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RESULTS OF THE HEAVY METALS IN MOSSES SURVEY 2000/2001

Summary report by the Coordination Centre of the International Cooperative Programme on Effects of Air Pollution on Natural Vegetation and Crops (ICP Vegetation)

Introduction

1. This report summarizes a survey conducted in Europe in 2000/2001 by a consortium of scientists under the direction of the Chairperson of ICP Vegetation and with the advice of Mr. Åke Rühling (Sweden) and Mr. Eiliv Steinnes (Norway). A detailed report was published recently (Buse *et al.*, 2003). The coordination of the survey was funded by the United Kingdom Department for Environment, Food and Rural Affairs. The overall aim was to determine the heavy metal concentrations of mosses in Europe, identify the main polluted areas, produce regional maps and further develop the understanding of long-range transboundary pollution.

2. The Heavy Metals in Mosses Survey was originally established in 1980 as a joint Danish-Swedish initiative under the leadership of Mr. Åke Rühling (Sweden) and has, since then, been repeated at five-yearly intervals with an increasing number of countries and individuals participating. Twenty-eight European countries, almost 7000 sites and about 100 individuals have been involved in the current survey (2000/2001). During 2001, responsibility for the coordination of the project was handed over to ICP Vegetation.

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3. The survey provides data on concentrations of ten heavy metals (arsenic, cadmium, chromium, copper, iron, lead, mercury, nickel, vanadium, zinc) in naturally growing mosses throughout Europe. The technique of moss analysis provides a surrogate measure of the spatial patterns of heavy metal deposition from the atmosphere to terrestrial systems, and is easier and cheaper than conventional precipitation analysis (Rühling and Tyler, 1968; Tyler, 1970).

I. SAMPLING, ANALYSIS AND MAPPING PROCEDURES

4. As in previous surveys, the carpet-forming mosses *Pleurozium schreberi* and *Hylocomium splendens* were the preferred species for analysis. Where necessary, other species with a similar growth habit were collected, *Hypnum cupressiforme* being the next choice. Because the mosses were collected in a range of habitats from the sub-arctic climate of northern Sweden to the hot and dry climate of parts of southern Italy, it is inevitable that a wide range of moss species were involved. Heavy metal concentrations were determined in 25 moss species at a total of almost 7000 sites. *Pleurozium schreberi* (Brid.) Mitt was the most frequently sampled species, accounting for 39.4% of the samples, followed by *Hypnum cupressiforme* (Hedw.) (17.4%), *Hylocomium splendens* (Hedw.) (16.8%) and *Scleropodium purum* (Hedw.) (11.4%).

5. Moss samples were taken according to the guidelines set out in the experimental protocol for the 2000/2001 survey (UNECE, 2001). The procedure was similar to that summarized in the report of the 1995 survey (Rühling *et al*., 1998). 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 in small open spaces to preclude any effect of canopy drip. Only the last three years' growth of moss material was used for the analyses.

6. The concentrations of heavy metals in mosses (µg g^{-1} dry weight) were determined by a range of analytical techniques, under the broad headings of atomic absorption spectrometry, inductively-coupled plasma spectrometry (both optical emission spectrometry and mass spectrometry), fluorescence spectrometry and neutron activation. Several different methods were used across Europe for each metal.

7. In most cases, quality control of the analysis of samples was ensured by the use of certified reference materials, and was the responsibility of individual participants. Quality control during the collection of samples was the same as for the 1995 survey (Rühling *et al*., 1998). The accuracy of data received by the Coordination Centre was assessed by inspecting them for extremes and by sending summarized data and the relevant draft maps to individual contributors for checking and approval before incorporating the final data into maps.

8. Two approaches to mapping were used: (a) 'dot maps', to indicate the concentration of each heavy metal at individual sampling sites; and (b) EMEP maps, which show the mean concentration of each metal within individual 50 x 50 km grid squares. Both methods provide a more accurate image of the situation in the field than contoured maps, which tend to obscure variations in the intensity of the original sampling and to exaggerate the importance of single spots in case of low sampling density. The dot maps were produced using ArcMAP, part of ArcGIS, an integrated geographical information system (GIS). Colour-coded concentration maps for each heavy metal were produced using eight concentration

classes and colours. The eight concentration classes are the same as those used in the report of the 1995 survey (Rühling *et al*., 1998).

II. EUROPEAN DISTRIBUTION OF HEAVY METALS IN MOSSES

9. 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 from industrial and vehicle sources. Explanations for the observed distribution of individual heavy metals have been derived from information provided by the relevant participants.

10. The table below shows the minimum, maximum and median values for ten heavy metals and the number of samples for each participating country. Concentrations in mosses were relatively low in most of Europe (>50% of sampling sites) for most heavy metals. Although some countries, particularly in the West and North, tended to have only localized high concentrations, other countries, especially in the East, tended to have extensive areas with relatively high concentrations.

11. Most of Scandinavia had relatively low concentrations, but there were high levels of cadmium near a smelter in Norway and of chromium near steelworks in Finland. Elevated levels of copper in the North were likely to be from the industrialized Kola Peninsula in the Russian Federation, and somewhat elevated lead concentrations in the South from vehicle emissions elsewhere in Europe. Levels in the Baltic States were similarly low, but elevated cadmium occurred both locally near a smelter in Latvia and over a wider area, presumably carried by the prevailing south-westerly winds.

12. Concentrations of several heavy metals were particularly high in Central Europe, especially arsenic near former lignite power plants in the 'Black Triangle', where the Czech Republic, Germany and Poland meet, and cadmium in the area of the Czech/Polish/Slovak borders. High concentrations of lead in north-west Slovakia, with no metal industries, were presumably due to transboundary transport. High levels of arsenic in Romania and Serbia and Montenegro on the Balkan Peninsula were related to the copper industry and refineries, respectively. Elevated concentrations in nearby Bulgaria were likely to have been from the same source. High levels of copper in central Bulgaria were associated with copper mining and a copper smelter.

13. Heavy metal concentrations in Germany (except for the east), Austria and Switzerland tended to be relatively low, with a few localized sites with elevated concentrations, such as a former copper-producing area in western Austria. High levels in Italy were particularly associated with steelworks and oil refineries in the north-west. In the United Kingdom, elevated concentrations tended to be localized, for example, in the South Wales industrial area, but widespread, slightly raised levels of lead were probably due to the use, now discontinued, of leaded petrol in transport. In France, higher levels of lead were associated with urbanized areas; elevated chromium in the south was associated with refineries and metallurgical industries. On the Iberian Peninsula, elevated levels of arsenic were mainly associated with

urban and industrial areas. In both south-east France and southern Portugal, high levels of iron were probably due to the arid conditions allowing wind-blown dust to collect on the mosses.

III. CONCLUSIONS

14. Mosses provide a cheap, effective surrogate to precipitation analysis for the identification of hot spots of atmospheric heavy metal deposition and contamination levels in remote areas. Some moss samples with high metal concentrations indicated very high metal deposition within the vicinity of local emission sources, whereas others showed elevated deposition over a wider area, due to widespread sources, such as contaminated soil, or transboundary transport. For example, transboundary transport appears to account for elevated concentrations of lead in southern Scandinavia (presumably from vehicle emission sources elsewhere in Europe).

15. Mapping of concentrations as 'dot maps' provides a detailed and accurate picture of heavy metal distribution. Application of the EMEP grid has a smoothing effect on the data, but without the appearance of extensive zones given by contoured maps. It also eliminates the artificial effect of different sampling densities on the dot map. Abrupt differences in concentrations along national boundaries, e.g. between Switzerland and Italy, were frequently real, as boundaries tend to follow topographical features such as mountain ridges.

16. In general, there was a clear east/west decrease in the concentration of heavy metals in mosses. In countries such as Bulgaria and Poland, coal was still a major source of fuel and, although industries were becoming cleaner, they were still the source of more heavy metal pollution in the East of Europe than the West.

17. Former industrial sites or historical sites of heavy metal pollution (e.g. mines) were still causing high heavy metal concentrations in mosses in some areas. The accumulation of heavy metals in mosses over the survey's standard three-year growth period means that reductions in emissions during the period between the 1995 and 2000/2001 survey, e.g. lead in petrol in the United Kingdom or cleaning of emissions in the Czech Republic, do not necessarily show in the maps.

18. A general decline in the concentration of some heavy metals in mosses, e.g. arsenic and cadmium, was observed throughout Europe by a preliminary comparison of the 1995 and 2000/2001 surveys.

IV. RECOMMENDATIONS FOR FUTURE ANALYSES OF EXISTING DATA AND FOR THE 2005 SURVEY

19. Standardization of data from surveys prior to 1995 will allow longer-term trends to be determined. Comparison of the spatial and temporal trends of heavy metal concentrations in mosses with trends in heavy metal deposition will further the investigation of the effectiveness of the link with atmospheric deposition. In particular, the maps of heavy metal concentrations in mosses prepared by ICP Vegetation on an EMEP 50 x 50 km grid should be compared with EMEP maps of atmospheric deposition of heavy metals.

20. Standard moss samples should be included in the 2005 survey and distributed among all participants to enhance quality control. Participants should be encouraged to collect mosses from sites with known rates of atmospheric heavy metal deposition, in order to establish direct relationships between the concentration of heavy metals in mosses and rates of atmospheric deposition of metals on a European scale. Previously, Berg and Steinnes (1997) and Berg *et al.* (2003) established these relationships for Norway and the Nordic countries, respectively. In addition, participants should be encouraged to perform interspecies comparisons (Berg and Steinnes, 1997; Reimann *et al*., 2001) and comparisons between several analytical techniques (where possible).

V. REPORT

21. Further details of the 2000/2001 survey can be found in the full report (Buse *et al*., 2003) available from the ICP Vegetation Coordination Centre at the Centre for Ecology and Hydrology, Bangor, United Kingdom. Contact: Mr. Harry Harmens (e-mail: hh@ceh.ac.uk).

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Table The concentration (µg g^{-1} dry weight at 40^{o} C) of heavy metals in the moss samples from individual countries in 2000/2001. N = the number of samples.

	As	Cd	Cr	Cu	Fe	Hg	Ni	Pb	V	Zn
Austria										
N of samples	221	221	221	221	221	221	221	221	221	221
Minimum	0.04	0.08	0.25	3.40	144	0.020	0.35	1.98	0.38	11.8
Maximum	1.14	1.27	3.69	41.0	3590	0.260	7.95	22.6	10.2	114
Median	0.10	0.18	0.73	6.13	409	0.050	1.26	5.76	1.27	31.5
Belgium										
N of samples	35	35	35	35	-	34	-	35	35	35
Minimum	0.30	0.25	2.78	5.10	-	0.039	-	3.54	1.80	53.8
Maximum	4.36	1.77	47.1	37.7	-	0.360	-	62.3	26.2	226
Median	0.78	0.75	8.16	9.72	-	0.127	-	23.8	5.77	111
Bosnia and Herzegovina										
N of samples	23	-	23	23	23	23	23	-	23	23
Minimum	0.31	-	0.94	0.00	439	0.4	1.69	-	2.89	10.0
Maximum	3.74	-	18.5	67.1	6020	4.85	25.2	-	34.4	56.9
Median	1.01	-	3.45	0.00	1350	0.173	4.85	-	7.16	23.8
Bulgaria										
N of samples	217	217	217	217	217	-	217	217	217	217
Minimum	0.08	0.06	0.74	5.34	333	-	1.49	4.55	2.02	12.5
Maximum	53.0	10.6	53.1	1860	11600	-	114	887	42.6	930
Median	0.21	0.38	2.41	14.5	1410	-	3.33	18.9	4.95	32.6
Bulgaria – additional data not included in the maps										
N of samples	126	-	126	-	126	-	126	-	126	126
Minimum	0.25	-	0.50	-	692	-	0.46	-	2.19	19.2
Maximum	59.0	-	26.9	-	14700	-	18.6	-	112	378
Median	1.00	-	3.49	-	2080	-	3.90	-	7.65	39.9
Czech Republic										
N of samples	250	250	250	250	250	250	250	250	250	250
Minimum	0.07	0.09	0.38	3.69	176	0.020	0.56	1.81	0.57	19.4
Maximum	1.40	2.24	7.66	11.7	1850	0.105	10.2	48.2	5.86	149
Median	0.29	0.23	1.88	6.52	401	0.048	1.95	5.66	1.52	35.0
Estonia										
N of samples	-	100	100	100	100	-	100	100	100	100
Minimum	-	0.12	0.43	2.29	158	-	0.44	1.95	0.96	21.8
Maximum	-	0.29	4.58	17.1	1030	-	4.01	9.60	10.2	54.6
Median	-	0.20	1.01	3.39	289	-	1.01	4.18	1.72	31.4
Faroe Islands										
N of samples	8	8	8	8	8	8	8	8	8	8
Minimum	0.11	0.04	0.50	4.48	270	0.022	1.02	2.18	1.81	10.6
Maximum	0.30	0.09	1.83	9.87	1750	0.067	2.97	5.94	8.03	20.2
Median	0.15	0.06	0.68	6.84	754	0.048	1.73	3.68	3.34	14.3
Finland										
N of samples	273	938	938	938	938	271	938	938	938	938
Minimum	0.00	0.01	0.34	1.26	51	<0.01	0.46	0.65	0.17	11.5
Maximum	0.81	0.42	9.21	67.7	1950	0.180	68.8	10.0	7.54	88.0
Median	0.16	0.12	1.06	3.38	210	0.042	1.38	2.96	1.24	27.6

	As	Cd	Cr	Cu	Fe	Hg	Ni	Pb	V	Zn
France										
N of samples	517	528	528	528	527	528	528	528	528	528
Minimum	<0.23	0.04	0.16	2.20	123	0.030	0.70	1.00	1.04	1.60
Maximum	9.19	1.36	15.4	28.4	7910	0.210	19.2	44.4	17.5	294
Median	<0.23	0.20	1.69	6.40	654	0.070	2.30	5.70	2.89	40.4
Germany										
N of samples	1026	1027	1025	1027	1026	1028	1028	1026	1027	1026
Minimum	0.05	0.07	0.41	2.92	111	0.016	0.39	1.61	0.15	15.8
Maximum	1.31	1.53	4.57	25.9	2830	0.312	5.07	29.4	16.3	234
Median	0.16	0.21	0.91	7.14	343	0.041	1.13	4.62	1.06	41.0
Hungary										
N of samples	32	32	32	32	32	32	32	32	32	32
Minimum	<1.0	0.31	3.00	3.30	315	<1.0	2.90	5.00	2.10	17.7
Maximum	<1.0	1.48	13.1	17.6	3480	<1.0	25.4	38.9	10.1	114
Median	<1.0	0.55	6.40	7.65	1760	<1.0	5.35	15.0	4.20	29.9
Italy										
N of samples	198	273	242	255	222	201	269	210	211	238
Minimum	0.00	0.00	0.17	0.25	119	<0.01	0.09	0.08	0.04	10.0
Maximum	37.0	4.22	103	136	52200	5.30	90.6	410	77.0	395
Median	0.40	0.26	3.65	9.11	1380	0.070	3.80	9.42	5.59	48.
Latvia										
N of samples	101	101	101	101	101	101	101	101	101	101
Minimum	0.001	0.10	0.58	3.10	80	0.010	0.50	1.50	0.59	20.0
Maximum	0.18	2.10	3.30	12.7	392	0.110	5.50	37.0	23.0	189
Median	0.06	0.16	0.95	5.10	134	0.050	0.98	2.90	1.80	31.0
Lithuania										
N of samples	138	138	138	138	138	143	138	138	138	138
Minimum	0.13	0.09	0.44	3.73	291	0.044	0.75	3.75	1.88	18.0
Maximum	1.43	0.31	4.73	12.3	2820	0.161	7.08	22.6	54.5	87.0
Median	0.32	0.15	1.27	6.45	623	0.088	1.36	8.25	3.44	34.5
Norway										
N of samples	462	462	453	464	464	464	464	464	464	464
Minimum	0.01	0.01	0.13	1.74	99	0.022	0.06	0.50	0.28	9.71
Maximum	3.43	2.62	258	206	11200	0.208	302	27.7	22.6	661
Median	0.13	0.09	0.69	4.26	365	0.052	1.11	2.70	1.36	29.4
Poland										
N of samples	-	116	116	116	116	-	116	116	116	116
Minimum	-	0.22	0.34	4.53	216	-	0.72	3.94	1.92	28.3
Maximum	-	7.17	10.5	39.6	4240	-	2.89	65.6	16.6	589
Median	-	0.36	0.89	8.03	429	-	1.57	9.94	5.84	41.4
Portugal										
N of samples	150	150	150	150	150	150	150	150	150	150
Minimum	0.00	0.00	0.27	2.81	140	0.000	0.00	0.00	0.26	12.9
Maximum	9.71	4.10	19.5	80.3	5110	1.74	26.8	109	20.0	332
Median	0.33	0.41	1.08	6.16	561	0.043	1.21	3.11	2.72	28.1

	As	Cd	Cr	Cu	Fe	Hg	Ni	Pb	V	Zn
Romania										
N of samples	214	21	214	167	214	-	214	21	214	214
Minimum	0.27	0.26	0.50	2.21	338	-	0.26	6.45	1.93	20.1
Maximum	118	1.03	51.9	2420	21300	-	31.9	31.5	31.9	2940
Median	1.56	0.46	8.46	21.5	2510	-	3.35	14.3	7.99	79.5
Russian Federation – north-west (Saint-Petersburg, etc.)										
N of samples	98	98	98	98	98	98	98	98	98	98
Minimum	0.083	0.008	0.795	3.16	126	0.010	0.860	2.45	0.950	17.1
Maximum	0.549	3.74	5.72	77.3	1670	0.110	26.3	23.3	71.1	126
Median	0.174	0.257	1.42	5.18	421	0.040	2.04	4.70	2.18	36.2
Russia – central (Tula, Tver, Yaroslavl)										
N of samples	221	219	220	149	220	-	220	149	221	221
Minimum	0.05	0.00	0.00	3.31	68.2	-	0.00	2.06	0.34	13.4
Maximum	2.98	1.22	27.7	35.5	19600	-	21.6	18.5	62.3	104
Median	0.24	0.23	1.45	6.54	616	-	1.99	7.41	3.28	34.9
Serbia and Montenegro										
N of samples	92	-	92	92	92	92	92	-	92	92
Minimum	0.46	-	1.14	6.31	720	0.010	1.96	-	2.85	14.0
Maximum	60.8	-	21.9	3140	9220	2.69	25.7	-	38.7	415
Median	1.44	-	5.07	16.9	2360	0.386	5.65	-	9.26	32.6
Slovakia										
N of samples	86	86	86	86	86	86	86	86	86	86
Minimum	0.34	0.11	1.10	3.92	430	0.062	0.70	9.72	1.80	28.0
Maximum	2.21	1.49	42.7	37.1	13700	3.44	12.6	109	30.3	179
Median	0.71	0.59	6.45	8.76	1560	0.180	3.15	28.3	5.70	55.0
Slovenia										
N of samples	82	82	82	-	82	-	-	-	-	82
Minimum	0.09	<0.1	0.63	-	210	-	-	-	-	18.6
Maximum	0.94	2.03	26.1	-	1940	-	-	-	-	100
Median	0.33	0.43	2.59	-	713	-	-	-	-	34.5
Spain (Galicia)										
N of samples	146	146	146	146	146	-	146	146	-	146
Minimum	0.04	0.03	0.29	1.22	2	-	0.25	0.29	-	10.8
Maximum	2.65	0.48	265	24.9	1890	-	127	20.6	-	95.7
Median	0.21	0.07	5.73	4.24	243	-	4.16	1.84	-	29.9
Sweden										
N of samples	603	603	603	603	603	594	603	603	603	603
Minimum	0.04	0.05	0.11	1.69	12	0.00	0.46	0.93	0.24	13.6
Maximum	1.40	0.69	136	30.3	4270	0.231	18.2	19.4	12.1	134
Median	0.16	0.18	0.68	4.36	228	0.017	1.41	4.27	1.31	38.8
Switzerland										
N of samples	142	142	142	142	142	142	142	142	142	142
Minimum	0.02	0.05	0.37	2.69	104	0.021	0.41	0.73	0.21	14.6
Maximum	0.86	1.53	2.79	16.3	975	0.081	8.02	30.9	3.64	116
Median	0.12	0.19	0.89	4.35	337	0.032	1.22	3.25	0.88	29.6
The former Yugoslav Republic of Macedonia										
N of samples	73	73	73	-	73	-	73	-	73	73
Minimum	0.12	0.02	2.33	-	423	-	0.09	-	1.79	13.9
Maximum	7.98	2.95	122	-	17300	-	24.1	-	43.4	203
Median	0.80	0.16	7.46	-	2410	-	2.39	-	6.95	39.4

Ukraine										
N of samples	115	115	115	114	115	115	115	115	115	115
Minimum	0.06	0.10	0.46	3.69	66	0.001	0.72	2.26	0.39	11.8
Maximum	0.67	2.91	4.38	48.8	1320	0.114	7.05	32.6	4.32	107
Median	0.24	0.29	1.50	7.31	313	0.039	2.06	6.80	1.29	29.3
United Kingdom										
N of samples	250	250	250	250	-	-	250	250	250	250
Minimum	0.01	0.01	0.11	0.87	-	-	0.00	0.34	0.14	7.36
Maximum	4.49	1.20	4.80	10.0	-	-	8.04	50.7	8.25	195
Median	0.16	0.11	1.44	4.32	-	-	0.77	2.92	0.99	22.7