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# Mosses as biomonitors of atmospheric heavy metal deposition: Spatial patterns and temporal trends in Europe

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*Since 1990, heavy metal concentrations in mosses have declined in Europe for most metals.*

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ABSTRACT

In recent decades, mosses have been used successfully as biomonitors of atmospheric deposition of heavy metals. Since 1990, the European moss survey has been repeated at five-yearly intervals. Although spatial patterns were metal-specific, in 2005 the lowest concentrations of metals in mosses were generally found in Scandinavia, the Baltic States and northern parts of the UK; the highest concentrations were generally found in Belgium and south-eastern Europe. The recent decline in emission and subsequent deposition of heavy metals across Europe has resulted in a decrease in the heavy metal concentration in mosses for the majority of metals. Since 1990, the concentration in mosses has declined the most for arsenic, cadmium, iron, lead and vanadium (52–72%), followed by copper, nickel and zinc (20–30%), with no significant reduction being observed for mercury (12% since 1995) and chromium (2%). However, temporal trends were country-specific with sometimes increases being found.



## 1. Introduction

The heavy metals in mosses survey was originally established in 1980 as a Swedish initiative. The idea of using mosses to estimate atmospheric heavy metal deposition was developed in the late 1960s by Rühling and Tyler (1968). It is based on the fact that mosses, especially the carpet-forming species, obtain most of their nutrients directly from precipitation and dry deposition; there is little uptake of metals from the substrate. The technique of moss analysis provides an alternative, time-integrated measure

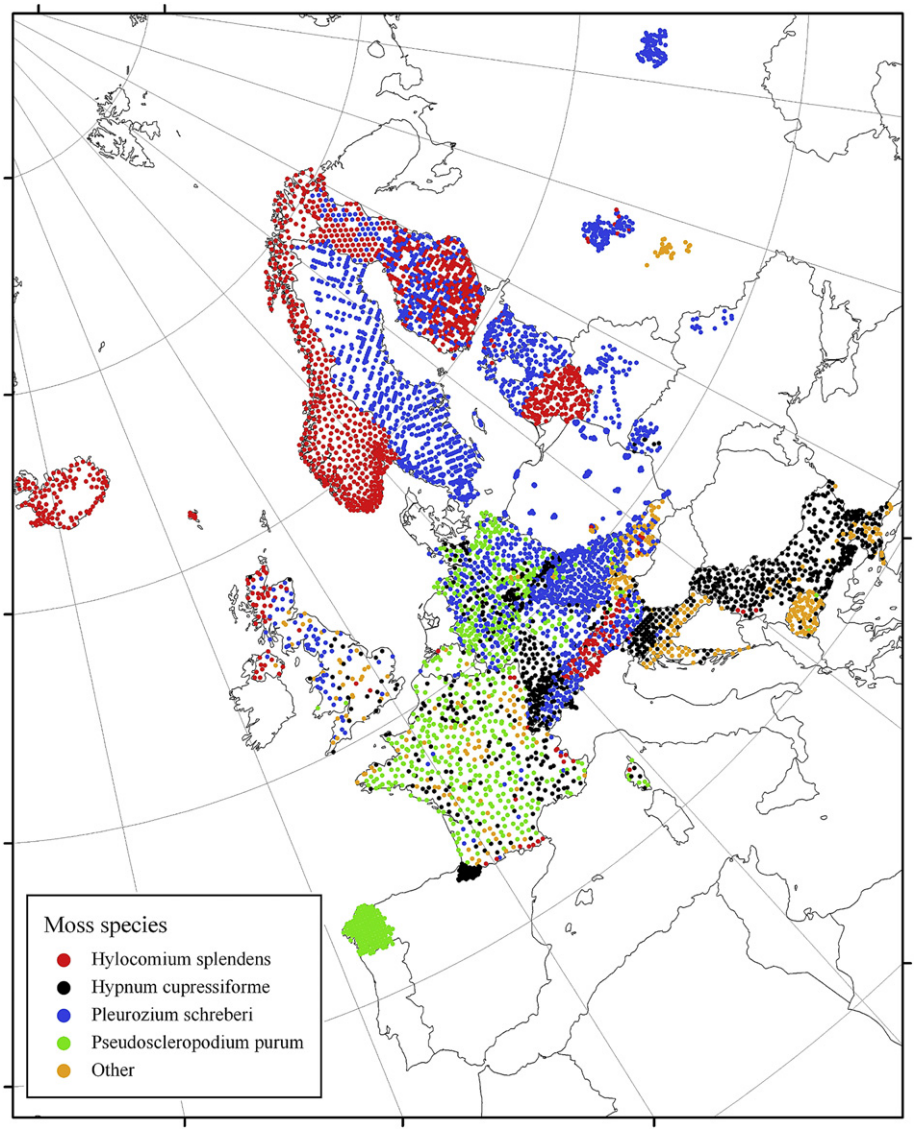


**Fig. 1.** Sampling sites and moss species collected in 2005.

**Table 1**
Analytical techniques applied in the 2005 European moss survey.

| 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[a] | 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 | – |
| 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 | – |
| 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 |

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 (see Barandovski et al., 2008).

[a] Low concentrations=ETAAS.

of the spatial patterns of heavy metal deposition from the atmosphere to terrestrial systems. It is easier and cheaper than conventional deposition analysis as it avoids the need for deploying large numbers of deposition collectors with an associated long-term programme of routine sample collection and analysis. Therefore, a much higher sampling density can be achieved than with deposition analysis (Gusev et al., 2009). Although the heavy metal concentration in mosses provides no direct quantitative measurement of deposition, this information can be derived by using regression approaches relating the results from moss surveys to deposition monitoring data (e.g. Berg and Steinnes, 1997; Berg et al., 2003). Comparison of the metal concentration in mosses with total deposition modelled across Europe using the EMEP (Co-operative programme for monitoring and evaluation of the long-range transmission of air pollutants in Europe) atmospheric transport model MSCE-HM (Travnikov and Ilyin, 2005) showed that the spatial and temporal trends are similar for Cd and Pb but less similar for Hg (Gusev et al., 2009; Harmens et al., 2009).

The European moss survey has been repeated at five-yearly intervals since 1990 (Buse et al., 2003; Rühling, 1994; Rühling and Steinnes, 1998) and the latest survey was conducted in 2005 with 28 countries participating (Harmens et al., 2008a). The European moss survey provides data on concentrations of ten heavy metals (As, Cd, Cr, Cu, Fe, Hg, Ni, Pb, V, Zn) in naturally growing mosses (Harmens et al., 2007, 2008c), and since 2005 also for the metals Al and Sb and for nitrogen (Harmens et al., 2008b). Since 2000, the European moss survey has been coordinated by the ICP Vegetation (International Cooperative Programme on Effects of Air Pollution on Natural Vegetation and Crops) Coordination Centre at the Centre for Ecology and Hydrology, Bangor, UK. The ICP Vegetation was established in 1987 and is one of seven ICPs/Task Forces of the Working Group on Effects that reports to the United Nations Economic Commission for Europe (UNECE) Long-Range Transboundary Air Pollution (LRTAP) Convention on the effects of atmospheric pollutants on the environment and human health (Working Group on Effects, 2004).

The main purpose of the survey is a) to provide, in the form of maps, spatial information on the distribution of heavy metal concentrations in mosses in Europe, b) identify main polluted areas, c) develop the understanding of long-range transboundary air pollution and d) monitor temporal trends. The contribution of various sources to emissions of heavy metals across Europe has changed in recent decades (Task Force on Heavy Metals, 2006; Ilyin et al., 2007). To date the most important emission sectors for the various metals are: metals industry (Al, As, Cr, Cu, Fe, Zn); other manufacturing industries and construction (As, Cd, Cr, Hg, Ni, Pb); electricity and heat production (As, Cd, Hg, Ni); road transportation (Cu, Sb, Pb, V, Zn); petroleum refining (Ni, V) and phosphate fertilisers in agricultural areas (Cd).

In this paper, we report on the spatial patterns in 2005 and the temporal trends since 1990 of heavy metal concentrations in mosses across Europe. As the emissions and depositions of heavy metals have declined across Europe in recent decades (Ilyin et al., 2005), we hypothesize that the concentrations of these metals in mosses have declined too. In particular we expected a marked decline in the Pb concentrations in mosses due to the introduction of unleaded petrol. The reduction in Hg concentrations is likely to be lower due to the lower reduction in emissions and hemispheric transport of Hg across the globe.

## 2. Materials and methods

### 2.1. Moss sampling

Moss samples were collected across Europe in 1990/1 (Rühling, 1994), 1995/6 (Rühling and Steinnes, 1998), 2000/1 (Buse et al., 2003) and 2005/6 (Harmens et al., 2008a). Throughout the paper we refer to the years of moss survey as 1990, 1995, 2000 and 2005 respectively. Because the mosses were collected in a range of habitats from the sub-arctic climate of northern Scandinavia to the hot and dry climate of southern Europe, it was inevitable that several carpet-forming moss species were sampled. Fig. 1 shows the moss sampling sites across Europe in 2005. *Pleurozium schreberi* was the most frequently sampled species, accounting for 40.9% of the samples, followed by *Hylocomium splendens* (22.7%), *Hypnum cupressiforme* (18.0%) and *Pseudoscleropodium purum* (11.9%); other species constituted only 6.5% of the mosses sampled (Fig. 1). The moss sampling procedure was according to the guidelines described in the protocol for the 2005 survey (ICP Vegetation, 2005). Only the last three years' growth of moss material was used for the analyses.

### 2.2. Heavy metal determination

In 2005, the concentration of heavy metals were determined by a range of analytical techniques (Table 1). For details on the applied analytical methods in previous years, we refer to the reports of the individual surveys (Buse et al., 2003; Rühling, 1994; Rühling and Steinnes, 1998). All metal concentrations were expressed as mg $kg^{-1}$ dry weight at 40 °C.

### 2.3. Quality assurance

As in 1995 (Steinnes et al., 1997), a quality control exercise was conducted in 2005 (Harmens et al., 2008a) for assessing the analytical performance of the participating laboratories. Moss reference material M2, containing elevated concentrations for most metals, and M3, containing background concentrations for most metals (Steinnes et al., 1997), were distributed amongst participating 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 considered the case when the values were outside the range of two standard deviations (as determined for the 2005 survey) from the mean recommended value for reference material M2 and/or M3 (Steinnes et al., 1997). Correction factors were applied when both M2 and M3 values were outliers for a specific metal, and sometimes corrections factors were also applied when only one reference value was identified as an outlier. Although applying correction factors enhanced compatibility of data between countries, it hardly affected the overall European mean and median values for the elements. As a consequence, it did not significantly affect the temporal trends reported for the whole of Europe.

In 2005, the mean values of M2 and M3 were generally in good agreement with the recommended values (Steinnes et al., 1997) and ranged from 91% (As) to 103% (Pb) of the recommended values for M2 and from 92% (Cr) to 117% (Hg) of the recommended values for M3. However, for Sb the mean value was only 83–88% of the previously recommended values for M2 and M3, therefore the recommended value for Sb was revised based on the data for both the 1995 and 2005 survey (Table 2). In addition, the recommended value for Ca was revised and a recommended value was established for N for the first time. Indicated values for M2 and M3 were also revised for Br and Cl and established for Bi, Nd and Pr. Recommended values were established when at least two analytical techniques based on different physical principles showed a good agreement, whereas indicated values refer to two or more laboratories obtaining similar values using the same analytical technique (Steinnes et al., 1997).

### 2.4. Mapping

EMEP maps were produced according to the method described by Harmens et al. (2008a); they show the mean concentration of each metal within individual EMEP grid squares (50 km × 50 km). Please note that the designations employed and the presentation of material in this paper do not imply the expression of any opinion whatsoever on the part of the United Nations concerning the legal status of any country, territory, city or area or of its authorities, or concerning the delimitation of its frontiers or boundaries.

### 2.5. Statistical analysis

Statistical analysis of the temporal trends across Europe was performed by calculating the geometric mean values per metal and survey year for each country. Subsequently, a general linear model ANOVA (Minitab version 15) was applied to each metal using only the geometric mean values for the countries which had determined the heavy metal concentration in mosses in all survey years for that metal. The geometric mean values were analysed with country as a factor, year as covariate and the number of samples as weights. Weighting was applied to take into account the accuracy of the calculated geometric means (i.e. the density of sampling varied between countries; see Fig. 1) and to give more weight to larger countries and less to smaller ones. For each metal, pairwise comparisons between years were conducted by applying the Tukey method.

**Table 2**
New and revised recommended and indicated values for the concentrations of elements (mg $kg^{-1}$) in moss reference material M2 and M3 (Steinnes et al., 1997). Values are mean ± one standard deviation; $N$ = number of samples.

| Element | M2 | M3 | |
|---|---|---|---|
| *Recommended values* | | | |
| Antimony (revised) | 0.185 ± 0.020 | 0.043 ± 0.004 | |
| | 12 | 9 | N |
| | 0.173 | 0.036 | GFAAS[a] |
| | 0.179 | 0.044 | ICP-MS[b] |
| | 0.204 | 0.044 | INAA[c] |
| Calcium (revised) | 2050 ± 160 | 2140 ± 200 | |
| | 11 | 11 | N |
| | 1860 | 1870 | FAAS[d] |
| | 2050 | 2180 | ICP-ES[e] |
| | 2070 | 2240 | ICP-MS |
| | 2150 | 2200 | INAA |
| Nitrogen (new) | 8360 ± 620 | 6810 ± 520 | |
| | 10 | 8 | N |
| | 8440 | 6990 | Dry[f] |
| | 8260 | 6710 | Wet[g] |
| *Indicated values* | | | |
| Bismuth (new) | 0.126 ± 0.014 | 0.015 ± 0.001 | ICP-MS |
| | 2 | 2 | N |
| Bromine (revised) | 110 ± 11 | 124 ± 12 | INAA |
| | 3 | 3 | N |
| Chlorine (revised) | 110 ± 5 | 65 ± 2 | INAA |
| | 2 | 2 | N |
| Neodymium (new) | 0.161 ± 0.04 | 0.098 ± 0.002 | ICP-MS |
| | 2 | 2 | N |
| Praseodymium (new) | 0.042 ± 0.002 | 0.027 ± 0.002 | ICP-MS |
| | 2 | 2 | N |

[a] GFAAS, Graphite furnace atomic absorption spectrometry.
[b] ICP-MS, Inductively coupled plasma mass spectrometry.
[c] INAA, Instrumental neutron activation analysis.
[d] FAAS, Flame atomic absorption spectrometry.
[e] ICP-ES, Inductively coupled plasma emission spectrometry.
[f] Wet, Wet ashing (Kjehldahl method).
[g] Dry, Dry ashing (Dumas method).

## 3. Results and discussion

### 3.1. Spatial patterns in 2005

In 2005, 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 (Table 3, Figs. 2–6). Relatively low concentrations of Fe, Hg, Ni and V were also observed in central Europe. The highest concentrations were often found in Belgium and south-eastern European countries. High concentrations of the more global pollutant Hg were detected in mosses in Belgium, France, Latvia, Slovakia and Slovenia. Relatively high concentrations of Al, As, Cr, Fe, Ni and V were found in eastern and southern France. This resulted in cross-border gradients with Germany and Switzerland for these metals, apart for Cr. Sb concentrations were generally high in densely populated areas (e.g. central and south-eastern United Kingdom, central Europe, north-western France and southern Norway around Oslo) and in many south-eastern European countries with high levels of metal pollution.

**Table 3**
Median concentration (mg kg$^{-1}$) and standard deviation (Stdev; mg kg$^{-1}$) of heavy metals in mosses and number of samples per country in 2005.

| Country | Parameter | As | Cd | Cr | Cu | Fe | Hg | Ni | Pb | V | Zn | Al | Sb | Number |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Austria | Median | 0.18 | 0.18 | 1.06 | 5.10 | 300 | 0.051 | 1.00 | 3.70 | 0.95 | 29.0 | 333 | 0.16 | 212 |
| | Stdev | 0.48 | 0.16 | 0.94 | 2.50 | 356 | 0.024 | 0.95 | 2.56 | 1.19 | 11.1 | 369 | 0.075 | |
| Belarus[a] | Median | 0.15 | – | 1.20 | – | 394 | – | 1.25 | – | 1.33 | 31.3 | 758 | 0.11 | 58 |
| | Stdev | 0.092 | – | 1.69 | – | 303 | – | 1.07 | – | 1.24 | 8.52 | 1234 | 0.040 | |
| Belgium | Median | 0.68 | 0.49 | 4.47 | 11.9 | 967 | 0.14 | 3.97 | 14.6 | 4.52 | 77.4 | – | – | 28 |
| | Stdev | 0.58 | 0.26 | 3.23 | 18.4 | 883 | 0.076 | 1.48 | 9.48 | 3.51 | 29.2 | – | – | |
| Bulgaria | Median | – | 0.31 | 2.43 | 10.7 | 1399 | – | 2.99 | 14.8 | 3.88 | 27.9 | 1495 | – | 212–213 |
| | Stdev | – | 0.57 | 6.32 | 21.6 | 1446 | – | 8.86 | 23.6 | 3.24 | 38.9 | 1393 | – | |
| Croatia | Median | 0.37 | 0.28 | 2.75 | 7.54 | 991 | 0.064 | 2.68 | 2.57 | 3.10 | 29.0 | 1346 | 0.15 | 94 |
| | Stdev | 0.79 | 0.23 | 5.38 | 4.42 | 1970 | 0.039 | 2.83 | 9.88 | 4.98 | 30.1 | 3322 | 0.16 | |
| Czech Republic | Median | 0.29 | 0.23 | 1.15 | 5.23 | 409 | 0.045 | 1.42 | 4.94 | 1.47 | 33.3 | 477 | 0.16 | 280 |
| | Stdev | 0.19 | 0.19 | 0.55 | 1.16 | 256 | 0.016 | 0.55 | 4.70 | 0.72 | 12.0 | 268 | 0.11 | |
| Estonia | Median | – | 0.16 | 0.65 | 2.79 | 177 | – | 0.72 | 2.60 | 1.02 | 27.7 | – | – | 111 |
| | Stdev | – | 0.039 | 0.27 | 0.69 | 129 | – | 0.24 | 0.80 | 0.48 | 5.79 | – | – | |
| Faroe Islands[b] | Median | 0.075 | 0.055 | 0.83 | 3.68 | 401 | – | 0.94 | 2.17 | 2.49 | 16.5 | 372 | – | 8 |
| | Stdev | 0.029 | 0.012 | 0.28 | 1.55 | 290 | – | 0.42 | 0.67 | 1.44 | 5.19 | 154 | – | |
| Finland | Median | 0.11 | 0.14 | 0.91 | 3.08 | 186 | 0.040 | 1.45 | 2.70 | 1.23 | 31.6 | 176 | – | 693[i] |
| | Stdev | 0.062 | 0.047 | 0.88 | 1.49 | 174 | 0.017 | 2.56 | 1.22 | 0.91 | 8.62 | 128 | – | |
| France | Median | 0.37 | 0.11 | 2.04 | 5.77 | 713 | 0.084 | 2.21 | 4.41 | 2.36 | 27.8 | 896 | 0.13 | 536 |
| | Stdev | 0.96 | 0.093 | 2.24 | 2.09 | 1116 | 0.029 | 1.86 | 4.50 | 2.53 | 14.6 | 1351 | 0.067 | |
| FYR Macedonia | Median | 0.68 | 0.29 | 6.79 | 6.65 | 2239 | 0.068 | 5.82 | 7.62 | 6.38 | 35.6 | 3600 | 0.15 | 72 |
| | Stdev | 0.61 | 0.47 | 12.7 | 4.01 | 1608 | 0.072 | 9.00 | 8.71 | 5.99 | 16.4 | 3988 | 0.13 | |
| Germany | Median | 0.16 | 0.21 | 2.36 | 7.27 | 328 | 0.035 | 1.16 | 3.69 | 1.09 | 46.7 | 289 | 0.16 | 723–726 |
| | Stdev | 0.20 | 0.14 | 5.10 | 2.89 | 302 | 0.015 | 0.78 | 3.33 | 0.60 | 27.6 | 315 | 0.096 | |
| Iceland | Median | 0.11 | 0.052 | 3.33 | 7.70 | – | – | 3.15 | 1.35 | – | 21.2 | – | – | 138 |
| | Stdev | 0.13 | 0.040 | 5.31 | 7.00 | 4697 | – | 4.57 | 3.74 | 14.45 | 13.7 | – | – | |
| Italy[c] | Median | 0.46 | 0.12 | 3.41 | 10.9 | 1038 | 0.072 | 2.92 | 6.05 | 2.87 | 33.2 | – | – | 20 |
| | Stdev | 0.12 | 0.031 | 1.26 | 2.96 | 230 | 0.015 | 0.95 | 1.85 | 0.67 | 9.40 | – | – | |
| Latvia | Median | 0.11 | 0.24 | 0.79 | 4.64 | 188 | 0.076 | 0.75 | 3.79 | 1.32 | 40.3 | – | – | 101 |
| | Stdev | 0.039 | 0.16 | 0.48 | 1.35 | 79 | 0.049 | 0.57 | 4.68 | 3.06 | 25.2 | – | – | |
| Lithuania | Median | 0.16 | 0.13 | 1.01 | 5.19 | 183 | 0.050 | 1.01 | 4.64 | 1.18 | 17.7 | – | – | 146[j] |
| | Stdev | 0.061 | 0.031 | 0.38 | 1.61 | 107 | 0.017 | 0.28 | 1.07 | 0.73 | 4.92 | – | – | |
| Norway | Median | 0.12 | 0.089 | 0.58 | 4.37 | 273 | 0.054 | 1.24 | 2.17 | 1.40 | 31.4 | 255 | 0.070 | 461–464 |
| | Stdev | 0.28 | 0.15 | 3.37 | 33.2 | 693 | 0.024 | 50.6 | 3.13 | 1.69 | 38.2 | 834 | 0.10 | |
| Poland – NP[d] | Median | – | 0.25 | – | 6.58 | 300 | – | 1.64 | 5.09 | – | 34.1 | – | – | 271–273 |
| | Stdev | – | 0.25 | – | 1.70 | 190 | – | 0.86 | 4.05 | – | 15.0 | – | – | |
| OR[d] | Median | 0.90 | – | 2.74 | – | 775 | – | 2.56 | – | 2.61 | 64.3 | 1237 | 0.36 | 30 |
| | Stdev | 0.57 | – | 2.12 | – | 597 | – | 1.15 | – | 1.94 | 23.5 | 1271 | 0.12 | |
| Russian Federation[e] | Median | 0.23 | 0.24 | 3.64 | 8.94 | 679 | – | 2.74 | – | 2.27 | 40.1 | 850 | 0.12 | 220[k] |
| | Stdev | 0.26 | 0.20 | 5.85 | 4.47 | 2080 | – | 3.37 | – | 5.82 | 33.3 | 1660 | 0.13 | |
| Serbia | Median | 1.41 | 0.26 | 6.44 | 11.1 | 2267 | – | 4.43 | 16.7 | 5.76 | 29.0 | 3946 | 0.24 | 193 |
| | Stdev | 2.42 | 0.22 | 10.2 | 38.8 | 2671 | – | 3.58 | 20.5 | 5.67 | 22.8 | 5046 | 0.20 | |
| Slovakia | Median | – | 0.50 | – | 14.9 | 840 | 0.088 | 3.92 | 12.3 | 3.34 | 48.9 | 2540 | – | 77 |
| | Stdev | – | 0.24 | – | 16.3 | 1114 | 0.071 | 6.93 | 19.3 | 5.31 | 19.7 | 2572 | – | |
| Slovenia | Median | 0.43 | 0.33 | 2.14 | 8.17 | 943 | 0.095 | 2.75 | 10.1 | 3.38 | 38.6 | – | 0.21 | 56–57 |
| | Stdev | 0.28 | 0.24 | 1.61 | 5.75 | 605 | 0.031 | 1.79 | 6.68 | 2.06 | 18.4 | – | 0.084 | |
| Spain[f] | Median | 0.18 | 0.082 | 6.45 | 6.23 | 352 | 0.050 | 3.72 | 2.31 | 1.46 | 36.9 | – | – | 207[l] |
| | Stdev | 0.78 | 0.069 | 5.98 | 2.86 | 295 | 0.012 | 2.67 | 6.23 | 3.82 | 16.3 | – | – | |
| Sweden | Median | 0.065 | 0.14 | 0.61 | 3.56 | 117 | – | 0.61 | 2.15 | 0.87 | 30.6 | – | – | 538 |
| | Stdev | 0.077 | 0.067 | 3.97 | 1.52 | 203 | – | 0.55 | 2.10 | 1.04 | 10.6 | – | – | |
| Switzerland | Median | 0.15 | 0.15 | 1.20 | 5.12 | 261 | 0.031 | 1.59 | 3.16 | 0.67 | 31.4 | – | – | 140–142 |
| | Stdev | 0.13 | 0.10 | 1.13 | 2.00 | 302 | 0.014 | 1.22 | 4.08 | 0.65 | 18.0 | – | – | |
| Turkey[g] | Median | 1.71 | 0.30 | 4.41 | 6.32 | 1709 | – | 4.04 | 5.09 | 6.28 | 27.5 | 2260 | 0.19 | 73–74 |
| | Stdev | 3.56 | 0.21 | 4.55 | 7.41 | 1259 | – | 4.08 | 6.06 | 4.14 | 18.4 | 2289 | 0.11 | |
| Ukraine[h] | Median | 0.22 | 0.32 | 1.86 | 7.20 | 450 | – | 1.70 | 7.65 | 2.13 | 36.2 | 625 | 0.23 | 47–53[m] |
| | Stdev | 0.19 | 0.26 | 1.31 | 2.19 | 408 | – | 0.80 | 5.68 | 0.82 | 12.1 | 400 | 0.16 | |
| United Kingdom | Median | 0.12 | 0.093 | 0.82 | 3.58 | – | – | 0.78 | 2.59 | 1.16 | 20.0 | 164 | 0.11 | 170 |
| | Stdev | 0.40 | 0.098 | 0.84 | 3.33 | – | – | 0.97 | 4.64 | 1.32 | 17.1 | 250 | 0.12 | |

[a] Western part and around Minsk.
[b] Part of the Kingdom of Denmark.
[c] Bolzano region.
[d] NP – National Parks, OR – Opole Region.
[e] Sergiev Posad, Tula, Tver, Udmurt Republic.
[f] Galicia and Navarra.
[g] European part.
[h] Volyn and Sumy region.
[i] $N = 267$ and 268 for As and Hg respectively.
[j] $N = 152$ for Hg.
[k] $N = 74$ and 76 for Cd (Tver) and Cu (Udmurt Republic) respectively.
[l] $N = 147$ for Fe and Hg (Galicia).
[m] $N = 12$ for As, Sb and $N = 49$ for Al.

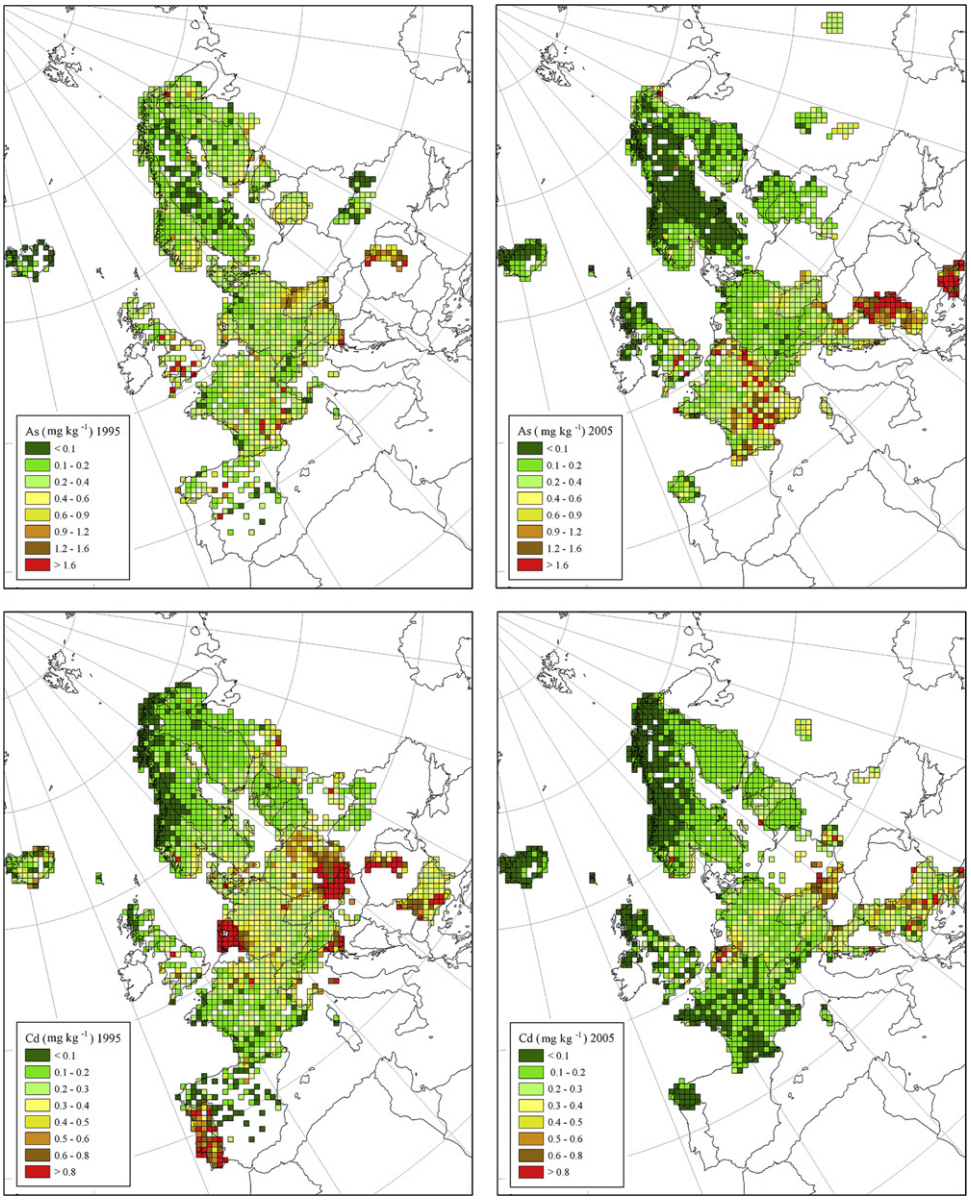


**Fig. 2.** The mean concentration of arsenic (top) and cadmium (bottom) in mosses per EMEP grid square (50 km × 50 km) in 1995 (left) and 2005 (right).

Within Europe and the LRTAP Convention, deposition of the heavy metals Cd, Hg and Pb is modelled using the EMEP atmospheric transport model MSCE-HM (Travnikov and Ilyin, 2005). The modelled data are verified against concentrations in air and precipitation measured at EMEP monitoring stations. However, the number of EMEP monitoring stations and their spatial distribution across Europe is limited. For Cd and Pb there were 66 measurement sites in 2006 and 2007, of which only 29 measured the metals in both air and precipitation (Aas and Breivik, 2009). In 2006 and 2007, there were 16 and 22 sites respectively measuring at least one form of Hg. The EMEP monitoring network for Cd and Pb is scarce or absent in southern and eastern Europe, whereas Hg is primarily measured in northern Europe. Compared to the data from the EMEP monitoring network, the moss survey has three advantages: i) the density of the moss monitoring network is much higher, ii) their spatial distribution is wider, including parts of southern and eastern Europe (Fig. 1) and iii) spatial and temporal trends are determined for more metals. Although deposition fluxes of heavy metals and their concentrations in mosses cannot be compared directly, it is possible to compare the spatial distribution of deposition and concentrations in mosses.

In 2005, the spatial patterns of Cd and Pb concentrations in mosses and EMEP modelled total deposition agreed reasonably well, i.e. regions with higher total deposition had generally higher concentrations in mosses and vice versa. For Hg, the spatial patterns showed less similarity (Gusev et al., 2009; Harmens et al., 2009). In 2000, correlations between concentration in mosses and atmospheric deposition fluxes for Pb were highest when restricted to areas suited for the EMEP task, that is with background concentrations of atmospheric deposition not being affected by local pollution sources but primarily by long-range transport such as in Scandinavia (Ilyin and Travnikov, 2005). Detailed statistical analysis of the factors affecting heavy metal concentration in mosses confirmed that EMEP modelled heavy metal deposition was the main predictor for concentrations in mosses for Cd and Pb. In 2005, for these two metals bivariate correlations were the highest

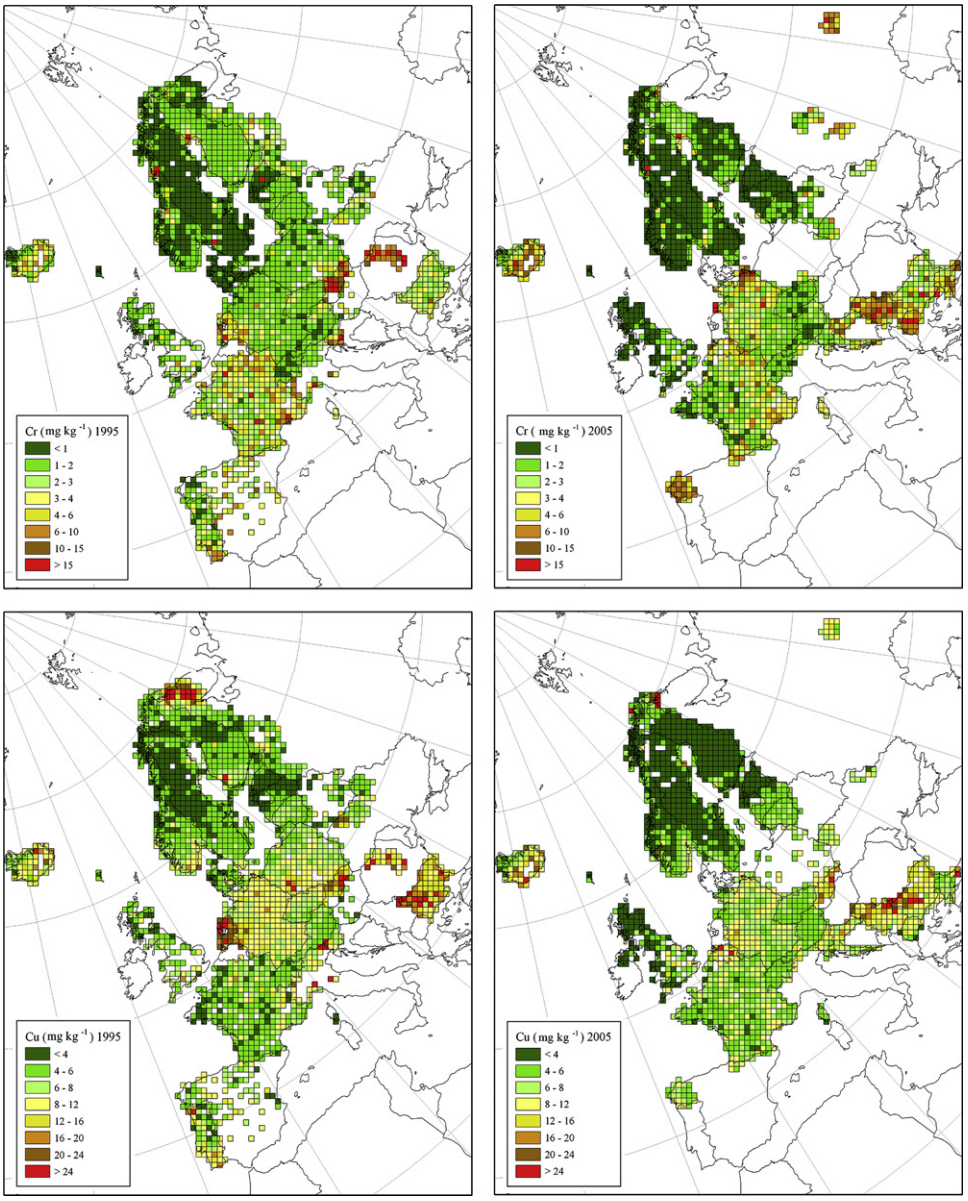


**Fig. 3.** The mean concentration of chromium (top) and copper (bottom) in mosses per EMEP grid square (50 km × 50 km) in 1995 (left) and 2005 (right).

for EMEP modelled depositions ($r = 0.63–0.73$) compared to any other predictor such as altitude, distance to the sea, land use and moss species (Holy et al., in press; Schröder et al., in press). Bivariate correlations for Hg were low ($r = 0.17–0.20$) and of a similar order of magnitude as for some of the other predictors such as precipitation and agricultural and urban land use. The sampled moss species was the main predictor for the Hg concentration in mosses in 2005.

As Hg in ambient air is predominantly found in the vapour phase and has a residence time of the order of one year it has to be considered as a global pollutant (Schroeder and Munthe, 1998) without distinct spatial deposition patterns. The lack of correlation between modelled deposition values for Hg and observed concentrations in moss may relate to the specific chemistry of Hg and corresponding interactions with the moss. In Scandinavia the Hg deposition as measured by precipitation analysis showed a steep increase from north to south (Iverfeldt, 1991), similar to that of other metals predominantly supplied by long-range atmospheric transport. In moss collected in Norway during the same period, however, the Hg level was fairly uniform with no distinct north-south gradient (Steinnes and Andersson, 1991). This geographical distribution of Hg has been confirmed in more recent moss surveys (Steinnes et al., 2003), and indicates that wet deposition of $Hg^{2+}$ alone cannot be responsible for the geographical distribution observed. The moss must also be able to retain dry deposited gaseous $Hg^0$ to a significant extent. Indeed, several studies have shown the importance of dry deposited gaseous $Hg^0$ to Hg concentrations in vegetation (De Temmerman et al., 2007, 2009; Lodenius et al., 2003). In addition, Arctic Mercury Depletion Events (Schroeder et al., 1998) might be contributing to the Hg deposition in the north of Europe and possibly explain part of the elevated Hg concentrations observed in moss in northern Norway (Berg et al., 2008). It might well be that the deposition pattern depicted by the moss survey is a better measure of the net Hg supply to the terrestrial ecosystem than that indicated by EMEP modelled calculations.

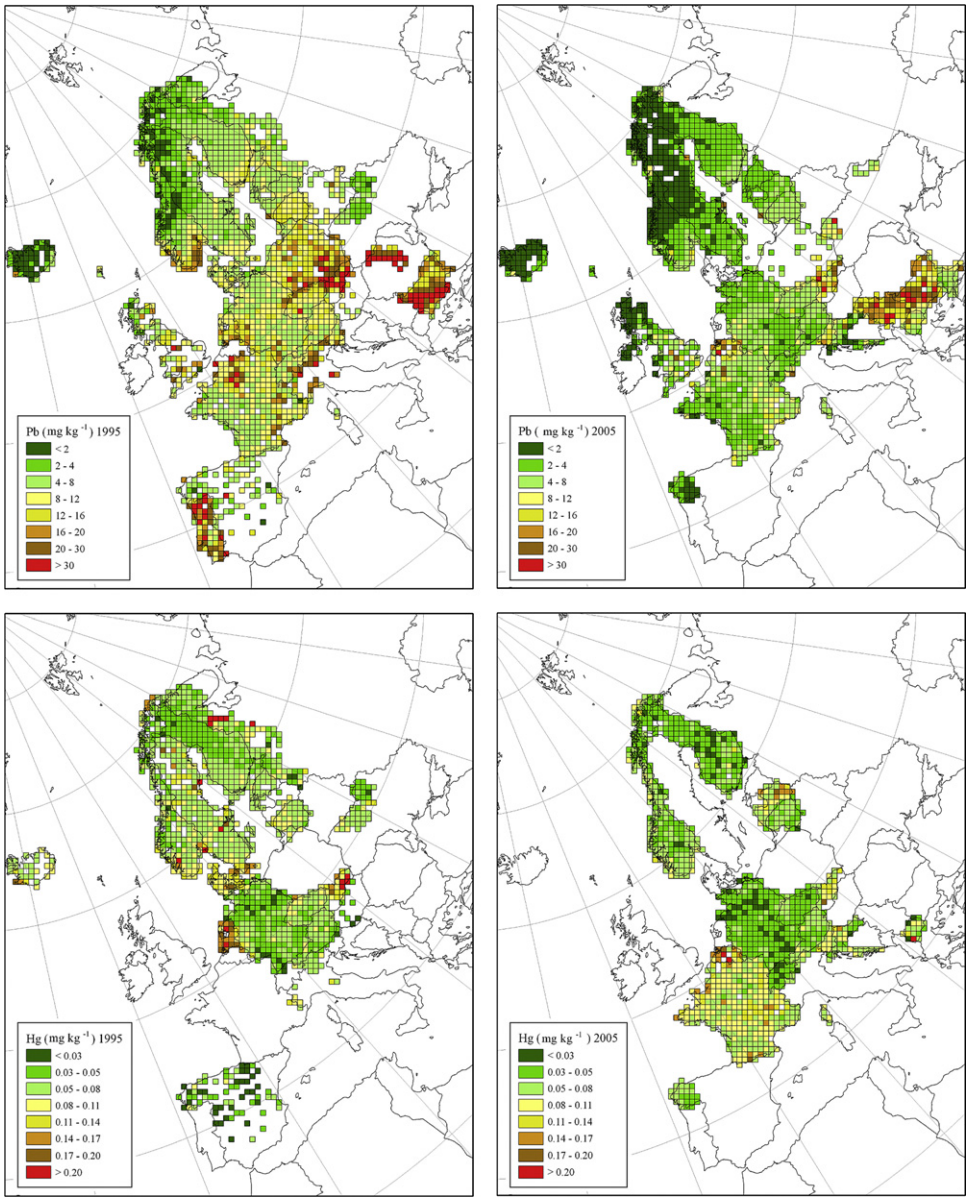


**Fig. 4.** The mean concentration of lead (top) and mercury (bottom) in mosses per EMEP grid square (50 km × 50 km) in 1995 (left) and 2005 (right).

For the first time in the European moss survey, Al and Sb concentrations in mosses were determined in 2005. Away from local pollution sources, Al 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 (Fig. 6). For some metals, this might explain the higher concentration in mosses in certain regions of Europe, for example, the high concentrations of As, Cr, Fe, Ni and V in eastern and southern compared with western parts of France. Strong linear relationships were found between the Al and Fe ($R^2 = 0.62$), Al and V ($R^2 = 0.66$) and Fe and V ($R^2 = 0.69$) concentrations in mosses. However, 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 Al and V 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 very low for mercury within the EMEP area (Ilyin et al., 2007). In south-eastern Europe anthropogenic activities might contribute considerably to the high Al concentration in mosses.

There is a growing use of Sb in automobile brake pads, plastics and flame retardants. At present, the brake pads in cars are thought to be the main source of atmospheric Sb, whereas the contribution from other sources such as coal burning, metallurgy and waste incineration is less obvious than in 1990. Recently, Sb was reported to be the single most highly enriched element in urban dust (Shotyk et al., 2004). In 2005, the lowest Sb concentrations in mosses were generally observed in areas with a low population density, such as middle and northern Norway and Scotland (Fig. 6). Considerable Sb concentrations were found in the midlands and south-eastern parts of the United Kingdom, southern Norway,

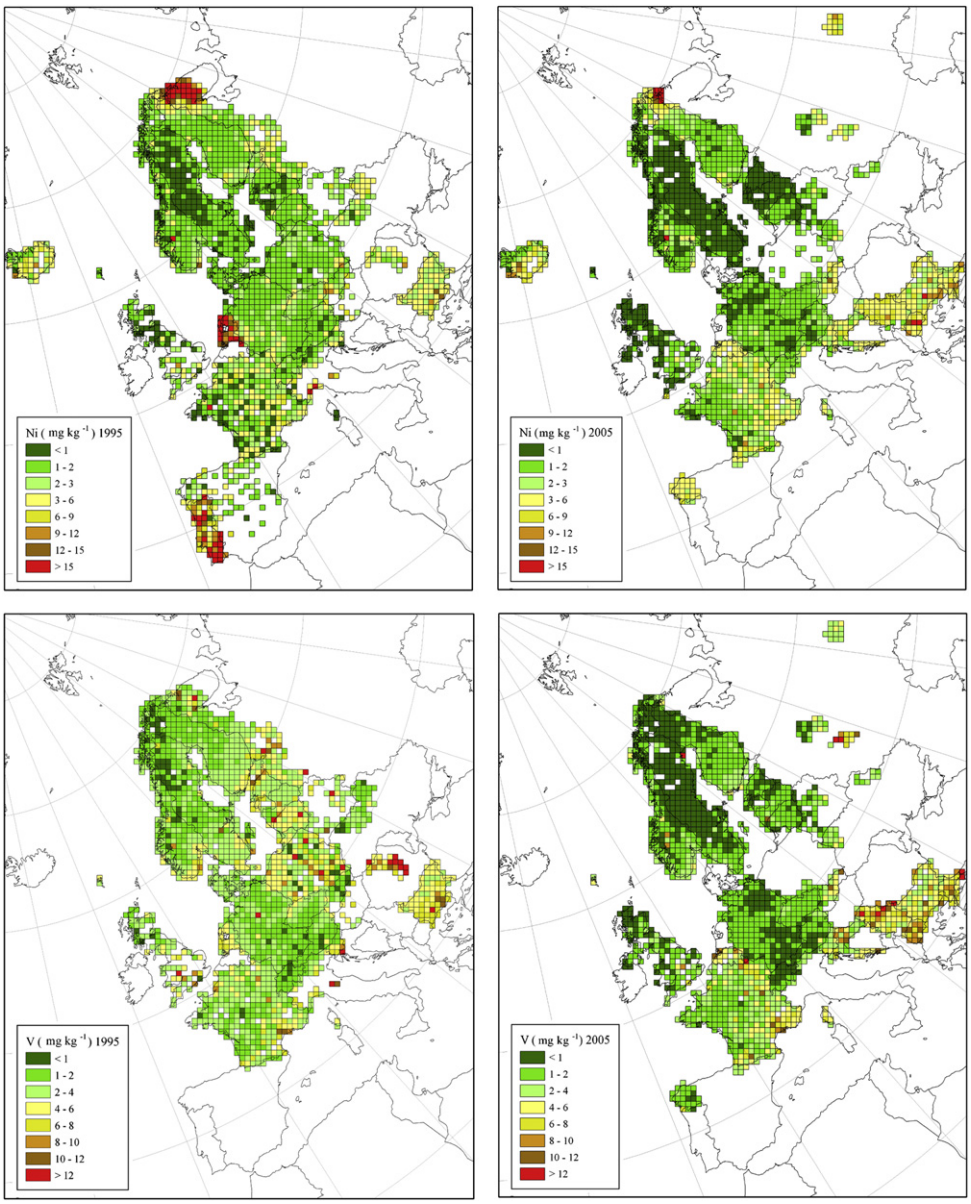


**Fig. 5.** The mean concentration of nickel (top) and vanadium (bottom) in mosses per EMEP grid square (50 km × 50 km) in 1995 (left) and 2005 (right).

north-western France and central (e.g. the Ruhr Valley in Germany) and south-eastern Europe.

### 3.2. Quality assurance of the 2005 data

The data reported for the moss reference material in 2005 confirmed the previously recommended values (Steinnes et al., 1997) for most of the elements, in which case no adjustment of the previously established values was required. Only minor adjustments were required for Sb and Ca and a recommended value for N was established for the first time (Table 2). The list of element with indicated values was extended with Cl, Br, Pr, Nd and Bi. As the majority of participating laboratories used strong nitric acid for sample decomposition, the recommended and indicated values are limited to analytical techniques deploying this wet digestion method. It is inevitable that techniques such as instrumental neutron activation analysis (INAA) based on the total determination of elements yield higher values for some elements (Steinnes et al., 1997). As only one laboratory applied INAA in 2005 and a small number of laboratories applied this technique in 1995, the data for INAA were too scarce to make a proper comparison between values obtained by INAA and other techniques following strong nitric acid digestion of samples. Smodiš and Bleise (2007) conducted a quality control study in 17 laboratories from 15 countries using the moss reference material M2 and M3. Their study revealed higher values for INAA or after nitric acid including hydrofluoric acid sample dissolution (i.e. total determination of elements) for elements such as Al, Cr and Fe, in particular for M2, the reference with elevated concentrations of heavy metals. However, no statistically significant differences were found between destructive and non-destructive analytical techniques for any of the elements. The higher values for Cr only applied to M2. High standard deviation in both the recommended values (Steinnes et al., 1997) and the data reported by Smodiš and Bleise (2007) indicate that considerable uncertainties are associated with the data for Cr. In areas with elevated concentrations of Cr (above ca. 1 mg $kg^{-1}$) in countries not

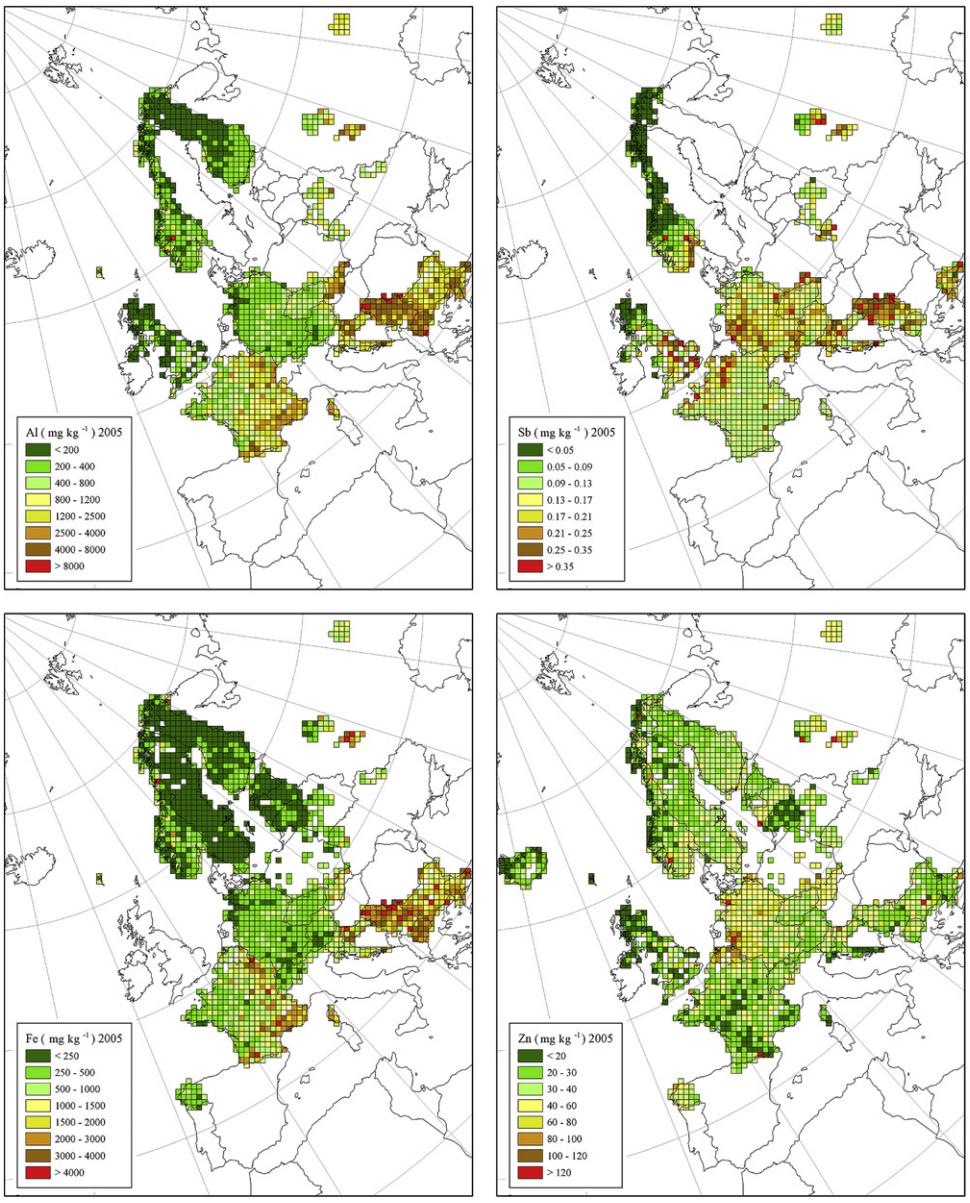


**Fig. 6.** The mean concentration of aluminium (top left), antimony (top right), iron (bottom left) and zinc (bottom right) in mosses per EMEP grid square (50 km × 50 km) in 2005.

applying INAA, it's likely that the Cr concentration in moss samples is underestimated. In other words, part of the higher Cr concentrations in mosses in 2005 in Belarus, Croatia, the Former Yugoslavic Republic of Macedonia, Poland – Opole Region, the Russian Federation and Serbia might be explained by the application of INAA as an analytical technique. The same appears to be true for Al.

The relatively high concentrations of Al, As, Cr, Fe, Ni and V in eastern and southern France compared to the rest of France and neighbouring countries to the west might indicate the accumulation of a relatively high proportion of wind-blown dust in these areas in 2005. Cross-border calibration studies via an exchange of moss samples between the laboratories in France and Belgium (all Swiss samples were analysed in Belgium) and the laboratories in France and Germany indicated that the cross-border gradient for the above elements were generally not due to the analysis of samples in different laboratories. In addition, the values from the French laboratory were not significantly different from the recommended values of the moss reference material for the majority

**Table 4**
Average geometric mean values of heavy metal concentrations in mosses for countries that analysed these metals in all survey years. The statistical significance (*P*-value) of survey year is also shown; for each metal, different letters indicate significant differences (at $P = 0.05$) between years.

| Metal (no. of countries) | Average geometric mean (mg kg$^{-1}$) | | | | *P*-value |
|---|---|---|---|---|---|
| | 1990[a] | 1995 | 2000 | 2005 | Year |
| As (15) | – | 0.26$^{a}$ | 0.22$^{b}$ | 0.21$^{b}$ | 0.001 |
| Cd (16) | 0.36$^{a}$ | 0.29$^{a}$ | 0.20$^{b}$ | 0.18$^{b}$ | 0.000 |
| Cr (14) | 1.83$^{a}$ | 1.47$^{a}$ | 1.82$^{a}$ | 1.81$^{a}$ | 0.688 |
| Cu (16) | 7.52$^{a}$ | 7.04$^{a}$ | 6.19$^{b}$ | 6.25$^{b}$ | 0.000 |
| Fe (13) | 677$^{a}$ | 503$^{b}$ | 544$^{b}$ | 373$^{b}$ | 0.000 |
| Hg (8) | – | 0.061$^{a}$ | 0.055$^{a}$ | 0.055$^{a}$ | 0.295 |
| Ni (16) | 2.17$^{a}$ | 1.81$^{ab}$ | 2.00$^{ab}$ | 1.74$^{b}$ | 0.000 |
| Pb (16) | 14.7$^{a}$ | 8.75$^{b}$ | 6.29$^{c}$ | 4.19$^{c}$ | 0.000 |
| V (10) | 3.02$^{a}$ | 2.51$^{b}$ | 1.62$^{c}$ | 1.15$^{c}$ | 0.000 |
| Zn (16) | 46.7$^{a}$ | 39.0$^{a}$ | 36.3$^{b}$ | 33.0$^{b}$ | 0.000 |

[a] For As and Hg statistical analysis of the changes with time were determined for the period 1995–2005 as in 1990 only five and two countries had determined the As and Hg concentration in mosses respectively.

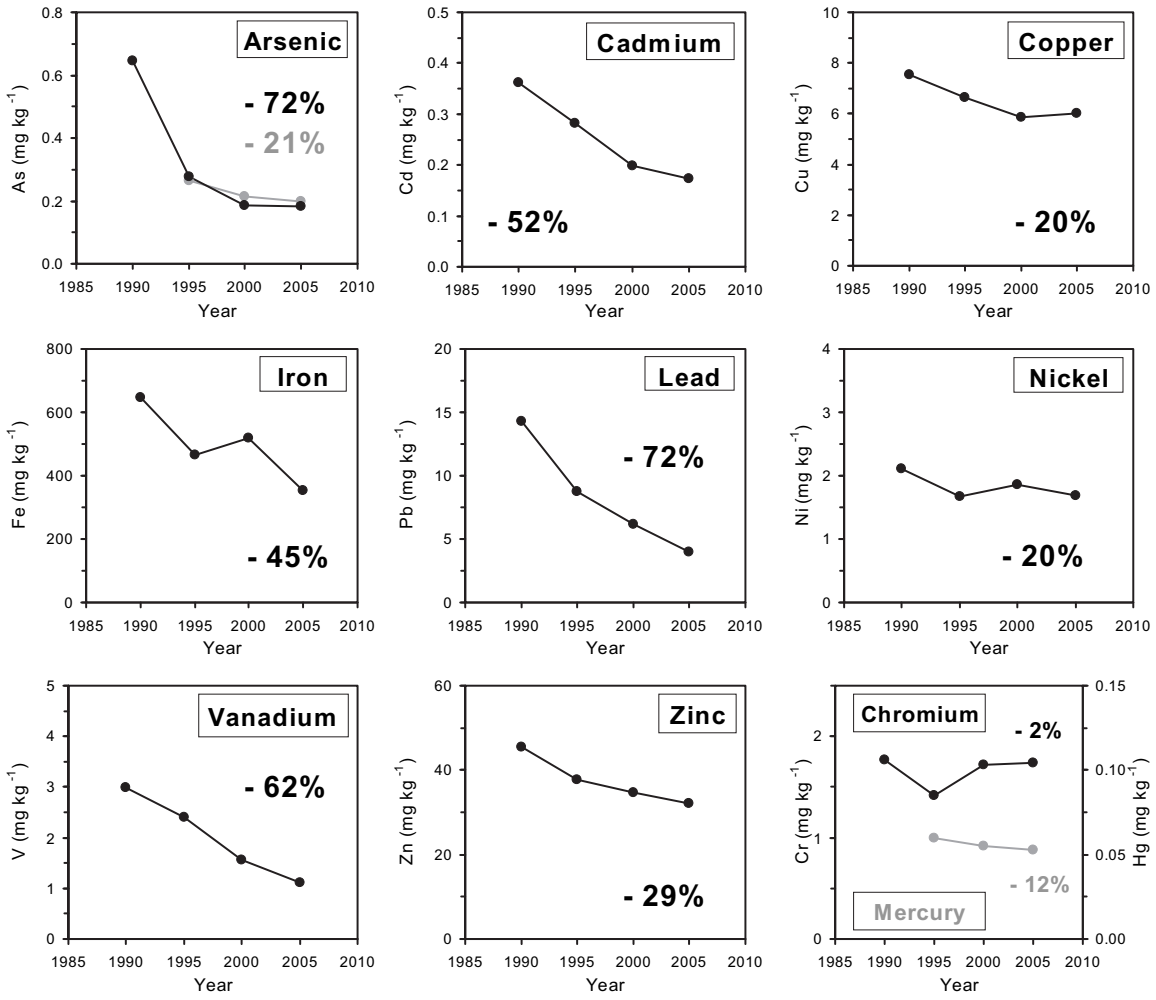


**Fig. 7.** Average of medium heavy metal concentrations in mosses for countries that reported concentrations in all survey years or the recent three survey years in case of mercury. For arsenic, the black line indicates an average based on five countries since 1990 and the grey line indicates an average based on 15 countries since 1995. The black and grey values indicate the decline since 1990 and 1995 respectively.

of metals. Only for Cd the French data for M3 (background Cd concentration) were significantly lower than the recommended values, indicating that higher uncertainties are associated with the background Cd concentrations reported from France.

### 3.3. Temporal trends between 1990 and 2005

The decline in emission and subsequent deposition of heavy metals across Europe has resulted in a significant reduction in the heavy metal concentration in mosses since 1990 for the majority of metals (Table 4, Figs. 2–5 and 7). 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. In Figs. 2–5 we chose to illustrate the change in heavy metal concentration in mosses between 1995 and 2005 as more countries had reported data in both 1995 and 2005 compared to 1990 and 2005 and because inter-laboratory calibration exercises were conducted in both 1995 and 2005. Between 1990 and 2005 the metal concentration in mosses has declined the most for Pb (72%), As (72%; based on five countries only), V (62%), Cd (52%) and Fe (45%; Fig. 7). An intermediate decrease was found for Zn (29%), Cu (20%) and Ni (20%) and no significant reduction for Cr (2%). Few countries reported data for As and Hg in 1990, but since 1995 the As concentration in mosses has declined by 21% (based on 14 countries), whereas Hg showed no significant decline (12%, based on eight countries). 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.

Temporal trends in metal concentration in mosses agree reasonably well with the trends in metal deposition modelled by EMEP (Gusev et al., 2009; Harmens et al., 2009). Taking the area of sampling into account, the metal concentration in mosses had declined by 73, 46 and 20% across Europe between 1990 (1995 for Hg) and 2005, whereas the modelled total deposition had declined by 70, 41 and 30% for Pb, Cd and Hg respectively. Total anthropogenic As emissions have declined by about 53% between 1990 and 2004 (Ilyin et al., 2006), which is in agreement with the temporal trends observed in mosses. Between 1990 and 2004, Cr emission have declined by 37% (Ilyin et al., 2006), which is in contrast with the temporal trends observed in mosses, i.e. since 1990 no significant change was found in Cr concentrations in mosses. In selected European countries, Cu and Zn emissions have

declined by 24 and 30% respectively between 1990 and 2003 (Task Force on Heavy Metals, 2006), which is similar to the decline of 20 and 29% in Cu and Zn concentrations in mosses respectively between 1990 and 2005. However, for essential plant micronutrients such as Cu and Zn one would have expected a lower decline in their concentration in mosses compared to atmospheric deposition as these micronutrient are recycled from old to new growing tissue and are therefore present in background concentrations in the mosses (e.g. Berg and Steinnes, 1997). Total anthropogenic emissions of Ni have decreased by about 57% between 1990 and 2004, with the decline levelling off in 2000 (Ilyin et al., 2006). However, smaller reductions in Ni concentrations in mosses were observed for the same period. The average median Ni concentration in mosses has declined by only 20% between 1990 and 2005, with the decline already levelling off in 1995.

The similarity in temporal trends for moss data and emission and/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 limitations of using mosses as biomonitors of atmospheric deposition. These potential limitations have been discussed in more detail elsewhere (Berg and Steinnes, 1997; Harmens et al., 2008c; Reimann et al., 2001; Steinnes, 1995, 2008; Zechmeister et al., 2003). For example, it is known that different moss species can accumulate metals at different rates, however, the differences in accumulation rates are metal-specific and vary between studies (Berg and Steinnes, 1997; Galsomiès et al., 1999; Thöni, 1996). Detailed statistical analyses has indicated that the variation in Cd and Pb concentrations in mosses not strongly affected by the use of different moss species, however, the use of different moss species might be an important confounding factor in the case of Hg (Holy et al., in press; Schröder et al., in press). For metals bound in cationic form to the moss surface cation exchange with metals in precipitation can be a confounding factor. It has been observed that metals are more readily leached from moss in areas near the coast, where more marine cations are deposited (e.g. Berg and Steinnes, 1997). However, detailed statistical analyses showed that the distance of the sampling site to the sea is hardly affecting the variation in heavy metal concentration in mosses across Europe (Holy et al., in press; Schröder et al., in press). If the metal is bound to aerosols mechanically attached to the moss surface, the mechanisms of metal loss are not clear. We are not aware of any attempts in the literature to measure residence times of elements in mosses, but they are bound to differ considerably among elements. The time necessary to notice a changes in atmospheric deposition may be assumed to be of the order of one year, depending on the relative magnitude of that change. The concentration measured in mosses is assumed to reflect an average deposition over a period of 3 years, however, correlations between Cd, Hg and Pb concentrations in mosses and EMEP modelled atmospheric deposition for these metals were similar when using either modelled deposition accumulated over 1 year or 3 years from the year of moss sampling (Holy et al., in press; Schröder et al., in press).

Although emission and deposition 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 in the food chain and the margins of safety are small (Task Force on Health, 2007; VROM, 2007). 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 (e.g. Zechmeister et al., 2008). Metals such as Sb might pose a significant risk to the environment and human health in the future (Krachler et al., 2005). 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 resuspension of wind-blown dust.

## 4. Conclusions

The following main conclusions can be drawn:

- Mosses provide a cheap, effective alternative to deposition analysis for the identification of areas at risk from high atmospheric deposition fluxes of heavy metals and temporal trends of atmospheric heavy metal deposition across Europe at a high resolution;
- Spatial patterns of heavy metal concentrations in mosses are metal-specific. However, in general the lowest background concentrations were observed in (north) Scandinavia, the Baltic States and northern parts of the United Kingdom and the higher concentrations in Belgium and south-eastern European countries in 2005;
- Since 1990, the metal concentration in mosses has declined statistically significantly for As, Cd, Cu, Fe, Ni, Pb, V and Zn, but not for Cr and Hg. This general decline across Europe is a good indication of the success of air pollution abatement strategies. Despite these general European trends, country and region-specific temporal trends were observed, including increases in metal concentrations in mosses in some areas.

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 spatial resolution and provides a useful tool for additional validation of modelled atmospheric deposition fluxes. Environmental monitoring programmes such as the moss survey are appropriate to regulatory bodies aiming to prevent the quality of the environment from deteriorating or ensure that its quality is improved.

## Acknowledgements

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