Centre for Ecology & Hydrology
NATURAL ENVIRONMENT RESEARCH COUNCIL

Spatial and temporal trends in heavy metal accumulation in mosses in Europe (1990-2005)

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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 with an increasing number of countries participating. The first moss survey at the European scale was conducted in 1990/1 and since then the number of participating countries has greatly expanded. Twenty-eight European countries and over 6,000 sites were involved in the 2005/6 survey. 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 and reviews the effects of atmospheric pollutants on different components of the environment and health. The results of the European heavy metals in mosses survey feed into review processes to establish the sufficiency and effectiveness of the 1998 Aarhus Protocol on Heavy Metals.

The survey provides data on concentrations of ten heavy metals (arsenic, cadmium, chromium, copper, iron, lead, mercury, nickel, vanadium and zinc) in naturally-growing mosses throughout Europe. In 2005/6, the concentration of aluminium and antimony was also determined. The technique of moss analysis provides a surrogate measure of heavy metal deposition from the atmosphere to terrestrial systems, 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. An additional aim of this report is to summarise changes in heavy metal concentrations in mosses in Europe between 1990 and 2005.

Methodology for the 2005/6 survey

As in previous surveys, moss samples were collected according to a standardised protocol and the heavy metal concentrations were determined in the last three years' growth segments using a range of analytical techniques. *Pleurozium schreberi* was the most frequently sampled species (40.9%), followed by *Hylocomium splendens* (22.7%), *Hypnum cupressiforme* (18.0%), *Scleropodium purum* (11.6%) and other species (6.9%). 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 the years 1990, 1995, 2000 and 2005. The maps were produced using ArcMAP, part of ArcGIS, an integrated geographical information system (GIS) and were based on the EMEP[2] 50 x 50 km^2 grid, displaying the mean heavy metal concentration for each cell.

Spatial and temporal trends in Europe

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 for the majority of metals. Between 1990 and 2005 the metal concentration in mosses has declined the most for lead (72.3%, based on 16 countries), arsenic (71.8%, five countries), vanadium (60.4%, 11 countries), cadmium (52.2%, 16 countries) and iron (45.2%, 13 countries). An intermediate decrease was found for zinc (29.3%, 16 countries), copper (20.4%, 16

[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

countries) and nickel (20.0%, 16 countries) and no significant reduction for chromium (2%, 14 countries). Few countries reported data for arsenic and mercury in 1990, but since 1995 the arsenic concentration in mosses has declined by 21.3% (14 countries), whereas mercury showed no significant decline (11.6%, eight countries). Temporal trends in heavy metal concentrations in mosses are in agreement with trends in EMEP emission data (or modelled deposition data if available) for arsenic, cadmium, copper, lead, mercury, nickel (although the decline of nickel in mosses is lower than for emissions) and zinc, but not for chromium (as emissions declined). No emission data are being reported by EMEP for iron and vanadium. On a national or regional scale large deviations from the general European trend were found, i.e. temporal trends were country or region-specific, with no changes or even increases being observed since 1990. Therefore, even in times of generally decreasing metal deposition across Europe, temporal trends are different for different geographical scales.

In 2005/6, the lowest concentrations of heavy metals in mosses were generally found in (north) Scandinavia, the Baltic States and northern parts of the United Kingdom, although higher concentrations were reported near local sources. Relatively low concentrations of iron, mercury, nickel and vanadium were also observed in central Europe. Depending on metal, the highest concentrations were often found in Belgium and eastern European countries, with localised lower concentrations being present. High concentrations of the more global pollutant mercury were detected in mosses in Belgium, France, Latvia, Slovakia and Slovenia. Relatively high concentrations of aluminium, arsenic, chromium, iron, nickel and vanadium were found in eastern and southern France, resulting in considerable cross-border gradients with Germany and Switzerland (although less pronounced for chromium). This could indicate accumulation of a high proportion of windblown dust on mosses collected in eastern and southern France during the dry summer of 2006. Antimony concentrations were generally high in densely populated areas (e.g. central and southern United Kingdom, central Europe, North-East France and southern Norway around Oslo) and in many eastern European countries with high levels of metal pollution.

Conclusions

- Mosses provide an effective and cheap method for monitoring trends in heavy metals pollution in Europe at a high resolution;
- Spatial trends of heavy metal concentrations in mosses were metal-specific. However, in general the lowest concentrations were observed in (north) Scandinavia, the Baltic States and northern parts of the United Kingdom and the higher concentrations in Belgium and eastern European countries;
- Since 1990, the metal concentration in mosses has declined for arsenic, cadmium, copper, iron, nickel, lead, vanadium and zinc, but not for chromium and mercury. Despite these general European trends, country and region-specific temporal trends were observed, including increases in metal concentrations.

Future challenges

The spatial variation in heavy metal concentration in mosses across Europe should be analysed in further detail to identify main causes of variation and the role of any possible confounding factors such as the use of different moss species and analytical techniques and sampling at different climatic conditions. Such an analysis should include linking the moss data with other available environmental data, for example climate and soil data. Detailed statistical analysis of the spatial and temporal trends and the quantification of the importance of confounding factors are required. For cadmium, lead and mercury the concentration in mosses should be compared in more detail with deposition data modelled by EMEP to investigate their relationships at European and national scale. A main challenge for the future will be to establish how the results of the moss survey can be used in the assessment

of effects of heavy metals on ecosystems and subsequently the identification of ecosystems at risk from heavy metal pollution. This might provide useful information for the critical load approach adopted by the LRTAP Convention. As ecosystems and human health are still predicted to be at risk of adverse effects of heavy metals in the future, the moss survey needs to be continued to monitor any future trends in heavy metal pollution in Europe, with the next survey taking place in 2010. Future surveys should include metals that might become a problem in the near future due to increases in their production and emission.

1. Introduction

Background

The heavy metals in mosses biomonitoring network was originally established as a Swedish initiative (Rühling and Skärby, 1979). The idea of using mosses to measure atmospheric heavy metal deposition is based on the fact that carpet forming, ectohydric mosses obtain most trace elements and nutrients directly from precipitation and dry deposition; there is little uptake of metals from the substrate (Tyler, 1970). The technique of moss analysis provides a surrogate, time-integrated measure of 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. Therefore, a much higher sampling density can be achieved than with conventional precipitation analysis. Heavy metals deposited from the atmosphere tend to be retained by the mosses, thereby making sampling and chemical analysis more robust and less prone to contamination. Heavy metal data from precipitation analysis can be very uncertain if the detection limit of the applied analytical techniques is high (Ilyin et *al*., 2006). Despite improvement of the analytical techniques, the latter remains a problem due to the general decline in anthropogenic emissions and subsequent deposition of heavy metals in recent decades. Although the heavy metal concentration in mosses provides no direct quantitative measurement of deposition, this information can be derived by using regression approaches relating moss and precipitation monitoring data (e.g. Berg and Steinnes, 1997; Berg *et al*., 2003). A more detailed review of the moss technique and its applications has been provided by Onianwa (2001), Tyler (1990) and Zechmeister *et al*. (2003).

During 2001, responsibility for the coordination of the European moss survey was handed over from the Nordic Working Group on Monitoring and Data, Nordic Council of Ministers, to the UNECE ICP Vegetation Programme Coordination Centre at the Centre for Ecology and Hydrology (CEH) Bangor, UK. The ICP Vegetation was established in the late 1980s to consider the science of the effects of air pollution on vegetation. It is one of seven ICPs/Task Forces that report to the Working Group on Effects (WGE) of the Convention on Long-range Transboundary Air Pollution (LRTAP). The WGE monitors and reviews the effects of atmospheric pollutants on different components of the environment (e.g. forests, fresh waters, vegetation, buildings) and human health (Working Group on Effects, 2004). The ICP Vegetation provides information for the review and possible revision of the Protocols of the LRTAP Convention.

In 1998, the first Protocol for the control of emissions of heavy metals was adopted in Aarhus. The Protocol states that “an effects-based approach should integrate information for formulating future optimised control strategies taking account of economics and technological factors”. Cadmium, lead and mercury emissions were targeted as they are the most toxic of metals. The Task Force on Heavy Metals was established by the LRTAP Convention as a response to the concern over the accumulation of heavy metals in ecosystems, and their impacts on the environment and human health. Recently the Task Force on Heavy Metals reviewed the sufficiency and effectiveness of the 1998 Protocol on Heavy Metals and reported on i) changes in emissions since 1990 and the relative contribution of sources to metal emissions (Task Force on Heavy Metals, 2006a) and ii) effects of heavy metal deposition from long-range atmospheric transport on ecosystems and human health (Task Force on Heavy Metals, 2006b). The Joint World Health Organization/Convention Task Force on the Health Aspects of Air Pollution (Task Force on Health) has evaluated the potential health risks of the priority metals cadmium, lead and mercury in Europe in more detail (Task Force on Health, 2007). In 2007, the Executive Body of the LRTAP Convention stated that there was no mandate to negotiate a revision of the Protocol on Heavy Metals and that the focus of further work on heavy metals under the

Convention should be on increasing the number of ratifications of the Protocol (LRTAP Convention, 2008).

The European moss survey has been repeated at five-yearly intervals and the number of participating countries has expanded greatly since 1990 (Buse *et al*., 2003; Rühling, 1994; Rühling and Steinnes, 1998). The most recent European survey was conducted in 2005/6 with 28 countries participating (Table 1.1), sampling mosses from about 6,000 sites across Europe. The survey provides data on concentrations of ten heavy metals (arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), iron (Fe), mercury (Hg), nickel (Ni), lead (Pb), vanadium (V) and zinc (Zn)) in naturally-growing mosses. In 2005/6 many countries also submitted data on the concentration of aluminium (Al) and antimony (Sb). Aluminium is a good indicator of mineral particles, mainly windblown soil dust (Berg and Steinnes, 1997; Zechmeister et al., 2003) as it is present at high concentrations in the earth's crust. Antimony is present at very low concentrations in the earth's crust and generally considered as a good indicator of long-range transport of anthropogenic pollution (Berg and Steinnes, 1997). The increase in production and use of antimony in recent decades has resulted in enrichment of Arctic air by more than 50%. Given that the toxicity of antimony is comparable to that of lead, antimony has now replaced lead in the rank of potentially toxic trace metals in the Arctic atmosphere, which might have broader implications worldwide for ecosystem and human health in the future (Krachler *et al*., 2005). Some countries determined the concentration of additional metals in mosses, but these are not included in this report. For the first time, the majority of countries (16) also determined the nitrogen concentration in mosses (almost 3,000 sites), as a pilot study for selected Scandinavian countries had shown that there was a good linear relationship between the total nitrogen concentration in mosses and atmospheric nitrogen deposition rates (Harmens *et al*., 2005). The nitrogen results are reported separately elsewhere (Harmens *et al*., 2008a).

Table 1.1. Countries that submitted data for the 2005/6 European moss survey.

Austria	FYR Macedonia[a]	Serbia
Belarus	Germany	Slovakia
Belgium	Iceland	Slovenia
Bulgaria	Italy	Spain
Croatia	Latvia	Sweden
Czech Republic	Lithuania	Switzerland
Denmark (Faroe Islands)	Norway	Turkey
Estonia	Poland	Ukraine
Finland	Russian Federation	United Kingdom
France		

[a] The Former Yugoslav Republic of Macedonia

Sources and effects of heavy metals

The contribution of various sources to emissions of heavy metals across Europe has changed in recent decades (Task Force on Heavy Metals, 2006a; Ilyin *et al*., 2007). These changes are described in more detail in chapter 3, here we summarise the main emission sources between 2003 and 2005. The most important emission sectors include:

- Metals industry (Al, As, Cr, Cu, Fe, 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).

The heavy metals cadmium, lead and mercury were targeted in the 1998 Aarhus Protocol as the environment and human health were expected to be most at risk from adverse effects of these metals. A recent study applying the critical load approach has confirmed that the focus on cadmium, lead and mercury is justified (VROM, 2006). Recently, the Task Force on Health reviewed the health risks of cadmium, lead and mercury from long-range transboundary air pollution in greater detail (Task Force on Health, 2007). 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 in the form of particulates. Washing leafy vegetables before consumption reduces the risk of exposure by humans considerably (Harmens *et al*., 2005).

Effects of cadmium, lead and mercury
As cadmium shows strong similarities with the micronutrient zinc, it can replace zinc in many biological systems, where it can bind up to ten times more strongly than zinc. It has a medium, direct toxicity to all organisms, but is a cumulative poison. Cadmium accumulating in crops mainly originates from the soil (Harmens *et al*., 2005). In mammals, cadmium accumulates in the kidney and liver and exposure to low levels is associated with an increased risk of osteoporosis in humans. Since the acceptable daily intake for humans is very low, the margin of safety between the present daily intake of cadmium in the diet and the intake that can result in adverse effects is very narrow (Task Force on Health, 2007).

The effects of lead stem from its ability to replace other biologically important metals such as calcium, iron and zinc in many enzymatic reactions, resulting in impairment of enzyme functions. Lead in soluble ionic form is toxic to most organisms, but in the natural environment it is usually tightly bound in the organic top soil layer (humus). Therefore, uptake via roots into plants is relatively small, but direct atmospheric deposition may contribute significantly to the lead concentration in plants, including crops (Harmens *et al*., 2005). In mammals it acts as a cumulative poison. Lead is a well-known neurotoxin and in humans the impairment of neurodevelopment in children is the most critical effect (Task Force on Health, 2007).

Mercury and many of its compounds (methylmercury) are strongly toxic to most kinds of organisms and the toxicity depends on its speciation. Mercury acts as an inhibitor of many enzymatic processes. Emissions of mercury to the air are in inorganic forms that can be converted biologically to methylmercury in soil and water. Airborne concentrations of mercury, concentrations of inorganic mercury in surface and groundwater and in crops are generally well below those known to cause adverse health effects from inhalation, drinking water and eating crops respectively (Task Force on Health, 2007). Methylmercury bioaccumulates in the food chain and humans are primarily exposed to methylmercury via fish in the diet; the main target organs are the kidney and the central nervous system.

Effects of other metals
Arsenic inhibits essential metabolic enzymes and is moderately toxic to plants, but highly toxic and carcinogenic to mammals. Its toxicity depends in its speciation and inorganic arsenic is generally regarded as being more toxic than organic arsenic, with arsenic(III) being the most toxic form. Chromium metal and chromium(III) compounds are not usually considered health hazards, whereas chromium(VI) is more toxic to organisms. Although sometimes emitted as chromium(VI), it will be readily reduced to chromium(III), at least in the soil under natural conditions. Chromium(VI) is carcinogenic to humans and it can also induce allergic effects in humans. Copper is an essential micronutrient to all organisms as a constituent of many metalloenzymes and has a role in biological electron transport. At higher concentrations it causes oxidative stress and is toxic to vascular plants and very toxic to algae and fungi. It is also very toxic to invertebrates, but only moderately toxic to most mammals. Iron is a major element in bedrock and soil. Similar to copper, iron is an essential micronutrient of all organisms as a constituent of many proteins and plays an important role

in biological redox systems. In plants iron is needed for the biosynthesis of chrorophyll and in vertebrates it is needed for the formation of haemoglobin, the iron-containing protein in red blood cells, which transports oxygen around the body. Iron toxicity is only a serious problem in crop production on waterlogged soils (Marschner, 1995).

Nickel is an essential micronutrient to many organisms (e.g. micro-organisms and plants) and in a number of enzymes it is the metal component required for the activity. At higher concentrations nickel is toxic to most plants and fungi. It is moderately toxic to mammals, but can induce allergic reactions in humans. Nickel compounds and probably also metallic nickel are carcinogenic to humans. Vanadium is an essential component of some enzymes, particularly vanadium nitrogenase used by some nitrogen-fixing micro-organisms. Its requirement for certain lower plants species (e.g. fungi and freshwater algae) is well established, but reports on its role in the stimulation of growth of higher plants are rare. It is tightly bound to soil particles and therefore not easily taken up by plants. Little is known about the effects of vanadium. Zinc is an essential micronutrient to all organisms as a constituent of proteins, including metalloenzymes, and is now also considered to be a neurotransmitter. Zinc is required for maintaining the integrity of biomembranes. At high concentrations it is moderately toxic to plants, but only slightly toxic to mammals. Excessive uptake of zinc can induce deficiencies of other metals such as copper, iron and magnesium.

Modelling of long-range transport of heavy metals

Measurements of the concentration of the priority metals cadmium, lead and mercury in air and precipitation are carried out by the monitoring network of the Cooperative Programme for Monitoring and Evaluation of Long-range Transmission of Air Pollutants in Europe (EMEP). In 2007, this network contained 64 stations reporting data on cadmium and lead and 19 stations reporting at least one form of mercury, primarily located in northern and western Europe (Ilyin *et al*., 2007). As the EMEP monitoring network covers only a limited part of Europe and at a low density, modelling is necessary to assess heavy metal pollution levels for the entire EMEP region. Therefore, Parties to the LRTAP Convention report emission data to EMEP. These data are then used to model atmospheric heavy metal concentrations, depositions and transboundary fluxes within the EMEP region by means of the atmospheric transport model developed at the Meteorological Synthesizing Centre – East (MSC-E). High uncertainties are associated with reported emission data and therefore with modelled deposition data. Although the calculated concentrations of heavy metals correlate well with measured values, in general, the modelled levels of cadmium and lead underestimate measurements by 30-50% and 20-30% respectively. Underestimation is most significant at sites located in central Europe and northern Scandinavia, most likely due to uncertainties of spatial distribution of emissions or missed local sources in these regions. For mercury difference between the modelled and measured values does not exceed ±15% for air concentrations and ±45% for concentrations in precipitation (Ilyin *et al*., 2007).

The moss monitoring network provides measurement data at a much higher spatial resolution than the EMEP monitoring network and the moss data can provide an additional indication of the performance of the MSC-E Heavy Metal model. For lead a significant positive correlation was found between the modelled total accumulated deposition for the years 1997-1999 and concentration in mosses for 2000/1 (Ilyin and Travnikov, 2005). The correlation coefficient was not as high as normally obtained between measured and calculated deposition by EMEP. However, when a comparison was performed between lead concentrations in mosses and modelled total lead deposition for selected EMEP grid cells in Scandinavia where EMEP monitoring stations are situated and where lead deposition is primarily determined by long-range transport, a very high correlation was found.

Aims and structure of this report

The main aims of this study were:

- To summarise, in the form of maps, changes in heavy metal concentrations in mosses in Europe between 1990 and 2005;
- To identify main polluted areas in 2005/6;
- To develop an understanding of changes in long-range transboundary air pollution between 1990 and 2005.

In the following chapters, the methodology for the 2005/6 moss survey is described (Chapter 2), followed by a summary of spatial and temporal trends, including maps based on the 50 x 50 km^2 EMEP grid (Chapter 3). In Chapter 4 the results are discussed and conclusions are drawn and future research challenges are identified in Chapter 5.

Details on temporal trends between 1990 and 2000 were reported previously (Harmens *et al.*, 2007, 2008b). Local or regional emission sources were described in detail in the report of the 1990/1 (Rühling, 1994) and 1995/6 survey (Rühling and Steinnes, 1998) and summarised in the 2000/1 survey (Buse *et al*., 2003) and are not repeated in this report. A more detailed description of spatial and temporal trends in heavy metal concentrations in mosses and changes in local emission sources at the national level has been provided elsewhere by the participants.

2. Methodology for the 2005/6 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 *Scleropodium purum* being the next choice. Because the mosses were collected in a range of habitats from the sub-arctic climate of northern Scandinavia to the hot and dry climate in western Turkey, 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 40.9% of the samples, followed by *Hylocomium splendens* (Hedw.) (22.7%), *Hypnum cupressiforme* Hedw. (18.0%), and *Scleropodium purum* (Hedw.) (11.6%). Other moss species constituted 6.9% of the mosses sampled.

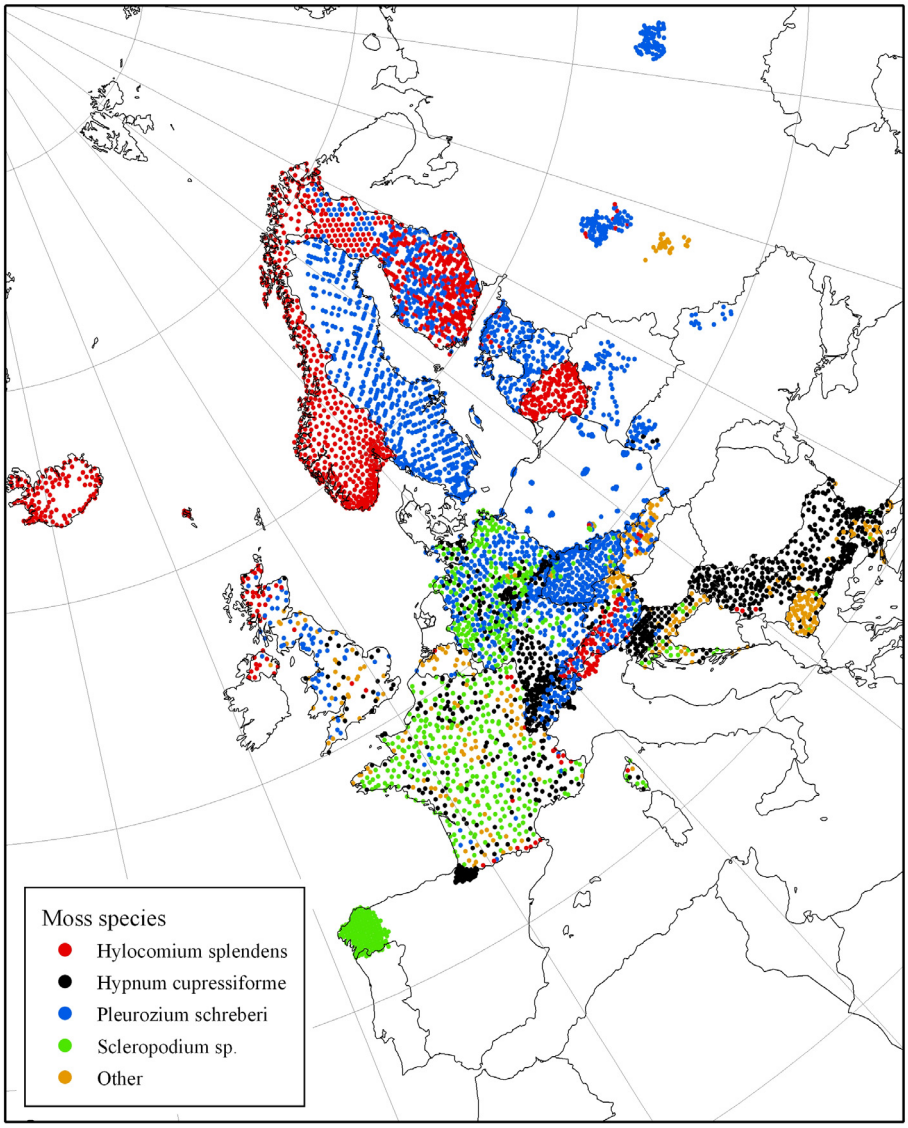

Figure 2.1. Moss species collected at each sampling point; 96% of *Scleropodium sp.* was *Scleropodium purum*, with *Scleropodium tourretii* sampled at 27 sites in Croatia and Poland.

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 2005/6 survey (ICP Vegetation, 2005). 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 three years' growth segments were used for the analyses. Samples were refrigerated, deep-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 three years' growth) was dried at 40^{o}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 on a hotplate or in a microwave oven 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 element concentrations (including mercury) are expressed as mg kg^{-1} dry weight at 40^{o}C.

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. This was the case when the values were outside the range of two standard deviations (as determined for the 2005/6 survey) from the mean recommended value for reference material M2 and/or M3. 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 2005/6, the mean values of M2 and M3 were generally in good agreement with the recommended values published by Steinnes *et al*. (1997) and ranged from 91% (arsenic) to 103% (lead) for M2, the reference material with high metal concentrations, and from 92% (chromium) to 117% (mercury) for M3, the reference material with background metal concentrations. For metals included for the first time in the 2005/6 moss survey, additional data are now available for M2 and M3. For 2005/6, the mean value for aluminium was almost the same as the recommended value (102%), however, the mean value for antimony was only 83-88% of the recommended values. Therefore, the recommended value for antimony was adjusted (Annex 3).

Smodiš and Bleise (2007) conducted a quality control study in 17 laboratories from 15 countries using M2 and M3. The study revealed systematic differences between the analytical values obtained non-destructively (e.g. Instrumental Neutron Activation Analysis – INAA) or after sample dissolution and measurement following nitric acid sample dissolution (without the use of hydrofluoric acid). Discrepancies included the elements aluminium, chromium, iron and lead, with higher values being reported than the recommended values, in particular for M2. The discrepancies for aluminium could not be verified in the 2005/6 moss survey, as countries applying INAA or total sample digestion (with the use of hydrofluoric acid) did not report data on aluminium, so it's likely that the aluminium data underestimate the total aluminium concentration in mosses (by up to 45% for reference material). One lab applying INAA in the 2005/6 survey reported similar differences as Smodiš and Bleise (2007) for M2 (+44%) and M3 (+7%) for chromium, but this was not the case for a lab applying total sample digestion using hydrofluoric acid; the opposite was true for iron. Although Smodiš and Bleise (2007) found differences for chromium, these were not significant and only applied to M2, for which the recommended chromium concentration is 45% higher than that of M3. Chromium is a difficult element to analyse as indicated by the high standard deviation in both the recommended values (Steinnes *et al*., 1997) and the data reported by Smodiš and Bleise (2007). Discrepancies for lead were not confirmed by data from the 2005/6 moss survey.

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 4.

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 heavy metal concentration for each cell (Buse *et al*., 2003). For convenience we refer to the 1990/1, 1995/6, 2000/1 and 2005/6 European moss surveys as 1990, 1995, 2000 and 2005 surveys from hereon. For some countries slight updates were made to the data and maps reported previously (Buse *et al*., 2003; Harmens *et al*., 2004, 2007, 2008b). For cadmium and chromium the concentration ranges used in the maps are the same eight classes as those used in the previous reports (Buse *et al*., 2003; Rühling, 1994; Rühling and Steinnes, 1998). However, for the other metals the concentration ranges were adjusted to clearly show both spatial and temporal variations for all years.

3. Spatial and temporal trends in Europe

Introduction

The 2005/6 data on the concentration of each metal in moss samples from each country are summarised in Annex 4. Extreme values are often for single hot spots. The emphasis of this chapter is on Europe-wide spatial and temporal trends. The temporal trends are compared with temporal trends in heavy metal emission and/or modelled deposition data as reported by EMEP. Many contributors to the survey have reported national trends in greater detail elsewhere, including local emission sources of heavy metals and the relationship between concentration in mosses and measured or modelled atmospheric deposition data.

Elevated concentrations of heavy metals in the 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. More detailed descriptions of local pollution sources are provided in the reports of the previous European surveys (Buse *et al*., 2003; Rühling, 1994; Rühling and Steinnes, 1998) and in national reports.

The heavy metal concentrations in mosses per EMEP grid square are shown for the ten metals determined in 1990, 1995, 2000 and 2005. In addition, the aluminium and antimony concentration in mosses per EMEP grid square are shown for 2005. Temporal trends in the average European median concentration (i.e. average of median concentrations from the countries that reported data for each survey year for a specific metal) were compared with reported Europe-wide temporal trends in emission and/or deposition. In general, spatial and temporal trends in median values were comparable to those for the (geometric) mean metal concentrations in mosses and therefore only data for the median values are shown. The median values were generally similar to the geometric mean values. If available, temporal changes in the contribution of key sources of heavy metal emissions were reported too. It should be noted that at the national scale the contribution of key emission sources might differ considerably from that reported for the whole of Europe.

Details on key sources of emissions and emission and modelled deposition trends since 1990 are most widely available (30 countries) for the priority metals targeted by the LRTAP Convention, i.e. cadmium, lead and mercury (Ilyin *et al*., 2005, 2007). For arsenic, chromium and nickel emission trends since 1990 have also been reported for 30 countries (Ilyin *et al*., 2006), whereas for copper and zinc emission trends up to 2003 were reported for 17 countries (Task Force on Heavy Metals, 2006a). Key sources for arsenic, chromium, copper, nickel and zinc for 2003 were reported for only nine countries (Task Force on Heavy Metals, 2006a). Recently, EMEP reported on country-averaged calculated deposition fluxes of cadmium, lead and mercury from European anthropogenic, natural/historical (“wind re-suspension”) and non-EMEP sources in 2005. The relative contribution of transboundary transport and national sources to anthropogenic depositions of these metals in Europe were also calculated (Ilyin *et al*., 2007).

Arsenic

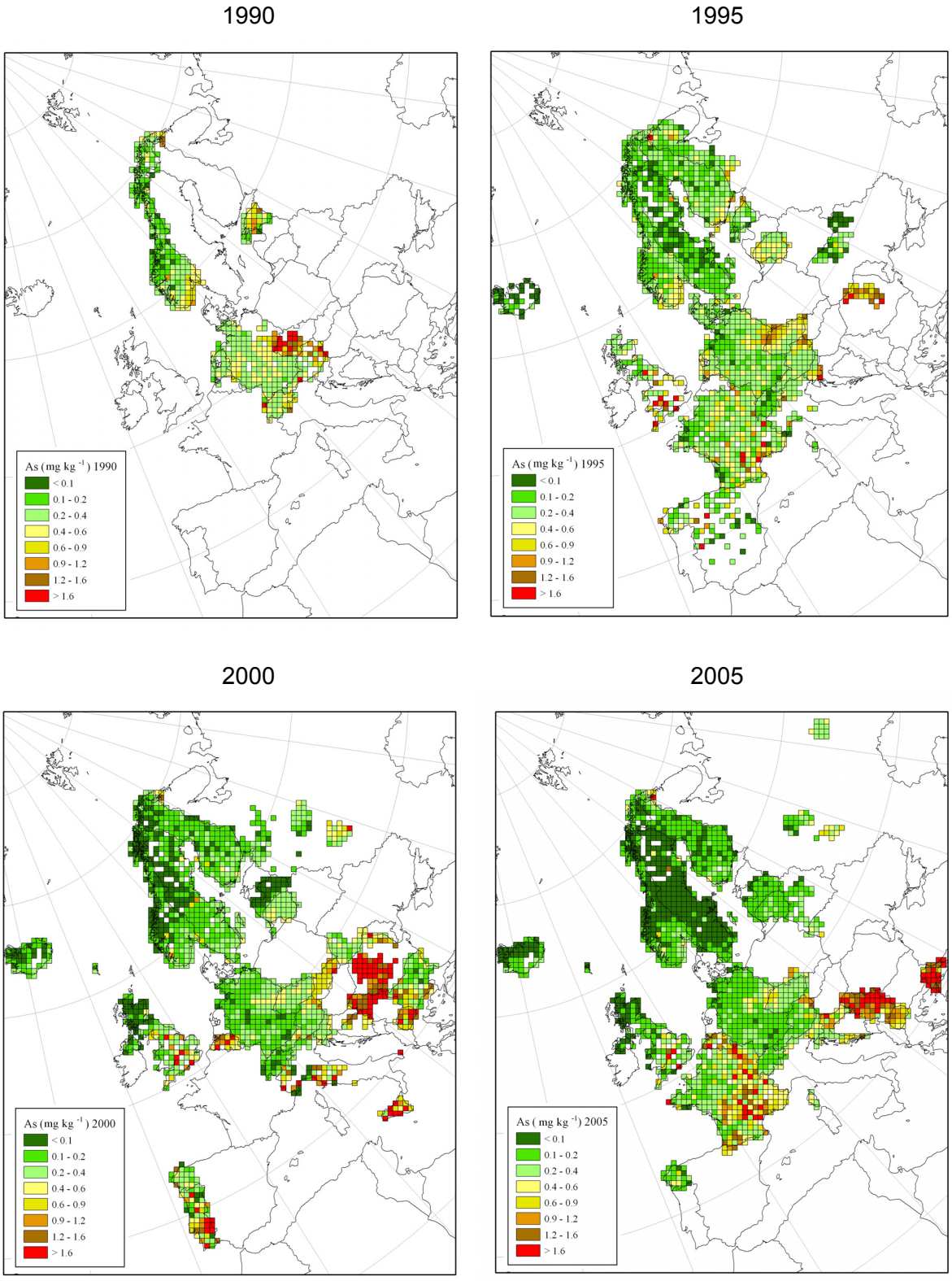

Figure 3.1. Mean concentration of arsenic in mosses per EMEP grid square in 1990, 1995, 2000 and 2005.

In the early 1990s, coal combustion was a major source of anthropogenic arsenic emission. However, key arsenic emission sources identified in selected European countries in 2003 were “non-ferrous metals industry” and “other manufacturing industries and construction” (Task Force on Heavy Metals, 2006a). Arsenic emissions have declined by about 53% between 1990 and 2004, with a sharp decline being observed between 2001 and 2002 and a small rise since then (Ilyin *et al*., 2006). In selected European countries, arsenic emissions have decreased by 64% between 1990 and 2003, with the highest decrease being observed between 1990 and 1995 and since 1995, arsenic emissions have declined at a much lower rate (Task Force on Heavy Metals, 2006a). This is in agreement with the temporal trends observed in mosses (Figure 3.1 and 3.2). Between 1990 and 2005, the average median arsenic concentration in mosses has declined by 72%, based on data available from five countries (Austria, Czech Republic, Germany, Norway and Switzerland). However, the average median arsenic concentration in mosses has declined by only 21% since 1995 and has hardly changed since 2000, based on data available from 15 countries (Figure 3.2). Country-specific changes were observed in the arsenic concentration in mosses, with decreases, no change or increases being observed between 2000 and 2005.

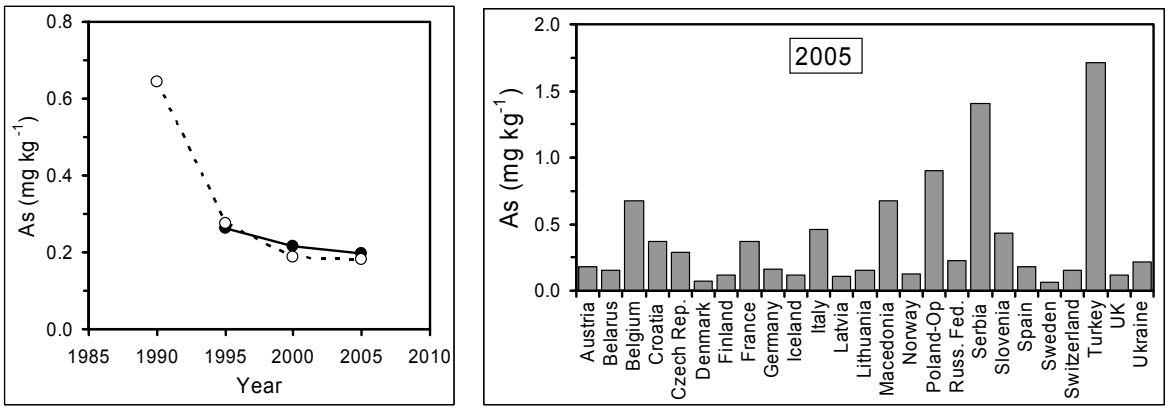

Figure 3.2. Average of median arsenic concentration in mosses for countries (n = 15) that reported arsenic data in 1995, 2000 and 2005, the broken line between 1990 and 2005 is based on data from only five countries (left), and median arsenic concentration in mosses per country in 2005 (right).

As in 2000, arsenic levels in mosses were generally low in Scandinavia, the Baltic States, Iceland, northern parts of the United Kingdom and parts of central Europe (Figure 3.1 and 3.2). Arsenic concentrations in mosses have declined further in these areas since 2000, which might indicate a decline in long-range transport of arsenic to these areas. High levels of arsenic were still observed in eastern Europe, in for example the FYR Macedonia, Serbia and western Turkey. In Belgium, France and the southern parts of the United Kingdom locally high concentrations of arsenic were present, often related to local emission sources. In France, there was a clear east-west gradient in the arsenic concentrations in mosses in 2005, resulting in a strong border effect with Germany and Switzerland. However, a cross-border calibration exercise for samples exchanged between Germany, France and Belgium did not show any significant differences between the performance of the laboratories. Furthermore, the French results for moss reference material M2 and M3 did not deviate significantly from the recommended values.

Cadmium

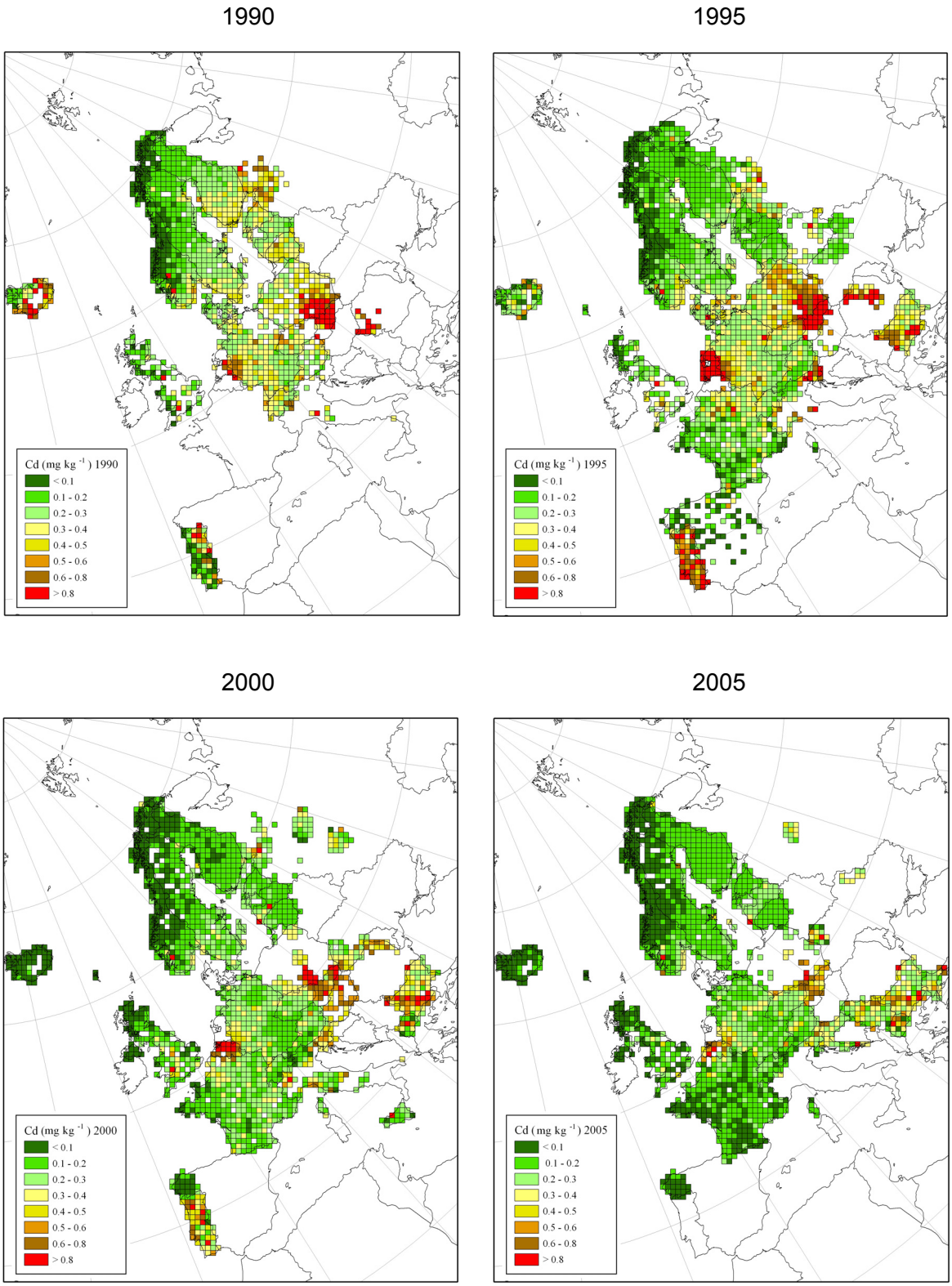

Figure 3.3. Mean concentration of cadmium in mosses per EMEP grid square in 1990, 1995, 2000 and 2005.

In 1990, waste incineration was the main anthropogenic cadmium emission source (Task Force on Heavy Metals, 2006a), but by 2005 its contribution was significantly reduced to only a few percent and "manufacturing industries and construction" (45%) and "public electricity and heat production" (21%) became the major sources across Europe (Ilyin *et al*., 2007). In agricultural areas cadmium is also spread to the environment by the use of phosphate fertilisers. Between 1990 and 2005, cadmium emission declined by 50% in the EMEP region, with a slowdown of decline being observed since 2000. A similar decline (57%) in modelled cadmium deposition was reported between 1990 and 2003 (Ilyin *et al*., 2005). This is in agreement with the temporal trends observed in mosses (Figure 3.3 and 3.4). The average median cadmium concentration in mosses declined by ca. 52% between 1990 and 2005, based on data available from 16 countries, with a smaller decline being observed since 2000. Some countries (Finland, the FYR Macedonia, Latvia) reported increases in the median concentration between 2000 and 2005.

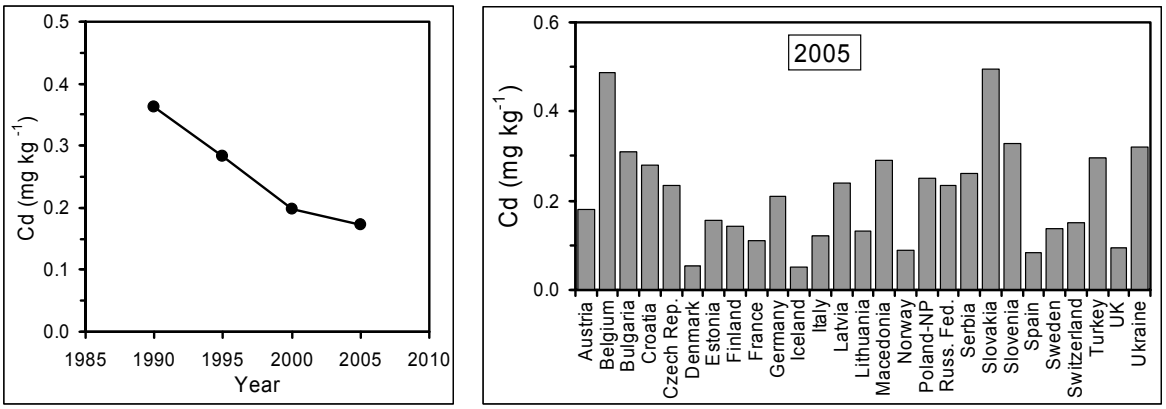

Figure 3.4. Average of median cadmium concentration in mosses for countries (n = 16) that reported cadmium data in all survey years (left) and median cadmium concentration in mosses per country in 2005 (right).

Spatial trends for the cadmium concentration in mosses were similar to those reported for the 2000 survey (Figure 3.3 and 3.4). The cadmium levels were lowest in north-west Scandinavia, Iceland, northern parts of the United Kingdom and Spain, but also in many areas of France. Higher levels were observed in parts of central Europe and the highest concentrations in mosses (median ≥ 0.3 mg kg^{-1}) were reached in Belgium and eastern Europe (Bulgaria, Slovakia, Slovenia, Turkey and Ukraine). However, for Belgium, Bulgaria, Slovakia and Slovenia, the cadmium levels were considerably lower in 2005 than in 2000. In France, the cadmium levels have declined considerably too between 2000 and 2005. In contrast, in many central European countries the median cadmium concentration in mosses declined considerably between 1995 and 2000, with no pronounced further decline between 2000 and 2005. The cross-border calibration exercise for samples exchanged between Germany, France and Belgium indicated that the cadmium concentrations in exchanged samples were always lower when determined in the French compared with the German and Belgian laboratories. However, the French results for moss reference material M2 (with high cadmium levels) did not deviate significantly from the recommended values. For moss reference material M3 (with background cadmium concentrations) the French data were lower than the recommended value, indicating that higher uncertainties are associated with background cadmium concentrations reported for France.

Chromium

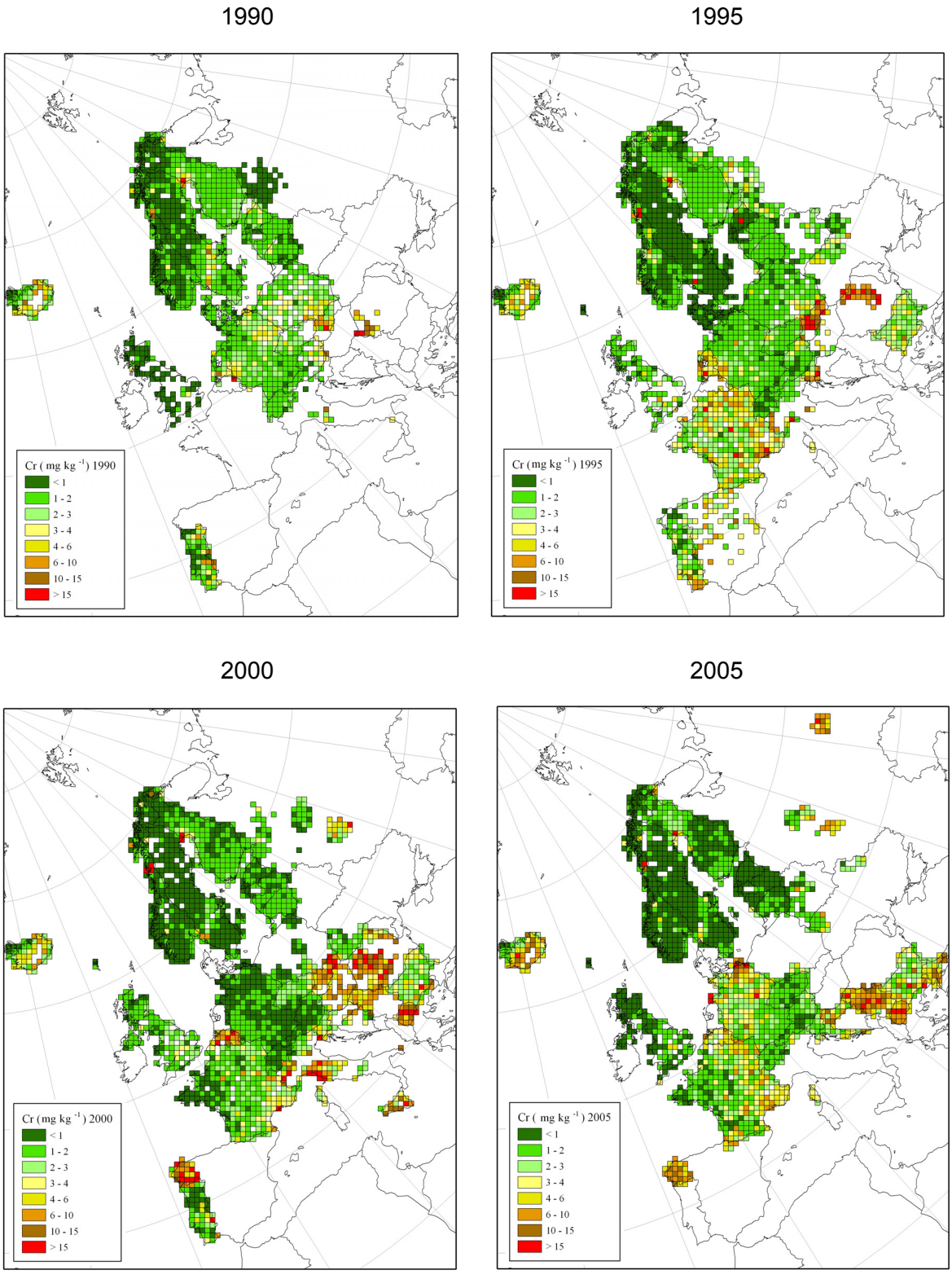

Figure 3.5. Mean concentration of chromium in mosses per EMEP grid square in 1990, 1995, 2000 and 2005.

The main source of chromium pollution is local industry, especially iron and steel mills. In 2003, “metal production” and “other manufacturing industries and construction” were the major sources of anthropogenic chromium emissions (Task Force on Heavy Metals, 2006a). Between 1990 and 2004, chromium emissions decreased by 37% in the EMEP region, with a sharp decline being observed between 2001 and 2002, followed by a small rise in 2004 (Ilyin *et al*., 2006). In selected European countries chromium emissions declined continuously between 1990 and 2003 and even by 70% overall within that period (Task Force on Heavy Metals, 2006a). In contrast, the chromium concentration in mosses has hardly changed between 1990 and 2005, although fluctuations were observed (Figure 3.5 and 3.6). Between 1990 and 2005, the average median chromium concentration in mosses declined by only 2%, with the lowest median value being reported for 1995. The determination of chromium in mosses is associated with considerable uncertainty (Steinnes *et al*., 1997; Smodiš and Bleise, 2007).

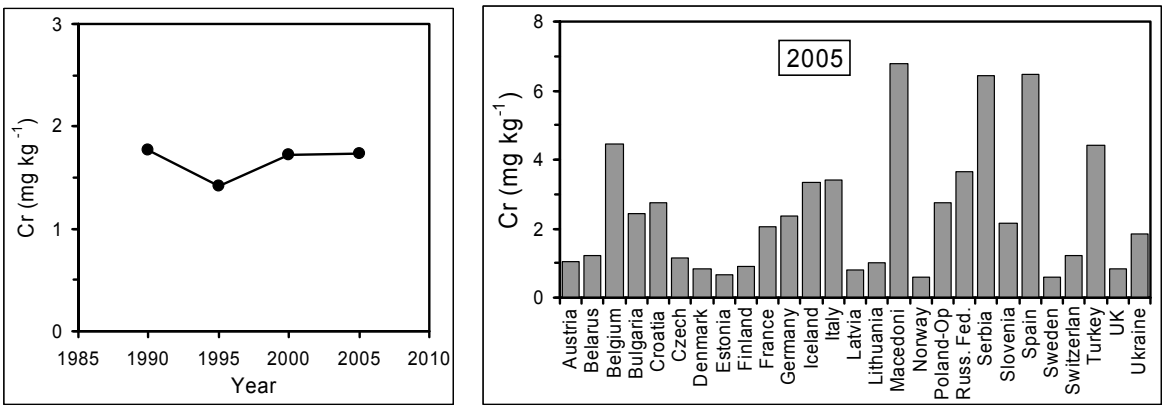

Figure 3.6. Average of median chromium concentration in mosses for countries (n = 14) that reported chromium data in all survey years (left) and median chromium concentration in mosses per country in 2005 (right).

In 2005, the lowest chromium concentrations in mosses were generally observed in Scandinavia, the Baltic States, the United Kingdom and eastern parts of central Europe, although some local pollution sources could be identified (Figure 3.5 and 3.6). As in 2000, high chromium concentrations were reported in 2005 for the FYR Macedonia, Serbia, and Galicia (Spain). Locally high concentrations were also observed in Bulgaria and Turkey. Although the high chromium concentrations reported for the FYR Macedonia and Serbia might be partly due to the application of the analytical technique INAA, this is not the cause of high concentrations reported for other countries. In addition, some of the countries (Belarus, Croatia, Poland – Opole region and the Russian Federation) with lower chromium concentrations also applied INAA (Annex 2). As in previous surveys, the values for Iceland were considerably higher than for other Nordic countries, in particular in the volcanic zone, reflecting geologically determined differences in soil dust composition. Remarkable is the increase in chromium concentration in Germany since 2000, with both the median and mean values being higher in 2005 than 1990. The reason for this increase is unknown, but it does not seem to be due to analytical errors as the values for reference material M2 and M3 were slightly lower than the recommended values. Although an increase in chromium in mosses was also observed in some of the neighbouring countries such as Switzerland and France (in particular in eastern parts), the median and mean values for those countries remained lower than the ones reported for 1990 and 1995, respectively. On the other hand, a considerable decline in chromium concentration was observed in the neighbouring countries Belgium (45%) and the Czech Republic (39%) between 2000 and 2005.

Copper

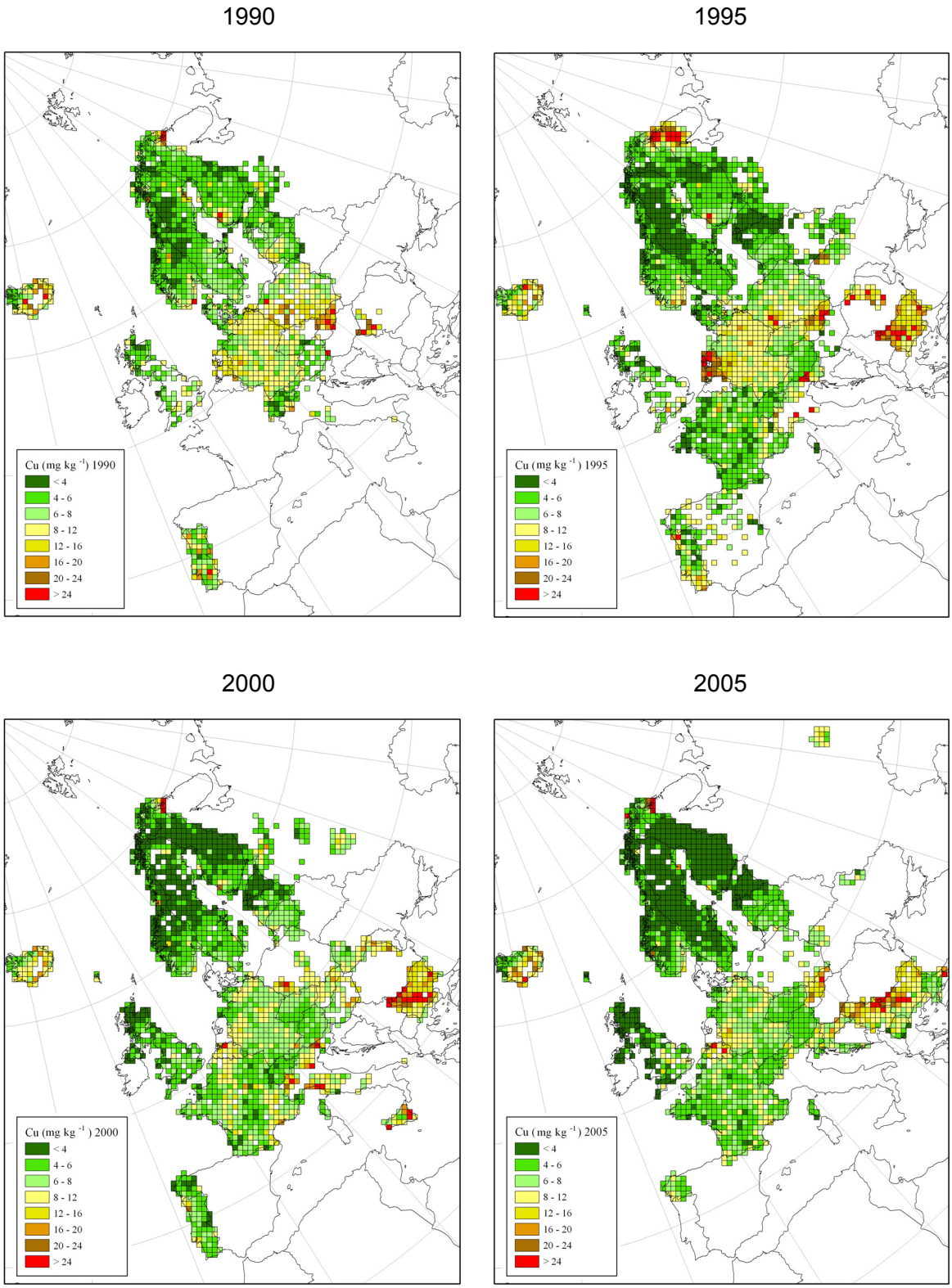

Figure 3.7. Mean concentration of copper in mosses per EMEP grid square in 1990, 1995, 2000 and 2005.

Local point sources such as metal smelters and fossil fuel combustion have traditionally been important anthropogenic emission sources of copper. However, in 2003, “road transportation” and the “non-ferrous metal industry” were the major sources of copper emissions (Task Force on Heavy Metals, 2006a). Recently, Hulskotte *et al*. (2006) suggested that brake wear from road traffic vehicles is an important source of diffuse atmospheric (particulate) copper emission in Europe. They concluded that current emission inventories underestimate copper emissions by 20–40% as brake wear emission are currently not included. In selected European countries, copper emissions have decreased by 24% between 1990 and 2003, with the highest decrease being observed between 1990 and 1995. Since 1995, copper emissions have hardly changed (Task Force on Heavy Metals, 2006a). Similar trends were observed for the copper concentration in mosses (Figure 3.7 and 3.8): between 1990 and 2005, the average median copper concentration in mosses declined by 20%, with the highest decline being observed between 1990 and 2000 and no further decline between 2000 and 2005.

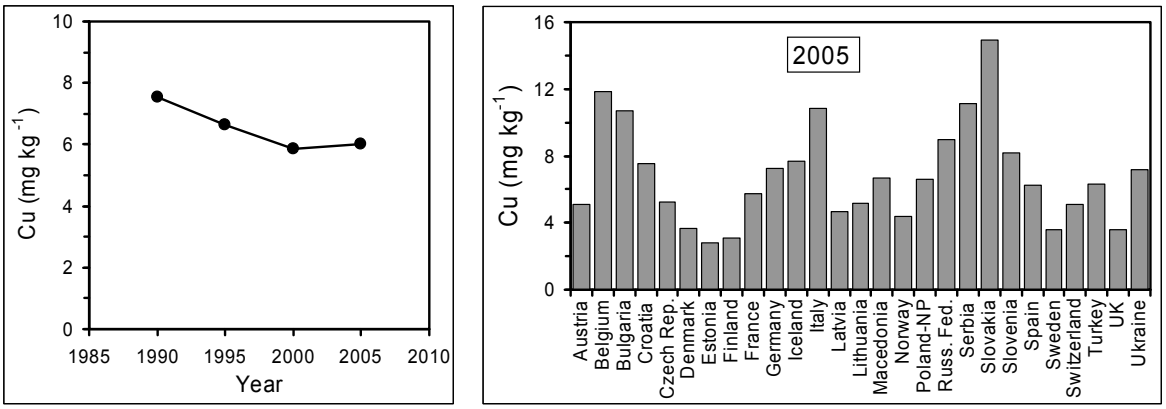

Figure 3.8. Average of median copper concentration in mosses for countries (n = 16) that reported copper data in all survey years (left) and median copper concentration in mosses per country in 2005 (right).

Copper is an essential micronutrient to all organisms as a constituent of many metalloenzymes. Therefore, background concentrations will be present in mosses as copper will be recycled from senescing to newly developing parts of the moss. As in previous moss surveys, copper levels were low in Scandinavia, the Baltic States and northern and western parts of the United Kingdom, with some locally high concentrations near smelters or mines (Figure 3.7 and 3.8). Intermediate levels were observed in central Europe, France, Galicia (Spain) and parts of eastern Europe (Macedonia, Turkey and the Ukraine). High levels (median > 8 mg kg^{-1}) were generally found in Belgium, northern Italy and many parts of eastern Europe (Bulgaria, Russian Federation, Serbia, Slovakia, Slovenia). In Bulgaria, concentrations have declined considerably since 2000. In Belgium, Galicia (Spain), northern Italy, the Russian Federation and Slovakia a considerable rise in copper concentrations in mosses was observed since 2000.

Iron

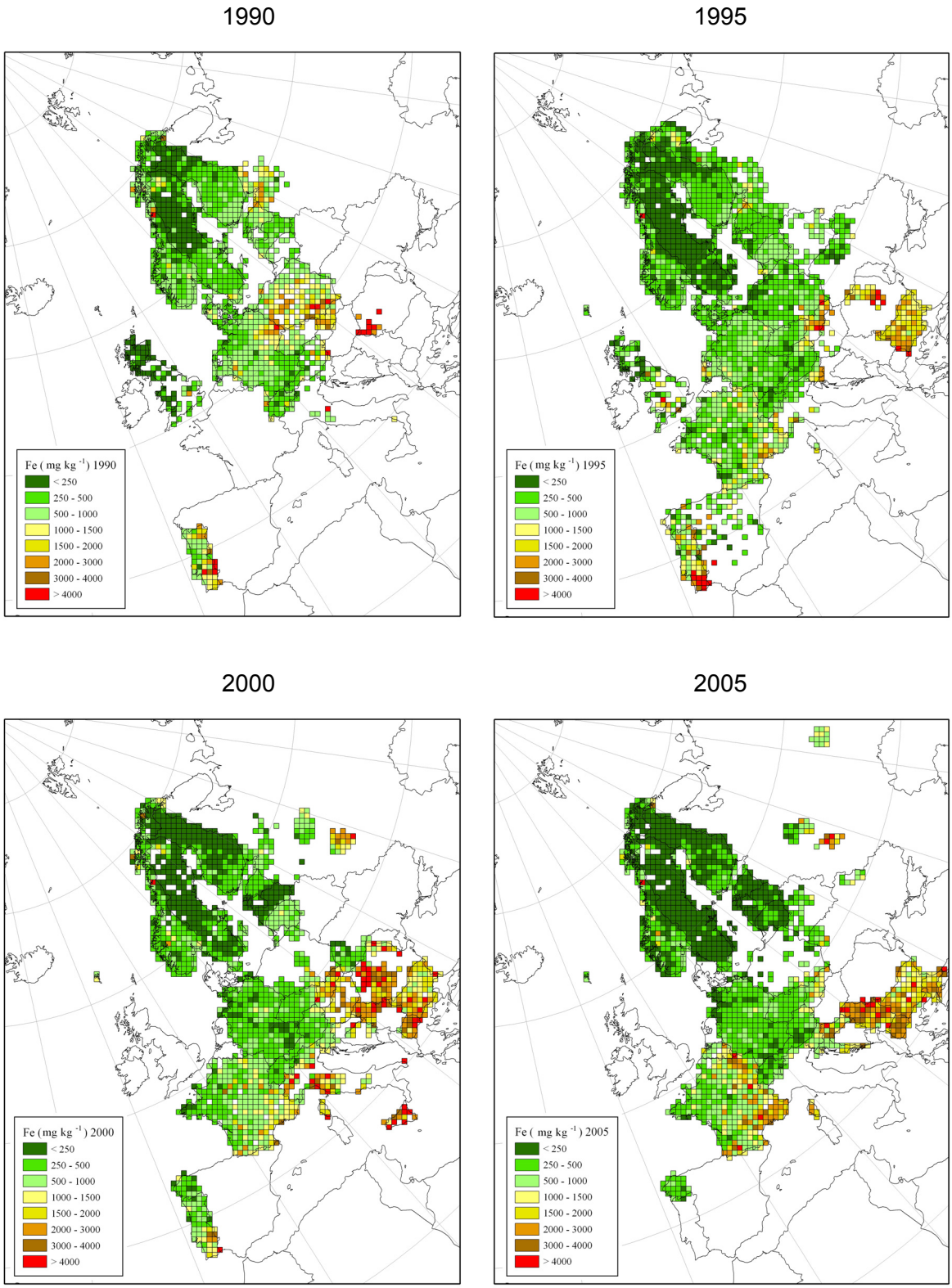

Figure 3.9. Mean concentration of iron in mosses per EMEP grid square in 1990, 1995, 2000 and 2005.

The main sources of iron emissions are mining and the iron and steel industry. The industry may add iron to the environment as emissions from smelting and dust from the process of grinding ore and from large containment areas for finely divided ore waste. Another, more diffuse major source is soil dust, especially in sparsely vegetated areas, as well as in agricultural regions. Iron is a major element in bedrock and soil. As iron emissions are not reported to EMEP, no comparison with the concentration in mosses can be made.

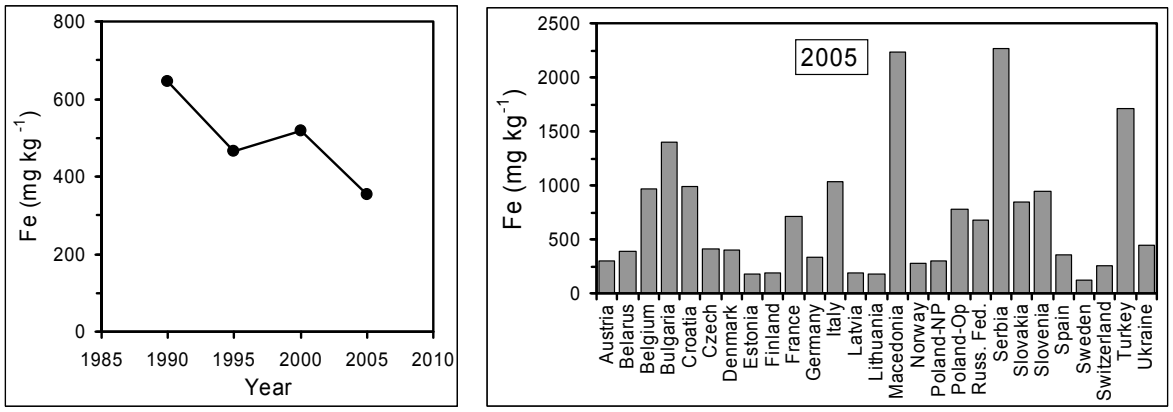

Figure 3.10. Average of median iron concentration in mosses for countries (n = 13) that reported iron data in all survey years (left) and median iron concentration in mosses per country in 2005 (right).

The spatial distribution of iron was similar to the one reported for 2000 (Figure 3.9 and 3.10). Low concentrations were generally found in Scandinavia and the Baltic States and relatively low concentrations were also observed in central Europe and Galicia (Spain). In the majority of these countries similar or lower concentrations were reported in 2005 compared with 2000. The highest iron concentrations were reported for the eastern European countries Bulgaria, the FYR Macedonia, Serbia and Turkey, followed by Belgium, Croatia, northern Italy, Slovakia and Slovenia. In Slovakia the median iron concentration in moss declined by 46% between 2000 and 2005. Very high iron concentrations were reported by Iceland, which are evidently due to high levels of windblown dust from volcanic origin. Therefore, iron data from Iceland were not included in further data processing and mapping in this report.

The high concentrations of iron in eastern and southern France are remarkable and resulted in a high gradient across the borders with Germany and Switzerland. It might well be that mosses in these parts of France were exposed to a relatively high amount of wind-blown soil dust, as also suggested by the high concentration of aluminium in mosses collected in this area. This might also explain the relatively high concentrations of arsenic, chromium and vanadium in eastern and southern France. In contrast to 2000, the year 2006 was a dry year in France, but so was 1996, when the iron concentrations in mosses were lower in this part of France than in 2006. However, 2006 was also a rather dry year in Germany. The cross-border gradient between France and Germany/Switzerland was less pronounced in 2000 and absent in 1995. Since 1995, the median and mean iron concentration has been rising in France, in particular the mean value has increased since 2000. Across Europe the median iron levels in mosses have declined between 1990 and 1995 and 2000 and 2005, with no significant change between 1995 and 2000. Between 1990 and 2005, the average median iron concentration in mosses has declined by 58% (Figure 3.10).

Lead

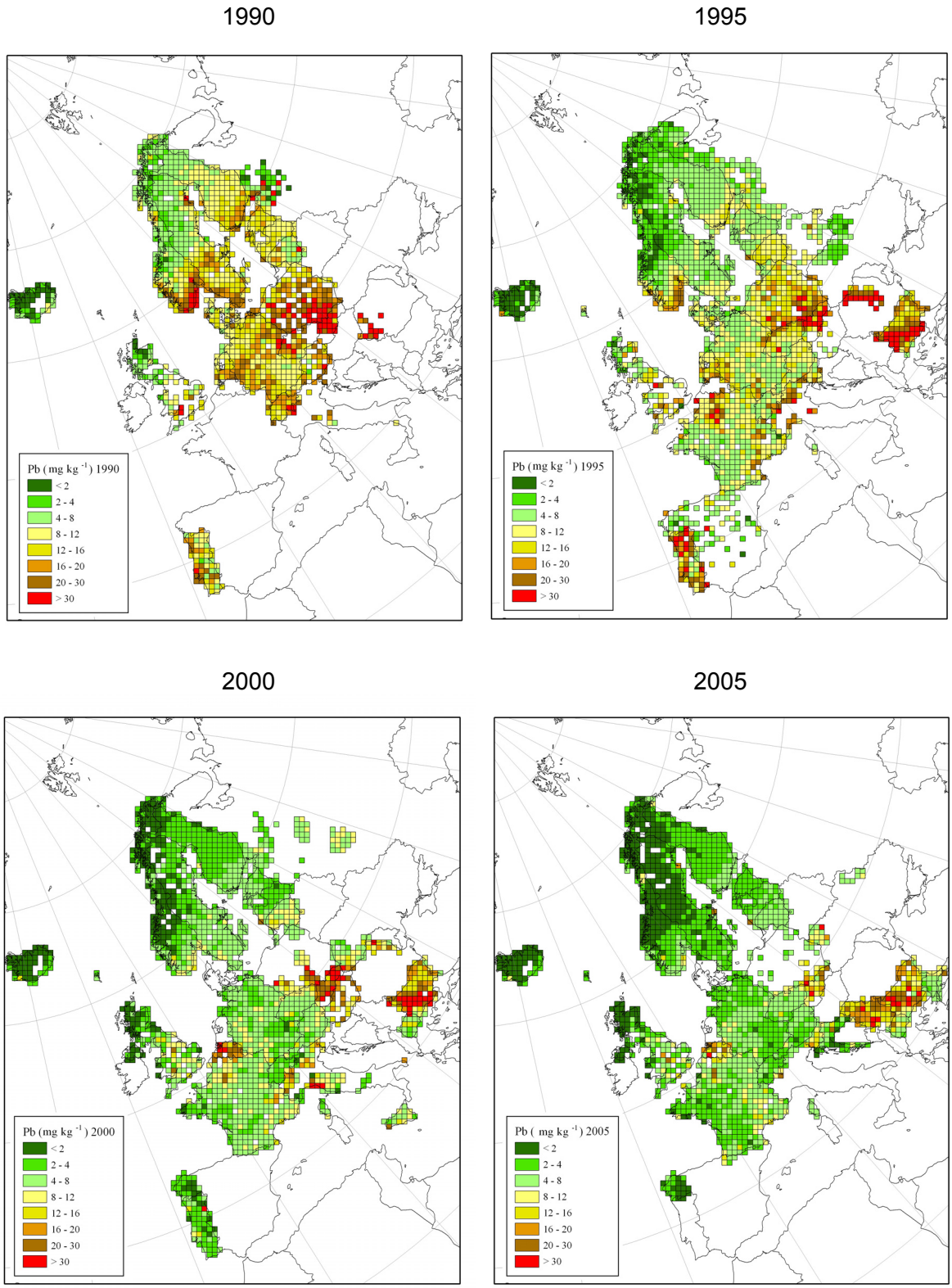

Figure 3.11. Mean concentration of lead in mosses per EMEP grid square in 1990, 1995, 2000 and 2005.

In 1990, the main source of anthropogenic lead was the sector “road transportation” (Task Force on Heavy Metals, 2006a), but its contribution to lead emissions has declined significantly over the last decades due to the abolishment of lead in petrol in many European countries. In 2005, “road transportation” had become the second source of lead emissions with a contribution of 17% and “manufacturing industries and construction” (41%) was the main source (Ilyin *et al*., 2007). Between 1990 and 2005 lead emission has declined by about 87% in the EMEP region, with a continuous decline being observed over that period. A decline in lead deposition of 57% was reported between 1990 and 2003 (Ilyin *et al*., 2005). These emission and deposition trends are in agreement with the temporal trends in lead concentration in mosses (Figure 3.11 and 3.12). Between 1990 and 2005, both the average median and mean lead concentration in mosses have declined by 72%, based on data available from 16 countries. Despite the overall decline in lead concentrations in mosses between 2000 and 2005, an increase in both the median and mean values was reported for the FYR Macedonia, Latvia, and Ukraine.

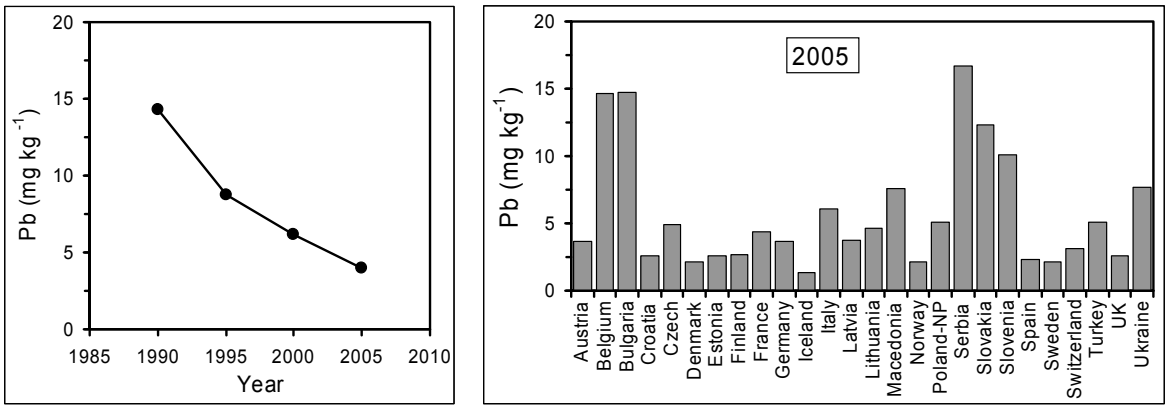

Figure 3.12. Average of median lead concentration in mosses for countries (n = 16) that reported lead data in all survey years (left) and median lead concentration in mosses per country in 2005 (right).

In 2005, the highest lead concentrations in mosses (median > 10 mg kg^{-1}) were found in Belgium and the eastern European countries Bulgaria, Serbia, Slovakia and Slovenia (Figure 3.11 and 3.12). In Belgium, major sources include lead and other metal smelters and disused metal mining areas and former steelworks. Nevertheless, the median lead concentration in mosses has declined by 39% in Belgium since 2000. In Bulgaria and Slovakia the median lead concentration in mosses has declined by 22 and 57% respectively since 2000 (no lead data were available for Serbia and Slovenia for 2000). In the majority of countries the median lead concentration was below 5 mg kg^{-1}, with the lowest concentrations (median < 3 mg kg^{-1}) being observed in Croatia, Estonia, Iceland, Scandinavia, Spain and the United Kingdom. In southern Scandinavia the lead concentration in mosses has further declined since 2000 due to a reduction in deposition of lead from long-range transport originating from central Europe and background concentrations have declined accordingly in northern Scandinavia.

Mercury

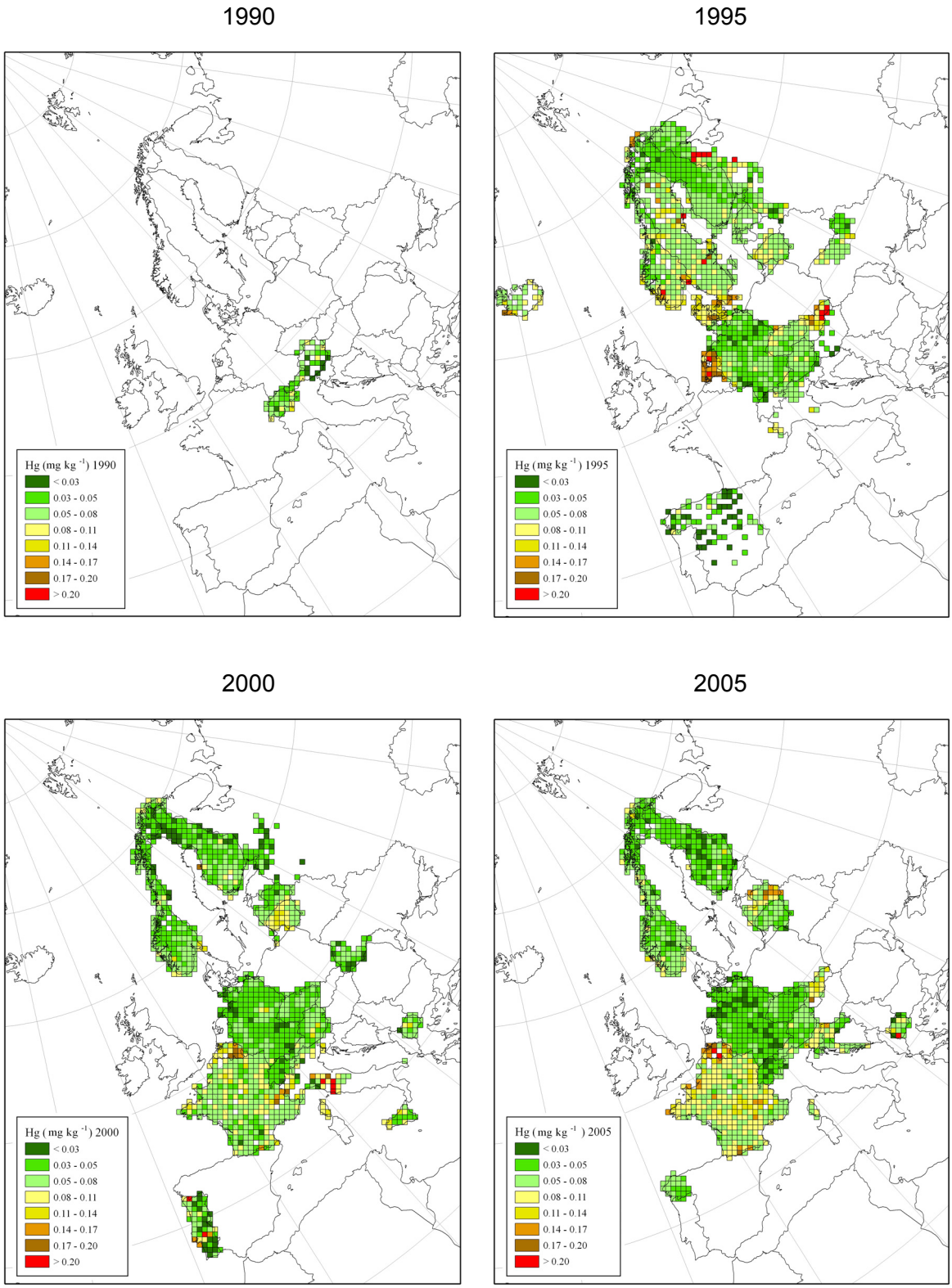

Figure 3.13. Mean concentration of mercury in mosses per EMEP grid square in 1990, 1995, 2000 and 2005.

In 2005, the main source of anthropogenic mercury emissions in Europe was “public electricity and heat production” (42%), followed by the sector “manufacturing industries and construction” (28%). “Waste incineration” and “metal production” both contributed 6% to mercury emissions in Europe (Ilyin *et al*., 2007). Between 1995 and 2005, mercury emissions have declined by about 32% in the EMEP region, with the decline levelling off since 1999. Mercury deposition has decreased by 20% between 1995 and 2003 (Ilyin *et al*., 2005). Slightly lower reductions were observed for the mercury concentration in mosses (Figure 3.13 and 3.14). Between 1995 and 2005, the average median mercury concentration in mosses has declined by 12%, based on data available from eight countries. In contrast to other metals, mercury is a global pollutant and can be transported in the atmosphere around the globe. Therefore, mercury emission sources located on other continents have a significant impact on pollution in Europe. In 16 countries European anthropogenic emissions made up the major contribution to mercury deposition in the EMEP domain, whereas in the other 29 countries the contribution of global emissions prevailed (Ilyin *et al*., 2007). Although natural emission sources and re-emission of gaseous mercury in the EMEP region contribute significantly to mercury input into the atmosphere, its contribution to deposition fluxes in the EMEP region is small. Due to the long residence time of gaseous mercury in the atmosphere, most of it will be transported outside the EMEP domain. Mercury depositions are mostly determined by short-lived mercury species such a particulate mercury or reactive gaseous mercury.

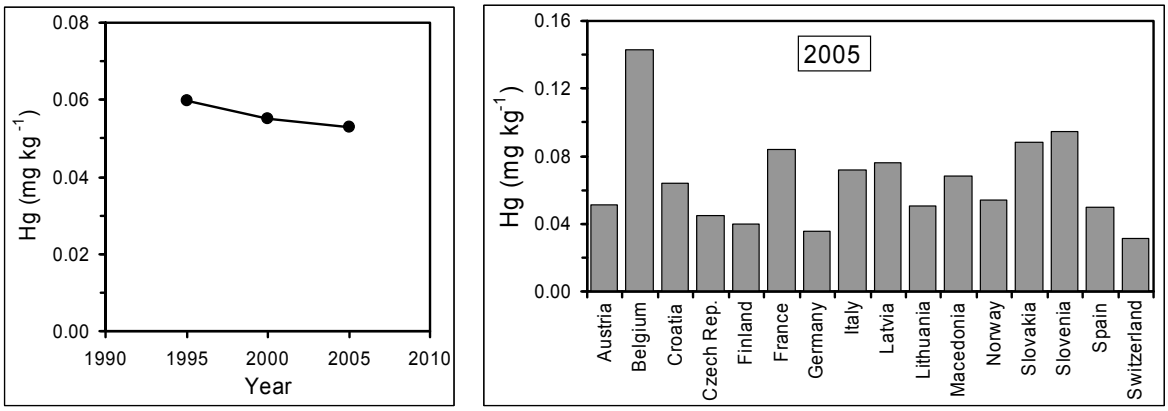

Figure 3.14. Average of median mercury concentration in mosses for countries (n = 8) that reported mercury data in all survey years (left) and median mercury concentration in mosses per country in 2005 (right).

In 2005, the highest mercury concentrations in mosses (median > 0.08 mg kg^{-1}) were detected in Belgium, France, Slovakia and Slovenia and the lowest concentrations (median < 0.05 mg kg^{-1}) in the Czech Republic, Finland, Germany and Switzerland (Figure 3.13 and 3.14). High concentrations of mercury were observed in France compared with the neighbouring countries Germany and Switzerland, resulting in a cross-border gradient between these countries. However, in contrast to arsenic, chromium, iron and vanadium, mercury concentrations in mosses in France were uniformly distributed across the country without a clear east-west gradient being present. Cross-border gradients were also observed between Latvia and Lithuania: whereas in Latvia the median mercury concentration declined between 1995 and 2000, an increase was detected between 2000 and 2005 (resulting in a higher median value in 2005 than 1995); the opposite was observed in Lithuania. Since 2000, considerable increases in the mercury concentration in mosses were reported for Belgium, France, the FYR Macedonia and Latvia.

Nickel

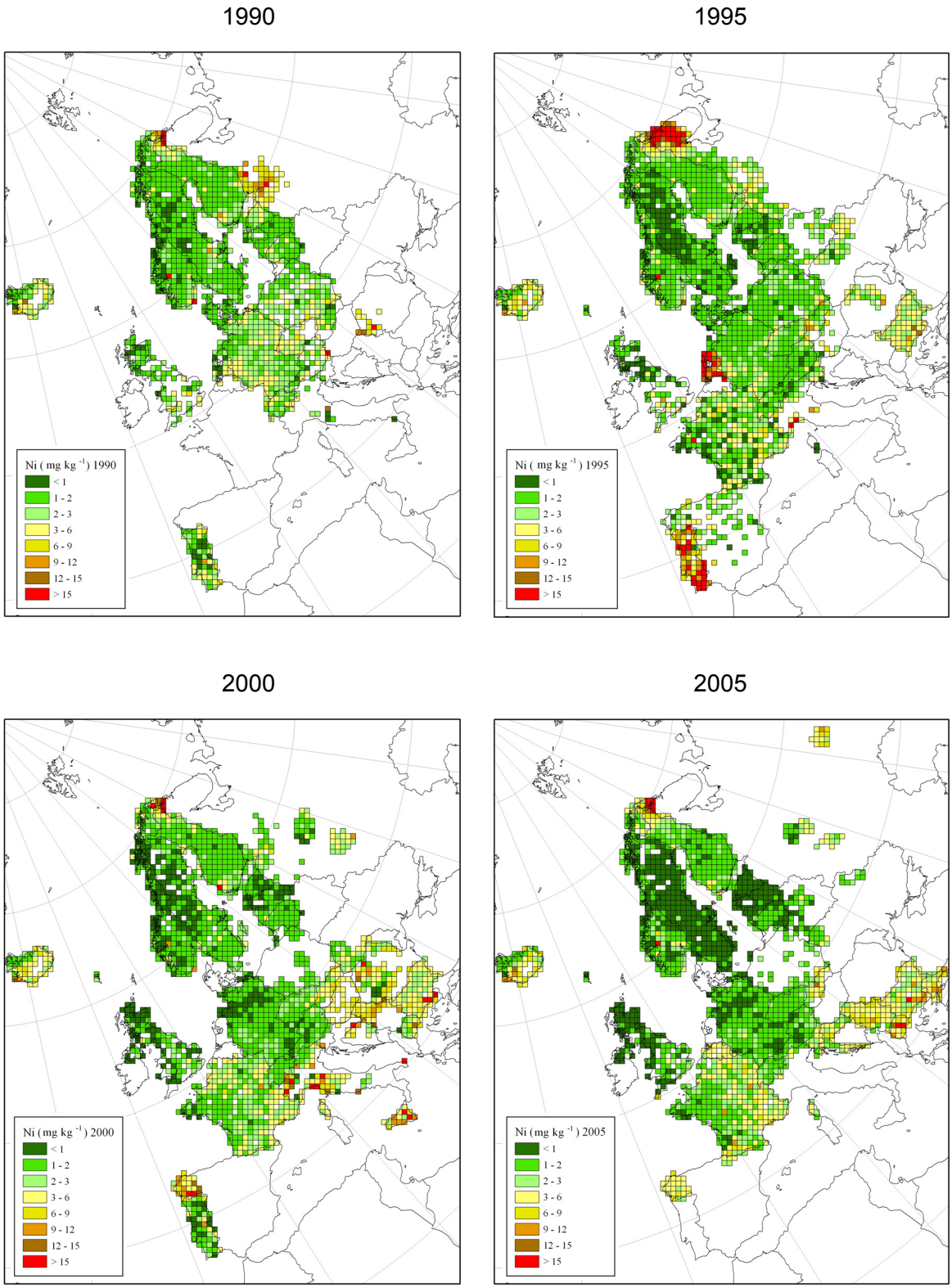

Figure 3.15. Mean concentration of nickel in mosses per EMEP grid square in 1990, 1995, 2000 and 2005.

Three sectors were responsible for almost 70% of anthropogenic nickel emissions in 2003: “petroleum refining”, “public electricity and heat production”, and “other manufacturing industries and construction” (Task Force on Heavy Metals, 2006a). Total anthropogenic emissions of nickel have decreased by about 57% between 1990 and 2004 in the EMEP region, with the decline levelling off in 2000 (Ilyin *et al*., 2006). However, smaller reductions in nickel concentrations in mosses were observed for the same period (Figure 3.15 and 3.16). The average median nickel concentration in mosses has declined by only 20% between 1990 and 2005, with the decline already levelling off in 1995. Since 2000, the median nickel concentration has increased considerably in the FYR Macedonia, the Russian Federation, Slovakia and Switzerland.

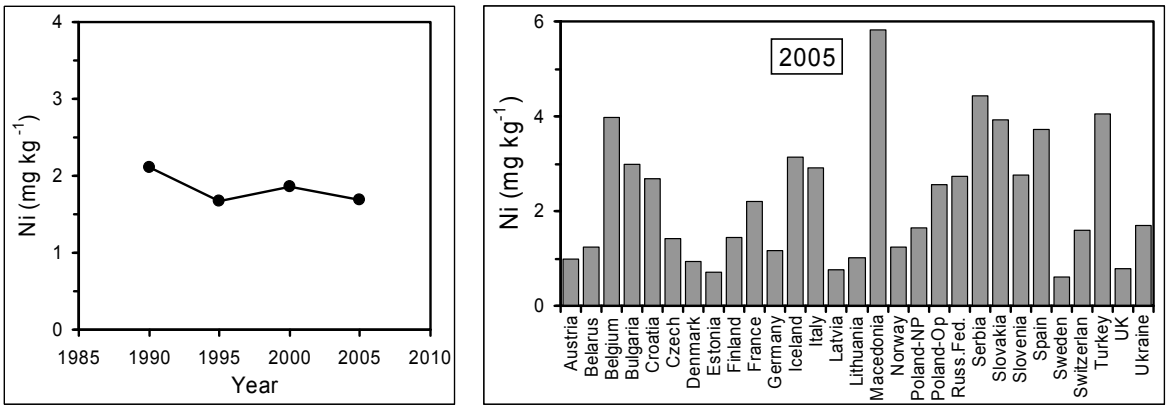

Figure 3.16. Average of median nickel concentration in mosses for countries (n = 16) that reported nickel data in all survey years (left) and median nickel concentration in mosses per country in 2005 (right).

In general, the lowest concentrations of nickel were found in Scandinavia, the Baltic States, the United Kingdom and central Europe. However, high nickel concentrations were observed near local emission sources in these regions, for example in north-east Norway and northern Finland near the copper-nickel smelters in the Kola Peninsula in the north-west of the Russian Federation. The median nickel concentration was higher than 3 mg kg^{-1} in Belgium, Iceland, Serbia, Slovakia, Spain and Turkey, and the highest median concentration was found in the FYR Macedonia. As in previous surveys, the values in Iceland were considerably higher than in other Nordic countries, in particular in the volcanic zone, reflecting geologically determined differences in soil dust composition. There was a clear east-west gradient in nickel concentrations in mosses in France, resulting in a cross-border gradient with Germany and Switzerland. This cross-border gradient was marginally present in 2000, but not in 1995. Although a cross-border calibration exercise between France and Germany revealed significantly higher nickel concentrations being measured in the French compared with the German laboratory, the results of the reference samples M2 and M3 did not reveal any significant difference with the recommended nickel values.

Vanadium

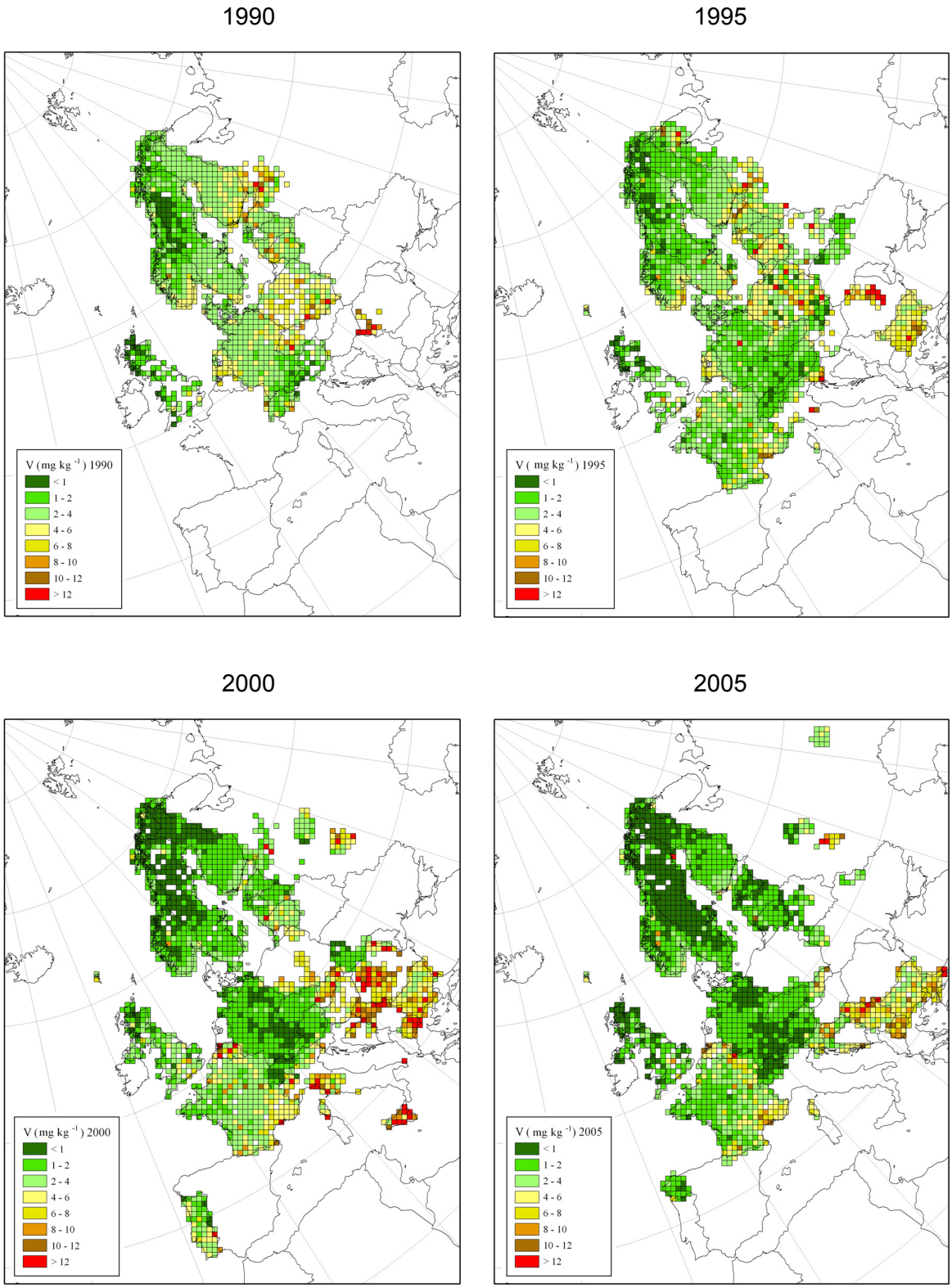

Figure 3.17. Mean concentration of vanadium in mosses per EMEP grid square in 1990, 1995, 2000 and 2005.

Traditionally the combustion of fuel oils has been a major source of anthropogenic vanadium emissions. As countries do not report emissions of vanadium to EMEP, not much is known about the temporal trends in vanadium emissions across Europe. However, selected European countries have reported on temporal trends in vanadium emission, for example, in the United Kingdom vanadium emission estimates have declined by about 40% between 1990 and 2005. The reduction in emissions reflects the decline in the use of fuel oils by the electricity supply industry, industry in general and the domestic sector. In 2005, road transport accounted for 59% and combustion of fuel oils for 20% of the estimated emission in the United Kingdom (http://www.naei.org.uk). Results of the moss survey indicate that vanadium emissions and depositions have significantly decreased across Europe (Figure 3.17 and 3.18). Between 1990 and 2005, the average median concentration of vanadium in mosses has declined by about 60%. Both nickel and vanadium emissions derive from crude oil combustion and although the moss maps for these metals were quite similar for 2000 and 2005, this was not the case for the earlier surveys (Figure 3.17). However, there is not a clear linear relationship between the nickel and vanadium concentrations in mosses. On the other hand, there is strong linear relationship between the iron and vanadium concentrations in mosses.

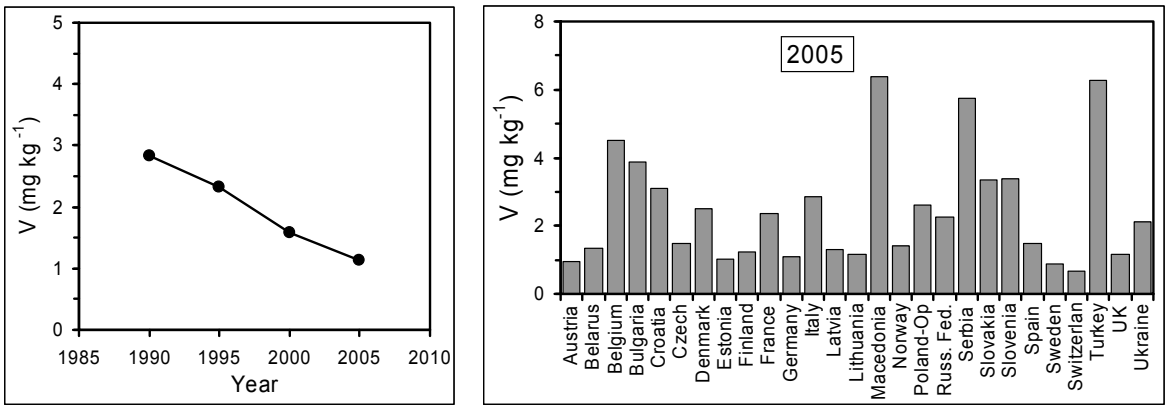

Figure 3.18. Average of median vanadium concentration in mosses for countries (n = 11) that reported vanadium data in all survey years (left) and median vanadium concentration in mosses per country in 2005 (right).

Since 2000, both the European median and mean vanadium concentrations have declined by 27-30%. Only in the Ukraine the median vanadium concentration has increased since 2000. In 2005, low vanadium concentrations in mosses were generally found in Scandinavia, the Baltic States, the United Kingdom, central Europe and Galicia (Spain). The median vanadium concentration was higher than 4 mg kg^{-1} in Belgium, the FYR Macedonia, Serbia, and Turkey (Figure 3.18). Similar to many other metals, there was a clear east-west gradient in vanadium concentrations in mosses in France, resulting in a considerable cross-border gradient with Germany and Switzerland. This cross-border gradient was only marginally present in 2000. As for nickel, the cross-border calibration exercise between France and Germany revealed significantly higher vanadium concentrations being measured in the French compared with the German laboratory, but the results of the reference samples M2 and M3 did not reveal any significant difference with the recommended vanadium values.

Zinc

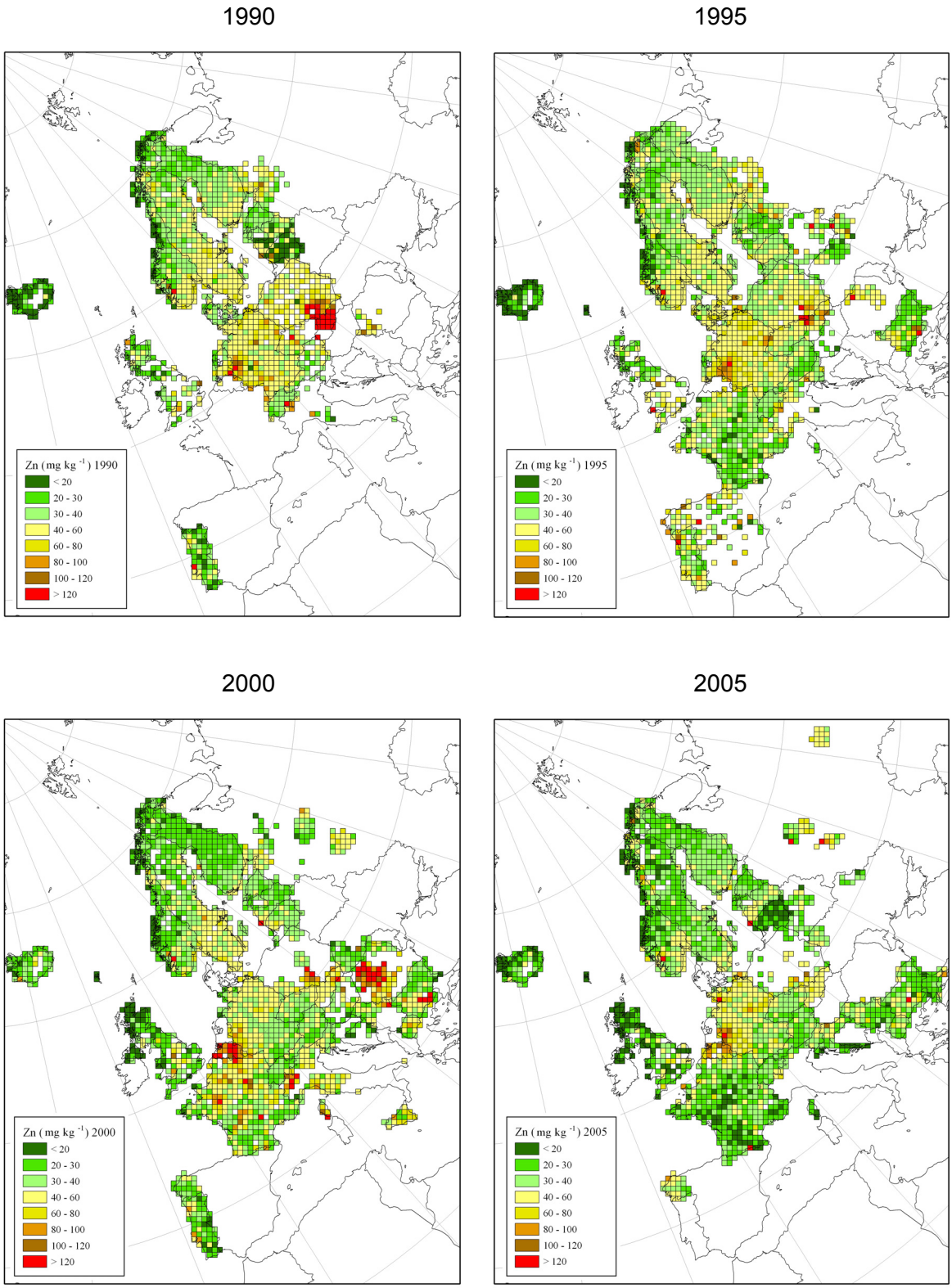

Figure 3.19. Mean concentration of zinc in mosses per EMEP grid square in 1990, 1995, 2000 and 2005.

In 2003, the maximum contribution to anthropogenic zinc emissions was made by the “road transportation” sector (42%), followed by “metal production” (21%), as determined in nine European countries (Task Force on Heavy Metals, 2006a). The road transport emission is almost entirely due to tyre wear, the zinc content of the tyre rubber is around 2% ZnO by weight. In selected European countries, zinc emissions have decreased by about 30% between 1990 and 2003, with the highest decline being observed between 1990 and 1996. Since 1996, zinc emissions have hardly changed (Task Force on Heavy Metals, 2006a). This is in agreement with the decline in the zinc concentration in mosses (Figure 3.19 and 3.20). Between 1990 and 2005, the average median and mean zinc concentration has declined by about 30%, with the highest decline being observed between 1990 and 1995, mainly due to a 70% decline in Slovakia over that period. Although the median zinc concentration has increased in 40% of the countries since 2000, a considerable decline was observed in others, resulting in a small decline in the average median zinc concentration between 2000 and 2005.

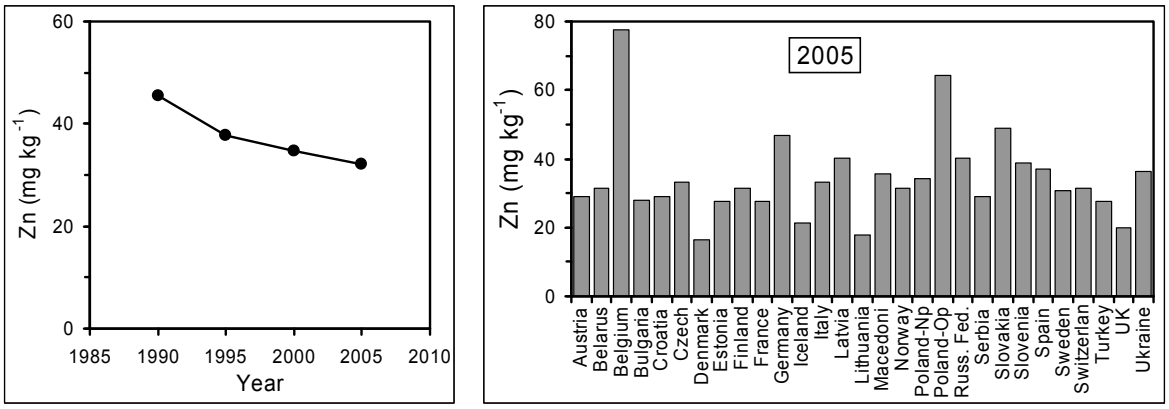

Figure 3.20. Average of median zinc concentration in mosses for countries (n = 16) that reported zinc data in all survey years (left) and median zinc concentration in mosses per country in 2005 (right).

Zinc (like copper) is an essential micronutrient to all organisms as a constituent of many metalloenzymes and of several other proteins. Therefore, background concentrations will be present in mosses as zinc will be recycled from senescing to newly developing parts of the moss. 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). The highest median zinc concentration was reported for Belgium, with median zinc concentration also being higher than 40 mg kg^{-1} in Germany, Latvia, Poland (Opole region), the Russian Federation and Slovakia. In Belgium, major sources include steelworks, metal smelters (some now closed) and disused old metal and coal mining areas. Whereas the median zinc concentration has decreased in Belgium and Slovakia, an increase was observed in Germany, Latvia and the Russian Federation since 2000. In France, the zinc concentration was remarkably lower in 2005 than 2000, but the spatial distribution in 2005 was similar to the one in 1995, with slightly lower concentrations being reported for 2005.

Aluminium and antimony

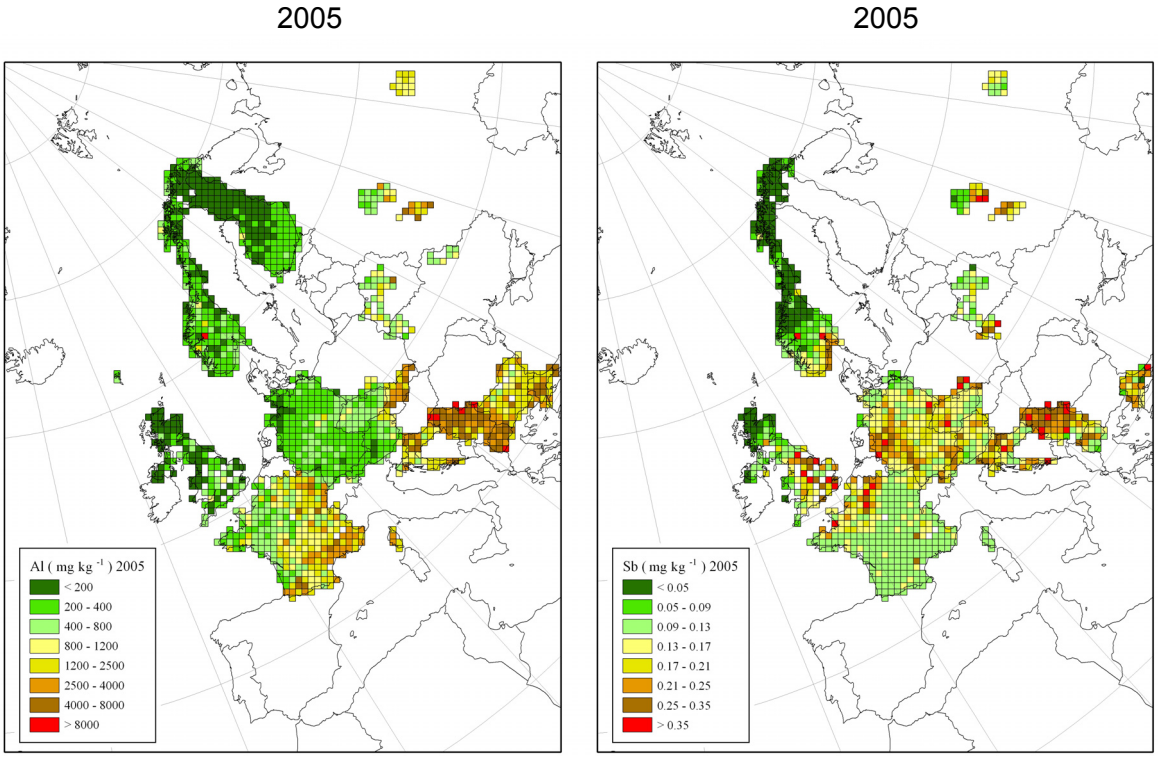

Figure 3.21. Mean concentration of aluminium (left) and antimony (right) in mosses per EMEP grid square in 2005.

Aluminium

In 2005, the highest median aluminium concentrations were found in the FYR Macedonia, Serbia, Slovakia and Turkey and the lowest ones in (north) Scandinavia and northern parts of the United Kingdom (Figure 3.21 and 3.22). Application of the analytical technique INAA might (partly) explain the high aluminium concentrations reported for the FYR Macedonia and Serbia (Smodiš and Bleise, 2007), however, this technique was not used in Slovakia and Turkey and therefore cannot explain the high concentrations observed in those countries. In addition, much lower aluminium concentrations were reported by other countries (Belarus, Croatia, Poland – Opole region and the Russian Federation) which also applied INAA (Annex 2). Away from local pollution sources, aluminium is a good indicator of mineral particles, mainly windblown soil dust (Berg and Steinnes, 1997; Zechmeister *et al*., 2003), because of its high concentration in the earth's crust. There is a clear north-south gradient and to some extent 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 arsenic, chromium, iron, nickel and vanadium in eastern and southern compared with western parts of France. Strong linear relationships were found between the aluminium and iron (R^2 = 0.62), aluminium and vanadium (R^2 = 0.66) and iron and vanadium (R^2 = 0.69) 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. The contribution of wind re-suspension to modelled deposition fluxes varies between countries and metals and is for

example very low for mercury within the EMEP area (Ilyin *et al*., 2007). The results for antimony indicate that in eastern Europe anthropogenic activities contribute considerably to the high aluminium concentration in mosses, but even in areas with low aluminium concentrations in mosses, part of the aluminium might be derived from long-range transport. For example, in southern Norway, the aluminium concentration in mosses declined by a factor two in the last 30 years (E. Steinnes, personal communication). Therefore, a simple correction factor based on the aluminium concentration in mosses to estimate the accumulation of other metals derived from soil dust cannot be applied.

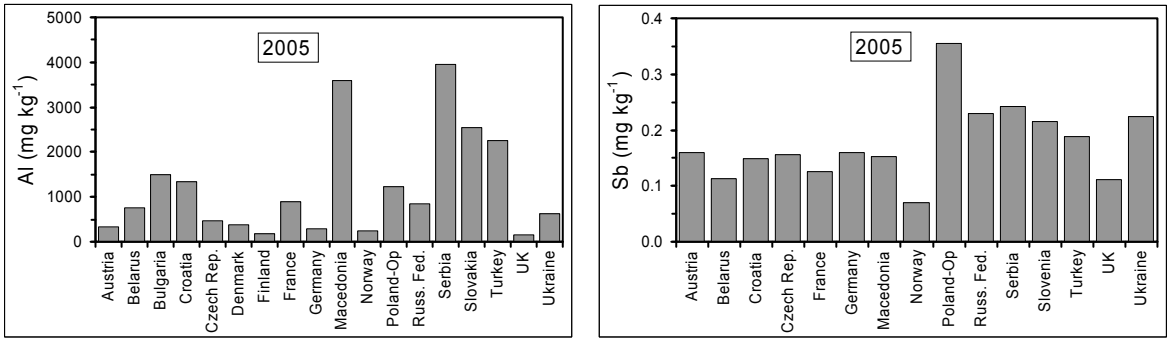

Figure 3.22. Median aluminium (left) and antimony (right) concentration in mosses per country in 2005.

Antimony

There is a growing use of antimony in automobile brake pads, plastics and flame retardants. At present the brake pads in cars are thought to be the main source of atmospheric antimony, whereas the contribution from other sources such as coal burning, metallurgy and waste incineration is less obvious than in 1990. In 2005, antimony was reported to be the single most highly enriched element in urban dust (Shotyk *et al*., 2004). In Norway, the association of antimony with long-range transport of metals was not so evident in 2005 compared with 1990, for example in the Oslo area antimony in mosses was relatively more dominating than before (E. Steinnes, personal communication). In 2005, the lowest antimony concentrations in mosses were generally observed in areas with a low population density, such as middle and northern Norway and Scotland (Figure 3.21 and 3.22). Considerable antimony concentrations were found in the midlands and southern parts of the United Kingdom, southern Norway, north-eastern France and central (e.g. the Ruhr Valley in Germany) and eastern Europe. In the majority of eastern and southern France antimony concentrations were low (below the quantification limit of 0.125 mg kg^{-1}), indicating again that the high concentration for some of the metals in this part in France might have originated from wind-blown dust (see aluminium).

4. Discussion and conclusions

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 for the majority of metals. 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.

Since 1990, the metal concentration in mosses has declined the most (45-72%) for arsenic (based on data from five countries), cadmium, iron, lead and vanadium, followed by copper, nickel and zinc (20-30%), with no significant reduction being observed for chromium (2%) and mercury (12% since 1995). Temporal trends in heavy metal concentrations in mosses are in agreement with trends in EMEP emission and/or modelled deposition data for arsenic, cadmium, copper, lead, mercury, nickel (although the decline of nickel in mosses is lower than for emission) and zinc, but not for chromium (no emission or deposition data are being reported by EMEP for iron and vanadium). As in previous surveys, the lowest concentrations of heavy metals in mosses were generally found in (north) Scandinavia, the Baltic States and northern parts of the United Kingdom in 2005/6. Depending on metal, the highest concentrations in mosses were often found in Belgium and eastern European countries. On a national (Harmens *et al*., 2007, 2008b) or regional scale within countries (e.g. Zechmeister *et al*., in press) large deviations from the general European trend were observed, i.e. temporal trends were country or region-specific with no changes or even increases in metal concentrations in mosses being found, depending on metal. Therefore, even in times of generally decreasing metal deposition across Europe, temporal trends are different for different geographical scales.

The similarity in temporal trends for moss data and emission or modelled total deposition data reported by EMEP suggests that at the European scale these trends are not hugely affected by either the high uncertainties associated with emission and modelled deposition data (Ilyin *et al*., 2007) or by potential confounding factors associated with the moss survey. The use of mosses as biomonitors of atmospheric heavy metal deposition could potentially be confounded by various climatic, geographical and environmental factors. These confounding factors have been discussed in more detail elsewhere (e.g. Berg and Steinnes, 1997, Harmens *et al*., 2008b; Reimann *et al*., 2001; Steinnes, 2008; Zechmeister *et al*., 2003, and references therein) and include:

- Use of different moss species across Europe within each survey and within countries between surveys. Different moss species might accumulate heavy metals at different rates. Therefore, countries are encouraged to conduct interspecies calibration exercises, i.e. sample different moss species at the same locations, to establish whether heavy metal accumulation rates are species-specific. However, for mapping at the European scale it might not be desirable to convert the data from one species to another as this may result in higher uncertainties (see Zechmeister *et al*., 2003).
- Application of different (or improved) analytical techniques within countries between different surveys and within a survey between different countries. In 1995/6 and 2005/6 moss reference material was included in the analyses to quantify any bias of the data due to the participation of different laboratories applying a range of analytical techniques. In general, there was a good agreement in the reference data (Steinnes *et al*., 1997; Annex 3), although the results for INAA tend to be higher for metals such as aluminium, chromium and iron than for methods using sample dissolution (Smodiš and Bleise, 2007).
- Sampling mosses in different climates or different seasons, which might affect the accumulation of heavy metals directly or indirectly via effects on moss growth rate. However, one should bear in mind that the metal concentrations in mosses are

determined for three years of moss growth, representing climatic conditions averaged over three years. In more arid regions of Europe, the contribution of dry deposition to the accumulation of heavy metals is significant and a considerable part of the dry deposition might originate from re-suspension of soil dust by wind. Away from local aluminium sources, the aluminium map provides an indication of the spatial variation in wind-blown dust across Europe. The high contribution of dry deposition to metal accumulation in mosses in arid regions of Europe was identified as a main problem in calculating absolute atmospheric deposition values across Europe based on moss data (Berg *et al*., 2003).

- In coastal areas, in particular the west coast of Europe, the presence of high levels of sea salt ions might interfere with the accumulation in mosses, in particular of loosely bound metals such as zinc. The presence of many EMEP measurement stations in coastal areas across Europe was also identified as a main problem in calculating absolute atmospheric deposition values across Europe based on moss data (Berg *et al*., 2003).
- Intensity, frequency and duration of precipitation and altitude, although contrasting results have been reported. An increase in precipitation can lead to an increase in metal concentration in mosses as well as rinsing of already deposited metals and an increase in altitude does not always result in an increase in metal concentration in mosses (see Zechmeister *et al*., 2003).

An initial study by Büker *et al*. (2003), using both regression analysis and artificial neural networks, showed only a weak correlation between the heavy metal concentration in mosses in 2000/1 and moss species, analytical techniques and climatic and geographical parameters.

A preliminary principal component analysis of all the European moss data since 1990 (D. Cooper, unpublished) identified two major dominant groupings, representing i) long-range atmospheric transported elements (cadmium, lead and zinc) and ii) wind-blown mineral particles or local emission sources from industry (chromium, iron and vanadium). Beyond these factors there was little Europe-wide consistency in further groupings, although in some regions with known local sources a third group was detected (copper and nickel). Although emissions and depositions of heavy metals have declined significantly for most of the metals in recent decades, ecosystems and human health are still at considerable risk of adverse effects of heavy metals as some of the metals bioaccumulate and the margin of safety is small (Task Force on Health, 2007; VROM, 2007). In addition, metals accumulate in the soil and therefore, vegetation and other organisms (including humans) could potentially be exposed to higher metal concentrations in the future via uptake from the soil or via re-suspension of wind-blown dust.

Conclusions

The following main conclusions can be drawn:

- Mosses provide a cheap, effective surrogate to precipitation analysis for the identification of hot spots and temporal trends of atmospheric heavy metal deposition across Europe at a high resolution;
- Spatial trends of heavy metal concentrations in mosses were metal-specific. However, in general the lowest concentrations were observed in (north) Scandinavia, the Baltic States and northern parts of the United Kingdom and the higher concentrations in Belgium and eastern European countries;
- Since 1990, the metal concentration in mosses has declined for arsenic, cadmium, copper, iron, nickel, lead, vanadium and zinc, but not for chromium and mercury. Despite these general European trends, country and region-specific temporal trends were observed, including increases in metal concentrations in mosses in some areas.

5. Future challenges

2010 survey

The European moss survey has an important role in identifying spatial and temporal trends in atmospheric heavy metal pollution across Europe. This work is essential for monitoring future trends at a high resolution. Despite the Europe-wide decline in atmospheric emission and subsequent deposition of many heavy metal in recent decades, ecosystems and human health are still predicted to be at risk of adverse effects of heavy metals in the future (Task Force on Health, 2007; VROM, 2007). In addition, European temporal trends differ from those at the national or regional scale as national or regional increases in heavy metal concentrations in mosses have been reported too in recent decades. Other metals such as antimony might pose a significant risk to the environment and human health in the future (Krachler *et al*., 2005). Therefore, the next European moss survey should be conducted in the year 2010 and should include the following:

- Inter-laboratory calibration exercise with reference material M2 and M3. In addition, participating laboratories are advised to investigate the relationship between the results of old and new techniques when improving techniques or switching to a new one and report the results;
- Cross-border calibration exercises to enhance quality assurance of the data and identify potential causes of steep gradients across borders;
- More countries to report on the metals aluminium, antimony, arsenic and mercury;
- Detailed uncertainty analysis of heavy metal concentrations in mosses;
- Interspecies calibration exercises across Europe to establish differences in accumulation rates of heavy metals between species in different climates;
- Sampling of mosses near national or EMEP monitoring stations to establish the relationship between heavy metal deposition and concentration in mosses.

Further data analysis

The spatial variation in heavy metal concentration in mosses across Europe should be analysed in further detail to identify the main causes of spatial variation and the role of any confounding factors (Schröder *et al*., 2008). Such an analysis should include linking the moss data with other available environmental data, including climate and soil data. Detailed statistical analysis of the spatial and temporal trends and the quantification of the importance of confounding factors are required. For cadmium, lead and mercury the concentration in mosses should be compared in more detail with deposition data modelled by EMEP to investigate their relationships at European and national scale. Potential factors affecting these relationships should be identified.

A main challenge for the future will be to establish how the results of the moss survey can be used in the assessment of effects of heavy metals on ecosystems and subsequently the identification of ecosystems at risk from heavy metal pollution. This might provide useful information for the critical load approach adopted by the LRTAP Convention.

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Annex 1. Participants in the 2005/6 survey

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

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Frolova	Marina	Latvian Environment, Geology and Meteorology Agency, Riga	Latvia
Nikodemus	Oļģerts	University of Latvia, Riga	Latvia
Tabors	Guntis	University of Latvia, Riga	Latvia
Kvietkus	Kestutis	Institute of Physics, Vilnius	Lithuania
Steinnes	Eiliv	Norwegian University of Science and Technology, Trondheim	Norway
Berg	Torunn	Norwegian University of Science and Technology, Trondheim	Norway
Uggerud	Hilde	Norwegian Institute for Air Research, Kjeller	Norway
Grodzińska	Krystyna	Institute of Botany, Polish Academy of Sciences, Krakow	Poland (National Parks)
Godzik	Barbara	Institute of Botany, Polish Academy of Sciences, Krakow	Poland (National Parks)
Kapusta	Pawel	Institute of Botany, Polish Academy of Sciences, Krakow	Poland (National Parks)
Szarek-Łukaszewska	Grażyna	Institute of Botany, Polish Academy of Sciences, Krakow	Poland (National Parks)
Szymon	Korzekwa	University of Opole	Poland (Opole Region)
Frontasyeva	Marina	Frank Laboratory of Neutron Physics, Joint Institute for Nuclear Research, Dubna	Russian Federation
Strelkova	Lyudmila	Frank Laboratory of Neutron Physics, Joint Institute for Nuclear Research, Dubna	Russian Federation (Bulgaria)
Pankratova	Yulia	Frank Laboratory of Neutron Physics, Joint Institute for Nuclear Research, Dubna	Russian Federation (Udmurt Republic, Poland – Opole Region, Serbia)
Vergel	Konstantin	Frank Laboratory of Neutron Physics, Joint Institute for Nuclear Research, Dubna	Russian Federation (Moscow Region, Sergiev Posad, Tver Region)
Ermakova	Elena	Frank Laboratory of Neutron Physics, Joint Institute for Nuclear Research, Dubna	Russian Federation (Tula Region)
Meresova	Jana	Frank Laboratory of Neutron Physics, Joint Institute for Nuclear Research, Dubna	Russian Federation (Western Slovakia)
Miodrag	Krmar	University of Novi Sad	Serbia
Radnovich	Dragan	University of Novi Sad	Serbia
Maňkovská	Blanka	Institute of Landscape Ecology, Slovak Academy of Science, Bratislava	Slovakia
Oszlanyi	Július	Institute of Landscape Ecology, Slovak Academy of Science, Bratislava	Slovakia
Florek	Matej	Comenius University, Bratislava	Slovakia (Western Slovakia)
Jeran	Zvonka	Jožef Stefan Institute, Ljubljana	Slovenia

Fernández Escribano	José Angel	University of Santiago de Compostela	Spain (Galicia)
Carballeira Ocaña	Alejo	University of Santiago de Compostela	Spain (Galicia)
Aboal Viñas	Jesús	University of Santiago de Compostela	Spain (Galicia)
Santamaría	Jesús Miguel	University of Navarra, Pamplona	Spain (Navarra)
González-Miqueo	Laura	University of Navarra, Pamplona	Spain (Navarra)
Elustondo	David	University of Navarra, Pamplona	Spain (Navarra)
Lasheras	Esther	University of Navarra, Pamplona	Spain (Navarra)
Bermejo	Raúl	University of Navarra, Pamplona	Spain (Navarra)
Rühling	Åke	University of Lund	Sweden
Olsson	Tommy	University of Lund	Sweden
Thöni	Lotti	FUB - Research Group for Environmental Monitoring, Rapperswil	Switzerland
Coşkun	Mahmut	Canakkale Onsekiz Mart University	Turkey
Coşkun	Münevver	Canakkale Onsekiz Mart University	Turkey
Çayır	Akın	Canakkale Onsekiz Mart University	Turkey
Blum	Oleg	National Botanical Garden, National Academy of Sciences of Ukraine, Kyiv	Ukraine
Harmens	Harry	Centre for Ecology and Hydrology, Bangor	United Kingdom
Lloyd	Andrew	Centre for Ecology and Hydrology, Bangor	United Kingdom
Jarvis	Kim	Kingston University, Kingston upon Thames	United Kingdom
Ashmore	Mike	University of York	United Kingdom
Jordan	Crawford	Agri-Food and Biosciences Institute, Belfast	United Kingdom (Northern Ireland)

Annex 2. Analytical techniques used in 2005/6

Country	As	Cd	Cr	Cu	Fe	Hg	Ni	Pb	V	Zn	Al	Sb
Austria	GFAAS	ETAAS	ICP-ES	ICP-ES	ICP-ES	CVAAS	ICP-ES	ICP-ES[1]	ICP-ES	ICP-ES	ICP-ES	GFAAS
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	-	-
Bulgaria	-	ICP-ES	ICP-ES	ICP-ES	ICP-ES	-	ICP-ES	ICP-ES	ICP-ES	ICP-ES	ICP-ES	-
- additional data[2]	INAA	AAS	INAA	AAS	INAA	-	INAA	AAS	INAA	INAA	INAA	INAA
Croatia	INAA	GFAAS	INAA	FAAS	INAA	CVAAS	INAA	GFAAS	INAA	INAA	INAA	INAA
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
Denmark - Faroe Islands	ICP-MS	ICP-MS	ICP-MS	ICP-ES	ICP-ES	-	ICP-MS	ICP-MS	ICP-MS	ICP-ES	ICP-ES	-
Estonia	-	ICP-ES	ICP-ES	ICP-ES	ICP-ES	-	ICP-ES	ICP-ES	ICP-ES	ICP-ES	-	-
Finland	GFAAS	ICP-ES	ICP-ES	ICP-ES	ICP-ES	CVAFS	ICP-ES	ICP-ES	ICP-ES	ICP-ES	ICP-ES	-
France	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	CVAAS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS
FYR Macedonia	INAA	GFAAS	INAA	FAAS	INAA	CVAAS	INAA	GFAAS	INAA	INAA	INAA	INAA
Germany	ICP-MS	ICP-MS	ICP-MS	ICP-ES	ICP-ES	CVAAS	ICP-MS	ICP-MS	ICP-MS	ICP-ES	ICP-ES	ICP-MS
Iceland	ICP-MS	ICP-MS	ICP-MS	ICP-ES	-	-	ICP-MS	ICP-MS	-	ICP-ES	-	-
Italy	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-ES	AMA	ICP-MS	ICP-MS	ICP-MS	ICP-MS	-	-
Latvia	GFAAS	FAAS	FAAS	FAAS	FAAS	CVAAS	FAAS	FAAS	GFAAS	FAAS	-	-
Lithuania	GFAAS	GFAAS	GFAAS	GFAAS	GFAAS	CVAAS	GFAAS	GFAAS	GFAAS	GFAAS	-	-
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 - National parks	-	FAAS	-	FAAS	FAAS	-	FAAS	FAAS	-	FAAS	-	-
- Opole region	INAA	-	INAA	-	INAA	-	INAA	-	INAA	INAA	INAA	INAA
Russian Federation	INAA	INAA	INAA	INAA	INAA	-	INAA	-	INAA	INAA	INAA	INAA
Serbia	INAA	FAAS	INAA	FAAS	INAA	-	INAA	FAAS	INAA	INAA	INAA	INAA
Slovakia	-	GFAAS	-	GFAAS	ICP-ES	AMA	GFAAS	GFAAS	GFAAS	ICP-ES	ICP-ES	-
- additional data[2]	INAA	AAS	INAA	AAS	INAA	AAS	AAS	AAS	INAA	AAS	INAA	-
Slovenia	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	CVAAS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	-	ICP-MS
Spain - Galicia	AFS	GFAAS	FAAS	FAAS	FAAS	AMA	GFAAS	GFAAS	GFAAS	FAAS	-	-
- Navarra	ICP-MS	ICP-MS	ICP-MS	ICP-MS	-	-	ICP-MS	ICP-MS	ICP-MS	ICP-MS	-	-
Sweden	ICP-MS	ICP-MS	ICP-MS	ICP-ES	ICP-ES	-	ICP-MS	ICP-MS	ICP-MS	ICP-ES	-	-
Switzerland	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-ES	AMA	ICP-MS	ICP-MS	ICP-MS	ICP-MS	-	-
Turkey	ICP-ES	ICP-ES	ICP-ES	ICP-ES	ICP-ES	-	ICP-ES	ICP-ES	ICP-ES	ICP-ES	ICP-ES	ICP-ES
Ukraine	ICP-ES	ICP-ES	ICP-ES	ICP-ES	ICP-ES	-	ICP-ES	ICP-ES	ICP-ES	ICP-ES	ICP-ES	ICP-ES
United Kingdom	ICP-MS	ICP-MS	ICP-MS	ICP-MS	-	-	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS

[1] Low concentrations: ETAAS

[2] Additional data, not included in maps

Abbreviations

AAS	Atomic absorption spectrometry (unspecified)
AFS	Atomic fluorescence spectrometry
AMA	Advanced mercury analyser
CVAAS	Cold vapour atomic absorption spectrometry
CVAFS	Cold vapour atomic fluorescence spectrometry
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. Moss reference material M2 and M3

Moss reference material was made available by Eero Kubin (Finland) and final processing of M2 and M3 data was conducted by Eiliv Steinnes (Norway).

Based on the 1995 inter-laboratory exercise, recommended values were issued for the ten elements included in the European moss survey (As, Cd, Cr, Cu, Fe, Hg, Ni, Pb, V, Zn) and an additional seventeen elements (Al, B, Ba, Ca, Co, Cs, La, K, Na, Mg, Mn, Rb, S, Sb, Se, Sr, Th) based on the criterion that at least two analytical techniques based on different physical principles showed good agreement (Steinnes *et al*., 1997). Most laboratories participating in the 2005/6 moss survey used some kind of multi-element analytical technique that could easily produce data for a number of elements in addition to the ten metals of primary interest. The participants were therefore asked to report data for as many elements as possible for M2 and M3, with particular emphasis on aluminium and antimony. Many laboratories were also reporting data for nitrogen in the two moss reference samples. In principle, therefore, data from the 2005/6 moss survey might facilitate recommended values for an additional number of elements in M2 and M3, and possibly revision of previously published data.

The data reported for M2 and M3 in 2005/6 confirm the previously recommended values for most of the elements, in which case no adjustment of the previously published data (Steinnes *et al.*, 1997) was deemed necessary. Only a few minor adjustments were required (Table annex 3). The 2005/6 values for calcium are consistently 5-10% higher than most of the data reported in 1995, and therefore new recommended values are suggested, considering the combined data from both studies. In the case of antimony the new data suggest that an adjustment is required, in particular for M3, presumably based on improved analytical methods. Moreover, the new data for total nitrogen allowed the establishment of recommended values for this element for M2 and M3. Nine laboratories submitted acceptable data for nitrogen, five of which employing methods based on wet ashing and the rest on dry ashing. Results from the two approaches agree very well (Table annex 3).

Finally, the new data, when combined with the 1995 values, allow an extension of the list of elements for which “indicated” values were published previously (Steinnes *et al*., 1997). This term was used when internally consistent values had been obtained by two or more laboratories but using the same analytical technique. Elements now added to the previous list are chlorine, bromine, praseodymium, neodymium and bismuth.

Given that most participating laboratories in the 1995 inter-laboratory comparison used strong nitric acid for sample decomposition, the recommended values were based primarily on methods depending thereon. This meant that techniques such as instrumental neutron activation analysis (INAA) based on total determination of elements yielded systematically high results for some elements, and the data had to be rejected although they might express correctly the total concentrations. In principle, the combined data from the two inter-laboratory comparisons might have been used to arrive at recommended values for total concentrations in cases where these deviate from those based on wet decomposition of the sample. As only one laboratory used INAA in the 2005/6 survey and only a small number used this technique in 1995, the data are too scarce for this purpose. Some general trends can still be indicated: among the elements frequently determined in moss samples by INAA, only the INAA results were higher than techniques based on wet ashing for the elements aluminium (30-40%), chromium (60-80%), iron (20-30%) and sodium (20-30%). Smodiš and Bleise (2007) made similar observations.

Table annex 3. New and revised recommended and indicated values for the concentrations (mg kg^{-1}) of elements in moss reference material M2 and M3 (Steinnes *et al*., 1997). Values are mean ± one standard deviation.

Element	M2	M3	
Recommended values			
Nitrogen	8360±620	6810±520	R
	10	8	N
	8260	6710	Wet
	8440	6990	Dry
Calcium	2050±160	2140±200	R
(revised)	11	11	N
	1860	1870	FAAS
	2050	2180	ICP-ES
	2070	2240	ICP-MS
	2150	2200	INAA
Antimony	0.185±0.020	0.043±0.004	R
(revised)	12	9	N
	0.179	0.044	ICP-MS
	0.204	0.044	INAA
	0.173	0.036	GFAAS
Indicated values			
Chlorine	110±5	65±2	INAA
	2	2	N
Bromine	110±11	124±12	INAA
	3	3	N
Praseodymium	0.042±0.002	0.027±0.002	ICP-MS
	2	2	N
Neodymium	0.161±0.004	0.098±0.002	ICP-MS
	2	2	N
Bismuth	0.126±0.014	0.015±0.001	ICP-MS
	2	2	N

Abbreviations

N	Number of observations
R	Recommended value
Wet	Wet ashing
Dry	Dry ashing
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 4. Metal concentrations (mg kg^{-1}) in mosses in 2005/6

	As	Cd	Cr	Cu	Fe	Hg	Ni	Pb	V	Zn	Al	Sb
Austria												
N[a]	212	212	212	212	212	212	212	212	212	212	212	212
Min[b]	0.092	0.055	0.41	2.90	65.0	0.026	0.39	1.20	0.25	16.0	76.2	0.040
Max[c]	5.31	1.60	6.89	35.0	2200	0.26	8.80	27.0	16.0	120	2584	0.62
Median	0.18	0.18	1.06	5.10	300	0.051	1.00	3.70	0.95	29.0	333	0.16
Belarus (Minsk and Grodno region)												
N	58	-	58	-	58	-	58	-	58	58	58	58
Min	0.052	-	0.18	-	167	-	0.55	-	0.40	17.6	194	0.039
Max	0.49	-	11.6	-	2243	-	5.65	-	9.57	65.1	9200	0.23
Median	0.15	-	1.20	-	394	-	1.25	-	1.33	31.3	758	0.11
Belgium												
N	28	28	28	28	28	28	28	28	28	28	-	-
Min	0.21	0.18	1.44	5.70	290	0.065	2.04	6.93	2.31	35.1	-	-
Max	2.34	1.44	18.5	104	4172	0.38	7.23	47.6	15.3	151	-	-
Median	0.68	0.49	4.47	11.9	967	0.14	3.97	14.6	4.52	77.4	-	-
Bulgaria												
N	-	213	213	213	213	-	213	212	213	213	213	-
Min	-	0.10	0.79	2.64	186	-	0.92	1.87	0.77	9.38	426	-
Max	-	5.23	57.8	281	9493	-	90.0	217	24.3	366	10394	-
Median	-	0.31	2.43	10.7	1399	-	2.99	14.8	3.88	27.9	1495	-
Bulgaria - additional data not included in maps (southern part around Plovdiv)												
N	98	98	98	98	98	-	98	98	98	98	98	98
Min	0.27	0.10	1.18	0.10	689	-	1.08	0.50	2.23	23.2	1532	0.070
Max	8.76	5.56	54.9	63.9	19370	-	29.2	368	64.5	774	43570	8.70
Median	0.98	0.30	5.66	6.87	3041	-	5.03	11.7	8.79	44.7	6978	0.29
Croatia												
N	94	94	94	94	94	94	94	94	94	94	94	94
Min	0.099	0.074	0.76	3.69	320	0.007	0.66	0.064	0.91	12.4	398	0.046
Max	5.79	1.91	32.7	22.7	12140	0.30	17.9	82.4	32.2	283	21460	1.39
Median	0.37	0.28	2.75	7.54	991	0.064	2.68	2.57	3.10	29.0	1346	0.15
Czech Republic												
N	280	280	280	280	280	282	280	280	280	280	280	280
Min	0.10	0.11	0.51	3.29	187	0.022	0.52	2.32	0.68	20.9	208	0.041
Max	1.82	1.75	4.54	10.5	2570	0.15	4.94	63.0	7.18	98.8	2862	1.73
Median	0.29	0.23	1.15	5.23	409	0.045	1.42	4.94	1.47	33.3	477	0.16
Denmark (Faroe Islands)												
N	8	8	8	8	8	-	8	8	8	8	8	-
Min	0.062	0.030	0.59	2.74	257	-	0.69	1.41	1.45	10.2	315	-
Max	0.14	0.063	1.47	7.05	1059	-	1.83	3.25	5.09	24.3	717	-
Median	0.075	0.055	0.83	3.68	401	-	0.94	2.17	2.49	16.5	372	-
Estonia												
N	-	111	111	111	111	-	111	111	111	111	-	-
Min	-	0.11	0.35	1.78	81.7	-	0.46	1.52	0.50	20.3	-	-
Max	-	0.32	2.10	6.77	912	-	1.87	5.15	3.80	51.6	-	-
Median	-	0.16	0.65	2.79	177	-	0.72	2.60	1.02	27.7	-	-
Finland												
N	267	693	693	693	693	268	693	693	693	693	693	-
Min	0.10	0.050	0.33	1.34	55.8	0.018	0.59	0.75	0.50	14.4	45.0	-
Max	0.45	0.40	11.4	20.2	2234	0.11	46.6	11.3	11.1	95.8	1514	-
Median	0.11	0.14	0.91	3.08	186	0.040	1.45	2.70	1.23	31.6	176	-

Annex 4, continued

	As	Cd	Cr	Cu	Fe	Hg	Ni	Pb	V	Zn	Al	Sb
France												
N	536	536	536	536	536	536	536	536	536	536	536	536
Min	0.070	0.025	0.19	2.23	144	0.041	0.49	1.07	0.71	7.63	148	0.13
Max	13.5	0.83	22.5	14.2	9320	0.22	18.4	60.1	21.5	143	9818	0.80
Median	0.37	0.11	2.04	5.77	713	0.084	2.21	4.41	2.36	27.8	896	0.13
FYR Macedonia												
N	72	72	72	72	72	72	72	72	72	72	72	72
Min	0.18	0.015	2.09	0.68	999	0.010	1.80	0.10	2.50	16.4	1466	0.044
Max	4.32	3.01	82.0	21.4	8130	0.42	43.1	46.6	31.9	91.3	25860	0.92
Median	0.68	0.29	6.79	6.65	2239	0.068	5.82	7.62	6.38	35.6	3600	0.15
Germany												
N	725	724	725	725	726	726	725	725	726	723	726	725
Min	0.035	0.060	0.48	3.34	113	0.016	0.35	1.19	0.31	17.2	24.5	0.050
Max	2.03	1.71	90.3	41.7	3568	0.11	9.37	40.4	6.04	426	3993	1.31
Median	0.16	0.21	2.36	7.27	328	0.035	1.16	3.69	1.09	46.7	289	0.16
Iceland												
N	138	138	138	138	-	-	138	138		138	-	-
Min	0.021	0.014	0.55	2.87	-	-	0.77	0.41		8.16	-	-
Max	0.83	0.25	36.0	42.6	-	-	24.8	37.0		110	-	-
Median	0.11	0.052	3.33	7.70	-	-	3.15	1.35		21.2	-	-
Italy (Bolzano region)												
N	20	20	20	20	20	20	20	20	20	20	-	-
Min	0.32	0.050	2.11	6.68	489	0.034	1.65	3.96	1.52	24.1	-	-
Max	0.79	0.17	6.34	16.4	1316	0.098	5.44	10.2	3.95	60.0	-	-
Median	0.46	0.12	3.41	10.9	1038	0.072	2.92	6.05	2.87	33.2	-	-
Latvia												
N	101	101	101	101	101	101	101	101	101	101	-	-
Min	0.098	0.14	0.41	3.28	88.0	0.060	0.47	2.24	0.48	26.1	-	-
Max	0.24	1.72	5.00	12.1	468	0.29	5.34	50.0	26.8	280	-	-
Median	0.11	0.24	0.79	4.64	188	0.076	0.75	3.79	1.32	40.3	-	-
Lithuania												
N	146	146	146	146	146	152	146	146	146	146	-	-
Min	0.077	0.047	0.49	2.70	65.5	0.020	0.55	2.67	0.40	6.07	-	-
Max	0.48	0.22	2.28	11.6	619	0.11	1.98	7.67	5.48	36.7	-	-
Median	0.16	0.13	1.01	5.19	183	0.050	1.01	4.64	1.18	17.7	-	-
Norway												
N	461	464	464	464	464	464	462	464	464	464	464	464
Min	0.004	0.017	0.099	1.83	50.4	0.019	0.055	0.49	0.25	8.04	58.3	0.015
Max	4.61	2.45	65.5	672	9972	0.25	1016	34.3	22.1	694	12121	0.94
Median	0.12	0.089	0.58	4.37	273	0.054	1.24	2.17	1.40	31.4	255	0.070
Poland (National parks)												
N	-	272	-	273	273	-	272	271	-	272	-	-
Min	-	0.010	-	3.34	98.3	-	0.13	0.45	-	18.4	-	-
Max	-	1.94	-	13.1	1210	-	4.63	21.3	-	124	-	-
Median	-	0.25	-	6.58	300	-	1.64	5.09	-	34.1	-	-
Poland (Opole region)												
N	30	-	30	-	30	-	30	-	30	30	30	30
Min	0.30	-	1.00	-	112	-	0.83	-	1.07	26.5	490	0.13
Max	3.12	-	10.3	-	3086	-	6.36	-	11.7	125	7406	0.68
Median	0.90	-	2.74	-	775	-	2.56	-	2.61	64.3	1237	0.36
Russian Federation (Sergiev Posad, Tula, Tver, Udmurt Republic)												
N	220	74[d]	220	76[e]	220	-	220	-	220	220	220	220
Min	0.024	0.028	0.21	3.41	25.9	-	0.43	-	0.083	11.4	78.7	0.024
Max	2.47	1.06	48.1	22.5	23490	-	22.8	-	68.5	331	12865	2.47
Median	0.23	0.24	3.64	8.94	679	-	2.74	-	2.27	40.1	850	0.23

Annex 4, continued

	As	Cd	Cr	Cu	Fe	Hg	Ni	Pb	V	Zn	Al	Sb
Serbia												
N	193	193	193	193	193	-	193	193	193	193	193	193
Min	0.22	0.040	2.00	3.04	670	-	1.70	1.03	1.94	13.2	1117	0.059
Max	21.6	1.11	78.8	451	16100	-	23.8	249	32.7	259	31180	1.37
Median	1.41	0.26	6.44	11.1	2267	-	4.43	16.7	5.76	29.0	3946	0.24
Slovakia												
N	-	77	-	77	77	77	77	77	77	77	77	-
Min	-	0.21	-	6.32	332	0.026	0.28	4.60	0.020	24.1	960	-
Max	-	1.48	-	151	6436	0.41	59.7	135	43.5	159	14720	-
Median	-	0.50	-	14.9	840	0.088	3.92	12.3	3.34	48.9	2540	-
Slovakia - additional data not included in maps (south-western part)												
N	20	20	20	20	20	20	20	20	20	20	19	20
Min	0.32	0.041	1.52	3.38	386	0.019	0.34	2.93	1.57	19.3	857	0.10
Max	8.73	0.80	8.18	12.0	3077	0.13	27.2	29.8	51.9	62.4	4802	0.45
Median	0.86	0.16	2.36	6.92	914	0.037	1.65	4.81	2.75	32.3	1684	0.21
Slovenia												
N of samples	57	56	57	57	57	57	57	56	57	57	-	56
Min	0.15	0.13	0.85	3.69	347	0.050	0.92	2.58	1.34	16.5	-	0.11
Max	1.36	1.21	10.3	44.5	4330	0.18	8.52	29.0	13.1	99.3	-	0.53
Median	0.43	0.33	2.14	8.17	943	0.095	2.75	10.1	3.38	38.6	-	0.21
Spain (Galicia and Navarra)												
N	207	207	207	207	147[f]	147[f]	207	207	207	207	-	-
Min	0.029	0.021	1.94	1.95	104	0.027	0.75	0.73	0.42	12.7	-	-
Max	6.84	0.44	35.4	21.2	1799	0.088	22.2	67.4	48.7	128	-	-
Median	0.18	0.082	6.45	6.23	352	0.050	3.72	2.31	1.46	36.9	-	-
Sweden												
N	538	538	538	538	538	-	538	538	538	538	-	-
Min	0.016	0.033	0.012	1.40	28.1	-	0.031	0.45	0.10	12.2	-	-
Max	1.28	0.61	90.7	18.9	3744	-	8.06	38.7	20.7	87.7	-	-
Median	0.065	0.14	0.61	3.56	117	-	0.61	2.15	0.87	30.6	-	-
Switzerland												
N	141	142	141	140	142	142	142	142	142	142	-	-
Min	0.053	0.049	0.33	2.70	95.4	0.016	0.50	0.84	0.21	10.1	-	-
Max	1.07	0.57	7.96	13.9	2380	0.099	7.77	31.6	3.55	179	-	-
Median	0.15	0.15	1.20	5.12	261	0.031	1.59	3.16	0.67	31.4	-	-
Turkey (European part)												
N	74	73	74	74	74	-	74	74	74	74	74	74
Min	0.16	0.090	1.33	2.99	615	-	0.79	1.78	1.53	15.2	766	0.004
Max	16.8	1.11	21.4	59.4	6448	-	20.5	48.7	22.6	126	11900	0.60
Median	1.71	0.30	4.41	6.32	1709	-	4.04	5.09	6.28	27.5	2260	0.19
Ukraine (Volyn and Sumy region)												
N	12	47	52	53	53	-	53	53	52	53	29	12
Min	0.12	0.060	0.16	2.70	162	-	0.68	3.26	0.68	12.8	196	0.12
Max	0.79	1.48	7.72	12.1	2477	-	4.87	35.6	5.02	81.3	2384	0.71
Median	0.22	0.32	1.86	7.20	450	-	1.70	7.65	2.13	36.2	625	0.23
United Kingdom												
N	170	170	170	170	-	-	170	170	170	170	170	170
Min	0.026	0.015	0.18	1.29	-	-	0.20	0.54	0.25	6.77	30.2	0.018
Max	2.99	0.54	8.97	34.3	-	-	9.31	34.4	10.6	128	1870	0.81
Median	0.12	0.093	0.82	3.58	-	-	0.78	2.59	1.16	20.0	164	0.11

[a] N = number of samples
[b] Min = minimum
[c] Max = maximum
[d] Tver
[e] Udmurt Republic
[f] Galicia