Article (refereed)

Harmens, Harry; Norris, David A.; Koerber, Georgia R.; Buse, Alan; Steinnes, Eiliv; Rühling, Ake. 2008 Temporal trends (1990 - 2000) in the concentration of cadmium, lead and mercury in mosses across Europe. *Environmental Pollution*, 151 (2). 368-376. doi:10.1016/j.envpol.2007.06.043

Temporal trends (1990 – 2000) in the concentration of cadmium, lead and mercury in mosses across Europe

Harry Harmens[a]*, David A. Norris[a], Georgia R. Koerber[a,1], Alan Buse[a], Eiliv Steinnes[b], Åke Rühling[c]

[a] Centre for Ecology and Hydrology, Orton Building, Deiniol Road, Bangor, Gwynedd LL57 2UP, UK. hh@ceh.ac.uk; danor@ceh.ac.uk

[b] Department of Chemistry, Norwegian University of Science and Technology, NO-7491 Trondheim, Norway. Eiliv.Steinnes@chem.ntnu.no

[c] Department of Plant Ecology, University of Lund, Ecology Building, S-223 62 Lund, Sweden. ake.ruhling@telia.com

[1] Present address: University of Wales, School of the Environment and Natural Resources, Memorial Building, Deiniol Road, Bangor, Gwynedd, LL57 2UW, UK. g.koerber@bangor.ac.uk

* Corresponding Author: Harry Harmens

E-mail address: hh@ceh.ac.uk

Tel.: +44-1248-370045

Fax: +44-1248-355365

Abstract

The European heavy metals in mosses survey provides data on the concentration of ten heavy metals in naturally growing mosses. The survey has been repeated at five-yearly intervals and in this paper we report on the temporal trends in the concentration of cadmium, lead and mercury between 1990 and 2000. Metal- and country-specific temporal trends were observed. In general, the concentration of lead and cadmium in mosses decreased between 1990 and 2000; the decline was higher for lead than cadmium. For mercury not enough data were available to establish temporal trends between 1990 and 1995, but between 1995 and 2000 the mercury concentration in mosses did not change across Europe. The observed temporal trends for the concentrations in mosses were similar to the trends reported for the modelled total deposition of cadmium, lead and mercury in Europe.

Keywords: biomonitoring, EMEP maps, heavy metals, metal deposition, moss survey

Capsule: Across Europe cadmium and lead concentrations in mosses declined but mercury concentrations did not change between 1990 and 2000.

1. Introduction

The heavy metals in mosses survey was originally established in 1980 as a joint Danish-Swedish initiative. The idea of using mosses to measure 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

49 nutrients directly from precipitation and dry deposition; there is little uptake of metals
50 from the substrate. The technique of moss analysis provides a surrogate, time-integrated
51 measure of the spatial patterns of heavy metal deposition from the atmosphere to
52 terrestrial systems. It is easier and cheaper than conventional precipitation analysis as it
53 avoids the need for deploying large numbers of precipitation collectors with an
54 associated long-term programme of routine sample collection and analysis. Therefore, a
55 much higher sampling density can be achieved than with conventional precipitation
56 analysis. The higher trace element concentrations in mosses compared to rain water
57 makes analysis more straightforward and less prone to contamination. Although the
58 heavy metal concentration in mosses provides no direct quantitative measurement of
59 deposition, this information can be derived by using regression approaches relating the
60 results from moss surveys to precipitation monitoring data (e.g. Berg and Steinnes,
61 1997; Berg et al., 2003).
62 The moss survey has been repeated at five-yearly intervals and the number of
63 participating European countries has expanded greatly since 1990 (Buse et al., 2003;
64 Rühling, 1994; Rühling and Steinnes, 1998). Currently, the 2005/2006 moss survey is
65 being conducted in 32 countries, analysing moss samples from over 7 000 sites across
66 Europe. For the first time the majority of countries (18) will also determine the nitrogen
67 concentration in mosses (ca. 3 200 sites). A pilot study for selected Scandinavian
68 countries has shown that there was a good linear relationship between the total nitrogen
69 concentration in mosses and atmospheric nitrogen deposition rates (Harmens et al.,
70 2005). During 2001, responsibility for the coordination of the moss survey was handed
71 over from the Nordic Working Group on Monitoring and Data, Nordic Council of
72 Ministers, to the UNECE ICP Vegetation (United Nations Economic Commission for
73 Europe International Cooperative Programme on Effects of Air Pollution on Natural

74 Vegetation and Crops) Coordination Centre at the Centre for Ecology and Hydrology
75 (CEH) Bangor, UK.

76 The UNECE ICP Vegetation was established in the late 1980s to consider the
77 science for quantifying damage to plants by air pollutants. It is one of seven ICPs and
78 Task Forces that report to the Working Group on Effects of the Long-Range
79 Transboundary Air Pollution (LRTAP) Convention on the effects of atmospheric
80 pollutants on different components of the environment (e.g. forests, fresh waters,
81 buildings) and human health (Working Group on Effects, 2004). The objectives of the
82 ICP Vegetation (Harmens et al., 2006) are designed to meet the requirements of the
83 LRTAP Convention, particularly at present the need to provide information for the
84 review of the 1999 Gothenburg Protocol to abate acidification, eutrophication, ground-
85 level ozone, and the 1998 Aarhus Protocol on heavy metals. The latter was the first
86 Protocol for the control of emissions of heavy metals; cadmium, lead and mercury
87 emissions were targeted as they are the most toxic.

88 The European moss survey provides data on concentrations of ten heavy metals
89 (As, Cd, Cr, Cu, Fe, Hg, Ni, Pb, V, Zn) in naturally growing mosses (Buse et al., 2003;
90 Rühling, 1994; Rühling and Steinnes, 1998). The main purpose of the survey is a) to
91 provide, in the form of maps, spatial information on the distribution of heavy metal
92 concentrations in mosses in Europe, b) identify main polluted areas, and c) develop the
93 understanding of long-range transboundary pollution. In general, there was a clear
94 east/west decrease in the concentration of heavy metals in mosses, related in particular
95 to industry. Former industrial or historic sites of heavy metal pollution (e.g. mines)
96 accounted for the location of some high concentrations of heavy metals in mosses in
97 areas without contemporary industries. Long-range transboundary transport appears to
98 account for elevated concentrations of heavy metals in areas without emission sources

99 (e.g. in Scandinavia). Many contributors to the survey have reported their national data
100 in greater detail elsewhere.
101 In this paper, we report on the temporal trends (1990 – 2000) of heavy metal
102 concentrations in mosses for the heavy metals targeted by the Aarhus Protocol, i.e.
103 cadmium, lead and mercury. As the emissions of these heavy metals have declined
104 across Europe in recent decades (Ilyin et al., 2005), we hypothesize that the
105 concentrations of these metals in mosses have declined too. In particular we expected a
106 marked decline in the lead concentrations in mosses due to the introduction of unleaded
107 petrol. The reduction in mercury concentrations is likely to be lower due to the lower
108 reduction in emissions and hemispheric transport of mercury across the globe. The
109 trends in the metal concentrations in mosses were compared with those reported by
110 EMEP (Co-operative programme for monitoring and evaluation of the long-range
111 transmission of air pollutants in Europe) regarding the modelled deposition of these
112 metals across Europe (Ilyin et al., 2005). In a following paper we will report on the
113 temporal trends of the other heavy metals.
114
115 **2. Materials and methods**
116
117 Moss samples were collected across Europe in 1990/1991 (Rühling, 1994),
118 1995/1996 (Rühling and Steinnes, 1998) and 2000/2001 (Buse et al., 2003; Harmens et
119 al., 2004). Throughout the paper we refer to the years of moss survey as 1990, 1995 and
120 2000 respectively. The carpet-forming mosses *Pleurozium schreberi* and *Hylocomium*
121 *splendens* were the preferred species for analysis. Where necessary, other species were
122 collected, *Hypnum cupressiforme* being the next choice. Because the mosses were
123 collected in a range of habitats from the sub-arctic climate of northern Sweden to the

124 hot and dry climate of parts of southern Italy, it was inevitable that a wide range of
125 moss species were sampled (Buse et al., 2003; Harmens et al., 2004). The moss
126 sampling procedure was according to the guidelines described in Rühling (1994) and
127 Rühling and Steinnes (1998) and was described in more detail in the protocol for the
128 2000 survey (ICP Vegetation, 2001). Only the last three years' growth of moss material
129 was used for the analyses. The concentration of cadmium, lead and mercury were
130 determined by a range of analytical techniques, under the broad headings of atomic
131 absorption spectrometry, inductively coupled plasma spectrometry (both ICP optical
132 emission spectrometry and ICP mass spectrometry), atomic fluorescence spectrometry,
133 and neutron activation analysis. All metal concentrations were expressed as mg kg^{-1} dry
134 weight at 40 ^{o}C. For details on the methods and quality control procedures we refer to
135 the reports of the individual surveys (Buse et al., 2003; Rühling, 1994; Rühling and
136 Steinnes, 1998). EMEP maps were produced according to the method described by
137 Buse et al. (2003); they show the mean concentration of each metal within individual
138 EMEP grid squares (50 km x 50 km). Please note that the designations employed and
139 the presentation of material in this paper do not imply the expression of any opinion
140 whatsoever on the part of the United Nations concerning the legal status of any country,
141 territory, city or area or of its authorities, or concerning the delimitation of its frontiers
142 or boundaries.
143 Statistical analysis of the temporal trends (1990 – 2000) across Europe was
144 performed by calculating the geometric mean values per metal per survey year for each
145 country. Subsequently, a general linear model ANOVA (Minitab version 14) was
146 applied to each metal using only the geometric mean values for the countries which had
147 determined the heavy metal concentration in mosses in all survey years for that metal.
148 The geometric mean values were analysed with country as a factor, year as covariate

149 and the number of samples as weights. Weighting was applied to take into account the
150 accuracy of the calculated geometric means (i.e. the density of sampling varied between
151 countries; see Buse et al., 2003) and to give more weight to larger countries and less to
152 smaller ones. For mercury changes with time were determined for the period 1995 –
153 2000 as only two countries had determined the mercury concentration in mosses in
154 1990.
155
156 **3. Results**
157
158 In tables 1 - 3 we only included the data for countries that determined heavy
159 metal concentrations in mosses in at least two of the three surveys. In general, the
160 cadmium and lead concentrations in mosses decreased between 1990 and 2000 (Tables
161 1 and 2; Figs. 1 and 2) and in the majority of countries the mercury concentration in
162 mosses decreased between 1995 and 2000 (Table 3; Fig. 3). The average median value
163 for countries that had determined cadmium and lead concentrations in mosses in both
164 1990 and 2000, decreased by 42% and 57% for cadmium and lead respectively (Table
165 4). Analysis of the geometric mean values confirmed that the decline in cadmium and
166 lead concentration in mosses with time was significant (Table 5). However, it should be
167 noted that country-specific trends were found (Tables 1 - 3). In some countries,
168 cadmium and/or lead concentrations did not change or increase between 1990 and 1995,
169 whereas in others they did not change or increase between 1995 and 2000. However,
170 only in Portugal the cadmium concentration was higher in 2000 than 1990 and only in
171 Lithuania and the Russian Federation (region of St. Petersburg) the lead concentration
172 was higher in 2000 than 1990. This appears to be primarily due to the relatively low
173 concentration of cadmium and lead found in the mosses in the 1990 survey in those

countries, possibly due to analytical error. The extremely high cadmium concentration in mosses in the Netherlands in 1995 (and to a lesser extent in 1990) also suggests an analytical error. The mercury concentration in mosses did not change in Austria and Italy and even increased in France, Lithuania, and Slovakia between 1995 and 2000. The sharp decline in the mercury concentration in mosses in Sweden is exceptional compared with the trends observed in neighbouring countries and the rest of Europe. The average median value for countries that determined mercury concentrations in mosses in both 1995 and 2000 decreased by 8%. Analysis of the geometric mean values shows that this decline with time was not significant (Table 5).

Similar trends were reported by EMEP Meteorological Synthesizing Centre - East (EMEP/MSC-E) regarding the modelled total heavy metal deposition in Europe (Ilyin et al., 2005). Between 1990 and 2000 the total deposition of cadmium and lead was reduced by 45% and 52% respectively, whereas the total deposition of mercury was reduced by 8% between 1995 and 2000 (Table 4). As in the moss survey, country-specific temporal trends were observed in the modelled total heavy metal deposition.

4. Discussion

The cadmium and lead concentration in mosses decreased significantly across Europe between 1990 and 2000, with the decline being higher for lead than cadmium. In contrast, no significant change was observed for the mercury concentration in mosses between 1995 and 2000. However, it should be noted that country-specific trends were observed. These findings are in agreement with the temporal trends reported by EMEP regarding the modelled total deposition of these metals in Europe (Ilyin et al., 2005). The modelled concentrations of cadmium, lead and mercury in air and precipitation

199 were generally in good agreement with available measurement data in the EMEP
200 monitoring network (Ilyin and Travnikov, 2005).
201 Gasoline lead additives have been the key emission source of lead over the last
202 decades. Phasing out leaded petrol across Europe has resulted in about 8 and 6 times
203 reduction in lead emissions and depositions respectively between 1980 and 2000 (Ilyin
204 et al., 2004). The highest reduction of emissions and depositions occurred between 1985
205 and 1990. Whereas in 1990 the sector 'road transportation' was the major source of lead
206 emission (85%), in 2003 the sector 'metal production' was the major source with a
207 contribution to lead emission of 28% (Verstreng et al., 2005). The increase in lead
208 concentration in mosses in countries such as the Russian Federation and the Ukraine is
209 likely due to the fact that these countries still used leaded petrol long after it had been
210 phased out elsewhere in Europe, together with an immense rise in the number of cars in
211 these countries.
212 Atmospheric cadmium may originate from multiple sources. Of key significance
213 are various combustion processes based on fossil fuels (in particular coal and oil), as
214 well as various processes in the pyrometallurgical non-ferrous metal industries and
215 waste incineration. Whereas in 1990 the sector 'waste incineration' was the major
216 source of cadmium emission (20%), in 2003 the sector 'metal production' was the
217 major source (26%) (Verstreng et al., 2005). Cadmium emissions and depositions in
218 Europe decreased about 4 and 3 times respectively between 1980 and 2000 and as for
219 lead the highest decline was observed between 1985 and 1990 (Ilyin et al., 2004).
220 The most important anthropogenic sources of mercury are the combustion of
221 fuels (in particular coal), waste incineration and chlor-alkali and cement production. In
222 1990 the maximum contribution to the total mercury emissions was from the sector
223 'public electricity and heat production' (29%), but in 2003 the sector 'other,

manufacturing industries and construction' became the largest source of emissions (31%) (Verstreng et al., 2005). Anthropogenic mercury emissions and depositions in Europe decreased about 2 and 1.5 times respectively between 1990 and 2000, with the decline being higher in the early than late 1990s (Ilyin et al., 2004). In contrast to cadmium and lead, mercury is a global pollutant, i.e. it can be transported by atmospheric flows around the world. Therefore, mercury emission sources located in other continents significantly affect mercury pollution levels in Europe. In addition, natural emission sources and re-emission contribute significantly to mercury levels in the atmosphere (Ilyin et al., 2004).

The similarity in temporal trends reported for the data of the European moss survey and the modelled total depositions suggests that at the European scale these trends are not affected by potential confounding factors. For example, high uncertainties are associated with the available official estimates of anthropogenic emissions, which form the basis of the EMEP modelled deposition data. The official emission data cannot explain measured wet deposition levels of cadmium and lead in Europe (Ilyin and Travnikov, 2005). Based on the measurement data in the EMEP monitoring network, the official emission data for cadmium and lead are expected to underestimate emissions by a factor 2 to 3. In the current study, the temporal trends of the lead and cadmium concentrations in mosses were therefore compared with EMEP modelled total deposition data based on adjusted emission scenarios (Ilyin and Travnikov, 2005; Ilyin et al., 2005).

Several studies have indicated that the use of mosses as biomonitors of atmospheric heavy metal deposition could be confounded by various climatic, geographical and environmental factors (e.g. Berg and Steinnes, 1997; Zechmeister et al., 2003). Confounding factors in relating the heavy metal concentrations in mosses to

249 measured wet deposition rates across Europe include the distance of the sampling site to
250 the sea and the significantly higher dry deposition in Central Europe, which in many
251 cases affected the concentration in mosses more than the wet deposition (Berg et al.,
252 2003). The drier climate in Mediterranean areas at low altitude is likely to reduce moss
253 growth rates (e.g. Vitt, 1990) in comparison with the wetter climates in northern
254 European countries or higher altitudes. Variation in moss growth rates due to variation
255 in (micro)climate might influence the heavy metal concentration in mosses (e.g. Gerdol
256 et al., 2002; Zechmeister, 1998), in particular for extracellular bound elements (Gerdol
257 et al., 2002). Conflicting results have been reported regarding seasonal variations in the
258 heavy metal concentrations in mosses (Berg and Steinnes, 1997; Thöni, 1996;
259 Zechmeister et al., 2003) and the variation of heavy metal concentrations in mosses with
260 altitude (Gerdol et al., 2002; Zechmeister, 1995). How these potential confounding
261 factors together exactly affect both the spatial and temporal variation of the
262 concentration of various heavy metals in mosses at the European scale requires further
263 investigation. One should bear in mind that the metal concentrations in mosses are
264 determined over a three-year growth period, representing climatic conditions averaged
265 over three years. A preliminary analysis by Büker et al. (2003) showed that the variation
266 in the concentration of heavy metals in mosses in the 2000/2001 moss survey could
267 hardly be explained by variation in climatic and geographical factors. In addition,
268 despite the broad variation in climate between northern and southern Europe, results of
269 the European moss surveys do not indicate a clear north – south gradient in the heavy
270 metal concentration in mosses in contrast to a clear east – west gradient related to
271 sources of heavy metal pollution (Buse et al., 2003).
272 Another potential confounding factor regarding temporal trends could be that
273 often participants have not consistently sampled mosses from the same sites in every

274 survey and sometimes have sampled different moss species in different years. It is
275 known that different moss species accumulate heavy metals at different rates and that
276 the difference in accumulation rates are metal-specific (e.g. Ashmore et al., 2000; Berg
277 and Steinnes, 1997; Galsomiès et al., 1999; Thöni, 1996). However, statistical analyses
278 and the use of artificial neural networks indicate that the variation in heavy metal
279 concentrations in mosses in the 2000 European survey can hardly be explained by the
280 use of different moss species (Büker et al., 2003). Reimann et al. (2001) concluded that
281 for regional mapping purposes the moss species *H. splendens* and *P. schreberi* can be
282 combined without interspecies calibration, as for the majority of heavy metals the
283 within-catchment variation is large for both moss species. Thöni (1996) came to a
284 similar conclusion for the moss species *H. splendens, P. schreberi* and *H.*
285 *cupressiforme*.
286 The use of different analytical techniques could be another source of variation in
287 the heavy metal concentration in mosses, but intercalibrations between the laboratories
288 in the 1995 survey showed that there is a reasonable agreement between all analytical
289 techniques used (Steinnes et al., 1997). However, instrumental neutron activation
290 analysis (INAA) showed higher concentrations in some cases due to the fact that the
291 method determines the total concentration of elements, while other methods need wet
292 digestion of samples with nitric acid, i.e. silicate minerals in the mosses are only partly
293 decomposed (Schaug et al., 1990). Büker et al. (2003) showed that the variation in
294 heavy metal concentrations in the 2000 moss survey cannot be explained by the use of
295 different analytical techniques.
296 Although calibration factors have been developed in for example the Nordic
297 countries to convert heavy metal concentrations in mosses to bulk wet deposition values
298 for certain heavy metals (Berg and Steinnes, 1997; Berg et al., 2003), these models

should only be used for background sites. A good linear relationship (correlation coefficient R = 0.91) was found between lead concentrations in mosses and modelled total lead deposition rates for selected grid cells in Scandinavia where EMEP monitoring stations are situated, i.e. at locations influenced by long-range transboundary air pollution only. The correlation coefficient was much lower (R = 0.56) when this relationship was determined for the whole of Europe, which is due to the fact that lead concentrations in mosses were also determined in areas of Europe affected by local pollution sources (Ilyin and Travnikov, 2005). The country-specific relationships between the heavy metal concentrations in mosses and the modelled atmospheric deposition rates require further investigation to establish in more detail any confounding factors affecting these relationships. In light of the high uncertainties currently associated with the EMEP modelled heavy metal deposition data, the data of the heavy metals in mosses biomonitoring network remain an invaluable resource for i) determining both general and more detailed spatial and temporal trends in heavy metal deposition in Europe and ii) verifying the performance of the EMEP heavy metal deposition model, at least in areas influenced by long-range transboundary air pollution only. Whereas the European moss survey provides data on ten heavy metals, detailed application of the EMEP heavy metal deposition model has been limited so far to the heavy metals cadmium, lead and mercury, although pilot calculations of atmospheric transport and depositions of other metals have been conducted recently (Ilyin et al., 2006).

5. Conclusions

Mosses provide a cheap and effective method for monitoring temporal trends in heavy metal pollution in Europe. Temporal trends in the concentrations of cadmium, lead and mercury in mosses were in agreement with those reported for modelled total deposition of these metals in Europe. Significant reductions in the emissions of cadmium and lead between 1990 and 2000 have resulted in a significant reduction of the accumulation of both metals in mosses. The smaller reductions in emissions of mercury over the shorter time period (1995 – 2000) studied here meant that no significant changes were found in the accumulation of mercury in mosses between 1995 and 2000.

Acknowledgements

We thank the United Kingdom Department for Environment, Food and Rural Affairs (Defra) for funding the ICP Vegetation Coordination Centre (contracts EPG 1/3/170, 1/3/205 and AQ03509). The contributions of the participants of the European heavy metals in mosses surveys and their funding bodies are gratefully acknowledged (for full details see Rühling (1994), Rühling and Steinnes (1998) and Buse et al. (2003)). We thank Ilia Ilyin (EMEP/MSC-E) for providing the modelled heavy metal deposition data and Tim Sparks (CEH Monks Wood) for statistical advice.

References

Ashmore, M., Bell, S., Fowler, D., Hill, M., Jordan, C., Nemitz, E., Parry, S., Pugh, B., Reynolds, B., Williams, J., 2000. Survey of the UK metal content of mosses 2000. Part II of EPG 1/3/144 final contract report: development of a critical load

methodology for toxic metals in soils and surface waters: stage II. University of Bradford, UK.

Berg, T., Hjellbrekke, A., Rühling, Å., Steinnes, E., Kubin, E., Larsen, M.M., Piispanen, J., 2003. Absolute deposition maps of heavy metals for the Nordic countries based on the moss survey. TemaNord 2003:505, Nordic Council of Ministers, Copenhagen, Denmark.

Berg, T., Steinnes, E., 1997. Use of mosses (*Hylocomium splendens* and *Pleurozium schreberi*) as biomonitors of heavy metal deposition: from relative to absolute values. Environmental Pollution 98, 61-71.

Büker, P., Mills, G., Harmens, H., Buse, A., Norris, D., Cinderby, S., 2003. Results of a study focussing on the optimization of spatial distribution maps and the determination of factors influencing data variation. UNECE ICP Vegetation Coordination Centre, Centre for Ecology and Hydrology, Bangor, UK.

Buse, A., Norris, D., Harmens, H., Büker, P., Ashenden, T., Mills, G., 2003. Heavy metals in European mosses: 2000/2001 survey. UNECE ICP Vegetation Coordination Centre, Centre for Ecology and Hydrology, Bangor, UK. http://icpvegetation.ceh.ac.uk

Galsomiès, L., Letrouit, M.A., Deschamps, C., Savanne, D., Avnaim, M., 1999. Atmospheric metal deposition in France: initial results on moss calibration from the 1996 biomonitoring. The Science of the Total Environment 232, 39-47.

Gerdol, R., Bragazza, L., Marchesini, R., 2002. Element concentrations in the forest moss *Hylocomium splendens*: variation associated with altitude, net primary production and soil chemistry. Environmental Pollution 116, 129-135.

Harmens, H., Buse, A., Büker, P., Norris, D., Mills, G., Williams, B., Reynolds, B., Ashenden, T.W., Rühling, Å., Steinnes. E., 2004. Heavy metal concentration in

European mosses: 2000/2001 survey. Journal of Atmospheric Chemistry 49, 425-436.

Harmens, H., Mills, G., Hayes, F., Jones, L., Williams, P. and the participants of ICP Vegetation, 2006. Air pollution and vegetation. ICP Vegetation Annual Report 2005/2006. UNECE ICP Vegetation Coordination Centre, Centre for Ecology and Hydrology, Bangor, UK. http://icpvegetation.ceh.ac.uk

Harmens, H., Mills, G., Hayes, F., Williams, P., De Temmerman, L. and the participants of ICP Vegetation, 2005. Air pollution and vegetation. ICP Vegetation Annual Report 2004/2005. UNECE ICP Vegetation Coordination Centre, Centre for Ecology and Hydrology, Bangor, UK. http://icpvegetation.ceh.ac.uk

ICP Vegetation, 2001. ICP Vegetation experimental protocol for the 2001 season. UNECE ICP Vegetation Coordination Centre, Centre for Ecology and Hydrology, Bangor, UK.

Ilyin, I., Berg, T., Dutchak, S., Pacyna, J., 2004. Heavy metals. In: Lövblad, G., Tarrasón, L., Tørseth, K., Dutchak, S. (Eds.), EMEP assessment Part I European perspective. Norwegian Meteorological Institute, Oslo, Norway, pp. 107-128.

Ilyin, I, Travnikov, O., 2005. Modelling of heavy metal airborne pollution in Europe: evaluation of the model performance. EMEP/MSC-E technical report 8/2005. Meteorological Synthesizing Centre - East, Moscow, Russian Federation. http://www.msceast.org

Ilyin, I, Travnikov, O., Aas, W, 2005. Heavy metals: transboundary pollution of the environment. EMEP/MSC-E technical report 2/2005. Meteorological Synthesizing Centre - East, Moscow, Russian Federation. http://www.msceast.org

Ilyin, I, Travnikov, O., Aas, W, 2006. Heavy metals: transboundary pollution of the environment. EMEP/MSC-E technical report 2/2006. Meteorological Synthesizing Centre - East, Moscow, Russian Federation. http://www.msceast.org

Reimann, C., Niskavaara, H., Kashulina, G., Filzmoser, P., Boyd, R., Volden, T., Tomilina, O., Bogatyrev, I., 2001. Critical remarks on the use of terrestrial moss (*Hylocomium splendens* and *Pleurozium schreberi*) for monitoring of airborne pollution. Environmental Pollution 113, 41-57.

Rühling, Å., 1994. Atmospheric heavy metal deposition in Europe – estimation based on moss analysis. NORD 1994:9. Nordic Council of Ministers, Copenhagen, Denmark.

Rühling, Å., Steinnes, E., 1998. Atmospheric heavy metal deposition in Europe 1995-1996. NORD 1998:15, Nordic Council of Ministers, Copenhagen, Denmark.

Rühling, Å., Tyler, G., 1968. An ecological approach to the lead problem, Botaniska Notiser 122, 248-342.

Schaug, J., Rambæk, J.P., Steinnes, E., Henry, R.C., 1990. Multivariate analysis of trace element data from moss samples used to monitor atmospheric deposition. Atmospheric Environment 24A, 2625-2631.

Steinnes, E., Rühling, Å., Lippo, H., Mäkinen, A., 1997. Reference material for large-scale metal deposition surveys. Accreditation and Quality Assurance 2, 243-249.

Thöni, L., 1996. Vergleich von Elementkonzentrationen in drei Biomonitoringmoosen untereinander und mit Depositionsfrachten in Bulksammler nach Bergerhoff. Bundesamt fur Umwelt, Wald and Landschaft, Egg, Switzerland.

Vestreng, V., Breivik, K., Adams, M., Wagner, A., Goodwin, J., Rozovskaya, O., Pacyna, J. M., 2005. Emission data reported to LRTAP Convention and NEC

419 Directive. Initial review for HMs and POPs. EMEP/MSC-W technical report 1/05.
420 Meteorological Synthesizing Centre - West, Oslo, Norway. http://www.emep.int

421 Vitt, D.H., 1990. Growth and production dynamics of boreal mosses over climatic,
422 chemical and topographic gradients. Botanical Journal of the Linnean Society
423 140, 35-59.

424 Working Group on Effects, 2004. Review and assessment of air pollution effects and
425 their recorded trends. Working Group on Effects, Convention on Long-range
426 Transboundary Air Pollution. Natural Environment Research Council, UK.

427 Zechmeister, H.G., 1995. Correlation between altitude and heavy metal deposition in
428 the alps. Environmental Pollution 89, 73-80.

429 Zechmeister, H.G., 1998. Annual growth of four pleurocarpous moss species and their
430 applicability for biomonitoring heavy metals. Environmental Monitoring and
431 Assessment 52, 441-451.

432 Zechmeister, H.G., Hohenwallner, D., Riss, A., Hanus-Illnar, A., 2003. Variations in
433 heavy metal concentrations in the moss species *Abietinella abietina* (Hedw.)
434 Fleisch. according to sampling time, within site variability and increase in
435 biomass. The Science of the Total Environment 301, 55-65.

436 **Figure legends**

437

438 **Figure 1.** The mean concentration of cadmium in moss per EMEP grid square (50 km x

439 50 km) for 1990 (a), 1995 (b) and 2000 (c).

440

441 **Figure 2.** The mean concentration of lead in moss per EMEP grid square (50 km x 50

442 km) for 1990 (a), 1995 (b) and 2000 (c).

443

444 **Figure 3.** The mean concentration of mercury in moss per EMEP grid square (50 km x

445 50 km) for 1995 (a) and 2000 (b).

446 **Table 1.** Median values, standard deviations (st. dev.) and number of samples (n)
447 analysed for cadmium concentrations in mosses across Europe between 1990 and 2000;
448 - = not determined.
449

	Median (mg kg^{-1})			St. dev. (mg kg^{-1})			n		
Country	1990	1995	2000	1990	1995	2000	1990	1995	2000
Austria	0.30	0.22	0.18	0.15	0.11	0.12	38	218	221
Bulgaria	-	0.38	0.38	-	0.45	1.04	-	215	217
Czech Republic	0.32	0.31	0.23	0.13	0.32	0.21	33	196	250
Denmark	0.25	0.31	-	0.11	0.20	-	76	86	-
- Faroe Islands	-	0.12	0.06	-	0.02	0.02	-	8	8
Estonia	0.30	0.18	0.20	0.13	0.06	0.04	74	103	100
Finland	0.26	0.17	0.12	0.11	0.06	0.04	821	970	938
France	-	0.20	0.20	-	0.16	0.11	-	509	528
Germany	0.31	0.30	0.21	0.13	0.16	0.12	473	973	1027
Hungary	-	0.42	0.54	-	0.20	0.20	-	13	32
Iceland	0.41	0.22	0.05	0.36	0.18	0.06	106	110	124
Italy	0.31	0.24	0.27	0.23	0.36	0.40	23	143	248
Latvia	0.27	0.17	0.16	0.05	0.05	0.26	81	100	101
Lithuania	0.35	0.19	0.15	0.14	0.07	0.04	144	165	138
Netherlands	1.18	3.76	-	0.61	0.82	-	9	110	-
Norway	0.13	0.13	0.09	0.26	0.18	0.17	497	458	464
Poland	0.41	0.45	0.36	0.61	0.29	1.00	147	295	116
Portugal	0.09	0.73	0.41	0.33	0.60	0.48	177	130	150
Romania	1.02	0.60	0.46	0.62	1.07	0.17	56	81	21
Russian Fed.	-	0.18	0.25	-	0.15	0.26	-	621	311
- St. Petersburg	0.42	0.27	0.26	0.23	0.15	0.38	214	216	98
Slovakia	1.36	1.19	0.59	0.77	0.52	0.34	58	78	86
Slovenia	-	0.73	0.43	-	0.28	0.27	-	22	79
Spain	0.32	0.10	0.07	0.08	0.18	0.05	12	126	146
Sweden	0.24	0.19	0.18	0.11	0.10	0.09	907	1170	603
Switzerland	0.36	0.26	0.19	0.17	0.18	0.15	235	202	142
Ukraine	-	0.18	0.29	-	0.06	0.29	-	75	115
United Kingdom	0.16	0.19	0.11	2.36	0.16	0.15	247	108	250

450

451 **Table 2.** Median values, standard deviations (st. dev.) and number of samples (n)
452 analysed for lead concentrations in mosses across Europe between 1990 and 2000; - =
453 not determined.
454

	Median (mg kg^{-1})			St. dev. (mg kg^{-1})			n		
Country	1990	1995	2000	1990	1995	2000	1990	1995	2000
Austria	15.8	8.9	5.8	6.4	4.3	3.2	38	218	221
Bulgaria	-	19.0	18.9	-	50.5	82.9	-	215	217
Czech Republic	16.6	11.0	5.7	11.5	18.4	4.8	33	196	250
Denmark	10.6	7.5	-	7.0	3.5	-	76	86	-
- Faroe Islands	-	6.9	3.7	-	2.0	1.1	-	8	8
Estonia	13.2	7.0	4.2	3.8	2.5	1.2	74	103	100
Finland	9.9	5.7	3.0	4.4	2.7	1.4	821	970	938
France	-	8.8	5.7	-	9.7	4.3	-	510	528
Germany	12.9	7.7	4.6	6.7	6.3	3.4	582	972	1026
Hungary	-	10.9	15.1	-	5.0	7.2	-	13	32
Iceland	1.9	1.0	1.5	2.4	5.0	5.2	106	110	124
Italy	13.9	11.3	9.0	8.7	13.5	33.7	23	144	194
Latvia	11.1	6.9	2.9	3.3	3.3	3.6	81	100	101
Lithuania	7.6	11.4	8.3	9.9	3.7	3.2	144	165	138
Netherlands	14.1	14.0	-	5.8	5.3	-	76	110	-
Norway	9.3	5.8	2.7	12.0	8.3	3.6	497	458	464
Poland	21.5	13.8	9.9	29.3	9.9	10.8	147	295	116
Portugal	14.0	19.5	3.1	16.8	15.3	10.3	177	128	150
Romania	35.1	26.5	14.4	23.8	30.4	6.4	56	81	21
Russian Fed.	-	4.5	6.6	-	4.2	3.1	-	621	247
- St. Petersburg	3.4	6.8	4.7	22.6	4.6	3.2	203	216	98
Slovakia	40.9	23.5	28.4	61.2	25.2	21.2	58	78	86
Spain	20.0	5.7	1.8	19.6	13.8	2.3	12	126	146
Sweden	11.3	6.1	4.3	8.2	3.3	2.3	906	1170	603
Switzerland	13.6	6.5	3.3	17.2	9.1	4.5	232	202	142
Ukraine	-	3.4	6.8	-	1.6	6.3	-	75	115
United Kingdom	6.4	8.3	2.9	20.9	6.5	6.4	275	108	250

455

456 **Table 3.** Median values, standard deviations (st. dev.) and number of samples (n)
457 analysed for mercury concentrations in mosses across Europe in 1995 and 2000. In
458 1990, mercury concentrations were only determined in Austria (median = 0.050 ±
459 0.023 mg kg^{-1}; n = 38) and Switzerland (median = 0.051 ± 0.033 mg kg^{-1}; n = 235); - =
460 not determined.
461

	Median (mg kg^{-1})		St. dev. (mg kg^{-1})		n	
Country	1995	2000	1995	2000	1995	2000
Austria	0.050	0.050	0.021	0.030	215	221
Czech Republic	0.064	0.048	0.027	0.015	195	250
Finland	0.047	0.042	0.022	0.023	970	270
France	0.060	0.070	0.047	0.028	230	528
Germany	0.044	0.041	0.023	0.022	974	1028
Iceland	0.073	0.039	0.032	0.021	30	124
Italy	0.070	0.070	0.025	0.422	98	185
Latvia	0.066	0.050	0.015	0.021	6	101
Lithuania	0.070	0.088	0.023	0.026	135	143
Norway	0.068	0.052	0.041	0.022	209	464
Russian Fed.	0.050	-	0.082	-	550	-
- St. Petersburg	0.047	0.040	0.032	0.017	176	98
Slovakia	0.113	0.180	0.719	0.660	78	86
Sweden	0.065	0.017	0.047	0.019	586	588
Switzerland	-	0.032	-	0.011	-	142
Ukraine	0.060	0.039	0.023	0.022	75	115

462

463 **Table 4.** Average median values of cadmium (Cd), lead (Pb) and mercury (Hg)
464 concentrations in mosses for countries that analysed these metals both in 1990 (1995 for
465 Hg) and 2000. Changes in the average median values with time were compared with
466 changes in the modelled total deposition across Europe (Ilyin et al., 2005).
467

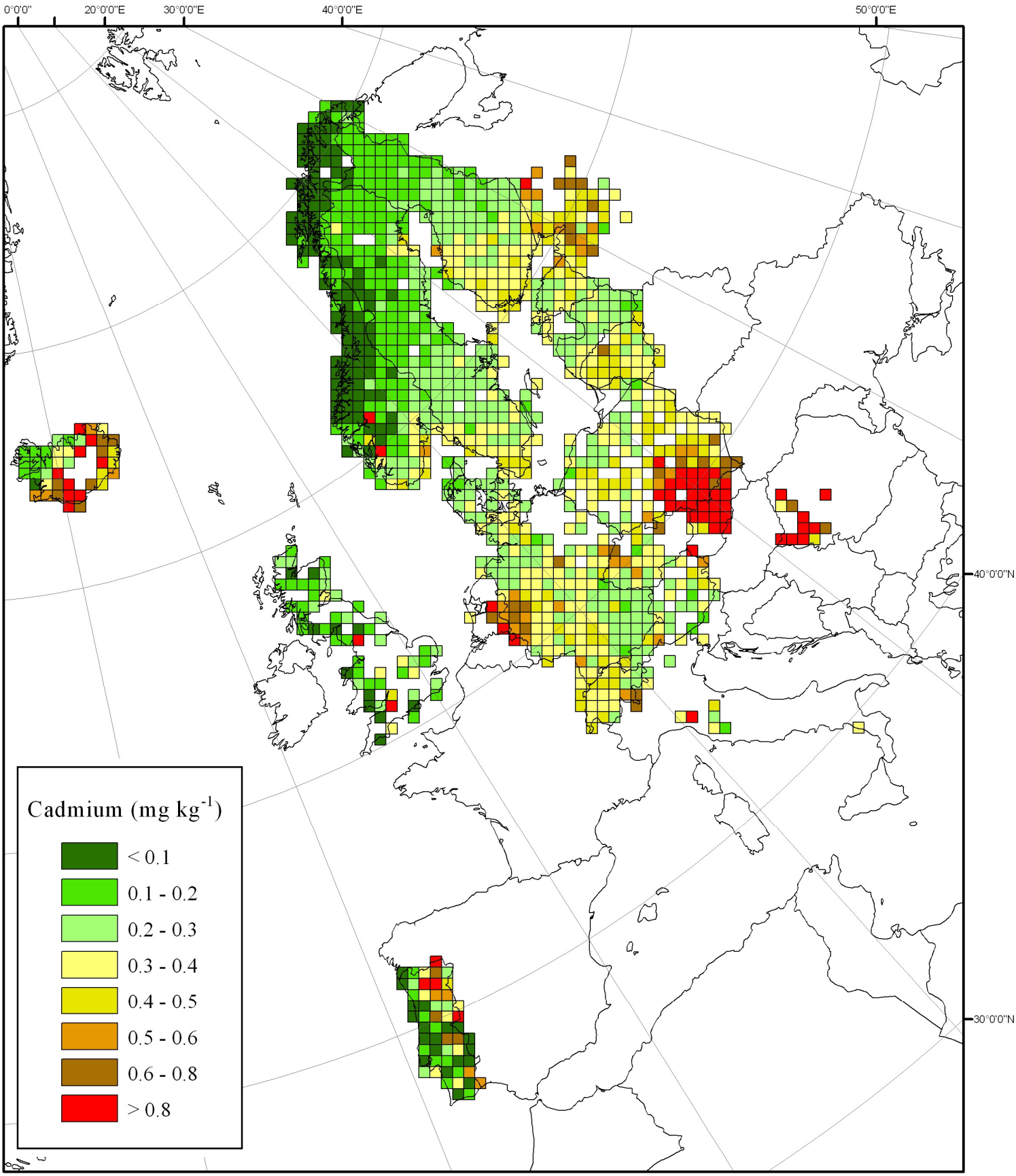
Metal	Concentration in moss			Deposition
	Median 1990[1] (mg kg^{-1})	Median 2000 (mg kg^{-1})	Decrease with time (%)	Decrease with time (%)
Cd	0.39	0.23	42	45
Pb	14.6	6.3	57	52
Hg	0.064	0.059	8	8

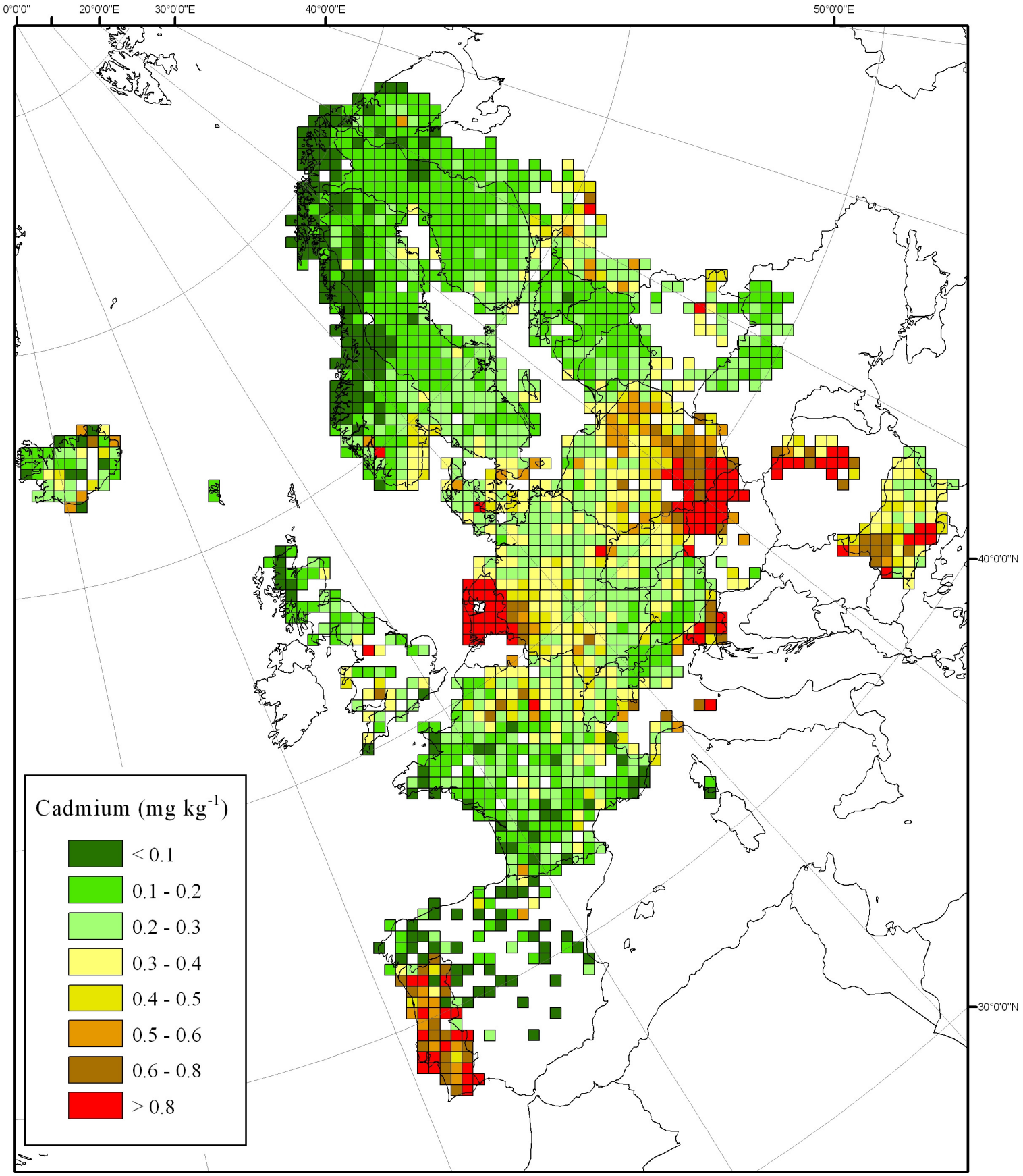
468
469 [1] 1995 for Hg.
470

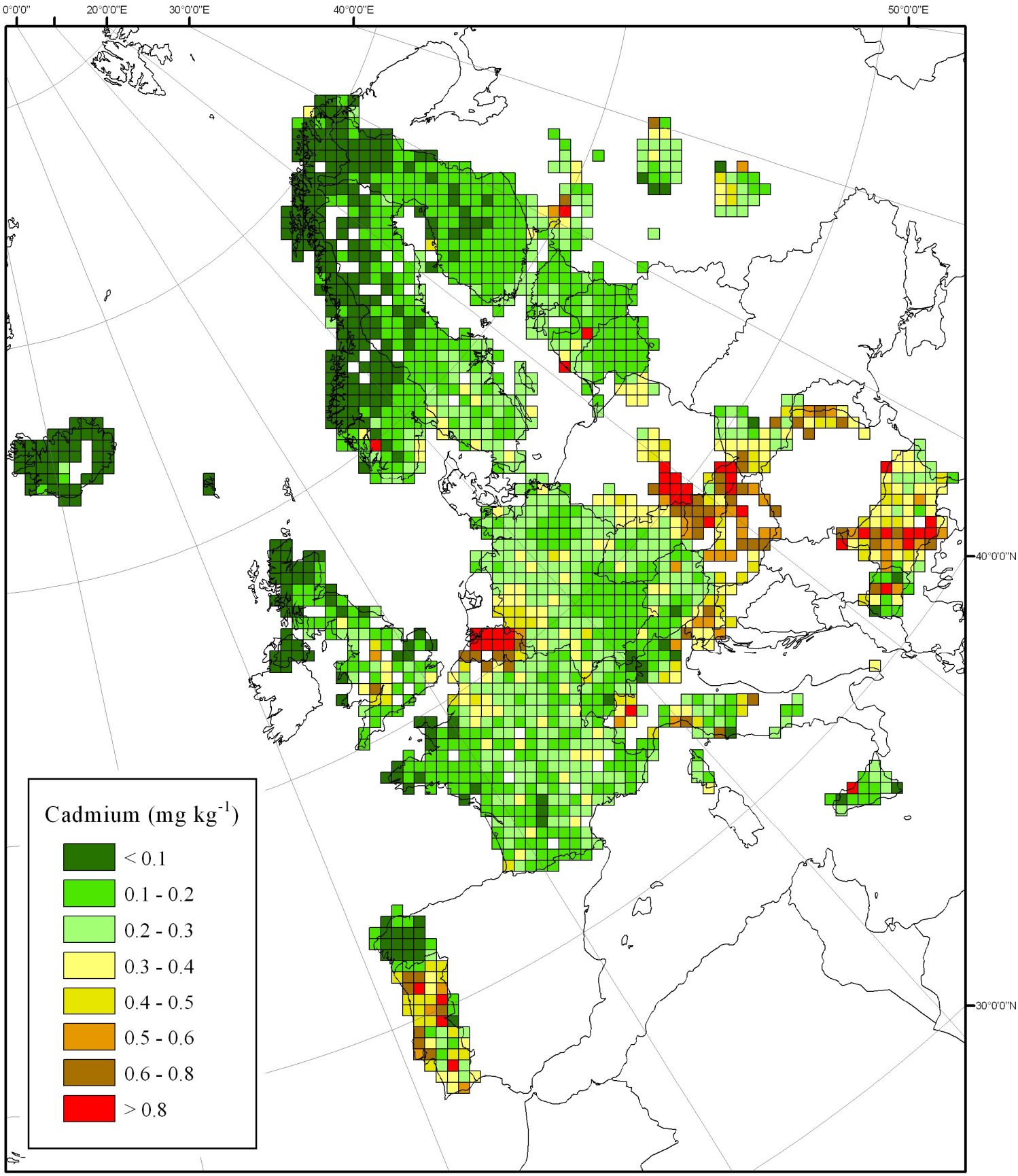
471 **Table 5.** Average geometric mean values of cadmium (Cd), lead (Pb) and mercury (Hg)
472 concentrations in mosses for countries that analysed these metals in all three surveys
473 (only 1995 and 2000 for Hg). The statistical significance (P-value) of country and year
474 of the survey are also shown.
475

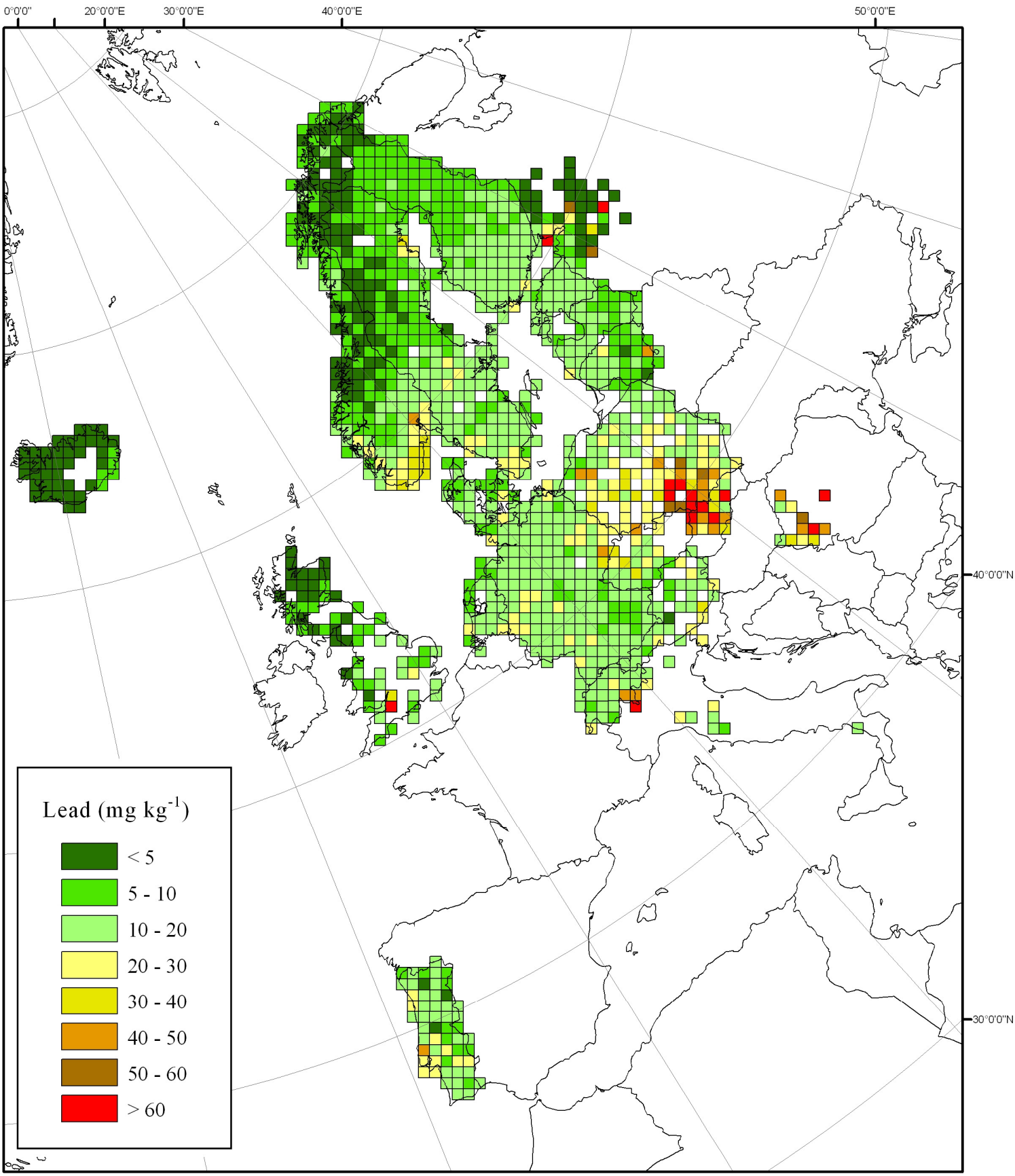
Metal	Average geometric mean (mg kg^{-1})			P-value	
	1990	1995	2000	Country	Year
Cd	0.38	0.33	0.23	0.000	0.000
Pb	15.1	10.2	6.4	0.000	0.000
Hg	-	0.067	0.062	0.072	0.222

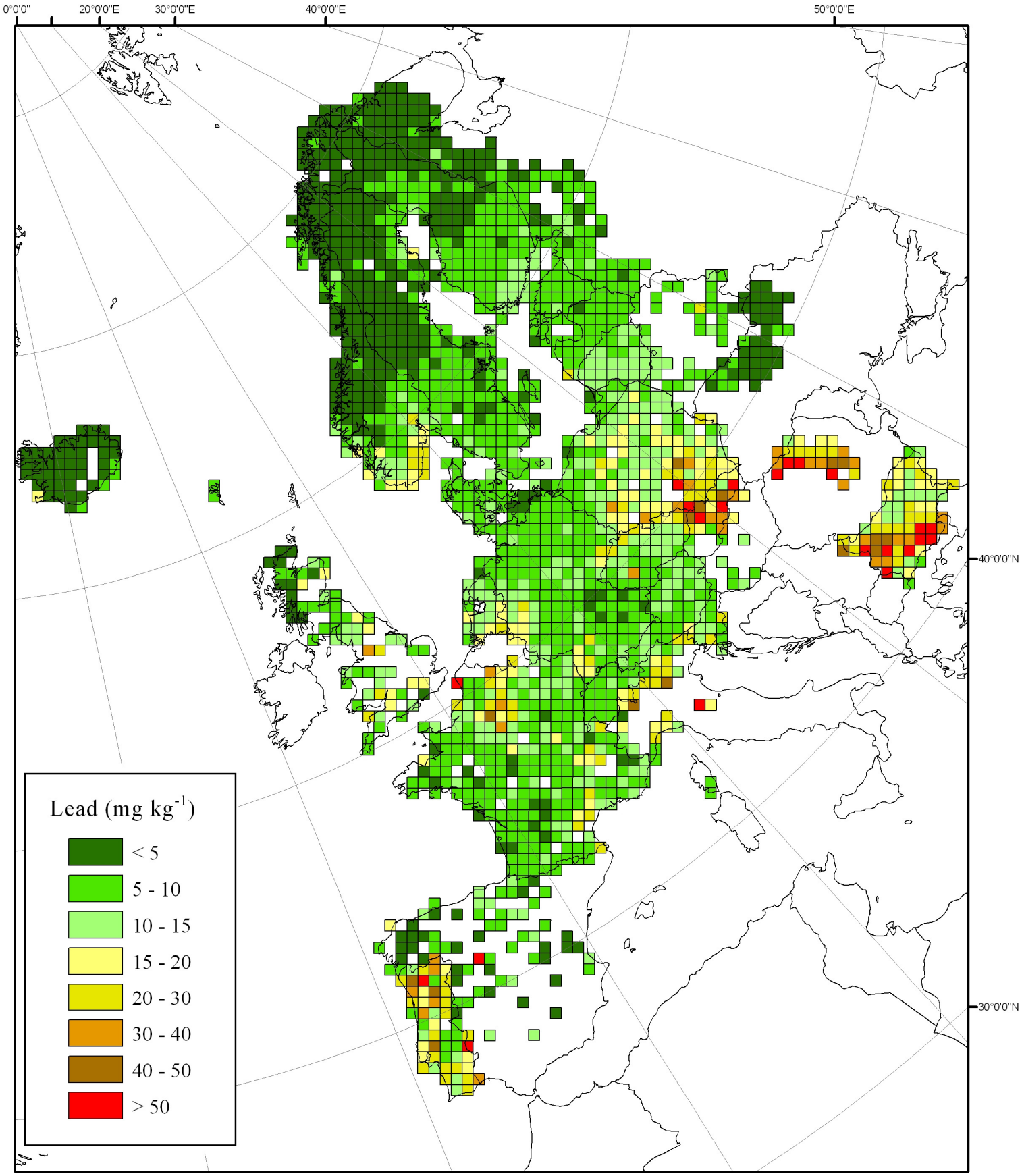
476

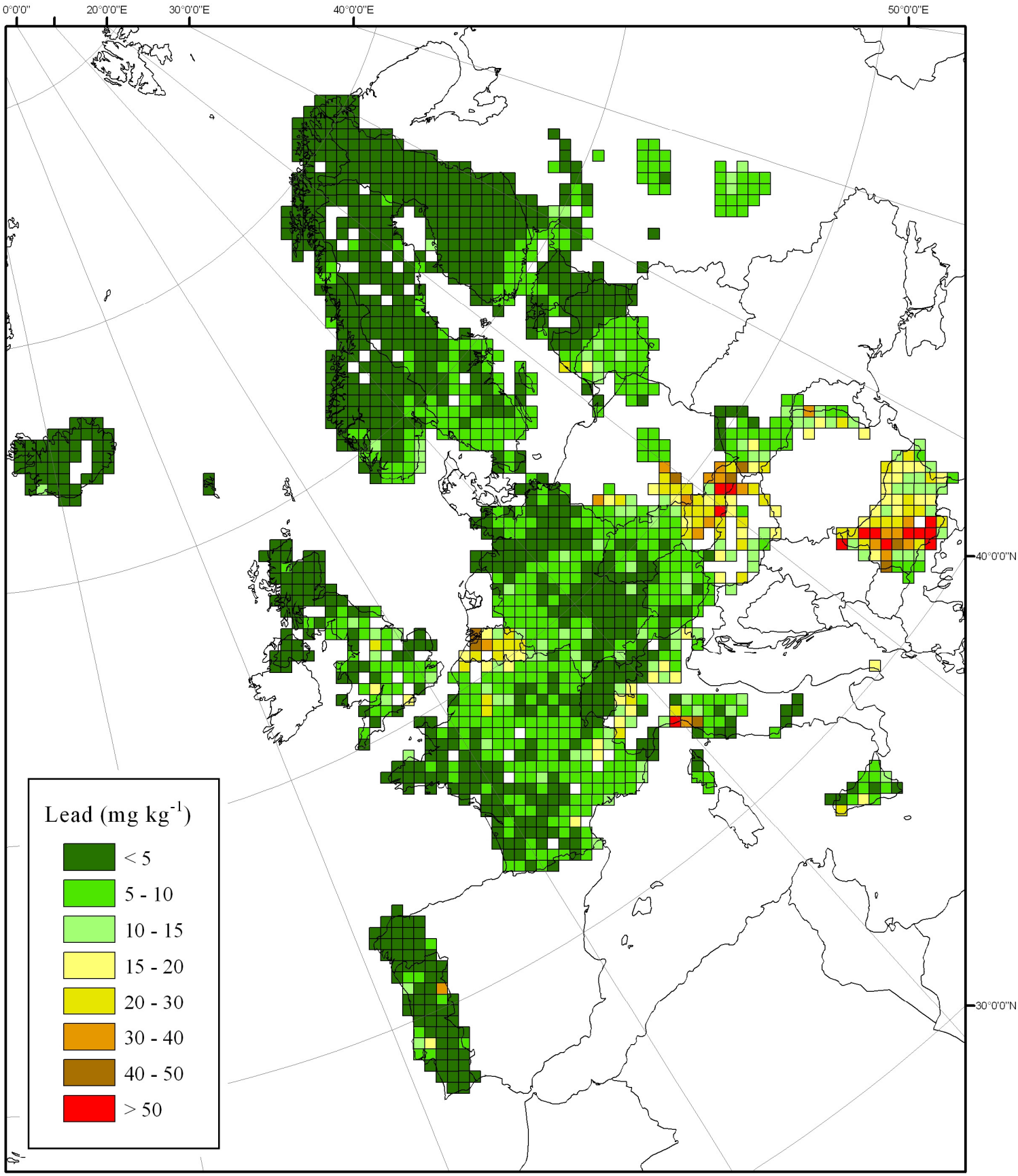

0°0'0"
20°0'0"E
30°0'0"E
40°0'0"E
50°0'0"E
40°0'0"N
30°0'0"N
Cadmium (mg kg-1)
< 0.1
0.1 - 0.2
0.2 - 0.3
0.3 - 0.4
0.4 - 0.5
0.5 - 0.6
0.6 - 0.8
> 0.8

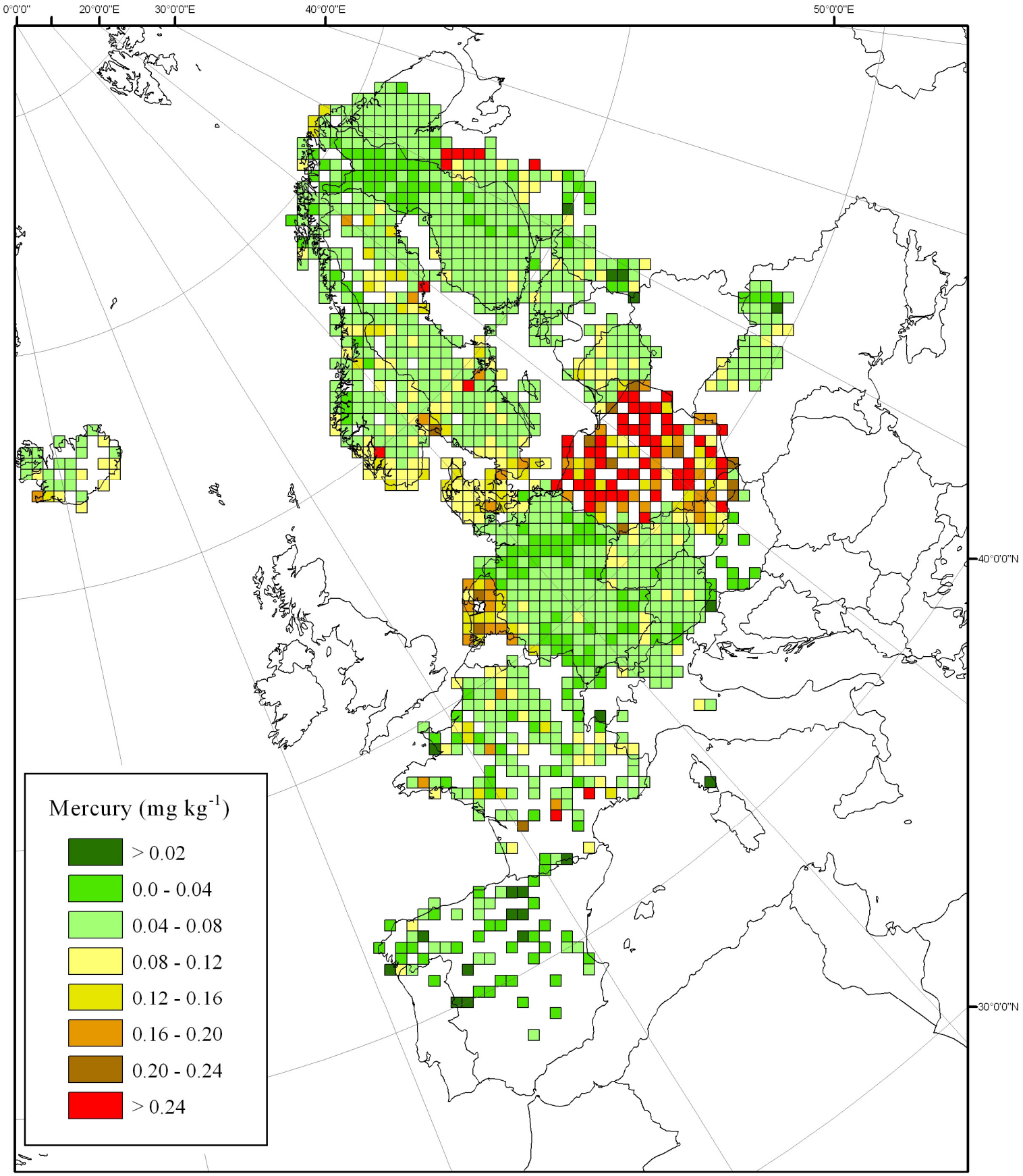

0°0'0"
20°0'0"E
30°0'0"E
40°0'0"E
50°0'0"E
40°0'0"N
30°0'0"N
Cadmium (mg kg-1)
< 0.1
0.1 - 0.2
0.2 - 0.3
0.3 - 0.4
0.4 - 0.5
0.5 - 0.6
0.6 - 0.8
> 0.8

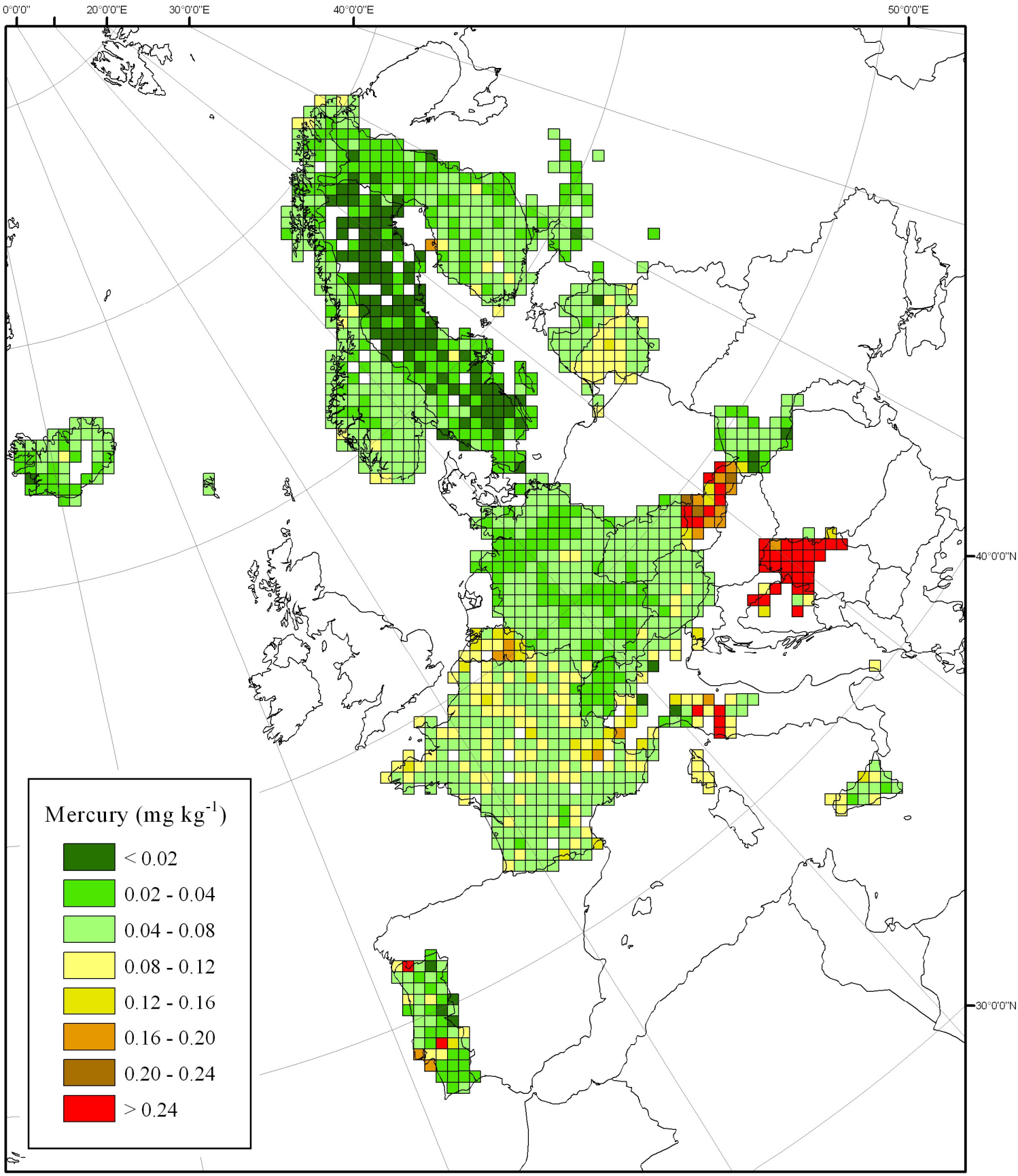

0°0'0"
20°0'0"E
30°0'0"E
40°0'0"E
50°0'0"E
40°0'0"N
30°0'0"N
Cadmium (mg kg-1)
< 0.1
0.1 - 0.2
0.2 - 0.3
0.3 - 0.4
0.4 - 0.5
0.5 - 0.6
0.6 - 0.8
> 0.8


0°0'0"
20°0'0"E
30°0'0"E
40°0'0"E
50°0'0"E
40°0'0"N
30°0'0"N
Lead (mg kg-1)
< 5
5 - 10
10 - 20
20 - 30
30 - 40
40 - 50
50 - 60
> 60


0°0'0"
20°0'0"E
30°0'0"E
40°0'0"E
50°0'0"E
40°0'0"N
30°0'0"N
Lead (mg kg-1)
< 5
5 - 10
10 - 15
15 - 20
20 - 30
30 - 40
40 - 50
> 50


0°0'0"
20°0'0"E
30°0'0"E
40°0'0"E
50°0'0"E
40°0'0"N
30°0'0"N
Lead (mg kg-1)
< 5
5 - 10
10 - 15
15 - 20
20 - 30
30 - 40
40 - 50
> 50


0°0'0"
20°0'0"E
30°0'0"E
40°0'0"E
50°0'0"E
40°0'0"N
30°0'0"N
Mercury (mg kg-1)
> 0.02
0.0 - 0.04
0.04 - 0.08
0.08 - 0.12
0.12 - 0.16
0.16 - 0.20
0.20 - 0.24
> 0.24


0°0'0"
20°0'0"E
30°0'0"E
40°0'0"E
50°0'0"E
40°0'0"N
30°0'0"N
Mercury (mg kg-1)
< 0.02
0.02 - 0.04
0.04 - 0.08
0.08 - 0.12
0.12 - 0.16
0.16 - 0.20
0.20 - 0.24
> 0.24