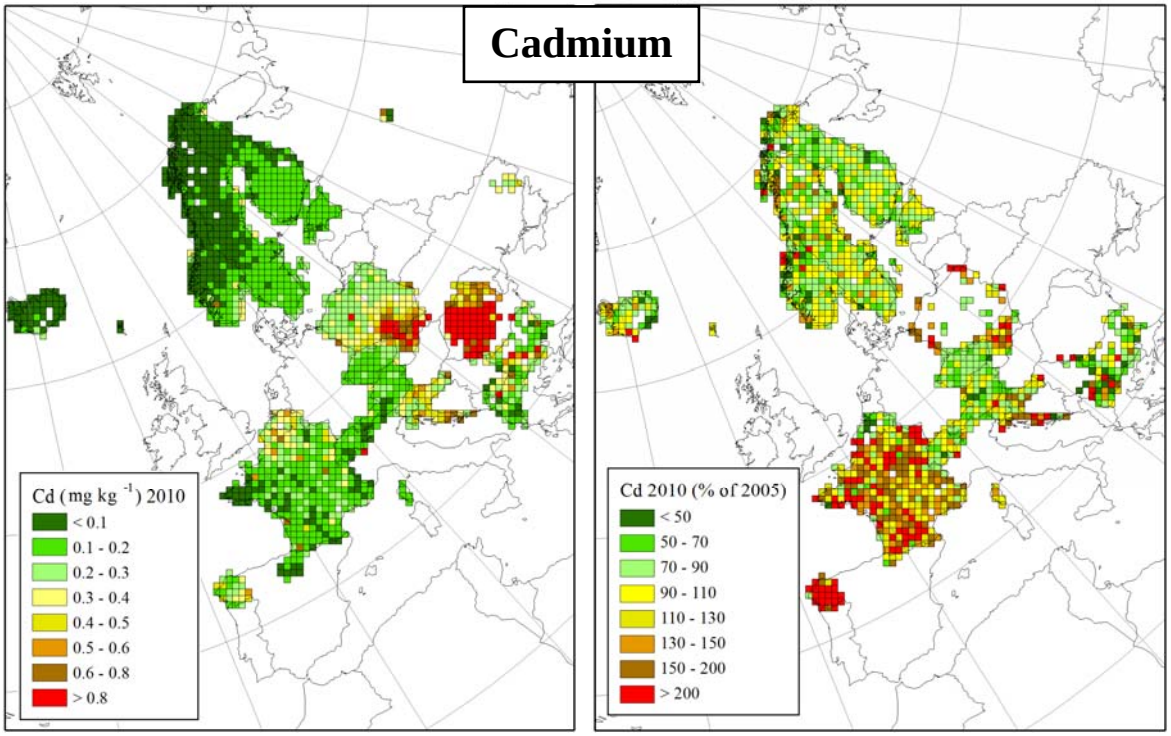

Figure 3.3. Mean cadmium concentration in mosses per EMEP grid cell in 2010 (left) and expressed as percentage of the values in 2005 (right); values below 100% represent a decline, values above 100% represent an increase since 2005.

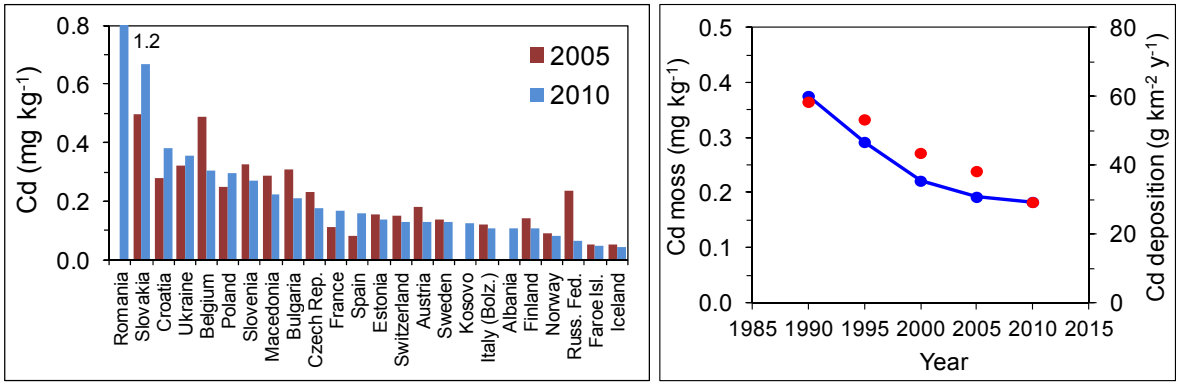

Figure 3.4. Median cadmium concentrations in 2005 and 2010 (left) and average median cadmium concentration in mosses for countries (n = 14-21, depending on year) that reported cadmium data for at least four survey years since 1990 (right); the red dots indicate the average cadmium deposition flux modelled by EMEP.

Chromium

Chromium concentrations in mosses show a clear east-west gradient, with the highest values being observed in eastern Europe, e.g. the Russian Federation, Romania, Albania, Macedonia and Belarus (Figure 3.5 and 3.6). The high values in Belarus, Romania and the Russian Federation might be explained partly by using neutron activation analysis, a technique that generally results in higher chromium concentrations as other techniques require acid digestion of the samples first, and this digestion is generally not complete for chromium (Smodiš and Bleise, 2007). However, this can't explain the increase in the median values of chromium in the Russian Federation and Belarus since 2005. In general, the determination of chromium concentrations in mosses is associated with considerable uncertainty (Steinnes et al., 1997; Smodiš and Bleise, 2007). A considerable decline of the median value of chromium between 2005 and 2010 was reported for Belgium (79%), Spain (77%), Ukraine (61%), Italy-Bolzano (53) and Macedonia (49%). Changes in Ukraine and the Russian Federation since 2005 are confounded by the fact that mosses were sampled from different regions in 2005 and 2010. In 2005, high chromium concentrations in mosses were also found in Galicia (Spain), but Galicia did not determine chromium concentrations in 2010. Nevertheless, a considerable decline in the median value for chromium was found between 2005 and 2010 in Navarra (67%). The decline in Macedonia might be partly due to using neutron activation analysis in 2005 and ICP-ES in 2010 to determine chromium concentrations in mosses. In eastern France, much lower chromium concentrations were observed in 2010 compared to 2005 (although this did not affect the median value that much due to the much lower chromium concentrations in western compared to eastern France in both survey years), resulting in a much more homogenous spatial pattern of chromium in mosses across France. This reduced the cross-border gradient with Switzerland that was observed in 2005. In Sweden, there was a high spatial variation in the changes in chromium concentrations in mosses since 2005. For the 20 countries reporting chromium data in both 2005 and 2010, the average median value has declined by 23% from 2.37 to 1.82 mg kg^{-1}. Since 1990, the average median chromium concentration in mosses has declined by 43% (Figure 3.6), which is much lower than the 73% decline in emissions in the EU (EEA, 2012).

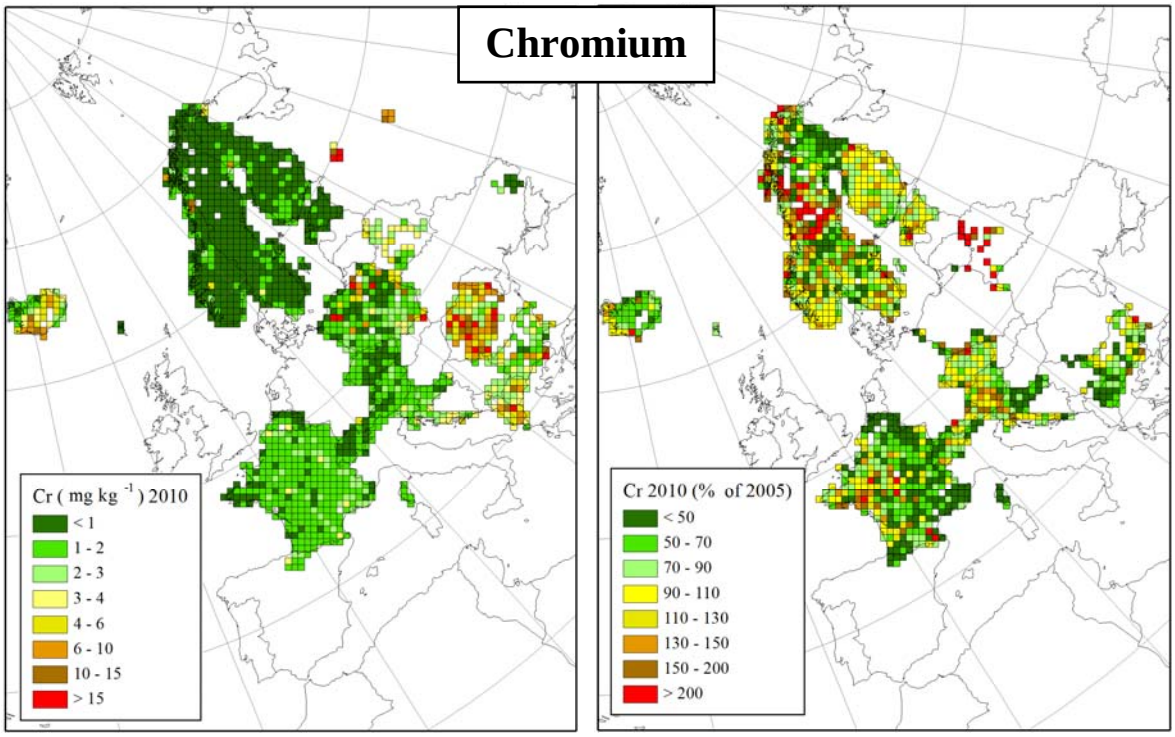

Figure 3.5. Mean chromium concentration in mosses per EMEP grid cell in 2010 (left) and expressed as percentage of the values in 2005 (right); values below 100% represent a decline, values above 100% represent an increase since 2005.

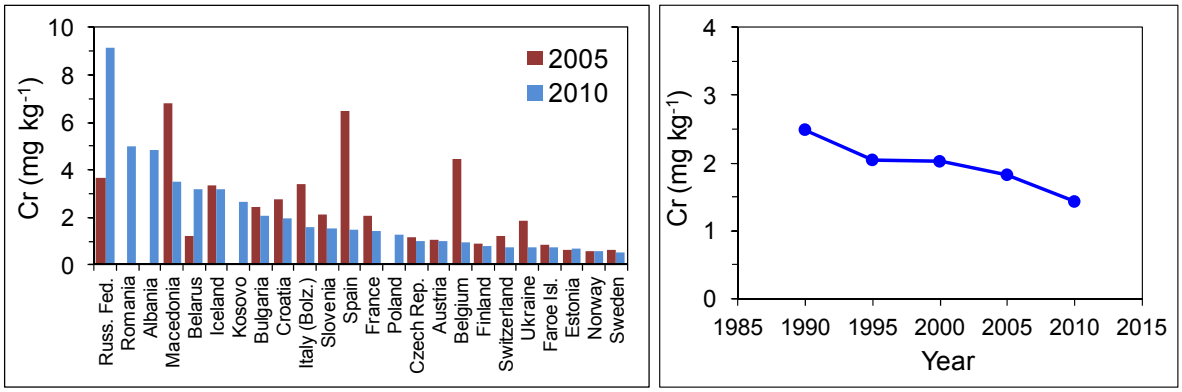

Figure 3.6. Median chromium concentrations in 2005 and 2010 (left) and average median chromium concentration in mosses for countries (n = 17-20, depending on year) that reported chromium data for at least four survey years since 1990 (right).

Copper

The highest copper concentrations in mosses were found in parts of eastern Europe, i.e. Ukraine, Romania, Slovakia and Bulgaria (Figure 3.7 and 3.8). However, low copper concentrations were found in Albania, Kosovo and Macedonia. As in previous years, the lowest copper concentrations were found in northern Europe, although locally high concentrations were detected at the Norwegian-Finnish-Russian border in the north due to the presence of very polluting copper-nickel smelters in the Kola Peninsula at the Russian side of the border (see Annex 4). In several countries the copper concentration in mosses has declined between 2005 and 2010, particularly in Belgium, Bulgaria and Macedonia (decline by more than one-third). The high increase in the Ukraine since 2005 can to some extent be explained by sampling being limited to the Donetsk region in 2010, which is quite an industrialised region. For the 21 countries reporting copper data in both 2005 and 2010, the average median value has declined by only 6% from 6.96 to 6.53 mg kg^{-1}. Since 1990, the average median copper concentration has declined by 11% (Figure 3.8), which is the lowest decline reported for all elements, in agreement with the 0.5% decline in emission in the EU (EEA, 2012).

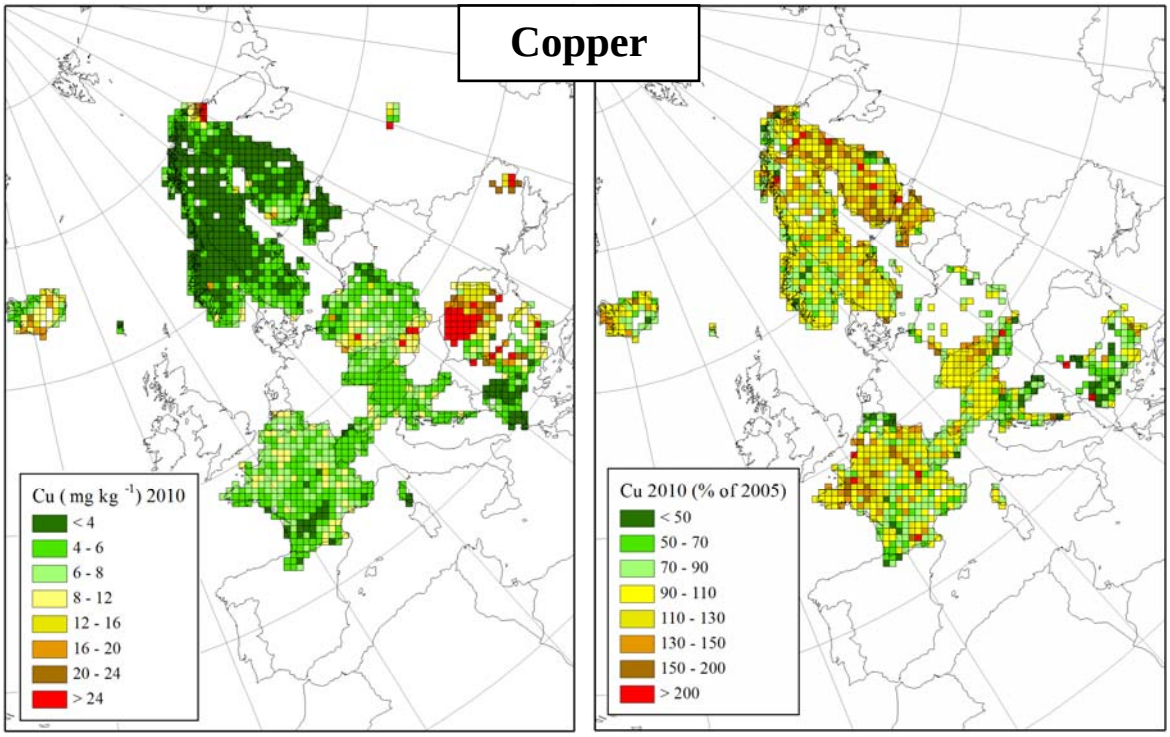

Figure 3.7. Mean copper concentration in mosses per EMEP grid cell in 2010 (left) and expressed as percentage of the values in 2005 (right); values below 100% represent a decline, values above 100% represent an increase since 2005.

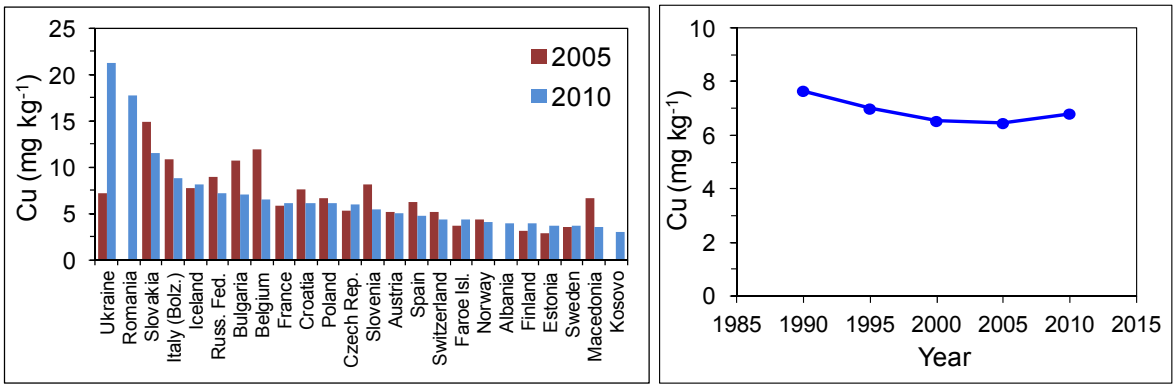

Figure 3.8. Median copper concentrations in 2005 and 2010 (left) and average median copper concentration in mosses for countries (n = 15-20, depending on year) that reported copper data for at least four survey years since 1990 (right).

Iron

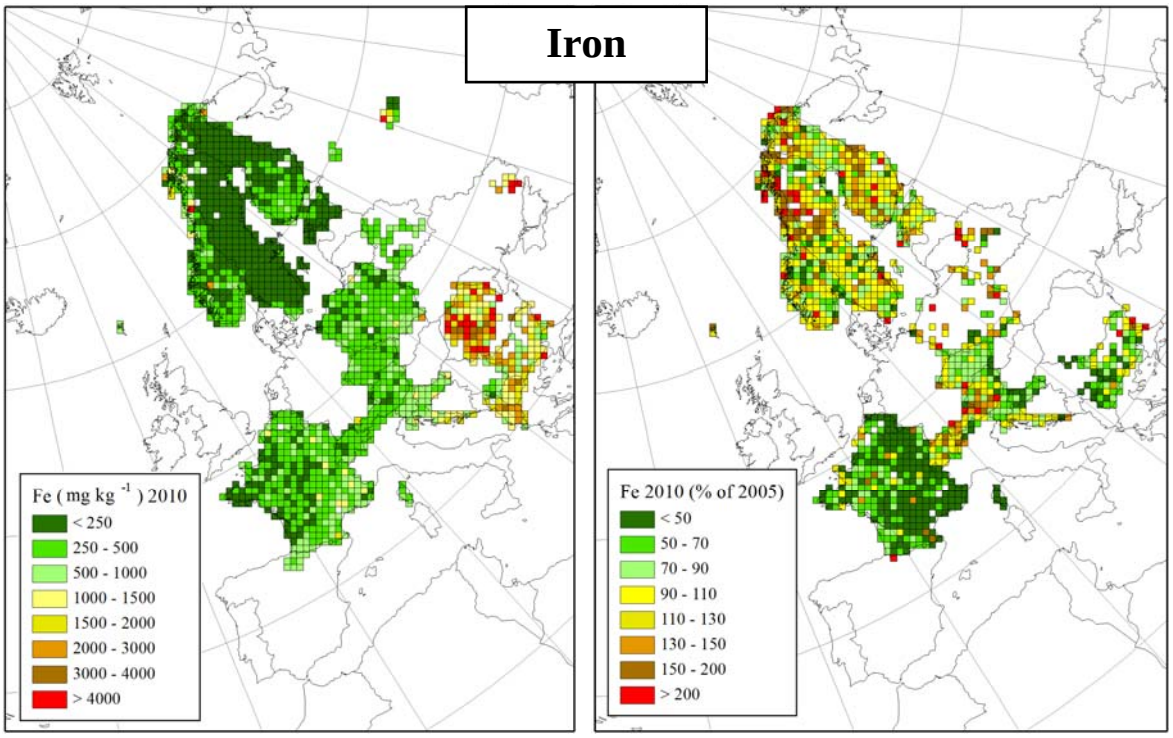

Figure 3.9. Mean iron concentration in mosses per EMEP grid cell in 2010 (left) and expressed as percentage of the values in 2005 (right); values below 100% represent a decline, values above 100% represent an increase since 2005.

As in previous years, there is a clear east-west gradient in Europe for the iron concentration in mosses, with the highest median values being reported for Romania, Albania, Macedonia (despite a decline since 2005), Ukraine and Bulgaria (Figures 3.9 and 3.10). Again, the lowest values were found in northern Europe. The biggest change since 2005 is the decline in the median iron concentration in mosses in Belgium, Italy (Bolzano) and France (particularly in eastern parts), with a decrease in the median value of 62%, 58% and 52% respectively. For France this has resulted in a more homogenous distribution of the iron concentration in mosses and disappearance of the cross-border gradient with Switzerland, which was present in 2005. This would indicate that in 2010 re-suspension of soil dust by wind has contributed much less to iron concentrations in mosses sampled particularly in eastern and southern parts of France. This is in agreement with the findings for other metals such as aluminium, chromium, and vanadium that can derive a considerable contribution from wind-blown dust. Once again, the rise in the median iron concentration in Ukraine can be explained to

some extent by sampling in the Donetsk region only in 2010. Remarkable is the increase (113%) in the median iron concentration in mosses sampled at seven sites on the Faroe Islands. For the 20 countries reporting iron data in both 2005 and 2010, the average median value has declined by 15% from 629 to 538 mg kg^{-1}. Since 1990, the average median iron concentration has declined by 52% (Figure 3.10), with the highest decline occurring between 1990 and 1995.

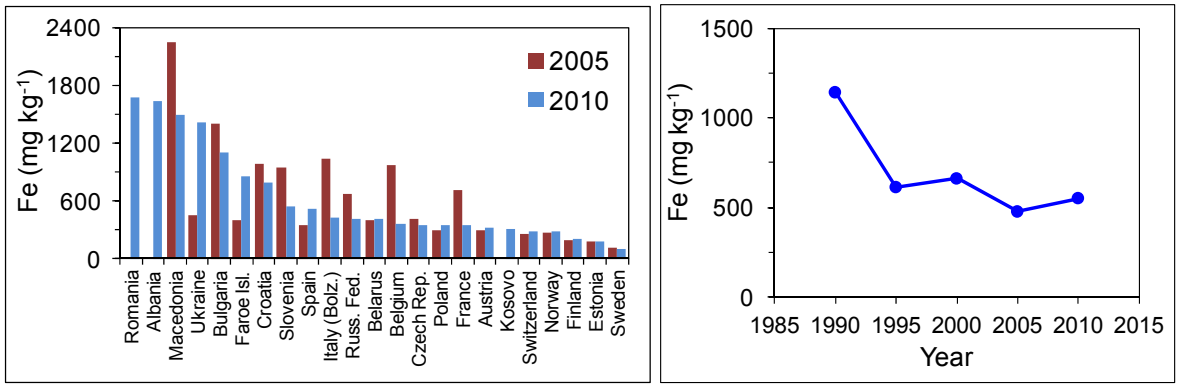

Figure 3.10. Median iron concentrations in 2005 and 2010 (left) and average median iron concentration in mosses for countries (n = 15-21, depending on year) that reported iron data for at least four survey years since 1990 (right).

Lead

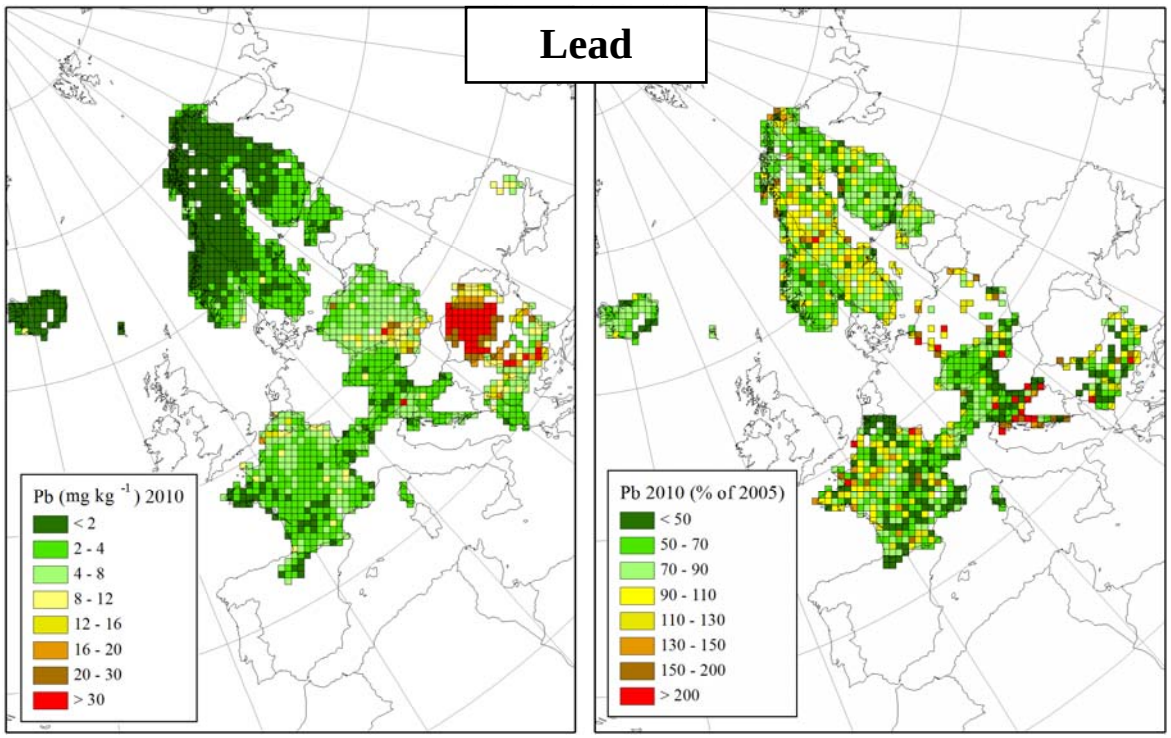

Figure 3.11. Mean lead concentration in mosses per EMEP grid cell in 2010 (left) and expressed as percentage of the values in 2005 (right); values below 100% represent a decline, values above 100% represent an increase since 2005.

Although measures were put in place to reduce the lead levels in petrol since the 1970s, in many European countries a full implementation of the ban on the use of leaded petrol in cars was only implemented in the 1990s. The phasing out of the use of leaded petrol across Europe has resulted in a considerable decline in the lead concentration in mosses since the first European moss survey in 1990 (Harmens et al., 2010). This decline has continued in 2010, with the average median lead concentration in mosses decreasing by a further 36% from 5.62 mg kg^{-1} in 2005 to 3.57 mg kg^{-1} in

2010 (Figure 3.11 and 3.12). However, very high lead concentrations in mosses were still reported in Romania, where the use of leaded petrol was banned completely only since January 2012. In addition, the presence of large industrial areas (including metallurgical works or melting plants) located in Baia Mare, Magoaja, Letca, Cergau or Zagra and Copsa Mica, contribute to the high concentration of lead in mosses (Lucacia et al., 2010). Relatively high lead concentrations were also found in Slovakia, Bulgaria, Kosovo, Ukraine and Slovenia, although the median lead concentration in mosses has declined between 31% and 50% in Slovakia, Bulgaria and Slovenia since 2005. Relatively high lead concentrations were also found in parts of southern Poland. The huge decline of lead in mosses in Belgium since 2005 (decrease of the median value by 74%) suggests that the implementation of clean air policies for heavy metals are finally starting to pay off in Belgium in line with neighbouring European countries. A slight increase in the median lead concentration in mosses since 2005 was only reported for Croatia, which might be due to the relatively low median value being reported for 2005 (compared to neighbouring countries). Since 1990, the average median lead concentration has declined by 77% (Figure 3.12). The decline in modelled lead deposition was 74% over the same period (Ilia Ilyin, pers. comm.; Travnikov et al., 2012).

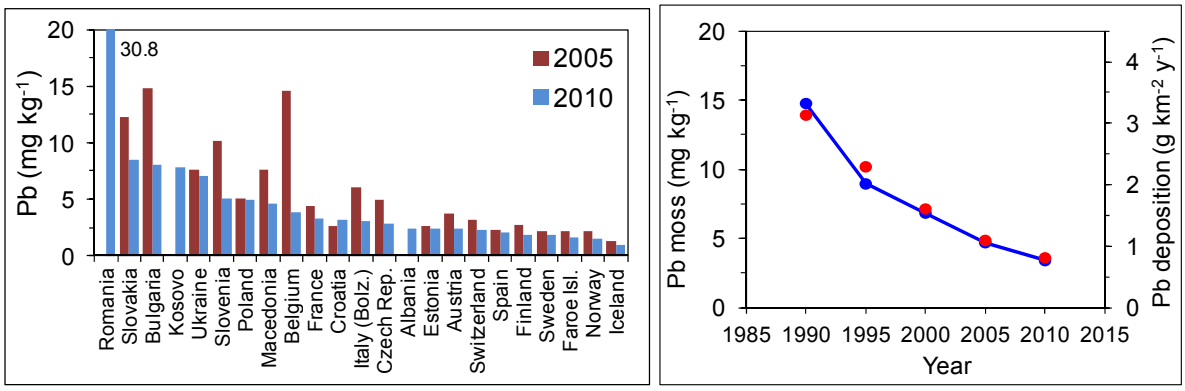

Figure 3.12. Median lead concentrations in 2005 and 2010 (left) and average median lead concentration in mosses for countries (n = 15-19, depending on year) that reported lead data for at least four survey years since 1990 (right); the red dots indicate the average lead deposition flux modelled by EMEP.

Mercury

In contrast to other metals, mercury is a global pollutant and can be transported in the atmosphere around the globe. Therefore, emission sources located on other continents have a significant impact on mercury pollution in Europe. Due to the long residence time of gaseous mercury in the atmosphere, most of it will be transported outside Europe. Although natural emission sources and re-emission of gaseous mercury in Europe contribute significantly to mercury input into the atmosphere, its contribution to deposition fluxes is small. However, dry deposited gaseous mercury is thought to contribute considerably to mercury concentrations in mosses (Harmens et al., 2010, and references therein). The global nature of mercury pollution appears to result in a more homogenous spatial pattern of mercury concentration in mosses in Europe compared to the other metals. The highest levels of mercury in mosses were found in Albania and Macedonia, followed by Italy, Poland and France (Figure 3.13 and 3.14). In France, particularly areas with relatively high mercury concentrations in 2005 showed a considerable decline in the concentrations in mosses in 2010. Relatively high levels of mercury were also reported for Norway (see Annex 4) and the levels have increased since 2005 in many parts of Norway. Arctic Mercury Depletion Events might be contributing to the elevated mercury concentrations in mosses in northern Norway (Berg et al., 2008). Whereas in many areas in southern Finland the mercury concentration in mosses has increased since 2005, the opposite was true for many areas in northern Finland. As with many other metals, since 2005 a considerable decline in mercury concentrations in mosses was reported for Belgium (decrease of the median value by 59%). The decline (47%) observed in Slovenia might be partly due to either a more careful approach during sampling, trying to avoid sampling mosses strongly affected by canopy drip from trees, or the fact that the majority of sampling sites were different for 2005 and 2010. For the 12

countries reporting mercury data in both 2005 and 2010, the average median value has declined by 20% from 0.066 to 0.053 mg kg^{-1}. Since 1995, the average median mercury concentration has declined by 23% (Figure 3.14). The reduction in modelled mercury deposition was 27% since 1995 and 36% since 1990 (Ilia Ilyin, pers. comm.; Travnikov et al., 2012). In 1990, the mercury concentration in mosses was only determined in Austria and Switzerland; in these countries the average median mercury concentration has declined by 37% between 1990 and 2010.

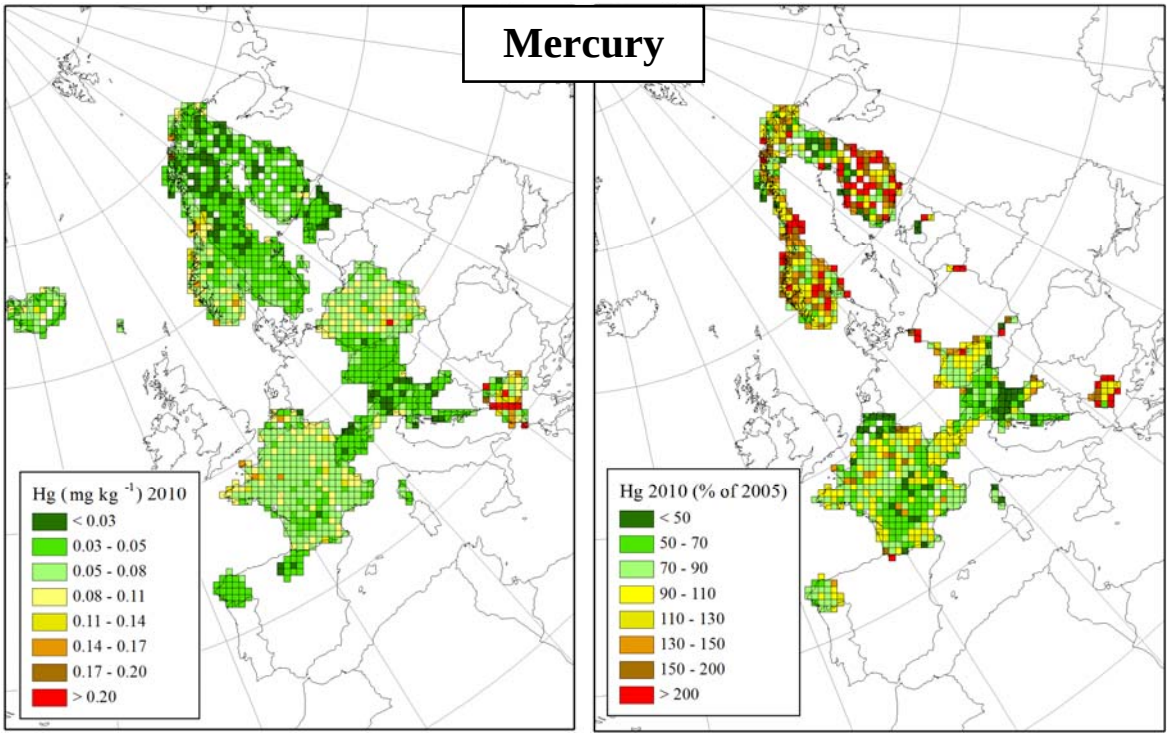

Figure 3.13. Mean mercury concentration in mosses per EMEP grid cell in 2010 (left) and expressed as percentage of the values in 2005 (right); values below 100% represent a decline, values above 100% represent an increase since 2005.

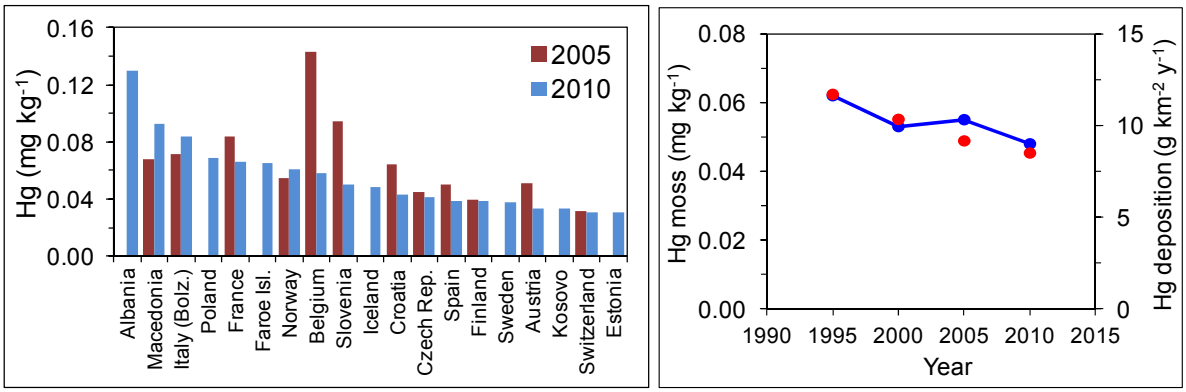

Figure 3.14. Median mercury concentrations in 2005 and 2010 (left) and average median mercury concentration in mosses for countries (n = 9-12, depending on year) that reported mercury data for at least three survey years since 1995 (right); the red dots indicate the average mercury deposition flux modelled by EMEP.

Nickel

In general, the highest nickel concentration were found in (south)eastern European countries, although high nickel concentrations were also observed in Iceland (Figure 3.15 and 3.16). As for copper, locally high concentrations of nickel were detected at the Norwegian-Finnish-Russian border in the north due to the presence of very polluting copper-nickel smelters in the Kola Peninsula at the Russian side of the border (see Annex 4). The spatial pattern for nickel is similar to that reported in

2005, although nickel concentrations in mosses have declined considerably in Belgium (decline of median value by 64%), eastern parts of France (resulting in a decline of the median value in France by 21%) and northern Spain (decline of the median value by 61%). Remarkable is also the homogeneously distributed low concentrations of nickel in Belarus in comparison with 2005. In Macedonia and northern Italy (Bolzano), the median value for nickel has declined by 41-42% since 2005. For Ukraine, the increase in the median value of nickel concentrations in mosses since 2005 is most likely due to sampling mosses in a more polluted region (Donetsk) in 2010. For the 21 countries reporting nickel data in both 2005 and 2010, the average median value has declined by 12% from 2.21 to 1.94 mg kg^{-1}. Since 1990, the average median nickel concentration has declined by 33% (Figure 3.16), which is considerably lower than the reported 59% decline in nickel emissions in the EU since 1990 (EEA, 2012).

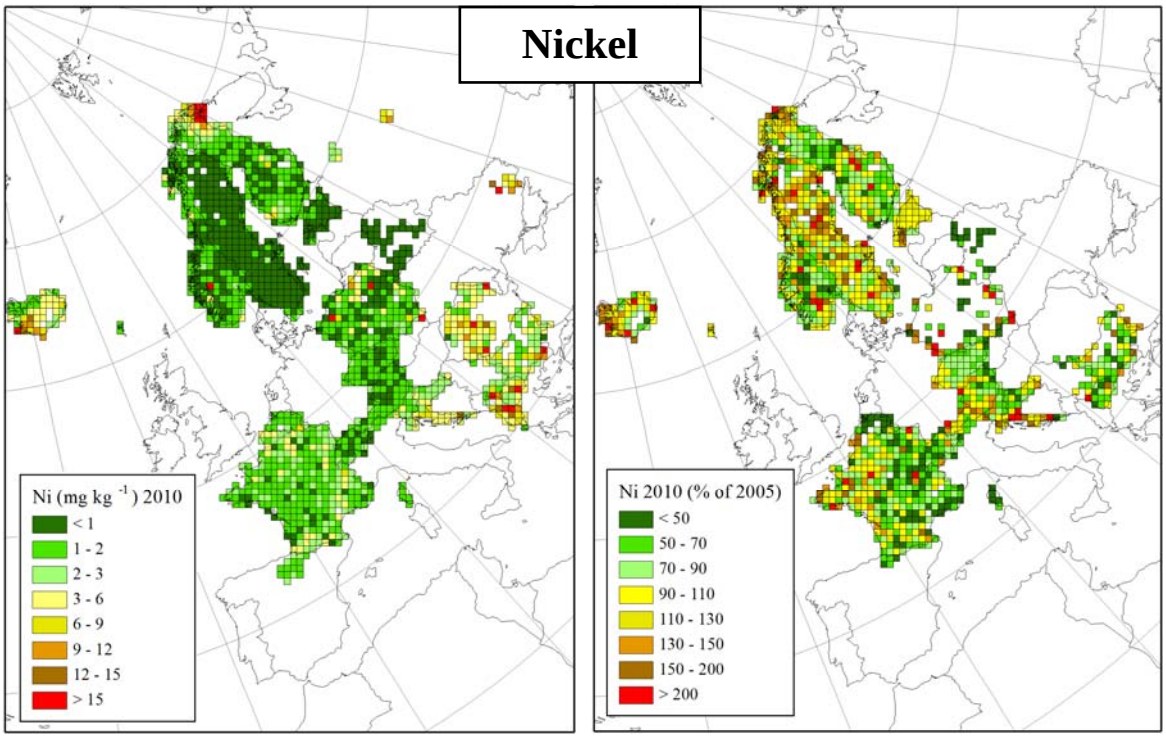

Figure 3.15. Mean nickel concentration in mosses per EMEP grid cell in 2010 (left) and expressed as percentage of the values in 2005 (right); values below 100% represent a decline, values above 100% represent an increase since 2005.

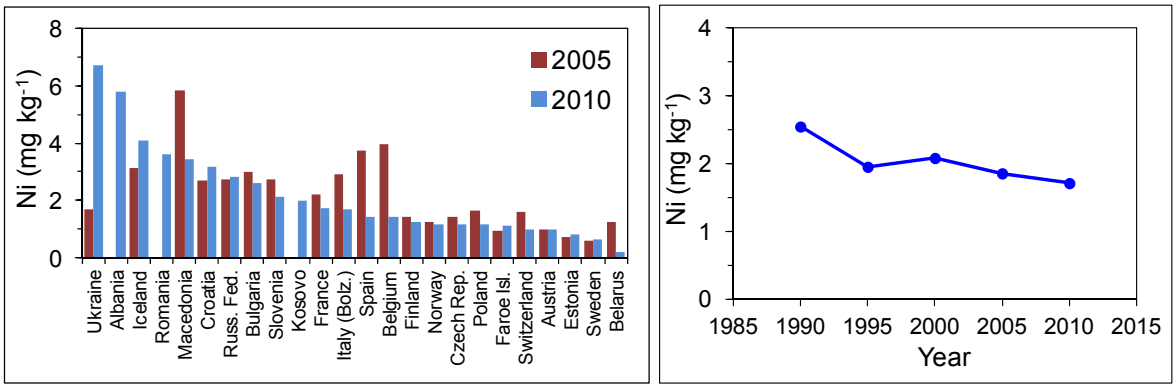

Figure 3.16. Median nickel concentrations in 2005 and 2010 (left) and average median nickel concentration in mosses for countries (n = 16-20, depending on year) that reported nickel data for at least four survey years since 1990 (right).

Vanadium

In 2010, the highest vanadium concentrations were reported for mosses in south-eastern Europe, i.e. Romania, Albania, Macedonia and Bulgaria (Figure 3.17 and 3.18). High median concentrations were also observed on the Faroe Islands, similarly to 2005. Low vanadium concentrations were generally found in the rest of Europe. As for many other metals, the decline in the median concentration of vanadium in mosses between 2005 and 2010 is remarkable for Belgium (75%). Since 2005, a decline in the median value of more than 45% was observed in Macedonia, Italy (Bolzano region), France and Slovakia. For France this has resulted in a more homogenous spatial distribution of vanadium concentration in mosses compared to 2005, when a clear east-west gradient was present with higher concentrations in mosses in the east. Increases in the mean values per EMEP grid since 2005 were observed in parts of northern Finland, the north-west coast of Norway and in many areas of Austria.

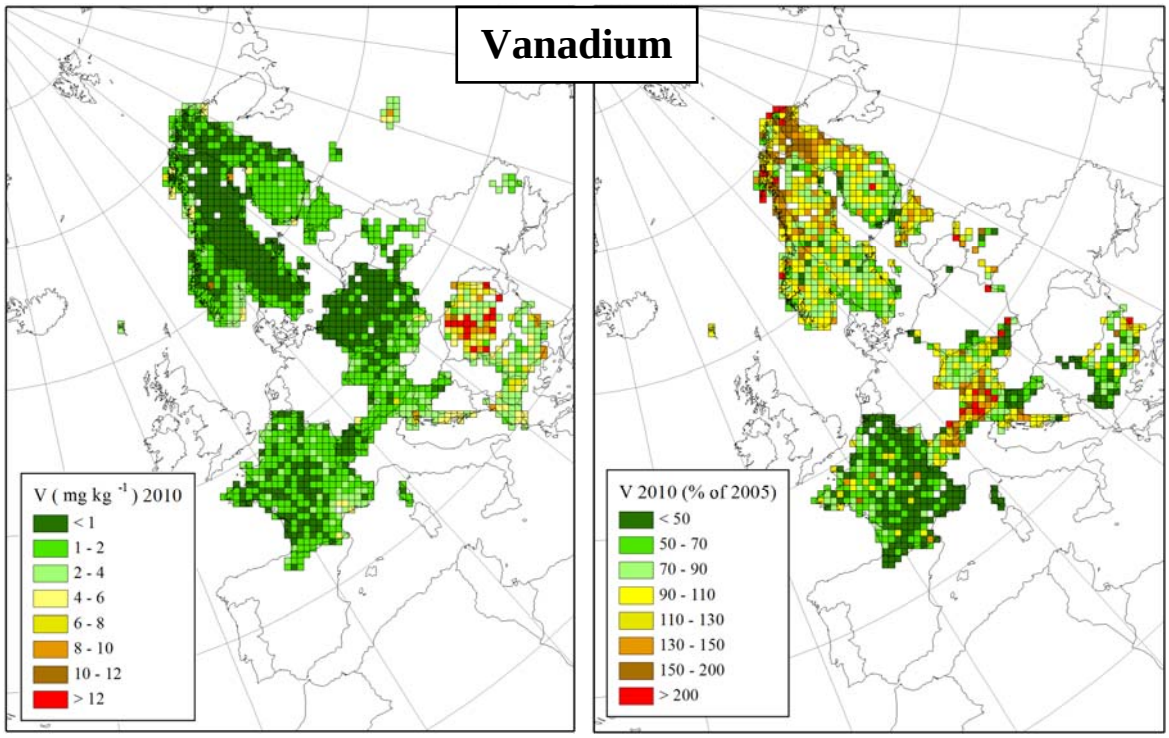

Figure 3.17. Mean vanadium concentration in mosses per EMEP grid cell in 2010 (left) and expressed as percentage of the values in 2005 (right); values below 100% represent a decline, values above 100% represent an increase since 2005.

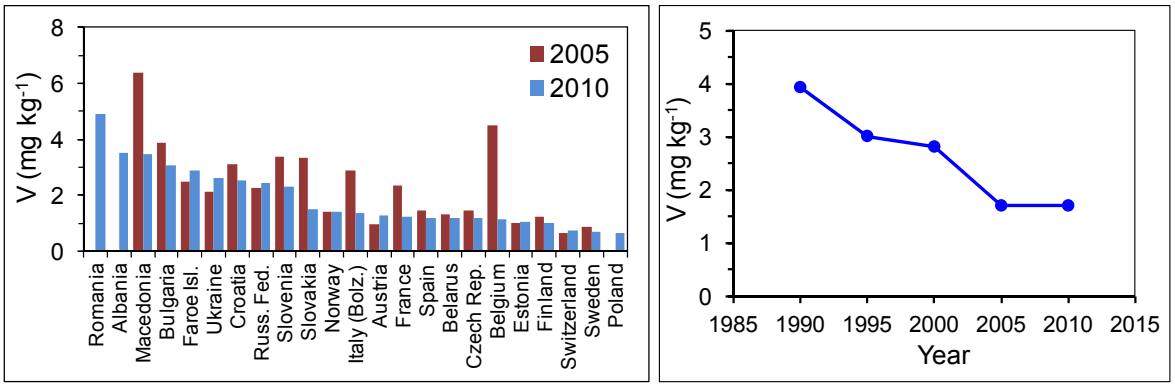

Figure 3.18. Median vanadium concentrations in 2005 and 2010 (left) and average median vanadium concentration in mosses for countries (n = 11-18, depending on year) that reported vanadium data for at least four survey years since 1990 (right).

As only a few countries showed a small increase in the median value since 2005, the average median value has declined by 27% from 2.36 to 1.72 mg kg^{-1} for the 20 countries reporting vanadium

concentrations in mosses in both 2005 and 2010. Since 1990, the average median vanadium concentration has declined by 57% (Figure 3.18).

Zinc

Of all metals, the zinc concentration in mosses has the most homogenous distribution across Europe, with locally or regionally elevated concentrations being observed (Figure 3.19 and 3.20). In 2010, the highest median values were found in Ukraine, Poland, Belgium, Romania and Kosovo, whereas the lowest median values were reported for Albania, Faroe Islands, Macedonia, Iceland and Bulgaria. As for many other metals, the decline in the median concentration of zinc in mosses between 2005 and 2010 is remarkable for Belgium (43%) and Macedonia (44%). As many other countries showed only a small decline or even a slight increase in the median value since 2005, the average median value has declined by only 7% from 33.4 to 31.0 mg kg^{-1} for the 21 countries reporting zinc concentrations in mosses in both 2005 and 2010.

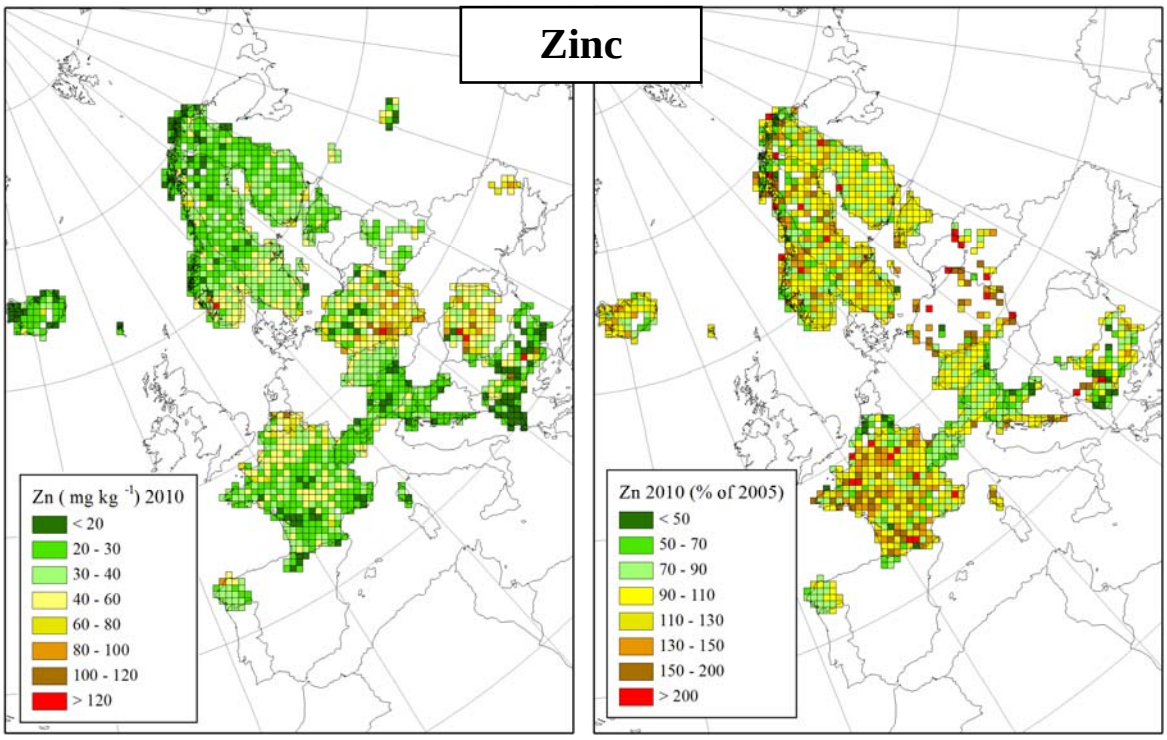

Figure 3.19. Mean zinc concentration in mosses per EMEP grid cell in 2010 (left) and expressed as percentage of the values in 2005 (right); values below 100% represent a decline, values above 100% represent an increase since 2005.

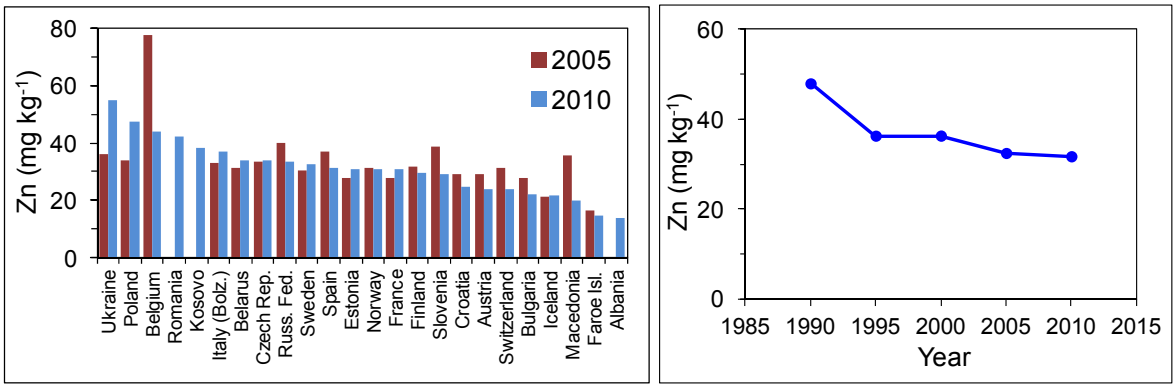

Figure 3.20. Median zinc concentrations in 2005 and 2010 (left) and average median zinc concentration in mosses for countries (n = 16-22, depending on year) that reported zinc data for at least four survey years since 1990 (right).

Since 1990, the average median zinc concentration has declined by 34% (Figure 3.20). This is slightly lower than the 43% decline in emissions in Europe (EEA, 2012). The biggest decline was observed between 1990 and 1995.

Aluminium

Away from local pollution sources, aluminium is a good indicator of mineral particles, mainly windblown soil dust, as it is present at high concentrations in the earth's crust. Therefore, the spatial pattern of aluminium concentrations in mosses might provide an indication of the contribution of wind re-suspension to the deposition of metals to mosses, reflecting to some extent historical deposition of heavy metals. There is an east-west gradient across Europe, indicating that in the dryer regions of Europe with mosses directly growing on mineral soil the deposition of soil dust on mosses is higher (Figure 3.21). For some metals this might explain the higher concentration in mosses in certain regions of Europe, for example, the high concentrations of chromium, iron, and vanadium in south-eastern European countries. Strong linear relationships (R^2 > 0.70) were found between aluminium and iron, aluminium and vanadium and iron and vanadium concentrations in mosses. A higher accumulation of soil dust does not necessarily translate into a higher deposition flux for all metals in the same way. The deposition flux of metals depends on the particle size distribution, e.g. if aluminium and vanadium were following the same particle size distribution, they would be subjected to re-suspension by wind in the same way. However, we cannot assume that this is the case. For Belarus, Romania, the Russian Federation and Slovakia higher aluminium concentrations in mosses might be expected due to the application of neutron activation analysis, which tends to result in higher concentrations compared to other analytical techniques (Smodiš and Bleise, 2007). However, in Slovakia the median aluminium concentration in mosses has declined considerably (72%) since 2005, when ICP-ES was applied to determine aluminium concentrations. For Romania, the results for antimony indicate that current anthropogenic activities also contribute considerably to high aluminium concentration (and associated metals) in mosses. In France, the results for aluminium and strongly correlated metals suggest that there was a considerably lower contribution from windblown dust to metal concentrations in mosses in 2010 than 2005. The average median value has declined by 28% from 1056 to 762 mg kg^{-1} for the 13 countries reporting aluminium concentrations in both 2005 and 2010.

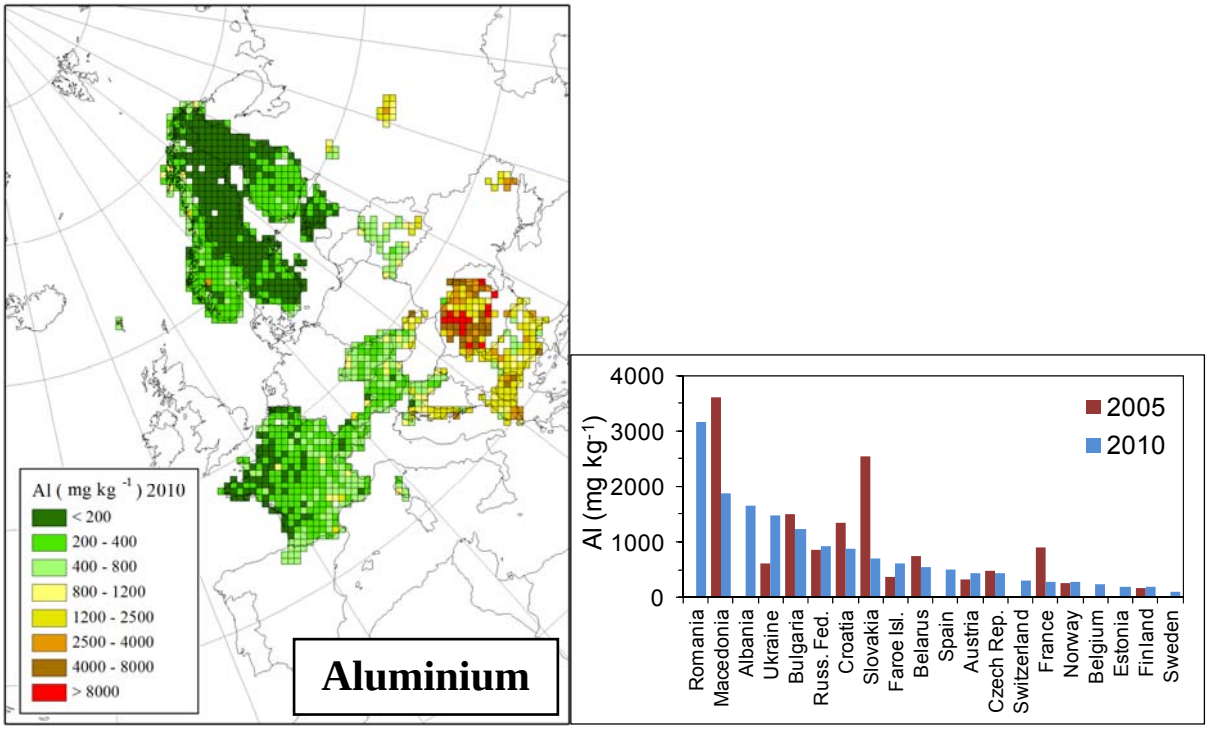

Figure 3.21. Mean aluminium concentration in mosses per EMEP grid cell in 2010 (left) and median aluminium concentrations in mosses in 2005 and 2010 (right).

Antimony

There is a growing use of antimony in automobile brake pads, plastics and flame retardants. Brake pads in cars are thought to be the main source of atmospheric antimony. Antimony is present at very low concentrations in the earth's crust. The increase in production and use of antimony in recent decades has resulted in enrichment of Arctic air by more than 50%. Given that the toxicity of antimony is comparable to that of lead, antimony has now replaced lead in the rank of potentially toxic trace metals in the Arctic atmosphere, which might have broader implications worldwide for ecosystem and human health in the future (Krachler et al., 2005). In 2005, antimony was reported to be the single most highly enriched element in urban dust (Shotyk et al., 2004). Therefore, high concentrations of antimony can be expected in the vicinity of densely populated areas and heavy polluting industries. Relatively high concentrations of antimony were found in Romania, indicating the presence of highly polluting industry in several areas (Figure 3.22). High concentrations were also reported for areas in other countries such as north-western France (including Paris), eastern Austria (Lower Inntal, see Annex 4) and southern Norway (around Oslo). In Norway, the association of antimony with long-range transport of metals was not so evident in recent compared with earlier survey years. Apart from Austria, all countries reported a decline in the median antimony concentration in mosses, with the highest decline being observed in Slovenia (44%) and the Czech Republic (39%). The average median value has declined by 23% from 0.14 to 0.10 mg kg^{-1} for the 7 countries reporting antimony concentrations in mosses in both 2005 and 2010.

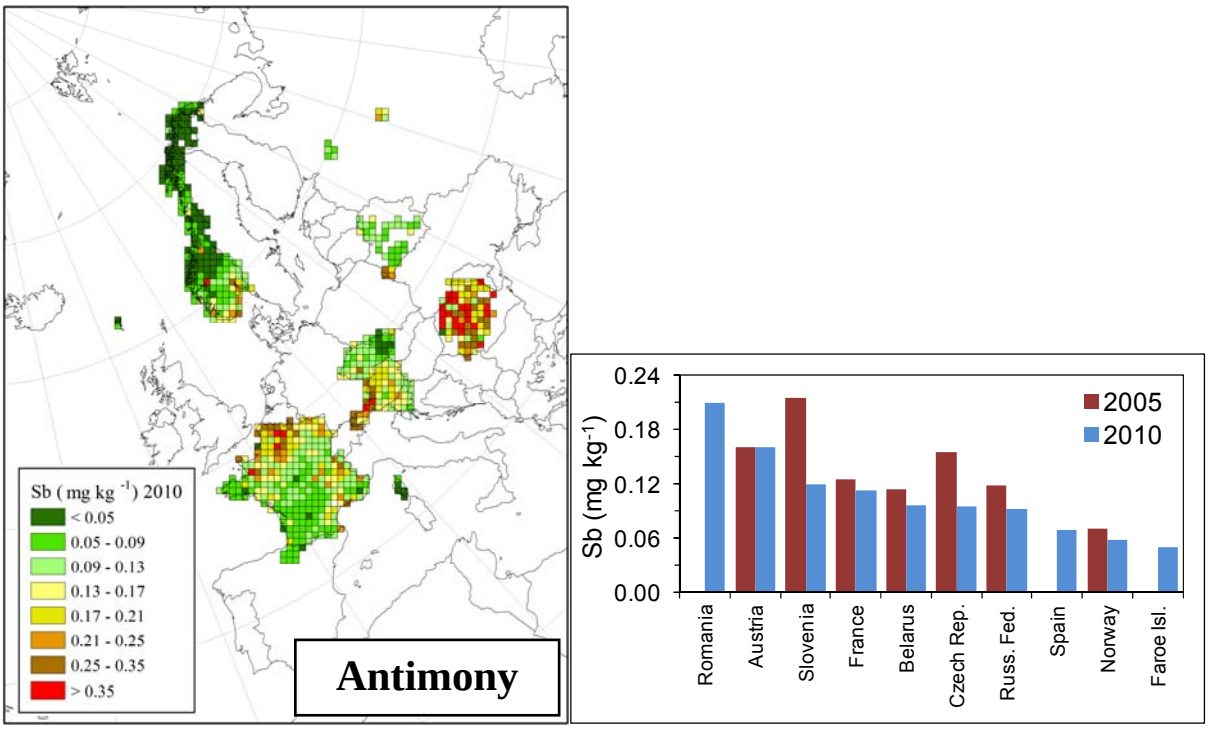

Figure 3.22. Mean antimony concentration in mosses per EMEP grid cell in 2010 (left) and median antimony concentrations in mosses in 2005 and 2010 (right).

Nitrogen

The spatial pattern of the nitrogen concentration in mosses was similar in 2005 and 2010, with lower values being observed for Finland than the rest of Europe (Figure 3.23 and 3.24). Generally, high concentrations of nitrogen were found in western, central and south-eastern Europe. In addition, the average median value for nitrogen has hardly changed since 2005: from 1.26% in 2005 to 1.19% in 2010 (a decline of 5%) for the 13 countries reporting nitrogen concentrations in mosses in both 2005 and 2010. This decline is in agreement with the ca. 7% decline reported by EMEP for modelled total nitrogen deposition in the EU27 between 2005 and 2010. The considerable decline (30%) reported for Slovenia is most likely due to either a more careful sampling campaign, trying to avoid the sampling of mosses affected by canopy drip from trees, or the fact that the majority of sampling sites were

different for 2005 and 2010. Increases in the median values were found in the Czech Republic (19% increase) and France (15%). For France it should be noted that the total nitrogen concentration in mosses was determined at 88 sites in 2005, whereas it was determined at 442 sites in 2010.

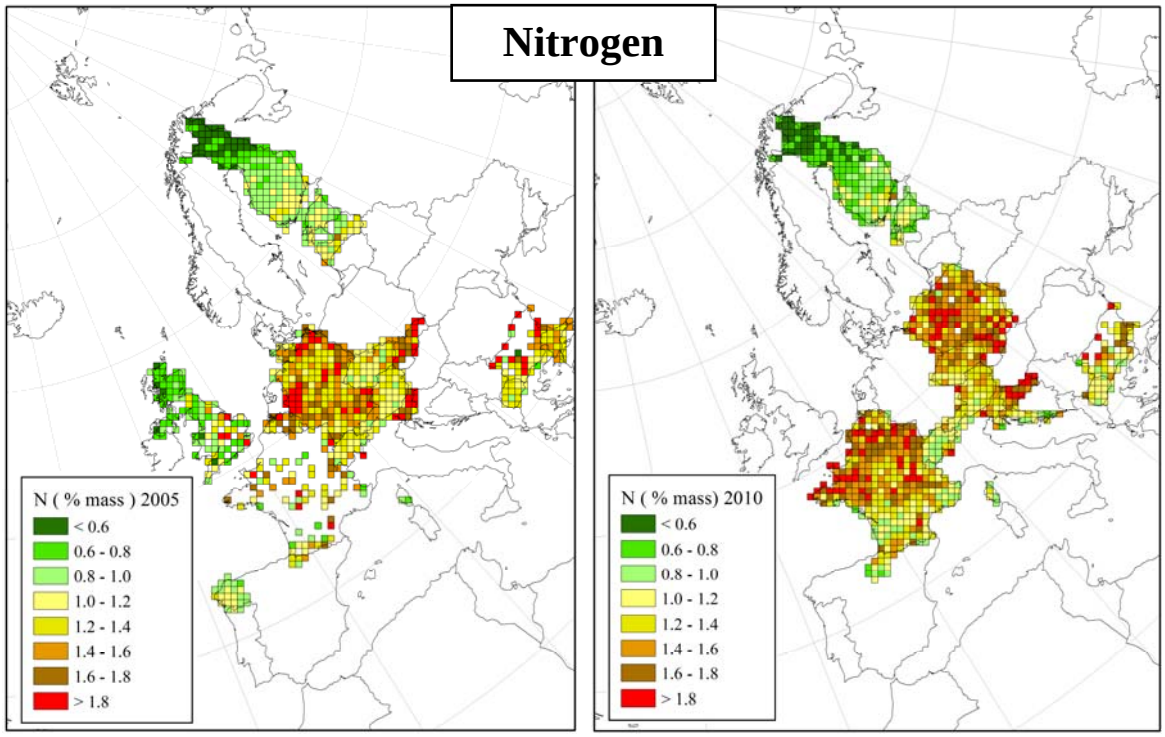

Figure 3.23. Mean total nitrogen concentration in mosses per EMEP grid cell in 2005 (left) and 2010 (right).

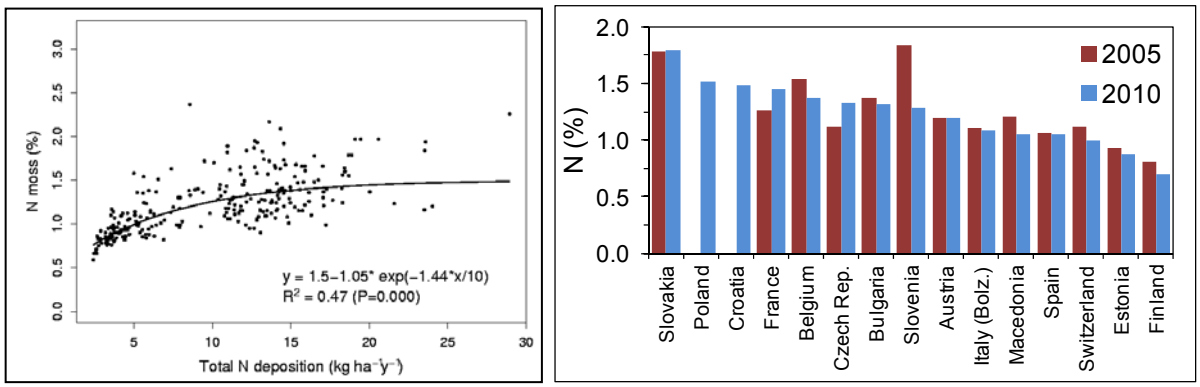

Figure 3.24. Relationship between total nitrogen concentration in mosses and EMEP-modelled total nitrogen deposition in 2005 (left; Harmens et al., 2011) and median total nitrogen concentrations in mosses in 2005 and 2010 (right)

The relationship between the total nitrogen concentration in mosses and EMEP-modelled deposition has not been analysed yet for 2010, however, it is expected that the relationship will be similar to the one reported for 2005 (Figure 3.24). In 2005, this relationship showed saturation occurring at a modelled deposition rate of ca. 15 kg N ha^{-1} y^{-1} (Harmens et al., 2011). In Switzerland, a linear relationship was found between the nitrogen concentration in mosses and measured bulk nitrogen deposition at the site level in 2005, and a similar relationship was found in 2010 (see Annex 4).

4 Discussion, conclusions and recommendations

Heavy metals

The decline in emission and subsequent deposition of heavy metals across Europe has resulted in a decrease in the heavy metal concentration in mosses since 1990, with the decrease continuing for all metals between 2005 and 2010. For many metals the biggest decline occurred between 1990 and 1995 (or 2000). Many emission sources have become cleaner, for example by using filters or other best available technologies, by changing from coal to gas as fuel source or phasing out leaded petrol in many parts of Europe. In addition, some very polluting local emission sources have been shut down since 1990, in particular in eastern Europe. For the priority metals cadmium, lead and mercury the decline in the concentration in mosses since 1990 (or 1995 for mercury) was in good agreement with the decline in atmospheric deposition rates modelled by EMEP (Travnikov et al., 2012). Since 1990, the metal concentration in mosses has declined the most for lead (77%), vanadium (57%), iron (52%) and cadmium (51%), followed by chromium (43%), zinc (34%) and nickel (33%). The lowest decline was observed for copper (11%). For arsenic and mercury, the concentration in mosses has declined by 26% and 23% respectively since 1995. However, even in times of generally decreasing metal deposition across Europe, temporal trends are different for different geographical scales, i.e. temporal trends were country or region-specific with no changes or even increases in metal concentrations in mosses being found. Whereas many areas in a country might have shown a decline, other areas have shown no change or a considerable increase in metal concentrations in mosses since the previous survey in 2005. As in previous surveys, the lowest concentrations of heavy metals in mosses were generally found in northern Europe and the highest concentrations in (south-)eastern Europe, resulting in an north-west to south-east gradient in 2010. For many metals (but not all) a north-south gradient is present in Scandinavia, reflecting both the higher population density in the south and the contribution of long-range transboundary air pollution from central Europe to the higher concentrations in the south. The same is true for nitrogen in Finland (see Annex 4).

The similarity in temporal trends for moss data and modelled total deposition data (or emission data in the absence of modelled deposition data) suggests that at the European scale these trends are not hugely affected by either the high uncertainties associated with emission and modelled deposition data (Travnikov et al., 2012) or by potential confounding factors associated with the moss survey (for details see Harmens et al., 2008a,b; 2010; 2012a, and references therein). It has been shown that at the European scale atmospheric deposition is the main factor determining the accumulation of cadmium and lead in mosses (Holy et al., 2010; Schröder et al., 2010b). Although this does not appear to be the case for mercury, temporal trends for the moss survey at the European scale still agree well with temporal trends in modelled mercury deposition, as shown in this study. For cadmium and lead, the correlations between concentrations in mosses and modelled atmospheric deposition were country- and metal-specific. Although significant positive correlations were observed in about two-thirds of the countries, correlations were sometimes not significant or even negative in some countries (Harmens et al., 2012a).

Some clear country-specific results were observed when comparing the results of the 2005 and 2010 European moss survey. In Belgium, the concentration in mosses has declined drastically for all metals since 2005. This suggests that the implementation of air pollution abatement policies is finally paying off. The same is true for Macedonia, however, the decline has been less drastic and has not been observed for all metals, e.g. the mercury concentration in mosses has increased since 2005 and hardly any change was found for arsenic. In Macedonia, a decline was found for all metals associated to some extent with wind-blown dust, i.e. aluminium, chromium, iron, nickel and vanadium (see Annex 4). In Slovenia, the decline in metal (and nitrogen) concentrations in mosses between 2005 and 2010 was confounded by a change in sampling strategy. Only about one-third of the sampling sites were the same in 2005 and 2010. When comparing the results for only the sites that were the same in 2005 and 2010, the median values for arsenic, chromium, nickel and zinc were similar for both years, whereas an increase was observed for cadmium since 2005. For the other metals, the observed decline was most probably due to applying a more careful sampling procedure to minimise the impact

of canopy drip in forests. Generally, mosses affected by canopy drip have a higher metal (and nitrogen) concentration due to the higher concentration of elements in throughfall deposition. Comparison of the metal concentration in mosses in Poland, Ukraine and the Russian Federation in 2005 and 2010 was also confounded by sampling mosses in different areas of the country, whereas in Spain data were included for the first time for Rioja in 2010. In France, the contribution of wind-blown dust to the concentration of some metals (aluminium, arsenic, chromium, iron, nickel and vanadium) in mosses in particularly eastern and southern parts of the country seemed to have been much higher in 2005 (Harmens et al., 2008a, 2010) than in 2010. Hence, the concentration of these metals has declined considerably between 2005 and 2010 in those parts of the country. For these metals, the east-west gradient has diminished drastically between 2005 and 2010 in France. Extremely high values for cadmium, copper and lead were observed in large areas of Romania, which might be partly due to applying flame atomic absorption spectrometry as an analytical technique for these metals. However, the use of plant reference material (other than M2 and M3 moss reference material) indicated a good recovery of the metals analysed. Undoubtedly the concentrations for these metals are expected to be high in the industrial areas in Romania (Lucacia et al., 2010) and for lead also due to only recent abolishment of the use of leaded petrol, but they were not expected to be at a similar level as in 1990 and to be higher than in 2000, the previous survey in which Romania participated. For most of the other metals (except nickel), analysed by neutron activation analysis, the concentration in mosses has declined since 2000 in Romania.

Nitrogen

Hardly any changes were observed in the nitrogen concentration in mosses since 2005. The small decline (5%) in the average median nitrogen concentration in mosses is in agreement with the 7% decline reported by EMEP for modelled total nitrogen deposition in the EU27 since 2005. As in 2005, areas most at risk from adverse effects of nitrogen on terrestrial ecosystems are located in western and central Europe. However, the risk in many northern, eastern and Mediterranean countries could not be assessed via the survey as those countries did not report on nitrogen concentrations in mosses. At the European scale, the relationship between site-specific nitrogen concentrations in mosses and modelled nitrogen deposition per EMEP 50 km x 50 km grid starts to show saturation at deposition rates of ca. 15 kg ha^{-1} y^{-1} (Harmens et al., 2011). Although the latter makes it difficult to assess the magnitude of risk in areas with medium to high nitrogen deposition, the moss technique still allows the identification of the areas potentially most at risk. Currently, data analysis is ongoing to establish the relationship between nitrogen concentrations in mosses and atmospheric deposition rates of nitrogen measured at the same sites.

Conclusions

- Moss biomonitoring provides 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 the priority metals cadmium, lead and mercury and for nitrogen the decline in average median concentrations in mosses across Europe is in agreement with that reported for modelled atmospheric deposition.
- Despite the general European decline in concentrations in mosses between 2005 and 2010 (and also since 1990), country and region-specific temporal trends were observed.
- Despite the apparent success of the implementation of air pollution abatement techniques in large areas of Europe, further measures are required in (south)-eastern Europe to reduce the relative high emissions of heavy metals. For nitrogen, more stringent air pollution abatement strategies are required across Europe to reduce the areas at risk from adverse effects of elevated atmospheric nitrogen deposition.

Recommendations

As ecosystems and human health are still predicted to be at risk from adverse effects of heavy metals and nitrogen in the future, the moss survey should be continued to monitor any future trends in heavy metal and nitrogen deposition in Europe, with the next survey anticipated for 2015/16. Especially

further stimulation of the participation in (south)-eastern European countries for both heavy metals and nitrogen is encouraged. In addition, more countries are encouraged to report on the nitrogen concentration in mosses in the future. An extension of the moss survey into Asia would also be welcome. It is recommended to use the newly available data for 2010/11 to further assess the performance of the EMEP models, particularly the model that estimates the atmospheric deposition of the priority heavy metals cadmium, lead and mercury. For nitrogen we recommend to investigate in further detail the relationship between measured total nitrogen deposition and the total nitrogen concentration in mosses at the site level.

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Annex 1. Participants in the 2010/11 survey

Many others have contributed to sampling and analysis, but only main contributors are listed below.

Country	Participant	Institute	Main e-mail contact
Albania	Pranvera Lazo	University of Tirana	pranveralazo@gmail.com
	Flora Qarri	University of Vlora	
Austria	Harald G. Zechmeister	University of Vienna	harald.zechmeister@univie.ac.at
	Alarich Riss	Federal Environment Agency, Vienna	
	Andrea Hanus		
Belarus	Yuliya Aleksiayenak	International Sakharov Environmental University, Minsk	beataa@gmail.com
Belgium	Ludwig De Temmerman	CODA-CERVA, Tervuren	ludwig.detemmerman@var.fgov.be
	Ann Ruttens		
	Nadia Waegeneers		
Bulgaria	Lilyana Yurukova	Institute of Biodiversity and Ecosystem Research - Base 3, previously Institute of Botany, Bulgarian Academy of Sciences, Sofia	yur7lild@bio.bas.bg
Croatia	Zdravko Spiric	OIKON Ltd. - Institute for Applied Ecology, Zagreb	zspiric@oikon.hr
Czech Republic	Ivan Suchara	Silva Tarouca Research Institute for Landscape and Ornamental Gardening, Průhonice	suchara@vukoz.cz
	Julie Sucharová		
Denmark	Maria Dam	Environment Agency, Argir	mariad@us.fo
(Faroe Islands)	Katrin Hoydal		
Estonia	Siiri Liiv	Tallinn Botanic Garden	siiri.liiv@botaanikaaed.ee
Finland	Juha Piispanen	Finnish Forest Research Institute (Metla),	juha.piispanen@metla.fi
	Jarmo Poikolainen	Oulu Research Unit	jarmo.poikolainen@metla.fi
	Eero Kubin		
	Jouni Karhu		
France	Sébastien Leblond	National Museum of Natural History, Paris	sleblond@mnhn.fr
	Xavier Laffray		
Iceland	Sigurður Magnússon	Icelandic Institute of Natural History, Reykjavík	sigurdur@ni.is
Italy	Renate Alber	Environmental Agency of Bolzano	Renate.Alber@provinz.bz.it
Kosovo	Pranvera Lazo	University of Tirana	pranveralazo@gmail.com
	Albert Maxhuni	University of Pristina	
Macedonia	Trajče Stafilov	Ss. Cyril and Methodius University, Skopje	trajcest@pmf.ukim.mk
	Lambe Barandovski		lambe@pmf.ukim.mk
	Katerina Baceva		
Norway	Eiliv Steinnes	Norwegian University of Science and Technology, Trondheim	eiliv.steinnes@chem.ntnu.no
	Torunn Berg		
	Hilde Thelle Uggerud	Norwegian Institute for Air Research (NILU), Kjeller	hilde.thelle.uggerud@nilu.no
Poland	Barbara Godzik	W. Szafer Institute of Botany,	b.godzik@botany.pl
	Paweł Kapusta	Polish Academy of Sciences, Krakow	
Romania	Ion V. Popescu	Valahia University of Targoviste	ivpopes@yahoo.com
	Claudia Stihi		stihi@valahia.ro
	Cristiana Radulescu		
	Andrei Chilian		
	Anca Gheboianu		
	Antoaneta Ene	Dunarea de Jos University of Galati	aene@ugal.ro
	Simona-Maria Cucu-Man	Alexandru Ioan Cuza University of Iasi	sman@uaic.ro
	Radu Todoran	Technical University of Cluj-Napoca, North Center, Baia Mare	todoran_radu@yahoo.com
	Otilia Ana Culicov	National Institute for R&D in Electrical Engineering ICPE-CA, Bucharest	culicov@nf.jinr.ru
	Inga Zinicovscaia	Institute of Chemistry of Academy of Sciences of Moldova	zinikovskaia@mail.ru
Russian Federation	Marina V. Frontasyeva	Frank Laboratory of Neutron Physics,	marina@nf.jinr.ru
	Konstantin N. Vergel	Joint Institute for Nuclear Research, Dubna	
	Zoya I. Goryainova		
(Ivanovo)	Anatoly M. Dunaev	Chemical Technological University of Ivanovo	kannikkiy@inbox.ru
(Kostromskaya)	Nina A. Lebedeva	Liceum # 1, Volgorechensk, Kostromskaya	ninal1964@mail.ru
(Tikhvin-Leningradskaya)	Inna V. Vikhrova	Municipal Educational Centre, Tikhvin, Leningradskaya	vix-inna@yandex.ru
Slovakia	Blanka Mankovska	ILE SAS, Bratislava	bmankov@stonline.sk
Slovenia	Zvonka Jeran	Jožef Stefan Institute, Ljubljana	zvonka.jeran@ijs.si
	Mitja Skudnik	Slovenian Forestry Institute, Ljubljana	
Spain (Galicia)	J. Ángel Fernández Escribano	University of Santiago de Compostela	jangel.fernandez@usc.es
	Jesús Aboal Viñas		
	Alejo Carballeira Ocaña		
Spain (Navarra)	Jesus Miguel Santamaría	University of Navarra, Pamplona	chusmi@unav.es
	David Elustondo		
	Sheila Izquieta		
Spain (Rioja)	Javier Martínez-Abaigar	University of La Rioja, Logroño	javier.martinez@unirioja.es
	Rafael Tomás-LasHeras		
	Encarnación Núñez-Olivera		
	José María Infante Olarte	Gobierno de la Rioja, Dirección General de Calidad Ambiental	
Sweden	Gunilla Pihl Karlsson	IVL Swedish Environmental Research Institute, Gothenburg	gunilla.pihl.karlsson@ivl.se
	Helena Danielsson		helena.danielsson@ivl.se
Switzerland	Lotti Thöni	FUB - Research Group for Environmental Monitoring, Rapperswil	lotti.thoeni@fub-ag.ch
Ukraine	Oleg Blum	National Botanical Garden, National Academy of Sciences, Kiev	blum@nbg.kiev.ua

Annex 2. Analytical techniques used in 2010/11

Country	As	Cd	Cr	Cu	Fe	Hg	Ni	Pb	V	Zn	Al	Sb	N
Albania	ETAAS	ETAAS	ICP-ES	ICP-ES	ICP-ES	CVAAS	ICP-ES	ICP-ES	ICP-ES	ICP-ES	ICP-ES		
Austria	GFAAS	ICP-MS	ICP-ES	ICP-ES	ICP-ES	CVAAS	ICP-MS	ICP-MS	ICP-MS	ICP-ES	ICP-ES	ICP-MS	EA
Belarus	INAA		INAA		INAA		INAA		INAA	INAA	INAA	INAA	
Belgium	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-ES	AMA	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS		Kjeldahl
Bulgaria	ICP-ES	ICP-ES	ICP-ES	ICP-ES	ICP-ES		ICP-ES	ICP-ES	ICP-ES	ICP-ES	ICP-ES		Kjeldahl
Croatia	ETAAS	ETAAS	ICP-ES	ICP-ES	ICP-ES	CVAAS	ICP-ES	ICP-ES	ICP-ES	ICP-ES	ICP-ES		Kjeldahl
Czech Republic	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	AMA	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	EA
Denmark (Faroe Islands)	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS		ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	
Estonia		ICP-ES	ICP-ES	ICP-ES	ICP-ES	CVAFS	ICP-ES	ICP-ES	ICP-ES	ICP-ES	ICP-ES		Kjeldahl
Finland	GFAAS	ICP-ES	ICP-ES	ICP-ES	ICP-ES	CVAFS	ICP-ES	ICP-ES	ICP-ES	ICP-ES	ICP-ES		Kjeldahl
France	ICP-MS	ICP-MS	ICP-MS	ICP-ES	ICP-ES	CVAAS	ICP-MS	ICP-MS	ICP-MS	ICP-ES	ICP-ES	ICP-MS	EA
Iceland	ICP-MS	ICP-MS	ICP-ES	ICP-ES	ICP-ES	ICP-MS	ICP-ES	ICP-MS	ICP-ES	ICP-ES			
Italy (Bolzano)	ICP-MS	ICP-MS	ICP-MS	ICP-ES	ICP-ES	AMA	ICP-MS	ICP-MS	ICP-MS	ICP-MS			EA
Kosovo		ETAAS	ETAAS	ETAAS	FAAS		ETAAS	ETAAS		FAAS			
Macedonia	ETAAS	ETAAS	ICP-ES	ICP-ES	ICP-ES	CVAAS	ICP-ES	ICP-ES	ICP-ES	ICP-ES	ICP-ES		Kjeldahl
Norway	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	CVAFS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	
Poland		FAAS/GFAAS	FAAS	FAAS	FAAS	AMA	FAAS	FAAS/GFAAS	GFAAS	FAAS			Kjeldahl
Romania	INAA	FAAS/GFAAS	INAA	FAAS/GFAAS	INAA		INAA	FAAS/GFAAS	INAA	INAA	INAA	INAA	
Russian Federation													
- Kostromskaya	INAA	INAA	INAA		INAA		INAA		INAA	INAA	INAA	INAA	
- Tikhvin-Leningradskaya	INAA	INAA	INAA		INAA		INAA		INAA	INAA	INAA	INAA	
- Ivanovo				FAAS	FAAS				INAA	FAAS	INAA		
Slovakia		GFAAS		FAAS				GFAAS	INAA		INAA		EA
Slovenia	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	AMA	ICP-MS	ICP-MS	ICP-MS	ICP-MS		ICP-MS	EA
Spain													
- Galicia	AFS	GFAAS				AMA				FAAS			
- Navarra	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	CVAAS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	EA
- Rioja	AFS	GFAAS				AMA	GFAAS	GFAAS					EA
Sweden	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS		
Switzerland	ICP-MS	ICP-MS	ICP-ES	ICP-MS	ICP-ES	AMA	ICP-ES	ICP-MS	ICP-MS	ICP-MS	ICP-ES		Kjeldahl
Ukraine (Donetzk)		ICP-ES	ICP-ES	ICP-ES	ICP-ES			ICP-ES	ICP-ES	ICP-ES	ICP-ES		

Abbreviations

AFS	Atomic fluorescence spectrometry
AMA	Advanced mercury analyser
CVAAS	Cold vapour atomic absorption spectrometry
CVAFS	Cold vapour atomic fluorescence spectrometry
EA	Elemental analysis (Dumas method)
ETAAS	Electrothermal atomic absorption spectrometry
FAAS	Flame atomic absorption spectrometry
GFAAS	Graphite furnace atomic absorption spectrometry
ICP-ES	Inductively coupled plasma emission spectrometry
ICP-MS	Inductively coupled plasma mass spectrometry
INAA	Instrumental neutron activation analysis

Annex 3. Metal (mg kg^{-1}) and nitrogen concentrations (mass %) in mosses in 2010/11

	As	Cd	Cr	Cu	Fe	Hg	Ni	Pb	V	Zn	Al	Sb	N (%)
Albania													
Number	59	59	59	59	59	61	59	59	59	59	59		
Min	0.039	0.038	1.62	1.52	469	0.031	1.56	1.34	1.15	1.00	535		
Max	2.20	0.90	31.8	11.1	5488	2.23	131	19.7	16.9	68.1	6974		
Mean	0.42	0.17	6.35	4.31	1915	0.20	11.2	3.37	4.26	14.2	1975		
Median	0.24	0.11	4.83	3.96	1629	0.13	5.81	2.42	3.52	13.8	1650		
90th percentile	1.12	0.29	12.0	6.35	3287	0.31	21.8	4.83	6.63	22.8	3089		
Austria													
Number	221	221	221	221	221	221	221	221	221	221	221	221	221
Min	0.065	0.047	0.49	2.90	97.0	0.004	0.31	0.55	0.34	13.0	81.9	0.040	0.74
Max	1.78	1.10	6.50	29.0	2800	0.35	4.50	12.0	17.0	81.0	3024	1.60	2.20
Mean	0.32	0.16	1.28	5.56	411	0.037	1.18	2.64	1.55	25.6	444	0.19	1.26
Median	0.22	0.13	1.00	5.00	320	0.033	1.00	2.40	1.30	24.0	347	0.16	1.20
90th percentile	0.60	0.26	2.70	6.80	690	0.051	2.00	4.00	2.50	37.0	819	0.29	1.60
Belarus													
Number	76		76		76		76		76	76	76	76	
Min	0.006		0.66		194		0.086		0.59	21.5	267	0.026	
Max	0.34		5.23		1030		1.21		3.68	94.7	1650	0.34	
Mean	0.14		3.04		466		0.39		1.35	40.1	650	0.11	
Median	0.12		3.21		416		0.23		1.19	34.1	557	0.096	
90th percentile	0.20		4.64		788		0.85		2.20	66.7	1045	0.19	
Belgium													
Number	29	29	29	29	29	29	29	29	29	29	29		29
Min	0.052	0.092	0.54	3.27	171	0.020	0.72	2.12	0.41	16.6	114		0.79
Max	0.89	0.69	3.89	11.5	1109	0.32	22.7	12.5	2.76	132	696		2.30
Mean	0.19	0.33	1.08	6.80	377	0.068	2.14	5.14	1.19	52.4	275		1.38
Median	0.16	0.30	0.92	6.50	365	0.058	1.41	3.87	1.14	44.2	242		1.37
90th percentile	0.26	0.55	1.62	8.97	513	0.094	1.97	9.31	1.94	77.6	443		1.78
Bulgaria													
Number	60	129	129	129	129		129	129	129	129	129		99
Min	0.15	0.043	0.72	2.00	307		0.84	1.69	0.96	8.22	402		0.20
Max	10.8	7.75	38.1	270	8546		82.1	333	22.4	286	8886		2.94
Mean	1.08	0.39	3.46	12.2	1534		4.37	16.8	3.96	30.6	1493		1.38
Median	0.63	0.21	2.06	7.01	1101		2.61	8.00	3.07	22.2	1245		1.32
90th percentile	1.76	0.57	5.87	21.0	2824		6.44	21.9	7.52	45.4	2714		1.90
Croatia													
Number	121	121	121	121	121	121	121	121	121	121	121		119
Min	0.039	0.10	0.41	3.35	85	0.010	1.04	1.11	0.23	11.6	112		0.71
Max	0.77	1.42	8.55	16.1	4028	0.15	14.7	36.6	37.3	77.1	4493		2.93
Mean	0.30	0.43	2.25	6.55	881	0.043	3.70	3.79	3.50	27.1	1062		1.54
Median	0.28	0.38	1.94	6.06	789	0.043	3.16	3.21	2.55	24.8	878		1.49
90th percentile	0.54	0.74	3.91	9.32	1658	0.063	6.39	5.48	6.17	41.6	1995		2.35
Czech Republic													
Number	273	273	273	273	273	273	273	273	273	273	273	273	273
Min	0.068	0.092	0.46	3.26	150	0.019	0.37	1.17	0.44	20.1	184	0.001	0.70
Max	1.08	1.38	4.35	10.7	2072	0.11	4.47	42.1	6.10	105	3227	0.82	2.52
Mean	0.29	0.22	1.21	6.00	421	0.043	1.27	3.83	1.38	36.5	526	0.097	1.38
Median	0.26	0.18	1.01	5.92	348	0.041	1.15	2.85	1.18	33.9	435	0.096	1.33
90th percentile	0.46	0.34	2.10	7.84	692	0.058	2.01	5.77	2.23	47.3	797	0.15	1.86
Denmark (Faroe Islands)													
Number	7	7	7	7	7	7	7	7	7	7	7	7	
Min	0.071	0.034	0.56	3.48	511	0.054	0.90	1.30	2.23	12.7	461	0.039	
Max	0.12	0.080	0.84	4.63	1074	0.074	1.84	2.05	4.40	28.8	724	0.060	
Mean	0.086	0.057	0.72	4.09	842	0.065	1.23	1.72	3.01	17.2	617	0.048	
Median	0.084	0.049	0.71	4.27	853	0.064	1.12	1.66	2.91	14.8	612	0.050	
90th percentile	0.10	0.078	0.82	4.52	982	0.072	1.63	2.03	3.73	23.3	711	0.057	
Estonia													
Number		99	99	99	99	99	99	99	99	99	99		99
Min		0.080	0.36	0.92	93	0.022	0.43	1.29	1.05	19.3	79		0.65
Max		0.25	2.40	10.6	617	0.076	2.10	3.97	2.85	55.6	492		1.50
Mean		0.15	0.75	3.81	204	0.034	0.86	2.50	1.17	31.5	204		0.94
Median		0.14	0.68	3.67	180	0.031	0.82	2.41	1.07	30.9	188		0.88
90th percentile		0.21	1.04	4.81	317	0.047	1.15	3.33	1.48	39.7	294		1.28
Finland													
Number	201	426	426	426	426	202	426	426	426	426	426		426
Min	<0.10	<0.050	0.34	0.74	53	0.016	0.42	<0.75	<1.00	11.5	44		0.38
Max	0.38	0.44	14.0	55.1	2230	0.12	88.2	6.57	14.2	102	958		2.06
Mean	0.12	0.12	0.95	4.90	240	0.042	2.45	2.04	1.28	31.0	206		0.77
Median	0.10	0.11	0.80	3.91	209	0.039	1.24	1.87	1.00	29.5	187		0.70
90th percentile	0.17	0.18	1.38	7.45	411	0.067	3.43	3.17	1.79	43.2	318		1.11

	As	Cd	Cr	Cu	Fe	Hg	Ni	Pb	V	Zn	Al	Sb	N (%)
France													
Number	442	442	442	442	442	442	442	442	442	442	442	442	442
Min	<0.050	0.042	0.52	2.24	86	0.025	0.55	1.00	0.42	14.1	62	0.030	0.80
Max	2.46	1.21	5.91	16.2	3540	0.15	10.2	18.2	6.35	97.3	2020	0.58	2.71
Mean	0.26	0.20	1.55	6.36	429	0.069	2.00	4.03	1.45	34.3	357	0.14	1.47
Median	0.18	0.17	1.43	6.06	343	0.066	1.75	3.29	1.24	30.7	286	0.11	1.45
90th percentile	0.48	0.35	2.27	8.69	788	0.095	3.25	7.17	2.38	53.0	685	0.23	1.90
Iceland													
Number	144	144	144	144		144	144	144		144			
Min	0.045	0.012	0.68	3.06		0.025	0.83	0.27		8.4			
Max	1.38	0.29	18.1	47.4		0.16	40.7	72.1		194			
Mean	0.25	0.06	4.09	9.92		0.055	6.63	1.69		25.6			
Median	0.15	0.05	3.16	8.16		0.048	4.09	0.91		21.9			
90th percentile	0.50	0.12	8.36	16.7		0.088	14.4	2.03		36.2			
Italy (Bolzano region)													
Number	20	20	20	20	20	20	20	20	20	20			20
Min	0.14	0.060	0.78	5.72	232	0.054	0.89	1.76	0.91	17.7			0.68
Max	0.95	0.22	3.37	13.9	646	0.12	3.36	11.5	1.90	68.4			1.43
Mean	0.28	0.11	1.59	9.26	420	0.083	1.77	3.64	1.39	38.2			1.09
Median	0.22	0.11	1.59	8.88	431	0.084	1.69	3.11	1.37	37.1			1.09
90th percentile	0.38	0.14	2.17	12.0	546	0.11	2.27	4.57	1.63	54.7			1.34
Kosovo													
Number		25	25	25	24	25	24	25		25			
Min		0.028	1.63	2.46	124	0.009	1.22	2.62		14.3			
Max		3.05	4.55	3.93	3082	0.35	34.2	47.8		76.0			
Mean		0.37	2.72	3.12	582	0.055	6.08	12.13		37.8			
Median		0.13	2.63	3.04	312	0.033	2.00	7.78		38.5			
90th percentile		0.83	3.52	3.54	1085	0.091	24.4	20.7		55.2			
Macedonia													
Number	52	72	72	72	72	72	72	72	72	72	72		68
Min	0.077	0.068	1.03	1.97	513	0.010	1.25	1.87	1.00	1.00	537		0.68
Max	3.30	2.24	39.7	10.6	6348	0.60	51.7	22.0	17.4	365	8679		1.75
Mean	0.88	0.29	4.68	4.02	1732	0.11	6.43	5.40	3.95	29.7	2176		1.08
Median	0.69	0.22	3.48	3.54	1490	0.093	3.45	4.61	3.49	19.9	1878		1.06
90th percentile	2.01	0.44	7.38	6.21	2941	0.16	10.5	8.37	6.20	48.1	3373		1.29
Norway													
Number	463	463	463	463	463	463	463	463	463	463	463	463	
Min	0.020	0.009	0.16	1.38	27	<0.024	0.15	0.33	0.29	7.4	46	<0.001	
Max	4.84	1.87	47.9	443	24684	0.34	857	20.8	25.9	368	4581	1.17	
Mean	0.18	0.12	0.98	6.43	449	0.070	5.40	2.29	1.76	35.9	346	0.092	
Median	0.13	0.081	0.59	4.04	278	0.060	1.16	1.54	1.41	30.7	283	0.058	
90th percentile	0.26	0.23	1.55	7.29	685	0.11	2.79	4.85	3.03	57.5	565	0.20	
Poland													
Number		320	320	320	320	320	320	320	308	320			320
Min		0.003	0.20	1.46	110	0.029	0.14	1.54	0.11	7.46			0.78
Max		14.3	293	133	2618	0.76	108	141	4.69	211			2.86
Mean		0.45	3.58	6.94	405	0.072	2.20	6.73	0.77	51.8			1.56
Median		0.30	1.27	6.04	344	0.069	1.15	4.93	0.65	47.5			1.52
90th percentile		0.71	4.25	9.64	663	0.097	3.47	10.6	1.36	86.1			1.97
Romania													
Number	333	330	331	330	332		253	330	333	332	333	332	
Min	0.10	0.13	0.68	0.23	237		0.39	2.21	0.39	0.6	220	0.013	
Max	51.1	24.0	62.2	627	29500		35.9	120	58.3	1440	34400	16.5	
Mean	1.48	1.70	8.18	38.6	3000		4.99	30.5	7.56	56.0	4861	0.45	
Median	0.68	1.20	4.98	17.8	1670		3.60	30.8	4.89	42.3	3150	0.21	
90th percentile	2.76	3.09	18.9	84.4	6610		8.80	43.7	17.7	85.4	11620	0.63	
Russian Federation (Ivanovo, Kostromskaya, Tikhvin-Leningradskaya)													
Number	66	30	65	21	90		66		90	91	90	66	
Min	0.067	0.004	0.73	1.02	50		1.17		0.81	2.40	288	0.028	
Max	9.32	0.96	242	43.9	13600		11.3		23.40	172	13300	0.32	
Mean	0.46	0.17	22.4	10.2	1049		4.08		4.15	39.2	1826	0.12	
Median	0.15	0.068	9.16	7.22	419		2.82		2.45	33.6	922	0.092	
90th percentile	0.92	0.42	41.5	24.0	2470		9.48		11.1	59.5	3496	0.22	
Slovakia													
Number		67		67				67	67		67		67
Min		0.078		6.44				2.31	0.60		251		1.00
Max		3.39		90.4				58.4	10.2		5580		2.85
Mean		0.77		14.5				10.9	2.04		1043		1.84
Median		0.67		11.5				8.51	1.50		707		1.79
90th percentile		1.24		19.8				18.9	3.39		1926		2.39
Slovenia													
Number	102	102	102	102	102	63	102	102	102	102		102	102
Min	0.13	0.090	0.72	2.83	243	0.030	0.85	1.96	1.00	14.7		0.060	0.85
Max	0.83	1.05	13.7	11.4	1391	0.16	8.16	304	7.00	66.7		0.76	1.99
Mean	0.28	0.33	1.94	5.71	617	0.056	2.34	8.79	2.40	31.5		0.13	1.32
Median	0.26	0.27	1.56	5.42	548	0.050	2.12	5.01	2.30	29.0		0.12	1.29
90th percentile	0.41	0.53	2.69	7.29	934	0.070	3.34	8.63	3.57	48.7		0.18	1.70

	As	Cd	Cr	Cu	Fe	Hg	Ni	Pb	V	Zn	Al	Sb	N (%)
Spain (Galicia, Navarra, Rioja)[1]													
Number	211	211	39	39	39	211	64	64	39	186	39	39	64
Min	0.086	0.031	0.43	2.64	171	0.022	0.58	0.95	0.55	12.7	173	0.040	0.64
Max	2.69	1.57	4.77	9.81	1449	0.081	3.94	10.3	4.20	156	1459	0.15	1.80
Mean	0.39	0.22	1.83	4.83	610	0.040	1.60	2.75	1.36	32.9	597	0.072	1.09
Median	0.29	0.16	1.46	4.70	520	0.039	1.44	2.13	1.21	31.5	511	0.069	1.05
90th percentile	0.73	0.37	3.38	6.25	1089	0.053	2.88	4.86	2.08	44.7	1043	0.10	1.48
Sweden													
Number	602	602	602	602	602	602	602	602	602	602	602		
Min	0.080	0.023	0.11	1.38	28	0.016	0.22	0.43	0.16	13.4	25		
Max	0.45	0.39	10.8	23.5	2406	0.14	7.11	19.9	9.63	81.9	1303		
Mean	0.10	0.13	0.67	3.92	135	0.041	0.72	2.09	0.79	33.9	143		
Median	0.10	0.13	0.52	3.61	101	0.038	0.66	1.87	0.69	32.6	110		
90th percentile	0.10	0.21	1.14	5.57	218	0.062	1.02	3.38	1.26	46.8	254		
Switzerland													
Number	142	142	142	142	156	142	142	142	142	142	142		64
Min	0.027	0.034	0.21	2.61	101	0.018	0.17	0.71	0.22	11.1	81		0.64
Max	5.81	3.57	5.25	10.0	1732	0.076	5.93	12.7	4.27	170	2256		1.88
Mean	0.19	0.18	0.92	4.89	351	0.034	1.30	2.60	0.88	27.8	357		1.05
Median	0.10	0.13	0.75	4.37	286	0.031	1.00	2.24	0.74	23.7	295		1.00
90th percentile	0.27	0.26	1.55	6.68	601	0.047	2.50	4.15	1.44	40.7	626		1.38
Ukraine (Donetsk)													
Number		16	16	17	17		17	17	17	17	17		
Min		0.080	0.25	12.8	1003		4.70	5.56	0.98	37.6	821		
Max		0.52	2.40	62.1	7307		26.1	20.9	3.99	152	4664		
Mean		0.33	0.92	22.9	2437		8.94	8.74	2.51	63.7	1822		
Median		0.36	0.73	21.2	1414		6.70	7.07	2.63	54.9	1476		
90th percentile		0.40	1.59	33.1	6708		15.4	14.4	3.80	92.4	3177		

[1] As, Cd, Hg: all regions; Zn: Galicia and Navarra; Ni, Pb, N: Navarra and Rioja; Al, Cr, Cu, Fe, Sb, V: Navarra.
Number = number of sampling sites; Min = minimum; Max = maximum.

Annex 4. Country reports

This part brings together the reports from national experts participating in the European moss survey. The reports have been edited in collaboration with the national experts, however, the responsibility for the content of the national reports lies with the national experts and not with the ICP Vegetation Programme Coordination Centre.

Albania

Lead institute: Pranvera Lazo, University of Tirana, Faculty of Natural Sciences, Department of Chemistry, Tirana, Albania. pranveralazo@gmail.com
Collaborating institutes: Trajce Stafilov, Institute of Chemistry, Faculty of Science, Ss. Cyril and Methodius University, Skopje, Macedonia. trajcest@iunona.pmf.ukim.edu.mk
Mariana Frontasyeva, Frank Laboratory of Neutron Physics, Joint Institute for Nuclear Research, Dubna, Russian Federation. marina@nf.jinr.ru

Background

Albania took part for the first time in the European moss survey in 2010/11 and attended the ICP Vegetation Task Force meeting for the first time in 2012. During the period September – October 2010, 32 moss samples were collected in southern Albania and in Tirana city, the capital of Albania. A further 30 samples were collected during the period June – August 2011 in other parts of the country. The University of Tirana was responsible for the sampling campaigns and the analysis of some trace elements by AAS. The ICP-ES analysis of 19 elements (Al, B, Ba, Ca, Cd, Cr, Cu, Fe, Hg, Mg, Mn, Na, Ni, P, Pb, Sr, V and Zn) was performed in Skopje, Macedonia. A further 65 elements are being analysed by INAA in Dubna, Russian Federation.

Heavy metal concentrations in mosses

The target elements in this study were heavy metals. For better interpretation of data, the elements Al, Ca, Fe, K, Na and P, as typically earth crust elements, were also included. The results of the descriptive statistic analysis of the trace elemental concentrations are shown in Figure 1.

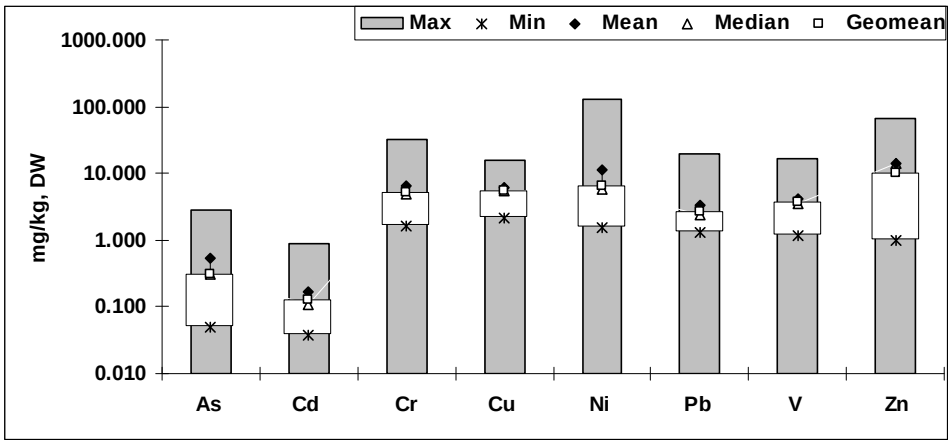

Figure 1. Box-plot of trace metal concentrations in mosses.

The metal concentration in moss samples based on the mean values follows the trend Cd<Li<Pb<V<Cr<Cu<Zn<Ni<B<Sr <Mn<Ba<Na <P< Fe<Mg<Al<K<Ca. The range of variation of Cd, Li, V, Zn, B, Mn and Na in moss samples is larger than of other minor elements, while Al, Fe and Ca appear to have the same trend of variation too. The distribution maps of some important metals are shown in Figure 2.

Discussion and conclusions

The spatial distribution of most elements (except Zn) follows their geogenic origin. The presence of mining industry and the loss of landscape due to mining, processing and mineral transport are

important factors in determining metal distributions. For example, the spatial distribution for Al follows the geological map of bauxites deposits in Albania. In contrast, the anthropogenic origin of Zn originated from the Elbasani metallurgical complex, traffic emissions, cement production and emissions during quicklime production through calcinations of limestone (by burning different kind of waste material such as tires, plastics and wood).
From our data for a limited number of elements we can conclude that:

- Most elements follow the earth crustal distribution;
- Traffic, PM_{10}, road dust emission and emission from industry are sources of Zn;
- Industrial processes, such as mining, contribute to the presence of heavy metals in the air and soil;
- Heavy metals in weathered rock or soil can be picked up and transported by the wind.

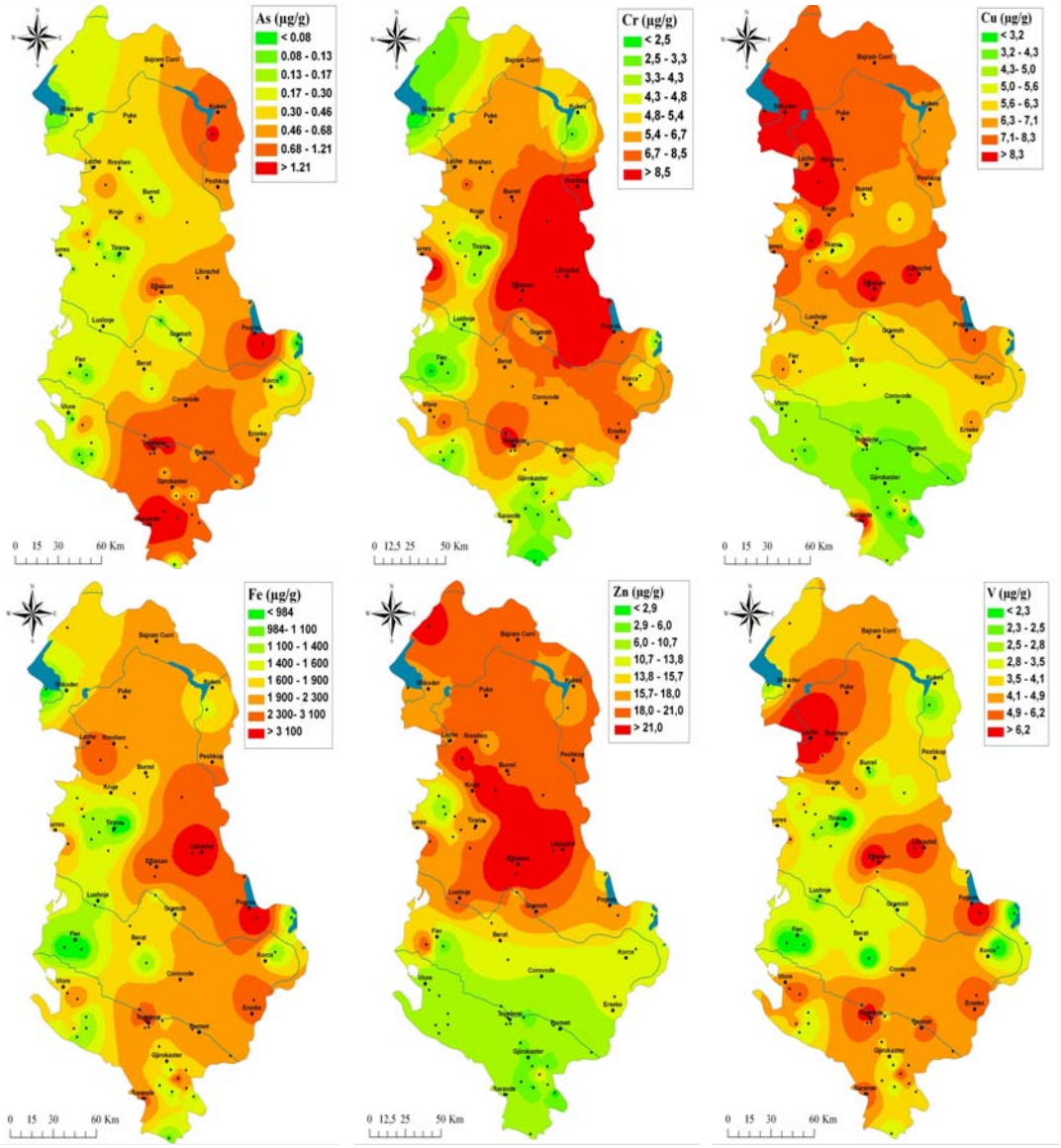

Figure 2. Arsenic (As), chromium (Cr), copper (Cu), iron (Fe), zinc (Zn) and Vanadium (V) distribution in mosses sampled in 2010/11 in Albania (Note: Black dots on the map are the sampling sites).

Better management of anthropogenic emissions from industry, waste incineration and traffic are necessary to reduce heavy metal pollution in Albania in the future.

Austria

Lead institutes: Harald Zechmeister, University of Vienna, Faculty of Life Sciences, Department of Conservation Biology, Vegetation and Landscape Ecology, Vienna.
harald.zechmeister@univie.ac.at
Alarich Riss and Andrea Hanus, Federal Environment Agency, Vienna.
alarich.riss@umweltbundesamt.at, andrea.hanus@umweltbundesamt.at

Background

Austria has been participation in the European monitoring of atmospheric heavy metal pollution since 1991, starting with a pilot study, testing various parameters like differences in moss species or altitudes of sampling sites. Since 1995, 220 sampling sites were investigated every five years. For the analyses of samples from the 2010 survey microwave digestion was used instead of the $HNO_3/HClO_4$ digestion used in previous years. Microwave digestion is in accordance with the method applied in most other countries. Therefore, conversion factors were calculated for data comparison with previous years within Austria. These factors were obtained by a wide range of samples analysed by both digestion methods. In 2010, the metals aluminium (Al), arsenic (As), cadmium (Cd), cobalt (Co), chromium (Cr), copper (Cu), iron (Fe), mercury (Hg), molybdenum (Mo), nickel (Ni), lead (Pb), antimony (Sb), vanadium (V) and zinc (Zn) were analysed as well as nitrogen (N) and sulphur (S).

Concentrations in mosses

Spatial distribution: Interpolated maps and sites results for Cd, Cu, V and N are shown in Figure 1. Overall, metal pollution is highest in the east of Austria, because of the high population density and its consequent pollution sources such as traffic and other forms of fossil fuel combustion. The east of Austria is also influenced by intensive agriculture on a large scale as well as by industrial sources from Austria and Slovakia (e.g. Bratislava refinery). Other hot spots can be found in the Inntal, east of Innsbruck. The Lower Inntal is a densely populated valley impaired by a wide range of industries, partly dating back to historic mining industries (see Cd and Cu in Figure 1). The area is affected by high (transit-)traffic too as indicated by Sb concentrations in mosses (data not shown). Other hot spots trace back to single emission sources like those close to Treibach/Carinthia (V, Mo), Leibnitz (Cd) or Reutte/Tyrol (Mo). More values clearly above average can be found in some vine producing areas (e.g. for Cu), or in densely populated areas, the latter mostly attributed by high S concentrations. Nitrogen concentrations in mosses provide a rough estimate of regions with either high agricultural density or high traffic volume. Source attribution by $\delta^{15}N$ signatures in moss tissue has been reported by Zechmeister et al. (2008b).

Temporal trends: For all elements, except for Mo and Cu, there was a significant decrease in concentrations since 1995, particularly for Pb and S. Between the five-year sampling periods these trends are not so obvious, leading to increases for some elements in 2000 or 2005. Some sampling sites show stronger fluctuations than the overall pattern. Causes can be for example increasing local emissions (Zechmeister et al., 2008a).

Discussion and recommendations

Although there has been a constant decrease of metal pollution on a national level, several sites show a (constant) increase over time. Therefore, for environmental and human health reasons monitoring should be continued. A good compromise for maintaining environmental health monitoring on an economically balanced basis could be a reduction in the number of sampling sites. Monitoring of N deposition is still highly recommended, as high N deposition is currently one of the most important environmental risks to local nature conservation (e.g. conservation of bogs and dry grasslands) and human health in Austria (e.g. drinking water quality).

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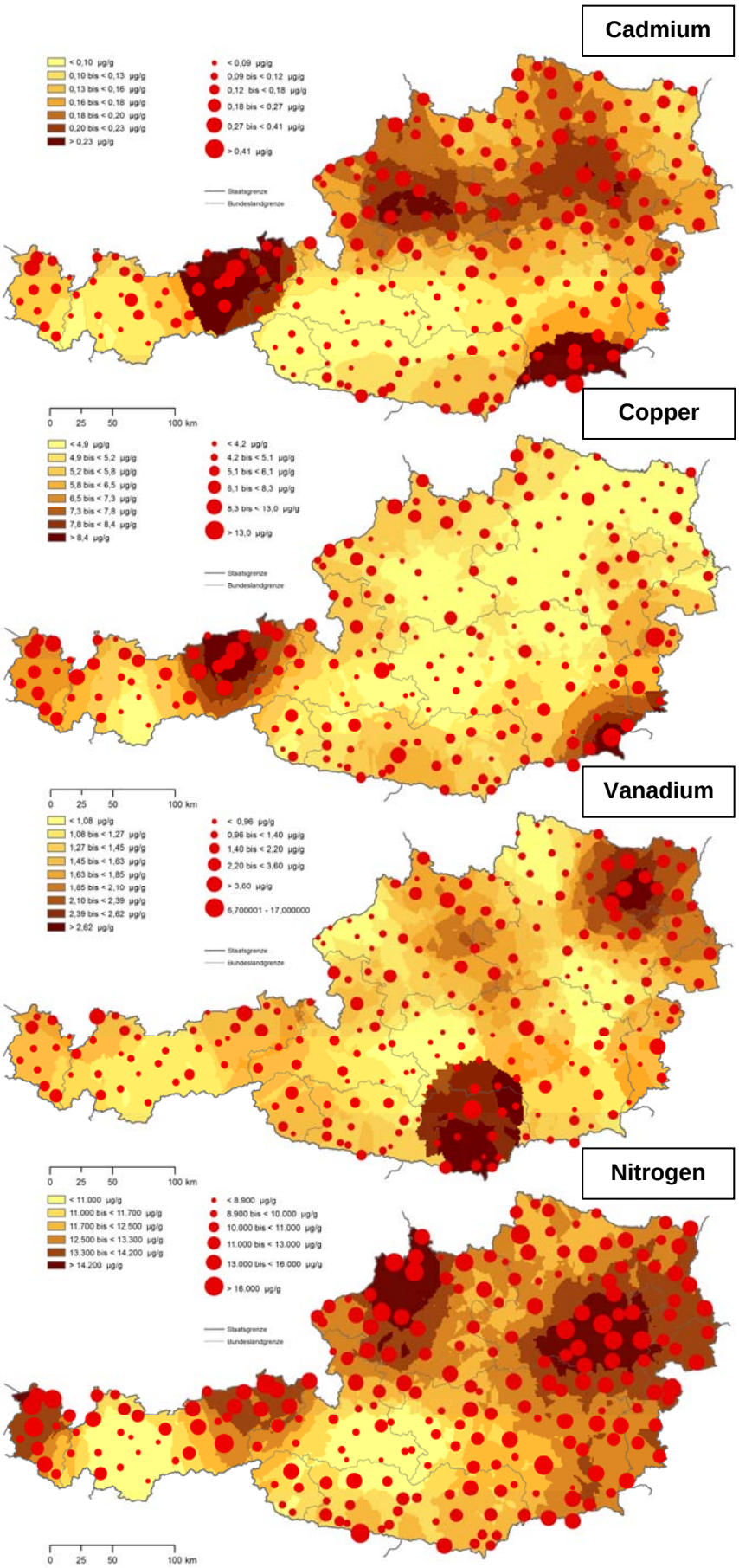

Figure 1. Concentration of cadmium, copper, vanadium and nitrogen in mosses in Austria in 2010. The size of the red dots represents the concentration in mosses at the sampling sites.

Bulgaria

Lead institute: Lilyana Yurukova, Institute of Biodiversity and Ecosystem Research – Base 3 – ex-Institute of Botany, Bulgarian Academy of Sciences, Sofia, BG 1113.
yur7lild@bio.bas.bg

Background

Bulgaria is situated in the eastern part of the Balkan Peninsula in south-eastern Europe with a total territory of 110,988 km^2. Bulgaria participated in the European moss survey for the first time in 1995 and since then the survey has been repeated at 5-year intervals. According to a resolution from the Bulgarian Council of Ministers from 1994 that was based on the ex-National Automated System of the Ecological Monitoring (NASEM), 14 areas were considered as "hot spots", i.e. areas with particularly high emissions of various pollutants, mainly due to non-ferrous and ferrous industry, open copper mines and copper production, lead-zinc mines, closed uranium mines, and serpentine rock. Leaded petrol was also a serious problem in Bulgaria (62% of the total petrol consumed in 2000). Many soils in Bulgaria are still strongly polluted with heavy metals as a result of the very high emissions before 2000 and the occurrence of wind re-suspension of contaminated soils. Bulgarian mosses had the highest concentrations of lead and cadmium in the European moss survey of 1995.

Concentrations in mosses

In 2010, mosses were sampled at up to 129 sites. The maximum concentration of heavy metals, sulphur and nitrogen were as follows: Al – 8886 mg kg^{-1}, As – 10.8 mg kg^{-1}, Cd – 7.75 mg kg^{-1}, Cr – 38.1 mg kg^{-1}, Cu – 270 mg kg^{-1}, Fe – 8546 mg kg^{-1}, Ni – 82 mg kg^{-1}, Pb – 333 mg kg^{-1}, S – 2427 mg kg^{-1}, V - 22.4 mg kg^{-1}, Zn – 286 mg kg^{-1}, N – 2.94%. In 2010, the spatial patterns were similar to previous surveys. No clear significant relationship was found with national emission sources. In Bulgaria, with the exception of Cr, heavy metal concentrations in mosses decreased between 1995 and 2010 by up to 30%.

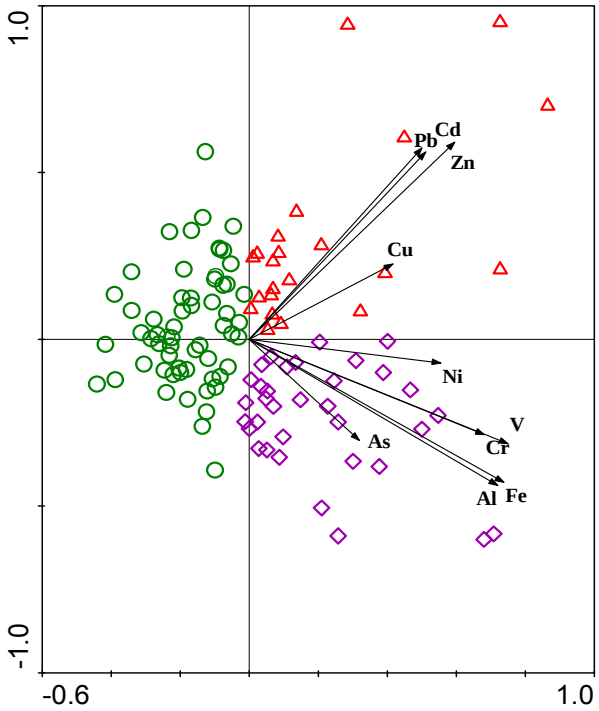

Figure 1. PCA-ordination diagram of 219 studied sites in Bulgaria for ten heavy metals in mosses in 2010. Triangles – sites located along ferrous and non-ferrous industry, open copper mines, old uranium mines, and over serpentine rock; diamonds – sites at Rhodopes and Strandzha Mountain, along N-W corner of the country due to the copper industry near town of Bor, Serbia, and along the border in South Bulgaria; circles – the rest of the monitored sites.

Principal component analysis (PCA) using CANOCO ver. 4.5 (Ter Braak and Smilauer, 2002) was carried out on data for ten elements measured in moss tissue collected from 129 sites in 2010 in Bulgaria. The element values were divided by their standard deviation and PCA was species-centered. The sum of canonical eigenvalues for all ten variables was 0.83. The first axis explained 57% of the variation in the data set and was correlated with cadmium, copper, lead, and zinc (Figure 1). The second axis was correlated with the rest of the elements. The heavy metals cadmium, lead, and zinc were also strongly related in all three previous periods (1995, 2000, 2005) and formed a compact group in the PCA.

Discussion and recommendations

Although deposition levels in Bulgaria have decreased since 1995, heavy metal concentrations in mosses were still high (except for Cr and Zn). In comparison to median heavy metal concentrations in other countries in Europe in all moss surveys, concentrations in Bulgaria were nearly always higher. In Bulgaria the modelled depositions were considerably lower than the moss-derived depositions for the previous three surveys (1995 – 2005). The official heavy metal emission trend for Cd was -64% and -67% for Pb in the period 1990-2010 (Travnikov et al., 2012). New technologies must be implemented in order to reduce atmospheric pollution levels in Bulgaria. It is important that new technologies for soil remediation and possibly, in addition, new effective controls on environmental legislation are implemented and that the deposition of heavy metals continues to be monitored systematically. Continuing the moss monitoring is crucial for future evaluations of the success of implemented environmental measures.

Acknowledgement. We would like to thank FUB, Switzerland, for partly supporting the sampling in Bulgaria for the last three moss surveys.

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Croatia

Lead institute: Zdravko Spiric and Vladimir Kusan, Oikon Ltd. - Institute for Applied Ecology, Trg senjskih uskoka 1, Zagreb, Croatia. zspiric@oikon.hr
Collaborating institutes: Trajce Stafilov and Ivana Vuckovic, Institute of Chemistry, Faculty of Science, Ss. Cyril and Methodius University, Skopje, Macedonia. trajcest@pmf.ukim.mk
Marina Frontasyeva, Frank Laboratory of Neutron Physics, Joint Institute for Nuclear Research, Dubna, Russian Federation. marina@nf.jinr.ru
Delko Barisic and Branko Vekic, Ruđer Bošković Institute Zagreb, Croatia.
Marin Glad, Teaching Institute of Public Health, Primorsko-Goranska County, Rijeka, Croatia. marin.glad@zzjzpgz.hr

Background

Since 2006, Croatia has participated in the European moss survey. Moss samples were collected in 2006 and 2010 on a nearly regular grid of 23 km x 23 km. Moss samples were collected during the summer of 2006 and the summer/autumn 2010 from 98 and 121 locations respectively, evenly distributed over the country (Figure 1), with additional samples taken in and around urban and industrial areas**.** The most dominant moss species present were *Hypnum cupressiforme, Pleurozium schreberi, Brachythecium rutabulum* and *Homalothecium sericeum*. This study was undertaken in order to i) provide an assessment of the air quality throughout Croatia, ii) generate information needed for better identification of local pollution sources as well as transboundary air pollution, and iii) improving the potential for assessing environmental and health risks in Croatia associated with dry and wet deposition of toxic metals.

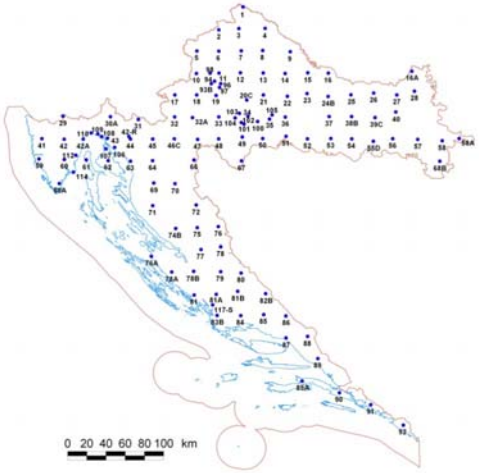

Figure 1. Locations of Croatian 2010 moss sampling sites.

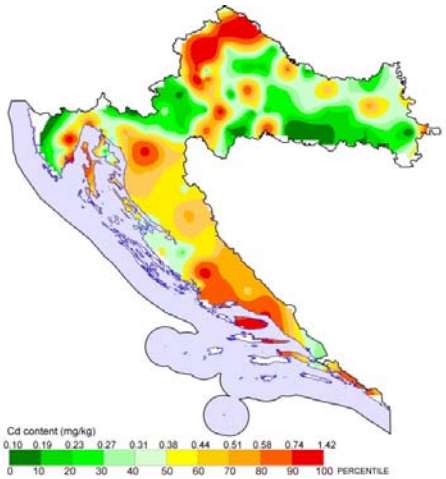

Figure 2. Cadmium concentrations in mosses in Croatia in 2010.

Metals, nitrogen and radionuclide concentrations in mosses

Here we present the results obtained in the 2010 moss survey in Croatia and compare these results with those obtained in the previous survey in 2006, in order to evaluate spatial patterns and temporal deposition trends. As an example, the spatial pattern of cadmium, lead and mercury concentrations in mosses in 2010 are shown (Figures 2 - 4). The concentration of 21 elements was determined by ICP-AES and AAS. Principal component analysis (PCA) was applied in order to show associations between the elements. Six factors (F1 to F6) were determined, of which two are anthropogenic (F3 and F6), two are mixed geogenic-anthropogenic (F1 and F5) and two are geogenic factors (F2 and F4). In addition, 22 out of 121 representative moss samples were subjected to gamma-spectrometric analyses for assessing the activity of the naturally occurring radionuclides (data not shown). In 2010, the nitrogen concentration in mosses was determined for the first time using the Kjeldahl method (data not shown). From data obtained in 2010, it can be concluded that the median values and ranges of all elements obtained in this study are very similar to the median values and ranges obtained in the previous study in 2006 (Špirić et al., 2012). Only a few elements (Cd, Cu, Mg, Ni and Pb) have a

slightly higher median value (Table 1). For some typical anthropogenic elements such as chromium, mercury, vanadium and zinc, lower median values were recorded.

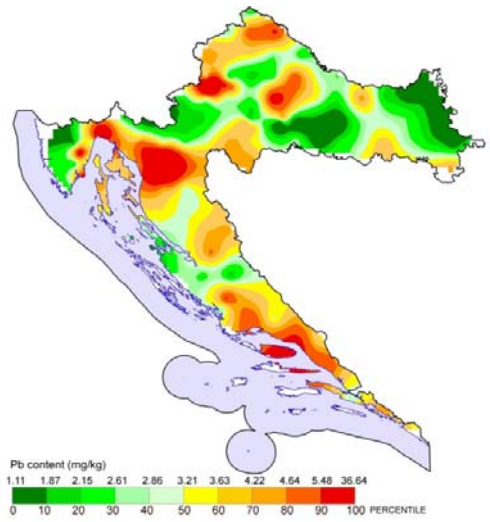

Figure 3. Moss lead concentrations in 2010.

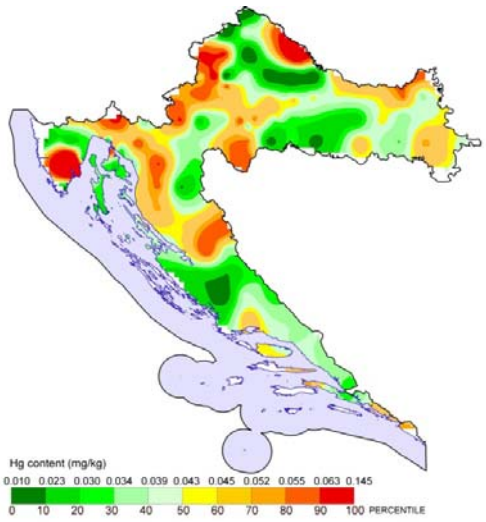

Figure 4. Moss mercury concentrations in 2010.

Table 1. Comparison of the 2006 and 2010 Croatian moss survey results.

	2010		**2006**	
No. of samples	n= 121		n= 94	
Element	Median	Range	Median	Range
Ag	0.032	0.001-0.16	-	-
Al	878	112-4493	1350	398-2146
As	0.36	0.050-1.00	0.37	0.10-6.00
Ba	20.6	4.49-94.3	32	7-192
Ca	6632	2649-20795	7623	2832-26740
Cd	0.38	0.10-1.42	0.27	0.070-1.90
Cr	1.94	0.41-8.55	2.8	0.76-33.0
Cu	8.53	4.72-22.7	7.5	3.70-22.7
Fe	789	85.0-4028	1000	320-12140
Hg	0.043	0.010-0.15	0.064	0.007-0.30
K	3891	1552-9279	8085	2565-23720
Li	0.55	0.11-4.27	-	-
Mg	3059	1619-4740	2120	676-12740
Mn	99.1	16.1-928	106	20-1421
Na	120	65.0-304	169	67-2332
Ni	3.16	1.04-14.7	2.7	0.66-18.0
P	1134	419-3117	-	-
Pb	3.21	1.11-36.6	2.46	0.060-82.4
Sr	16.0	4.74-54.0	21	4-125
V	2.55	0.23-37.3	3.1	0.91-32.0
Zn	24.8	11.6-77.1	29	12-283

Discussion and conclusions

From the moss data it can be concluded that anthropogenic heavy metal pollution has not changed significantly in Croatia between 2006 and 2010. The main anthropogenic sources of heavy metals are light and heavy industry, transportation, steel industry, textile industry, thermoelectric plants, oil deposits and refineries, whose activities are carried out near big industrialised cities such as Zagreb, Sisak, Rijeka, Kutina, Split and Sibenik. Moss samples collected near these regions showed the highest content of typical air pollution from heavy metals. In comparison with the results obtained in other European countries, it can be concluded that Croatia is more polluted than many parts of northern and western Europe, but less polluted than many of its neighbouring countries.There is a clear need to continue the moss survey in order to assess air quality throughout Croatia and to produce information needed for better identification of pollution sources and assessment of environmental and health risks associated with dry and wet deposition of toxic metals in Croatia.

Reference

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Czech Republic

Lead institute: Silva Tarouca Research Institute for Landscape and Ornamental Gardening, CZ-252 43 Pruhonice (www.vukoz.cz), Julie Sucharová (sucharova@vukoz.cz), Ivan Suchara (suchara@vukoz.cz), Marie Holá (hola@vukoz.cz)

Background

The Czech Republic (CZ) was historically industrialized (energy, metal industry, engineering and chemical industry) mainly in hard coal basins (Ostrava, Trutnov, Kladno), brown coal basins (Most, Sokolov, Břeclav, Mydlovary) and near metal ore deposits (Plzeň, Příbram, Pardubice, Kutná Hora, Zlaté Hory, etc.). Between 1945 and 1990 further local industrial works were introduced elsewhere in the country. The air pollution by major pollutants (SO_2, NO_x, particles) reached the highest levels in Central Europe in the coal basins near Most and Ostrava, which were called 'Black Triangles' in the past. The huge air pollution and acidification caused large-scale injury to coniferous forests mainly in the northern half of the Czech Republic. In the decade following the political changes in 1989/1990, industries were re-structured, advanced and cleaner technologies were introduced in remaining factories in the Czech Republic. Coal power plants were de-sulphurized (1993–1998) and the use of leaded petrol declined and finally ceased in 2000. The decrease of emission amounts (http://www.chmi.cz/_files/portal/docs/uoco/isko/grafroc/groce/gr10e/akap11.html) was followed by significant reduction of major pollutant concentrations in the atmosphere, mainly in industrial regions (http://portal.chmi.cz/_files/portal/docs/uoco/isko/tab_roc/tab_roc_EN.html) before 2000. Small, non-significant improvement in air quality has been observed after 2000. The rising number of cars and the increasing mass of solid fuels burned in home furnaces has caused increasing concentrations of particulate matter (PM), NO_x and persistent organic pollutants (POPs) in the atmosphere, mainly in the industrial areas and large cities in the Czech Republic.

Element concentrations in mosses

The element concentration in mosses was determined at 33, 192, 250, 280 and 273 monitoring sites in 1991, 1995, 2000, 2005 and 2010 respectively. In the first survey, the concentration of ten elements was determined, whilst in following campaigns the concentration of 36–40 elements (www.biomonitoring-cz.eu/index.php?option=com_content&view=article&id=77&Itemid=123&lang=en) was determined. Accumulated element concentrations in mosses are assumed to correspond closely with the bulk atmospheric deposition rates of these elements. Usually, the element concentrations in mosses in the Czech Republic have not shown a normal distribution. Rapid and significant decreases in element concentrations in mosses were found between 1991 and 2000 (2005). Minor spatial and temporal changes in element concentrations in mosses have been detected since 2000. However, the total nitrogen concentration in mosses has increased recently. Table 1 shows the temporal changes in the median element concentrations in mosses in the whole country, in formerly highly industrialised centres ('Black Triangles') and in large areas dominated by agriculture. After 1990, a substantial decrease in arsenic, iron, lead and zinc concentration in mosses was observed due to the de-sulphurization of coal power plants, reduction of metallurgical industry, amount of combusted brown coal and termination of the use of leaded petrol. Despite a general reduction of element concentration in mosses, three larger areas and a few more local hotspots with increased element concentration in mosses are present in the Czech Republic after 2000. In the brown coal basin in the north-west emission sources such as coal power plants and engineering and chemical works have caused an increase in the accumulation of mainly arsenic, chromium, iron, mercury, sulphur and vanadium in mosses. A consistent decline of these elements in mosses near the Polish border is due to de-sulphurization of the biggest Polish coal power plant close to Bogatynia. The second industrial area in north-east (hard coal and metallurgical industries, battery production, etc.) has high concentrations of particulate matter in the atmosphere and here the mosses show increased concentrations of mainly cadmium, chromium, iron, mercury, vanadium and zinc. The third larger hot spot is located in the south-east. In this area, covered by large fields and rare small coniferous forests, mosses get dusty due to high deposition rates of wind-eroded soil particles. The biased high concentration of typical lithogenic elements (chromium, iron, nickel and vanadium) has been observed in mosses in this area and in dry years (increased deposition of eroded soil particles) throughout the Czech Republic.

Table 1. Median element concentrations in mosses (mg kg^{-1}) for the whole of the Czech Republic, industrial and non-industrial (agricultural) areas between 1991 and 2010. (n.d. = not determined).

Year	Land use	As	Cd	Cr	Cu	Fe	Hg	N	Ni	Pb	S	V	Zn
1991	CZ all	1.70	0.32	1.90	8.40	747	n.d.	n.d.	3.40	16.6	n.d.	5.40	45.5
	Industrial	3.25	0.56	2.70	10.3	1,124	n.d.	n.d.	4.60	26.0	n.d.	7.95	60.3
	Agricultural	1.35	0.30	1.51	7.50	680	n.d.	n.d.	3.00	14.1	n.d.	4.35	42.8
1995	CZ all	0.50	0.31	1.37	7.13	395	0.064	n.d.	1.94	10.9	1,550	2.00	41.5
	Industrial	1.15	0.56	5.70	8.51	691	0.107	n.d.	2.65	20.0	1,788	3.97	59.9
	Agricultural	0.28	0.22	0.99	5.59	233	0.056	n.d.	1.45	7.00	1,276	1.14	31.1
2000	CZ all	0.29	0.23	1.88	6.53	401	0.048	11,881	1.95	5.66	1,182	1.52	35.0
	Industrial	0.66	0.49	2.22	6.86	434	0.081	12,826	2.19	10.1	1,411	2.19	43.4
	Agricultural	0.20	0.17	0.91	4.79	339	0.044	9,531	1.25	3.86	1,032	1.14	28.9
2005	CZ all	0.29	0.23	1.15	5.23	409	0.045	11,204	1.42	4.94	1,137	1.47	33.3
	Industrial	0.53	0.48	1.72	5.68	653	0.057	12,448	1.99	5.50	1,292	2.39	41.4
	Agricultural	0.19	0.18	0.83	4.48	325	0.038	9,560	1.06	3.77	1,001	1.13	29.0
2010	CZ all	0.26	0.18	1.01	5.92	348	0.041	13,331	1.15	2.85	995	1.18	33.9
	Industrial	0.42	0.20	1.76	6.18	589	0.055	15,667	1.64	3.94	1,203	2.18	37.7
	Agricultural	0.16	0.13	0.76	4.63	247	0.034	10,165	0.89	2.30	904	0.86	28.7

In a small area of the hard coal basin (Žacléř) in the north, an accumulation of arsenic in mosses has been detected. Some important local pollution sources have affected element concentration in mosses too. For example, a secondary lead smelter in Příbram has caused increased concentrations of arsenic, cadmium, mercury, lead and zinc in mosses; glass works in Desná and a battery factory near Frýdek Místek has controlled local cadmium contamination, a coal power plant near Mělník has affected arsenic concentrations in mosses in the surroundings. Since 2000, the concentration of total nitrogen in moss has increased elsewhere in industrial and rural areas, mainly in the northern half of the Czech Republic. Mosses have shown the highest nitrogen concentration in industrial-agricultural regions (e.g. 16,705 mg kg^{-1} in the Pardubice region in 2010), whereas the lowest nitrogen concentrations have occurred in forested areas (e.g. 851 mg kg^{-1} in the Karlovy Vary region in 2010). Temporal and spatial changes in cadmium concentration in mosses between 1995 and 2010 are shown in Figure 1 as an example.

Conclusions and recommendations

Heavy metal accumulation in mosses has remained in three larger areas and in the surroundings of a few local pollution sources. Nitrogen accumulation in moss has increased mainly in the northern half and in the south-eastern part of the country. Monitoring concentrations of some metals, total nitrogen and selected persistent organic pollutants in mosses is recommended for the future.

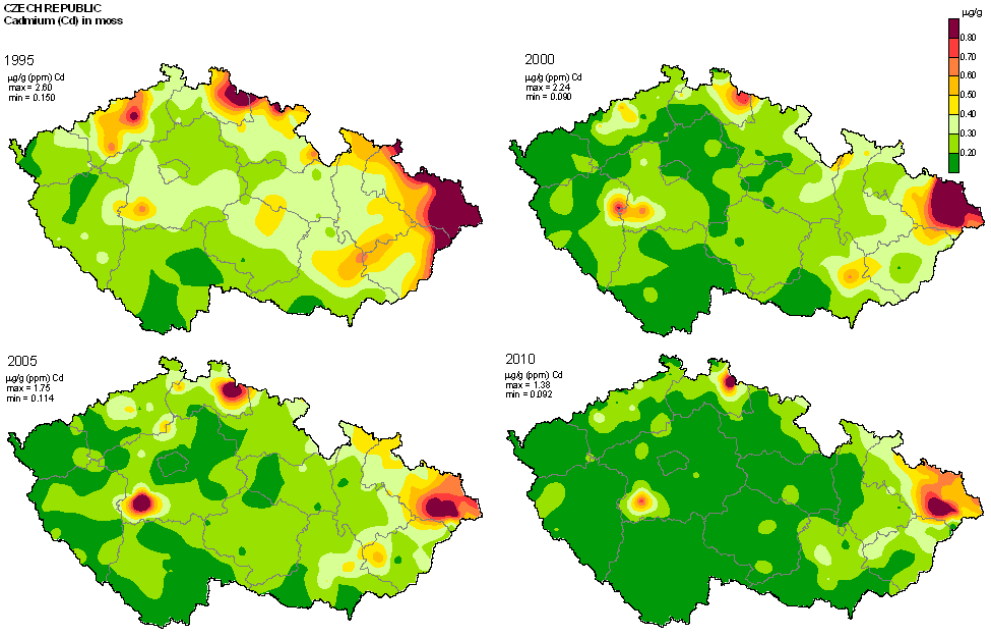

Figure 1. Cadmium concentration in moss (µg g^{-1}) in the Czech Republic between 1995 and 2010.

Finland

Lead institute: Finnish Forest Research Institute, Oulu Unit, Oulu. Jarmo Poikolainen jarmo.poikolainen@metla.fi), Juha Piispanen (juha.piispanen@metla.fi), Eero Kubin (eero.kubin@metla.fi)

Background

The Finnish Forest Research Institute (Metla) set up a project (ILME) in 1985 as a part of the Finnish Research Project on Acidification (HAPRO), to study the effects of air pollution on forests. The aim was to gather as wide as possible a body of data covering the changes in forests. For these studies Metla established in 1985-86 a network of 3009 permanent monitoring sites all over the country (Kubin, 1990). This network formed the basis for the heavy metal deposition surveys in Finland until the year 2005. The moss samples in 2010 were collected mainly from the permanent plots of the 11th National Forest Inventory (NFI11). The moss surveys in Finland have been carried out in 1985, 1990, 1995, 2000, 2005 and 2010. The surveys in Finland started as part of the surveys in the Nordic countries (Rühling et al., 1987) and continued with the European moss surveys (Harmens et al. 2008), which provides data also on the concentrations of nitrogen in mosses. In the surveys carried out in Finland, nitrogen concentrations have been regularly determined already since 1990.

The unused portions of the moss samples collected in the surveys of Finland have been stored in the Environmental Specimen Bank at Paljakka in the district of Puolanka. The main building of the specimen bank was established in 1994, and an extension was built in 1999. Only dried plant material is stored at Paljakka. Reference material for the pan-European moss surveys has been prepared from moss samples in the Paljakka specimen bank (Steinnes et al. 1997).

Finland is a suitable country for moss surveys because the differences in altitude are relatively small. Almost the whole country is located within the boreal coniferous zone, and moss species suitable for surveys can be found growing throughout the country. However, Finland is a long country in the latitudinal direction and there is a clear climatic gradient running from the south to the north of the country. The deposition of air pollutants also decreases when moving from the south to the north, because the population and most of the industrial plants and traffic are concentrated in southern Finland.

Concentrations in mosses

The heavy metals analysed in the national moss surveys can be divided into three groups on the basis of their concentrations (Poikolainen et al., 2004). The first group includes lead, cadmium and vanadium. In all surveys, the concentrations of these metals have been the highest in southern Finland, and decreased gradually going north with the lowest concentrations being found in north-west Lapland. The concentrations of these heavy metals have decreased the most between 1985 and 2010, and especially in the 1990s. Their decrease has been clearly evident throughout Finland, but is relatively the greatest in southern Finland. The second group consists of iron, zinc, mercury and arsenic. Their concentrations have been quite low throughout the years. They also have decreased from south to north, but the changes have been considerably smaller and they have not decreased as regularly as for lead, cadmium and vanadium. The third group comprises copper, nickel and chromium. The variation in the concentrations of these metals in background areas in different parts of the country have been relatively small, but their concentrations were clearly elevated in the vicinity of a number of major local emissions sources. There is a slight overall decrease in the concentrations of these metals when going from south to north. The concentrations of copper and nickel in the southwest of Finland have been effected considerably by emissions from smelters at Harjavalta, and in the northeast Lapland by high copper and nickel emissions from the smelters on the Kola Peninsula. The refined steel mill in Tornio has affected on chromium concentrations in the southwest of Lapland.

In general, the average nitrogen concentrations in mosses have been below 1.00% in Finland (Poikolainen et al., 2009). The concentrations have been highest in the southern part of the country and they have decreased gradually when moving northwards, with the lowest values being observed in northwest Lapland. There were no great changes in nitrogen concentrations between 1990 and 2010.

Table 1. Heavy metal (mg kg^{-1} dry wt.) and nitrogen concentrations (%) in mosses in Finland in 1985 - 2010.

		As	Cd	Cr	Cu	Fe	Hg	Ni	Pb	V	Zn	N
1985	Mean	-	0.37	1.49	5.99	379	-	2.24	15.5	4.76	38.1	-
	Min	-	0.03	0.22	1.64	86.1	-	0.58	2.07	0.28	16.5	-
	Max	-	1.46	23.8	223	2080	-	79.7	49.9	42.7	107	-
1990	Mean	-	0.28	1.59	5.98	405	-	1.97	10.2	3.48	36.5	1.00
	Min	-	0.04	<0.05	1.66	90.6	-	0.57	1.70	1.25	18.6	0.32
	Max	-	0.97	15.3	260	3120	-	47.3	31.8	13.7	126	2.16
1995	Mean	0.26	0.18	1.54	5.28	331	0.053	1.94	6.22	2.39	38.4	0.87
	Min	<0.10	0.03	0.57	1.73	64.0	0.017	0.54	1.07	0.59	17.5	0.45
	Max	1.07	0.67	15.2	144	3150	0.150	29.3	19.3	9.07	137	2.32
2000	Mean	0.19	0.12	1.25	3.96	259	0.048	1.83	3.37	1.45	28.8	0.78
	Min	<0.10	0.01	0.34	1.26	50.6	0.014	0.46	0.65	0.17	11.5	0.37
	Max	0.81	0.42	9.20	67.7	1950	0.180	68.8	10.0	7.54	88.0	1.76
2005	Mean	0.12	0.15	1.13	4.11	236	0.044	1.87	2.96	1.43	32.9	0.85
	Min	<0.10	0.03	0.32	1.65	55.8	0.017	0.58	0.38	0.25	14.4	0.37
	Max	0.45	0.40	11.4	24.9	2460	0.112	46.6	11.3	11.1	95.0	1.79
2010	Mean	0.12	0.12	0.95	4.90	240	0.042	2.45	2.04	1.28	31.0	0.77
	Min	<0.10	<0.05	0.34	0.74	52.7	0.016	0.42	<0.75	<1.00	11.5	0.38
	Max	0.38	0.44	14.0	55.1	2230	0.119	88.2	6.57	14.2	102	2.06

Discussion

The concentrations of the heavy metals and nitrogen in mosses in Finland are generally relatively low compared to the concentrations reported in other parts of Europe (Harmens et al. 2008). The concentrations and their decline with time are in agreement with heavy metal and nitrogen emissions and deposition measurements in Finland. The decrease in heavy metal concentrations in Finland is mainly due to the decrease in domestic emissions, as well as to the decrease in the long-range transport of heavy metals into Finland. For example, the decrease in emissions in western and northern Europe has been affected by the reduction in coal consumption, the increase in the use of unleaded petrol, the improvement of industrial manufacturing processes and the tightening of environmental legislation.

The emissions in industry and in other sources in Finland are at present relatively low and therefore additional reductions in heavy metal emissions is very expensive. Since 2000, the decrease in heavy metal concentrations in mosses have been small too. Currently, the mining industry in Finland is growing rapidly, hence heavy metal emissions are increasing locally. The monitoring of heavy metal deposition using mosses in the vicinity of the major emission sources (mining industry etc.) should be integrated with the national moss survey.

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Macedonia

Lead institute: Trajče Stafilov, Lambe Barandovski and Katerina Baceva, Faculty of Natural Sciences and Mathematics, Ss. Cyril and Methodius University, POB 162, 1000 Skopje, Macedonia. trajcest@pmf.ukim.mk

Collaborating institutes: Marina Frontasyeva, Frank Laboratory of Neutron Physics., Joint Institute for Nuclear Research, Dubna, Russian Federation. marina@nf.jinr.ru

Robert Šajn, Geological Survey of Slovenia, Dimičeva ul. 14, 1000 Ljubljana, Slovenia. Robert.Sajn@geo-zs.si

Background

The Republic of Macedonia was involved in the European moss survey for the first time in 2002, when the atmospheric deposition of trace elements was studied. The moss survey was repeated again in 2005 (Barandovski et al., 2008) and 2010 (Barandovski et al., 2012), sampling the terrestrial mosses *Hypnum cupressiforme* Hedw. and *Homalothecium sericeum* (Hedw.) B.S. & G. Moss samples were collected at 73 sites in 2002 and at 72 sites in 2005 and 2010, evenly distributed over the country using a dense grid of 17 x 17 km^2. The analyses of 42 elements were performed by using instrumental neutron activation analysis (INAA) and atomic absorption spectrometry (AAS) as analytical technique. The most important emission sources were smelters and drainage systems near the towns of Veles, Tetovo, Kavadarci and Radoviš, as well as mines in Sasa, Toranica and Zletovo in the east of the country. Some uranium deposition patterns were related to the activity of power plants (near Bitola and Kičevo) using lignite coal as fuel. Due to the intensive ferronickel production in the Kavadarci region, the median nickel concentration was 2.5 times higher in 2005 than in 2002. There are examples when the concentration in mosses of some anthropogenic elements was lower in 2005 than in 2002 (arsenic, chromium, copper, antimony and selenium). For example, the newly introduced protection activities on the slag dump from the closed ferrochromium smelter located near Tetovo contributed to a decrease of chromium in mosses in 2005 compared with 2002.

Concentrations of heavy metals and nitrogen

To determine the concentration of the various elements in the mosses collected in 2010, AAS and ICP-ES were used. The concentration of 18 elements (Al, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Ni, P, Pb, Sr, V and Zn) was determined in Skopje, Macedonia. In previous years, INAA was also performed in Dubna, Russian Federation, to determine 42 elements. However, the INAA results for 2010 are not available yet. Although the median values for all elements are lower in 2010 than in previous years, it should be noted that lower median values for Al, Ba, Ca, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Sr, V and Zn can be explained to some extent by the difference of the analytical techniques applied. AAS and ICP-ES potentially do not include a fraction of the elements due to their refractory minerals, which is included in INAA. The Kjeldahl analytical method was applied to determine the nitrogen concentration in moss samples in 2005 and 2010 (data not shown).

Results and discussion

To explain variation in the concentration of metals in mosses and to reveal associations of chemical elements, all data were examined by multivariate analysis. The multivariate statistical cluster and factor analyses were performed on 15 selected chemical elements (Al, Ba, Cd, Cr, Cu, Fe, K, Mg, Mn, Ni, P, Pb, Sr, V and Zn). Four factors were identified, explaining 78.6% of the variability of elemental concentrations in mosses. Factors were identified by visual inspection of similarities of spatial distribution of element patterns, the correlation coefficient, comparison of basic statistical parameters and the results of multivariate analyses (Barandovski et al., 2013). **Factor 1** (Al, V, Fe, Ba, Li, Sr): this group represents chemical elements that are naturally distributed. Concentrations of these elements in mosses are significantly influenced by mineral particles released into the atmosphere by wind erosion of local sources or particles attached to the moss in the periods when the soil surface is not wet. **Factor 2** (Cd, Cu, Pb, Zn) is the second strongest factor with 18.3% of total variability. This factor is related to industrial activity in Macedonia. **Factor 3** (Mg, Cr and Ni) represents mixed (geogenic-anthropogenic) association of elements. The concentration of these elements is affected primarily by

natural factors such as lithological background but anthropogenic influence as well. **Factor 4** (P and K) represents the second anthropogenic geochemical association of elements. High values of these elements have been found in the regions where agricultural activities are present in the country. The spatial distribution of the Factor scores is shown in Figure 1.

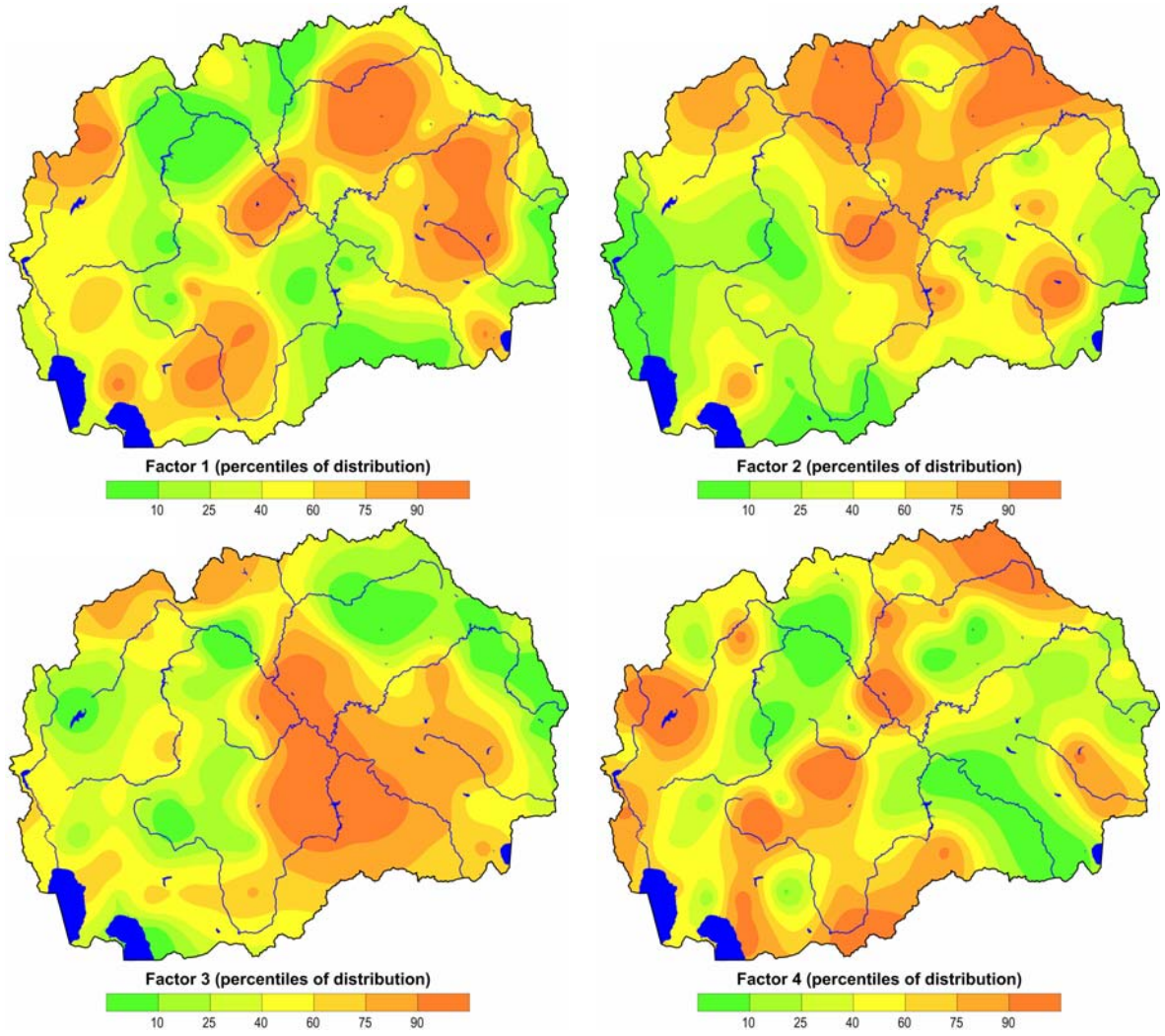

Figure 1. Spatial distribution of Factor 1 scores (Al, Ba, Fe, Li, Sr, V), Factor 2 scores (Cd, Cu, Pb, Zn), Factor 3 scores (Cr, Mg, Ni) and Factor 4 scores (K, P) based on elemental concentrations in mosses in Macedonia in 2010.

Although elemental concentrations in mosses tend to be lower in Macedonia than in neighbouring countries, considerable atmospheric metal pollution is still present in Macedonia compared to the more pristine areas in Europe. Recent trends in concentration in mosses for some elements can be explained by closing down some of the smelters, using non-leaded petrol and some protective activities introduced for slag dump in the country.

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Norway

Lead institute: Hilde Thelle Uggerud and Martin Schlabach, Norwegian Institute for Air Research, NO-2027 Kjeller. hilde.thelle.uggerud@nilu.no; martin.schlabach@nilu.no
Collaborating institute: Eiliv Steinnes and Torunn Berg, Norwegian University of Science and Technology, NO-7491 Trondheim. eiliv.steinnes @ntnu.no; torunn.berg@ntnu.no

Background

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

Spatial patterns and temporal trends of concentrations in mosses

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

Other metals in mosses such as iron, copper and nickel are mainly related to emissions from industrial point sources. Examples are zinc and cadmium from the Odda zinc smelter, and iron, manganese and chromium from the Mo i Rana industries. Because of topographic factors these point sources generally influence only limited areas in the vicinity of the source. The most severe influence from local point sources is emissions of copper and nickel from Russian smelters situated close to the Norwegian border in the far northeast. In contrast to the emissions in Norway, the contribution from these copper-nickel smelters has increased steadily over time. The geographical trend of mercury in moss differs substantially from bulk deposition values calculated from precipitation monitoring, showing fairly uniform values all over Norway. This can probably explained by retention of elemental mercury in the moss, being different from precipitation where only oxidised forms of the elements are found.

Since 2000, a more detailed moss survey has been conducted every five years around 15 main industrial pollution sources in the country. This survey was initiated by The Norwegian Climate and Pollution Agency and financed by the industries involved, and has become a useful instrument in assessing emission trends of metals from these industries. In 2010, separate moss samples were collected at 20 sites distributed over the country, and the concentrations of several groups of persistent organic pollutants such as polychlorobiphenyl (PCB), polycyclic aromatic hydrocarbon (PAH), and polybrominated diphenyl ether (PBDE) were determined. Apparently, all these compounds are retained in the moss from the atmosphere, and moss samples may thus be a useful instrument for looking at time trends also for these compounds (Harmens et al., 2013). The geographical patterns are apparently influenced by local sources as well as long-range transport, depending on the substance considered. The south to north distribution seems to depend on the volatility of the compounds.

Conclusion

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

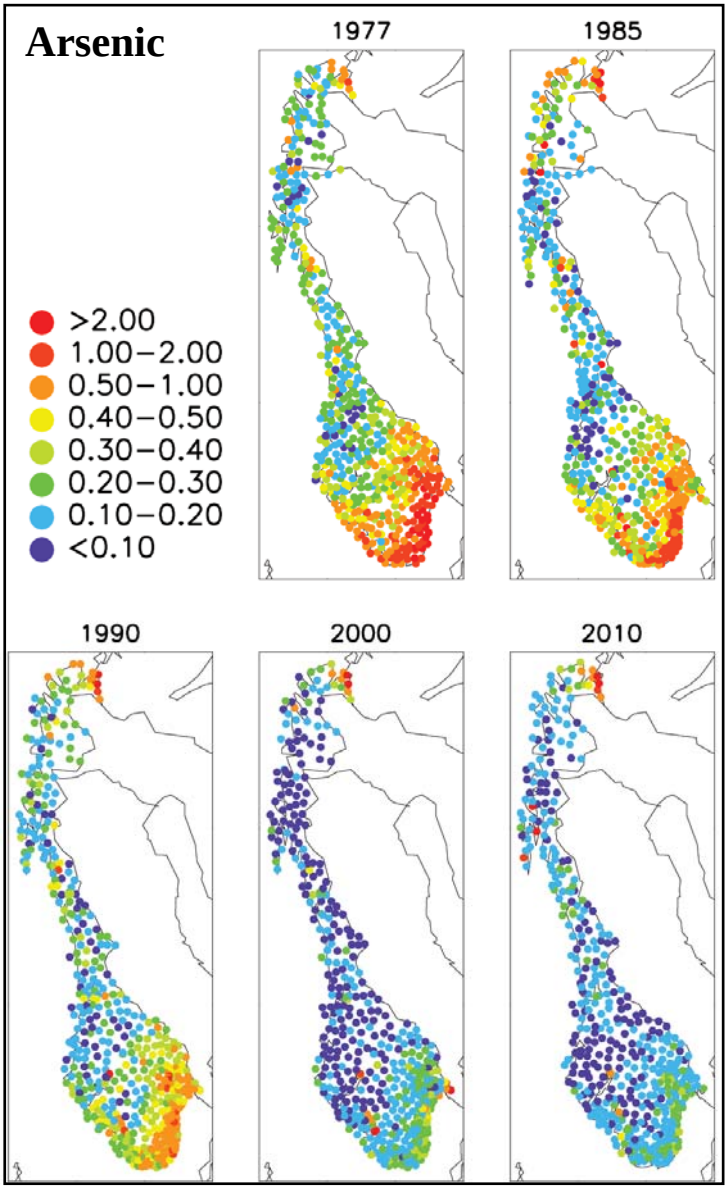

Figure 1. Temporal trends (1977 -2010) of arsenic concentrations (mg kg^{-1}) in moss in Norway.

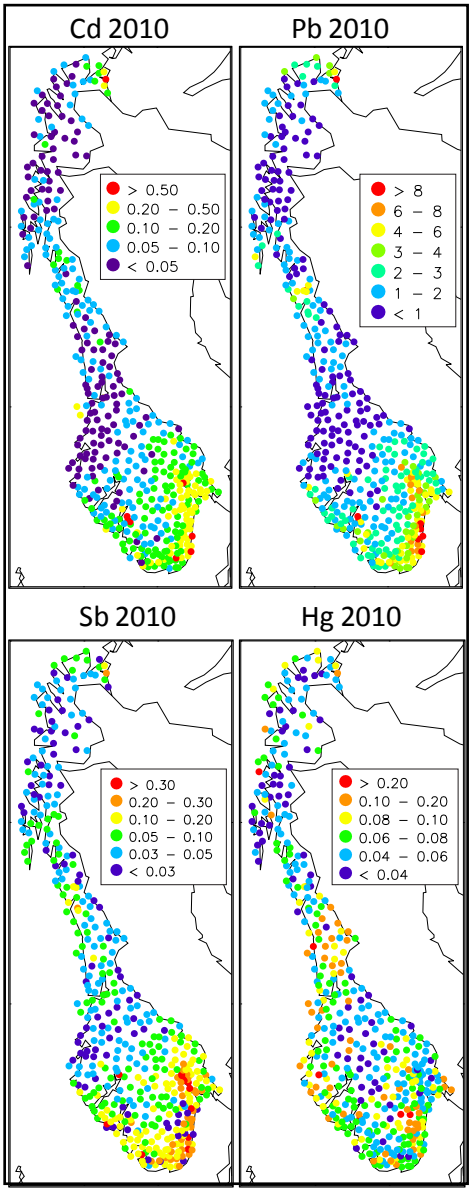

Figure 2. Cadmium (Cd), lead (Pb), antimony (Sb) and mercury (Hg) concentrations (mg kg^{-1}) in moss in Norway in 2010.

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Poland

Lead institute: Paweł Kapusta, Grażyna Szarek-Łukaszewska, Barbara Godzik, W. Szafer Institute of Botany, Lubicz 46, 31-512 Kraków, Poland;
p.kapusta@botany.pl; g.szarek@botany.pl; b.godzik@botany.pl

Background

Heavy metal pollution became a serious environmental problem in Poland in the middle of the 20th century. This was mostly a result of economic transformation which happened after World War II – the rapid development of the industrial sector based on local resources, i.e. coal, iron and non-ferrous metals. Excavation and processing of zinc-lead ores (Silesia and Olkusz Industrial Region) and copper ores (Legnica-Głogów Industrial Region), and coal combustion in power plants caused enormous emissions of gases and dust. It affected vast areas of southern and south-western Poland. The peak of industrial activity was in the 1970s and 1980s. After 1990, emissions of pollutants began to decrease gradually, due to a slowdown of industrial production and the use of filtering systems.

Moss monitoring was initiated in Poland in the 1970s with the studies of heavy metal accumulation in mosses collected from national parks (Grodzińska, 1978). It became a part of the European monitoring programme in 1990. Since then, the Polish moss surveys have been repeated ca. every five years, but using different sampling schemes. In 1990 and 1995, moss samples were collected at 147 and 297 sites, respectively, evenly distributed across Poland. In 2000, the moss survey comprised 116 sites grouped in four areas representing different degrees of industrialization (south-western, southern – heavy polluted; central – moderately polluted, and the north-eastern part of Poland – clean area). In 2005, moss monitoring was conducted in 23 national parks scattered across the country. In all these surveys the moss species *Pleurozium schreberi* was used and the accumulation of seven heavy metals (Cd, Cr, Cu, Fe, Ni, Pb, Zn) was determined. The results of the Polish moss surveys were published in a few papers (e.g. Grodzińska et al., 1990, 1999, 2003, Grodzińska and Szarek-Łukaszewska, 2001, Suchara et al., 2007) and included in the European reports and papers.

Heavy metal and nitrogen concentrations in mosses

The most recent Polish moss survey was carried out in 2010. Samples were collected from the same sites that were studied in 1995 (it allowed to estimate the significance of the temporal change between years). In 2010, the average concentrations of Cd, Cu, Ni and Pb in the moss were significantly lower than in 1995 (Table 1). Average values decreased from 0.45 to 0.30 (Cd), from 7.60 to 6.04 (Cu), from 1.44 to 1.15 (Ni) and from 13.8 to 4.93 (Pb) mg kg^{-1} between 1995 and 2010. The trend was dependent on the region; for some provinces decreases were not significant. Concentrations of other metals (Cr, Fe, Zn) did not alter significantly with time (Table 1). The spatial patterns of the accumulation of heavy metals in mosses were similar in both surveys; southern parts of Poland, industrialized and densely populated, were contaminated more than the rest of the country (Figure 1). Taking into account the results of other surveys (1990, 2000 and 2005), the temporal trend of heavy metal pollution in Poland should be considered as consistently decreasing.

Table 1. Average trace metal concentrations (mg kg^{-1}) in mosses in 1995 and 2010.

Year	Sites	Cd	Cr	Cu	Fe	Ni	Pb	Zn
1995	295	0.45	1.50	7.60	362	1.44	13.8	43.0
2010	320	0.30	1.27	6.04	344	1.15	4.93	47.5

In the 2010 moss survey, nitrogen concentrations in mosses were estimated for the first time in Poland. They ranged from 0.78 to 2.86% (the average value was 1.56%). The western part of Poland (having more intensive agriculture and transport) seemed to be influenced by nitrogen deposition to a greater extent than the eastern part (Figure 1), however, significant differences between provinces were not found due to the high local variation.

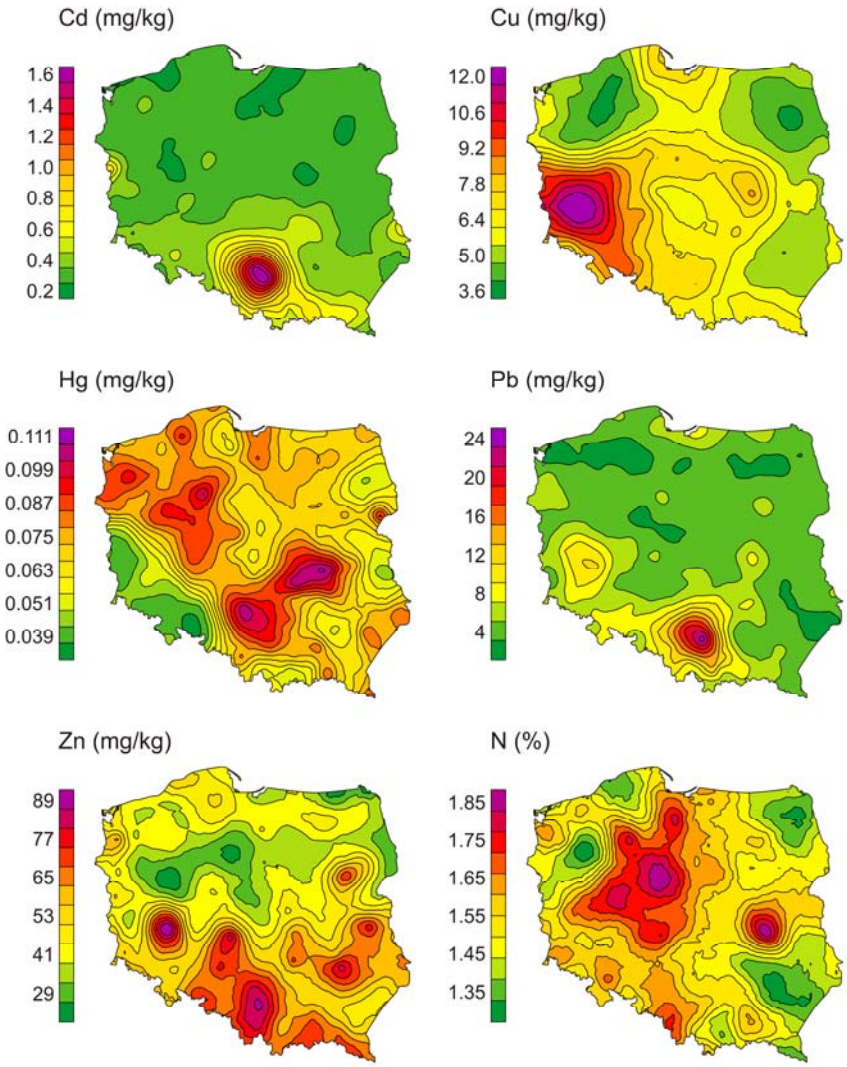

Figure 1. Heavy metal (Cd, Cu, Hg, Pb, Zn) and N concentration in mosses in Poland in 2010.

Discussion and conclusion

The spatial variability of heavy metal accumulation in mosses correlates well with the variability in the level of industrialization between regions, and the temporal trend in the accumulation reflects improvement of air quality with time. Moss monitoring with the current sampling density and expanded to include metals used in new technologies should be continued. It is the only air quality control programme in Poland, which covers a relatively long period, covers the whole country and is integrated with similar programmes carried out by other European countries.

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Slovakia

Lead institute: Blanka Maňkovská, Institute of Landscape Ecology, Slovak Academy of Sciences, Štefanikova street 3; P.O. Box 254; 814 99 Bratislava. bmankov@stonline.sk

Background

The use of mosses as biomonitors of atmospheric deposition of heavy metals started more than 30 years ago in connection with the problem of forest dieback in Slovakia. Since 1990, systematic moss biomonitoring studies were carried in Slovakia (grid of 16 km x 16 km), and the results were presented in the European moss survey reports and papers. It is assumed that in the Slovakia a large gradient of the atmospheric deposition load of elements exists, because part of Slovakia belongs to the most polluted areas in central Europe, known as the 'Black Triangle II'. In order to investigate the distribution of element deposition in Slovakia, the moss monitoring technique was applied in 1990, 1995, 1996, 1997, 2000, 2005, 2010.

Table 1. Metal-polluted areas in Slovakia in 2010.

Area	Pollution	Elements with Ci > 2
Central Spiš region (Volovské Mts),	Industrial activity metallurgy, nonferrous ores and processing factories.	Na, Mg, **Al, Cl, K, Sc, Ti,** V**, Cr**, Co, Ni, **Mn, Fe, Ni, As**, **Se, Br, Rb, Sr, Zr, Mo, Ag, Sb, I**, Cs, **Ba, La, Ce, Sm, Tb,Yb, Hf, Ta, W, Th, U, Cu, Zn,** Cd, Pb, S, Hg
Region Košice -Prešov	Manufacture of basic metals and fabricated metal products.	Na, Al, Cl, Cr, As, Se, Br, Mo, Ag, In, Sb, W, Cu, **Zn, As, Cu,** Zn, **Cd, Pb**, S, Hg
Snina -Stropkov-Strážske	Manufacture of basic metals and fabricated metal product, chemical products.	Na, Al, Cl, K, Sc, Ti, V, Cr, Mn, Co, Ni, Se, Sr, Zr, Mo, Sb, Ba, Hf, Ta, W, U, Cd, S, Hg
Ružomberok -Svit	Pulp, paper products, chemical and fibre industry.	Mg, Al, Cl, K, Sc, Ti, V, Cr, Co, Ni, Se, Br, **Rb,** Sr, Zr, **Mo,** Ag, Hf, Ta, W, Th, S
Orava	Ferro-alloys smelters, fabricated metal product.	K, Mn, As, Se, Br, Mo, In, I, Sm, W, Zn, S, Hg
Detva -Brezno	Manufacture of basic metals and fabricated metal products.	K, Br, Zr, Sb, Hf, **Zn**, S, Hg
Jelšava –Lučenec - Poltár	Magnesite plants, glass-ceramic production.	Na, Mg, Al, Sc, Ti, V, Cr, Co**, Ni**, Se, Sr, Zr, La, Sm, **Hf,** Ta, U, Pb, S, Hg
Kremnicko-Štiavnické Mts.	Non-ferrous ores and smelters, old mining districts.	Na, Al, Sc, Ti, V, Mn, Co, Ni, Se, Br, Rb, **Sr, Zr,** La, Ce, Sm, Tb, Yb, Hf, Ta, W, Th, U, Cd, S, Hg
Upper Nitra and Martin	Thermal power stations, manufacture of machinery and equipment.	**Na, Mg**, Al, Ca, Sc, Ti, V, Cr, Co, **Ni**, Se, **Br**, Zr, **Mo,** Ag, I, La, Sm, Tb, Hf, Ta**, W, Au**, Th, U, Zn, **Cd, Pb**, S, Hg
Kysuce and Považská valley	Engineering and instrument industry, glass, tire and rubber industry (Black Triangle II).	Al, Cl, Ca, Sc, Ti, V, Mn, Cr, Co, Ni, As, Se, **Br,** Rb, Sr, Zr,Mo, I, Ce, La, Sm, Tb, Yb, Hf, W, Th, U, Cd, S, **Hg**
Anomalous zones		
Brezová pod Bradlom	Geogenic anomalous zones.	**Na, Mg,Al, Sc, Ti, V**, Cr, Fe, Co, Ni, Zn, As, Se, **Br**, Rb, **Zr,** Mo**, I**, Ba, La, Ce, **Sm**, Tb, Yb, Hf, Ta, W, Th, **U**, S
Slanec	Output and crumbled of stone.	Na, Mg,Al, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, As, Se, Br, Rb, Sr,Zr, Mo, Ba, La, Ce, Sm, Tb, Yb**, Hf**, Ta, W, Th, U, S

Note: Ci = contamination factor, i.e. the median value of element concentration in Slovakian mosses divided by the median value in Norwegian mosses.

Hot spots of heavy metal pollution sources included Volovské Mts (Central Spiš), Kremnické and Štiavnické Mts (non-ferrous ores processing and aluminium factories) and dumps of stone chips (Slanec). In comparison to the average heavy metal concentrations in moss in Austria and the Czech Republic, the Slovak atmospheric deposition loads of the elements were found to be 2–3 times higher on average. The transboundary contamination by mercury via dry and wet deposition from the Czech

Republic and Poland is evident in the borders in the north-western part of Slovakia (BlackTriangle II), well known for its metallurgical works, coal processing and chemical industries.

Heavy metal and nitrogen concentrations in mosses

Spatial trends of heavy metal concentrations in mosses were metal-specific. The median concentration of cadmium, copper, lead and vanadium in mosses has decreased between 1990 and 2010 in Slovakia. The decline was higher for lead (79%) than cadmium (51%). Although the correlations between concentrations in mosses and EMEP-modelled deposition were weak for cadmium and lead, the temporal trend for the concentration in mosses was similar to the trend reported for modelled total deposition of lead in Slovakia (Harmens et al., 2012). The level of elements in mosses reflects the relative atmospheric deposition loads of the elements at the investigated sites (Table 1). Factor analysis was applied to determine possible sources of trace element deposition in Slovakian mosses. In the industrial area of Central Spiš were higher than in Norway (Central Norway- as relatively the cleanest region) for Al, As, Ca, Cd, Cl, Co, Fe, K, Mn, Sb, Sm, Sr, W and Zn. A comparison between the median concentration of elements in mosses in Norway and Slovakia is provided in Table 2 by means of the contamination factor.

Table 2. The contamination factor, i.e. the median value of element concentration in Slovakian mosses divided by the median value in Norwegian mosses for 2010.

Contamination factor Ci				
<1	1-2	2-5	5-10	>10
Br, I	Cl, Mn, Na, Ni, Se, Rb, U, Zn,	Ba, Ca, Co, Cr, Cu, Fe, Hg, K, Sm, Tb, Th, Ti, V	Al, Au, Ce, La, Sb, Se,Sr, Yb, Pb	Ag, Cd, Mo, Ta, W

Nitrogen concentrations in the mosses (*Pleurozium schreberi, Hylocomium splendens* and *Dicranum* sp.) ranged from 16.5 to 30.1 mg kg^{-1} (2000) and from 10.0 - 28.5 mg kg^{-1} (2010). Compared to the year 2000, there was a decline in the nitrogen concentration in mosses in 2010.

Conclusion

Mosses provide an effective method for monitoring trends in heavy metals pollution in Slovakia at a high spatial resolution.

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Spain

Collaborating institutes:

J.R. Aboal, A. Carballeira, J.A. Fernández, University of Santiago de Compostela, Department of Cellular Biology and Ecology, Santiago de Compostela. jangel.fernandez@usc.es
E. Núñez-Olivera; R.T. Las Heras, J. Martínez Abaigar; University of La Rioja, Logroño. javier.martinez@unirioja.es
S. Izquieta, D. Elustondo, E. Lasheras, R. Bermejo, J.M. Santamaría, University of Navarra, Department of Chemistry and Soil Science, Pamplona. chusmi@unav.es

Background

In the 1995 survey, moss samples were collected in the northern half of Spain (125 sites) in a survey coordinated by the University of Santiago de Compostela with the help of botanists from some Spanish universities and institutions (e.g. La Rioja, Navarra, País Vasco, Barcelona, Madrid and Salamanca). This survey was done without specific funding and the lack of a national supporting budget prevented new national-scaled samplings in the subsequent reports. In the 2000 survey, only data from Galicia (NW Spain; 150 sites) were included. In 2005, data were included from Galicia (147 sites) and Navarra (NE Spain; 60 sites), and in the 2010 survey a new region, La Rioja (north-central Spain; 25 sites), was also included. The three regions provided data on heavy metals and nitrogen (N) concentrations in moss samples. The lack of funding for national studies was overcome by regional surveys. In Galicia, these were done each four years (from 2000 to 2010) to study general patterns of air pollution, using the moss species *Pseudoscleropodium purum* collected in a regular grid (25 km x 25 km) twice a year (spring and autumn). Moreover, focused studies in the main polluting industrial areas have been developed in the last decade. Since its first participation in the European survey, several studies have been carried out in Navarra in order to assess the deposition of heavy metals and nitrogen by the using particularly the moss species *Hypnum cupressiforme*. In La Rioja, additional surveys were conducted in 2006, 2008 and 2010, using samples of *Hypnum cupressiforme* collected at 25 sites in La Rioja (10) and neighbouring provinces (15). The size of the grid was equal to that used in Galicia and mosses were sample twice a year. A fourth campaign is currently ongoing, where analytical results are expected by the end of 2013.

Results and conclusions

In Galicia, the concentrations of heavy metals in moss samples have allowed us to establish the extent of the polluted areas and also to identify the most important pollution sources. In general, the highest levels of pollution correspond to the coastal strip, where the most populated cities and the biggest industries (e.g. coal-fired power plants, iron smelters, paper works, aluminium smelters) are situated. Nevertheless, the metal concentrations are lower than in other industrialized areas of Europe. The zone with the lower levels of pollutants is located in the inner area of the region, the less inhabited and industrialized part of the region, where the main activities are related to agriculture and livestock. Due to the location of Galicia in the north-west corner of Spain, there is not a great influence of long-range air pollution from other countries. A comparison of the levels of pollutants in mosses in the different surveys shows a slight reduction, similar to that detected in the rest of Europe. There are also data on N concentrations in mosses, determined to evaluate the extent of airborne N deposition in the 2005 survey. For N, the concentrations are also lower than in the more industrialized European regions, and usually range between 0.8 and 1%. Finally, available data on $\delta^{15}N$ levels showed a range between -7.60 and -1.00‰, indicating that the deposition of N is mainly in the form of oxidised compounds.

The north-west area of Navarra is clearly influenced by the highly industrialized area of the Basque Country. A hot spot is also observed in the west, where many metal industries and an important cement factory are located. A third source is related to long-range transboundary air pollution coming from central Europe, which are deposited in the north east area of Navarra after crossing the Pyrenees. Besides these anthropogenic sources, some metals (V, Cr, Ni and As), are clearly related to the nature of the bedrock materials. The elements Zn, Cd and Pb show a clear relation with

anthropogenic activities, reaching higher concentrations in the above-mentioned regions. In the last survey (2010) a significant decrease of heavy metal concentrations has been detected in Navarra. This may be linked to the reduction in industrial activity experienced in recent years and the implementation of air pollution control technologies in some important factories. However, it is also important to note that in 2010 some locally polluted sampling sites have been excluded, which has resulted in a greater than expected reduction in air pollution. The comparison of heavy metal deposition between 1995 and 2010 surveys also reveals a decreasing trend in pollution (Figure 1).

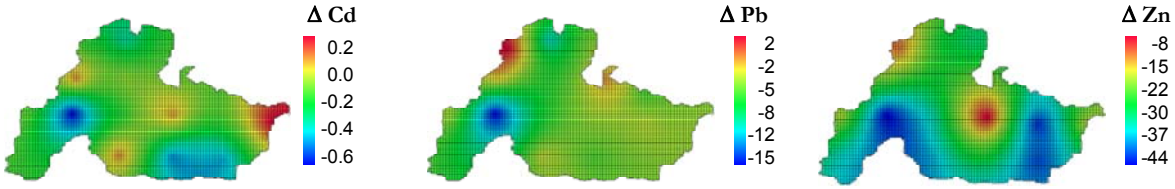

Figure 1. Changes in heavy metal concentrations in mosses in Navarra (µg g^{-1}) between 1995 and 2010.

In La Rioja, the Cd, Hg, Ni and Pb concentrations are clearly low in comparison with both other regions of Spain and other European countries. This is in accordance with the relatively low industrialization and the absence of strong sources of heavy metals in La Rioja. In contrast, As values are generally higher than those found in most European countries, although lower than those measured in more industrialized areas of Spain. The reason for this is being investigated. Comparisons between the 1995-96 data and the more recent data (2006, 2008 and 2010 campaigns) are confounded by the fact that the sampling sites in the first campaign do not coincide with those in more recent surveys. Nevertheless, mean data are shown in Table 1 for comparison. No clear temporal trend was observed for Cd and Ni, whereas As shows a clear increase in 2010, Hg seems to have increased in the last 10-15 years, and Pb has clearly decreased in the same period. If the three more recent campaigns are compared (Table 1), As values show an increasing trend, which may be due to a local effect that is still not fully understood. Cd and Hg concentrations have decreased in the two most recent campaigns, Pb values have slightly increased and Ni values have considerably increased in 2010 compared to 2008.

Table 1. Mean concentrations of arsenic (As), cadmium (Cd), mercury (Hg), nickel (Ni) and lead (Pb) in different moss surveys conducted in La Rioja (north-central Spain).

Year	As (ng g^{-1})	Cd (ng g^{-1})	Hg (ng g^{-1})	Ni (µg g^{-1})	Pb (µg g^{-1})
1995-96	475.4	-	9	1.78	6.6
2006	399.8	96.6	42.9	-	2.89
2008	429.4	80.3	31.4	1.26	2.62
2010	665.7	74.7	29.7	1.72	2.70

In 2010, the total N concentration and the isotopic ratio $\delta^{15}N$ were measured for the first time in mosses from La Rioja. Total N varied between 0.6 and 1.1% (mean = 0.8%). These values were lower than those found in northern Spain and in several other countries (see main part of this report). The $\delta^{15}N$ ratio varied between -8.7 and -5.8 (mean = -7.3), showing lower values than in Europe and northern Spain. This is associated with the reduced N forms originating from agricultural activities.

Recommendation

The excellent results obtained in the three studied regions suggest that the moss survey must be extended to other zones of Spain. There is currently no other inexpensive and easy technique to assess the extent of airborne pollution from the local pollution sources, to evaluate the effect of changes in legislation and to identify temporal trends in air pollution levels.

Sweden

Lead institute: Gunilla Pihl Karlsson and Helena Danielsson, IVL Swedish Environmental Research Institute, Göteborg, Sweden. gunilla.pihl.karlsson@ivl.se; helena.danielsson@ivl.se

Background

The initiative to use mosses as bioindicators for large scale inventories was developed in Sweden in the 1970´s by Lena Skärby and Åke Rühling. The national moss survey in Sweden has been performed since 1975 at five-year intervals. A general north-south gradient can be seen for most of the analysed metals with the highest concentrations found in the southern and south-western parts of Sweden. Lead, cadmium, copper, chromium, mercury, nickel, vanadium and zinc are all significantly lower in the mountains and in the northern parts of Sweden compared to other parts of the country. There are, however, for some metals, local effects on the metal concentrations in mosses. Areas around the iron ore fields in northern Sweden and on the Bothnian Bay coast line are exceptions to the general south-north gradient. In the southern parts of the Bothnian Bay coast line concentrations of arsenic, lead, cadmium, copper and zinc are higher than in other parts of the Bothnian Bay coast line. As expected, in the iron ore fields the iron concentrations are slightly elevated compared with other parts of northern Sweden. The moss samples from coastal areas near the Finnish border show locally higher concentration of chromium and nickel.

Concentrations in mosses

Between 1975 and 2010, the metal concentrations in mosses in Sweden have decreased significantly for all analysed metals. The largest decrease was found for lead (Figure 1) followed by chromium, nickel, cadmium (Figure 2), vanadium, arsenic (Figure 3), copper and zinc. However, there are specific regions in Sweden with no significant reduction in metal concentrations in mosses between 1975 and 2010. For example, at the coast line of northern Sweden there was no statistically significant reduction for arsenic (Figure 3) or chromium.

The metal concentration in mosses have not decreased to the same extent during the past 20-year period (1990-2010). Only lead (Figure 1) and cadmium (Figure 2) show a statistically significant reduction for the whole of Sweden during this period.

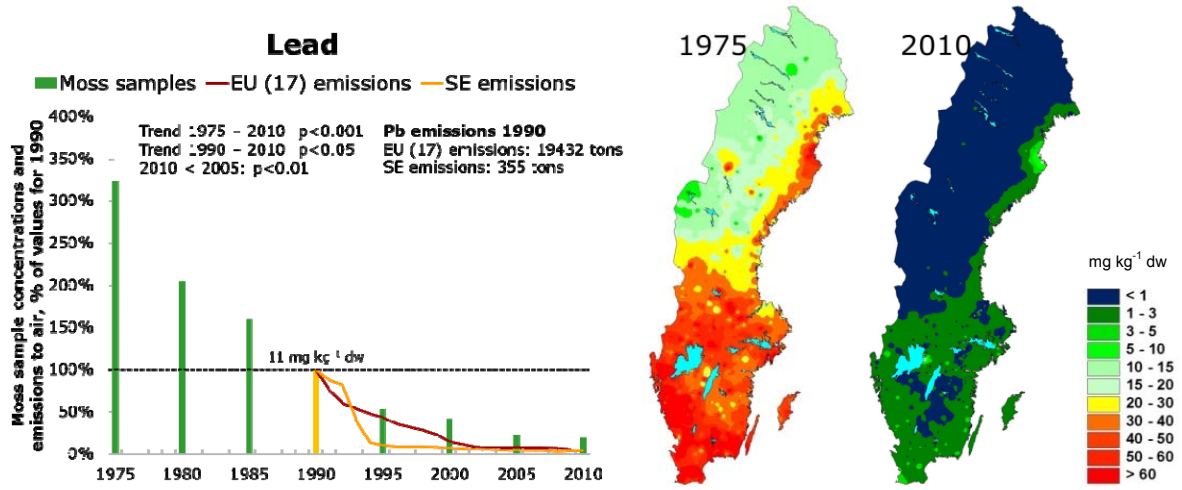

Figure 1. Moss sample concentrations and emissions to air (as % of the value for 1990) and concentrations of lead (mg kg^{-1} dry wt) in moss samples in 1975 and 2010 in Sweden.

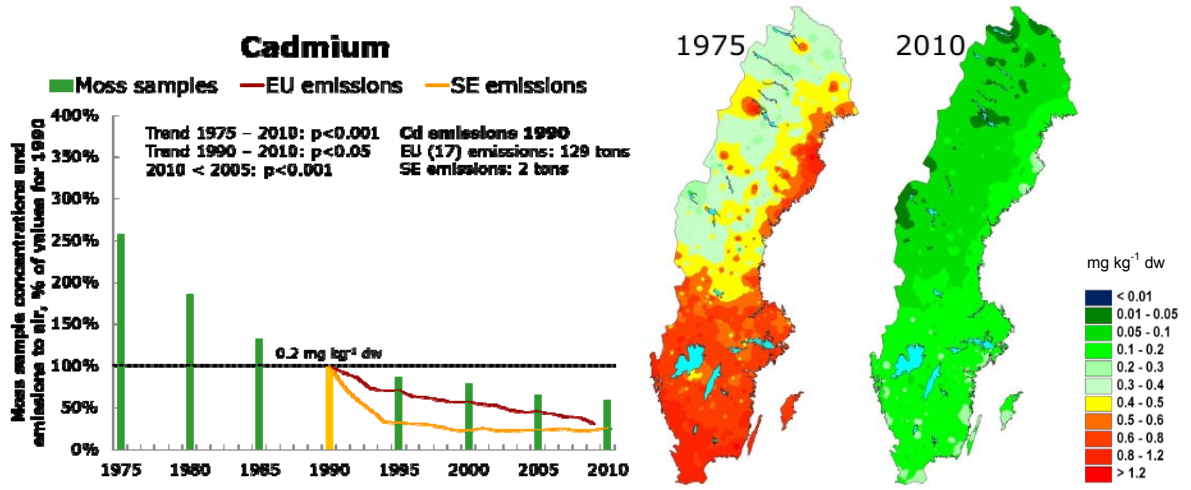

Figure 2. Moss sample concentrations and emissions to air (as % of the value for 1990) and concentrations of cadmium (mg kg^{-1} dry wt) in moss samples in 1975 and 2010 in Sweden.

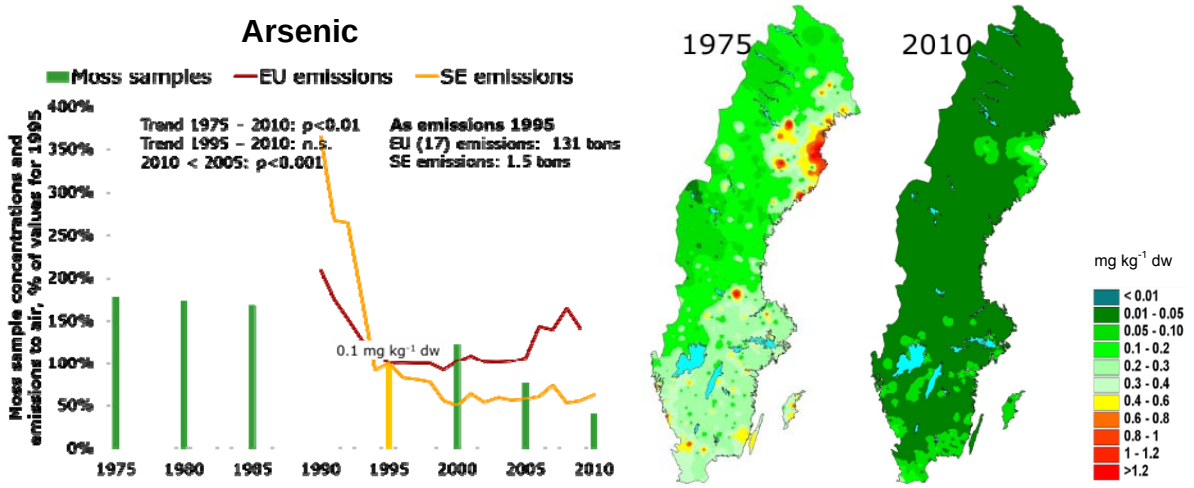

Figure 3. Moss sample concentrations and emissions to air (as % of the value for 1995) and concentrations of arsenic (mg kg^{-1} dry wt) in moss samples in 1975 and 2010 in Sweden.

Conclusions

For most metals, the heavy metal concentrations have continued to decline since 2005. The occurrence of most metals in moss samples follows a general gradient:

- The lowest levels are generally found in the mountains and inland parts of northern Sweden;
- The highest concentrations are generally found in the southern parts of Sweden.

Areas around the iron ore fields in northern Sweden and at the Bothnian Bay coast line are exceptions to the general south-north gradient.

During the last 35 years (1975 - 2010), the metal concentration in mosses for the whole of Sweden decreased significantly for all investigated metals. The largest decrease was found for lead. Still there are regions where no significant reduction in metal concentrations was found. During the last 20 years (1990 - 2010), the metal concentration in mosses has not declined to the same extent as for the period 1975 - 2010. Only lead and cadmium show a statistically significant reduction for the average value for the whole of Sweden during the last two decades.

Switzerland

Lead institute: Lotti Thöni, FUB – Research Group for Environmental Monitoring, Rapperswil.
lotti.thoeni@fub-ag.ch

Background

Switzerland has been participating in the European moss survey since 1990. At the end of the 1980s, many small industries were operating in Switzerland with the main "hot spot" for ferrous metallurgy in the southern part. In addition, 28 incineration plants were important further sources for heavy metal emissions, especially for cadmium and several crematoria for mercury emission. The major source for lead was leaded petrol. All these plants were either closed down or fitted with filters and leaded petrol is not sold anymore in Switzerland since 2000.

Heavy metal concentrations in mosses

In Figure 1 the spatial distribution of the elements arsenic, cadmium, copper, lead and zinc in mosses, primarily originating from anthropogenic activities, is shown in cumulative form. The highest heavy metal levels were recorded in the southern Alps caused by domestic emissions and transboundary long-range transport of pollutants from Italy. This was very obvious in 1990 but still visible in 2010.

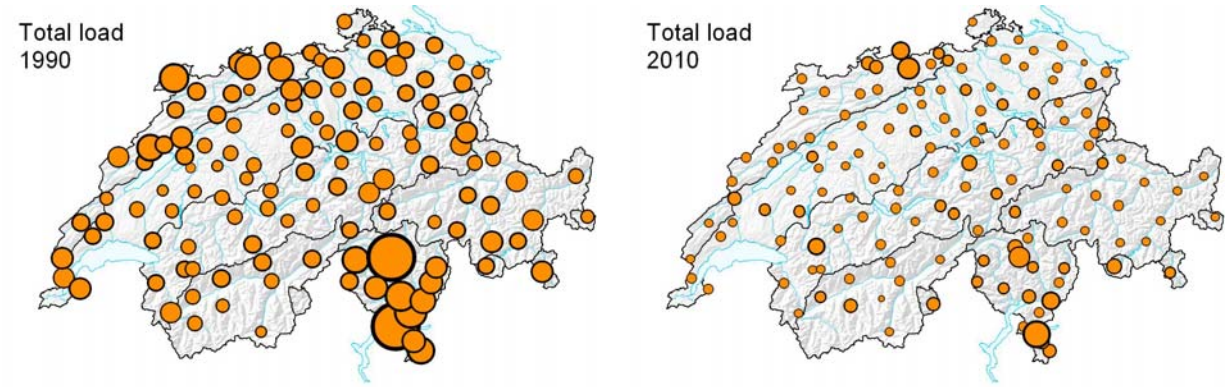

Figure 1. The spatial distribution of the summarised elements As, Cd, Cu, Pb, Zn, normalised for their geometric mean, in 1990 and 2010 in Switzerland.

Figure 2 shows the temporal trends for several metals. All considered elements apart from copper have been decreasing since 1990, most markedly lead with a decline of 86%.

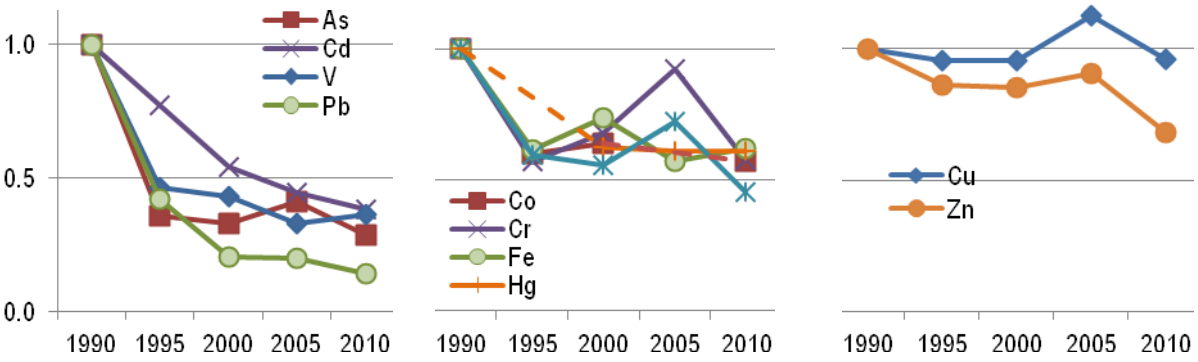

Figure 2. Temporal trends of 11 metals since 1990, normalised to the values for 1990.

The temporal trends in cadmium, mercury and lead concentrations in mosses are in good agreement with the reported emission data for these elements in Switzerland (Figure 3).

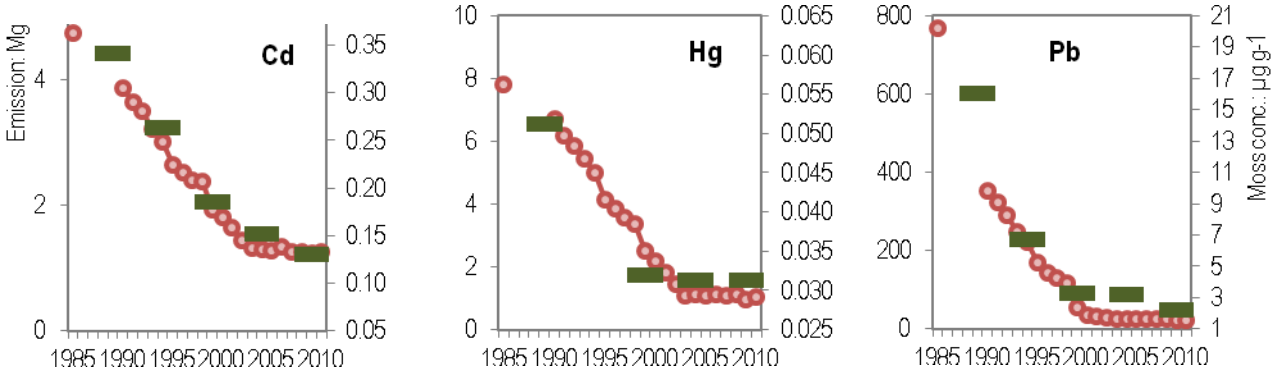

Figure 3. Temporal trends in Cd, Hg and Pb concentrations in moss in comparison with reported emission data for Switzerland. Dots represent emissions, bars concentration in moss.

Nitrogen concentration in mosses

Figure 4 shows boxplots of the nitrogen concentration in mosses in the 5 regions in Switzerland: J=Jura, M=central plateau, NA=northern Alps, ZA=central Alps, SA=southern Alps. In accordance with the other elements, the highest nitrogen level was found in southern Switzerland. There was a good linear correlation between the nitrogen concentration in moss and measured bulk deposition of nitrogen at nearby monitoring stations (Figure 5). The relationship was similar for 2005 and 2010, although the R^2 value was lower in 2010.

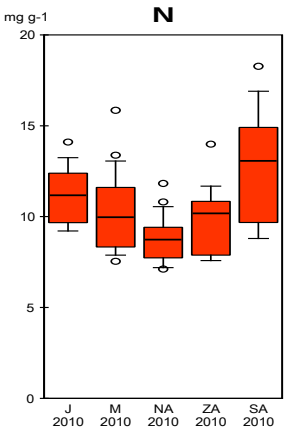

Figure 4. Boxplots of nitrogen concentration in moss at the 5 regions in Switzerland in 2010.

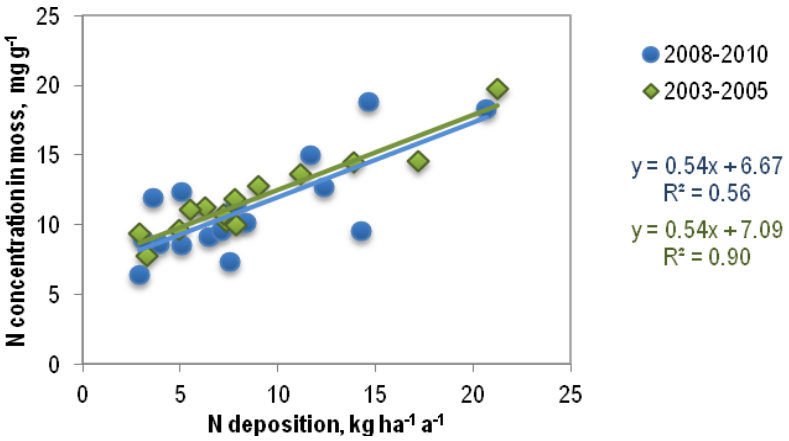

Figure 5. Relationship between nitrogen concentration in moss and nitrogen deposition determined with bulk sampler at nearby monitoring stations.

Conclusions

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

Centre for Ecology & Hydrology
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'Heavy metals and nitrogen in mosses: spatial patterns in 2010/2011 and long-term temporal trends in Europe'

Naturally-occurring mosses have been sampled across Europe to monitor the deposition of heavy metals and nitrogen from the air. This survey has been repeated at five-yearly intervals since 1990 for heavy metals and since 2005 for nitrogen. In 2010/2011, mosses were collected at ca. 4,500 sites in 25 countries for heavy metals and ca. 2,400 sites in 15 countries for nitrogen. In general, the lowest concentrations in mosses were found in northern Europe for both heavy metals and nitrogen. The highest concentrations of heavy metals were often observed in south-eastern Europe, whereas the highest concentrations of nitrogen were found in parts of western and central Europe. Europe-wide the concentration of lead (77% decline), vanadium (57%), iron (52%) and cadmium (51%) has declined the most since 1990, whereas the concentration of copper has declined the least (11% decline). Since 1995, the concentration of arsenic and mercury has declined by 26% and 23% respectively. The nitrogen concentration in mosses has hardly changed since 2005. This report is for scientists, policy makers and others with an interest in air pollution.

For further information or copies contact:
Harry Harmens
Centre for Ecology and Hydrology
Environment Centre Wales
Deiniol Road
Bangor
Gwynedd LL57 2UW
United Kingdom

Telephone: **+44 (0) 1248 374500**
Email: **hh@ceh.ac.uk**
Website: **icpvegetation.ceh.ac.uk**

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