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PROGRESS IN INVESTIGATION OF HEAVY METAL DEPOSITION TO VEGETATION

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

I. BACKGROUND

1. In 1998, the first protocol for the control of emissions of heavy metals was adopted in Aarhus, Denmark, and signed by 36 Parties to the Convention. The Protocol on heavy metals stated that an effects-based approach should integrate information for formulating future optimized control strategies taking account of economic and technological factors (art.6). Shortly before the Protocol was adopted, methods for an effects-based approach were considered at the 1997 Workshop in Bad Harzburg, Germany (EB.AIR/WG.1/1998/13). The Workshop concluded that more research was needed to establish methods for deriving critical values for heavy metals. A shortage of information on deposition to crop plants was noted, and ICP Vegetation responded by including such measurements in its work-plan in 1998. The

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results were presented at the 1999 follow-up Workshop on Effects-Based Approaches for Heavy Metals (Schwerin, Germany,EB.AIR/WG.1/2000/10). A second sampling and analysis regime is planned for this experimental season of ICP Vegetation. Furthermore, ICP Vegetation is in the process of incorporating an existing project investigating heavy metal deposition to mosses in over 30 countries into its programme of activities.

2. The 1998 Aarhus Protocol on Heavy Metals targets three particularly harmful metals: cadmium, lead and mercury. Lead and cadmium analyses were included in the analysis of the clover clones used in the ozone experiment of ICP Vegetation. The mercury content was not measured because its volatility can lead to re-release from plants, making quantification from dried material difficult and unreliable. Instead, the arsenic and copper contents were determined as these two elements can also be harmful if accumulated in the environment or foodstuffs, and have been discussed previously in work under the Convention.

3. Data on the deposition to growing plants are essential for the validation of heavy metal deposition maps that have been developed from data of direct deposition to rain gauges or their equivalent. Values from such deposition gauges do not necessarily relate to the uptake by vegetation. First, the deposition must be intercepted by plants, either directly through the leaves or indirectly by deposition to the soil followed by root uptake. The deposits may then be removed by rain, wind or dew formation etc. and any accumulated metals may subsequently be lost by litter fall. Thus, plants accumulate heavy metals by root uptake and by leaf interception of dust particles originating from local or long-range transport. The accumulation of dust deposits by living plants is a dynamic process. Biomass increase has a diluting effect on the metal concentration, but at the same time covering of the soil surface increases, allowing more interception of the particles. From the concentration of heavy metals in the plant biomass, the covered soil surface at harvest, and the exposure time, the part of the vertical flux accumulated by the plants can be calculated. This flux can then be compared to dust deposits measured with rain gauges.

II. AIMS

4. The aims of this study were:

(a) To determine the feasibility of using the white clover clone system to assess heavy metal deposition at ICP Vegetation sites;

(b) To analyse clover samples from the sites for lead, cadmium, copper and arsenic content;

(c) To consider how this approach can be used to validate EMEP deposition models for heavy metals;

(d) To initiate the transfer of the “Heavy Metals in Mosses” programme to ICP Vegetation.

III. EXPERIMENTAL METHOD AND VALIDATION

5. Samples from the 1998 experimental season (plus one from the 1999 season) of ICP Vegetation were used to assess heavy metal deposition at 18 of the experimental sites. Participants grew the NC-S (ozone-sensitive) and NC-R (ozone-resistant) clones outdoors in 15-litre pots according to the standard protocol (UN/ECE, 1998). Two samples of the dried harvested material (leaves and stems) per clone per 28-day harvest were sent to the Veterinary and Agrochemical Research Centre (VAR) in Tervuren (Belgium) for analysis. Samples from the first harvests were excluded from the analysis because the plants were establishing outdoors at this stage. Material from 3 to 4 successive harvests per site were analysed for their lead, cadmium, copper and arsenic content. The soil substrate was not standardized at each site, and thus samples from the different locations were also included in the analysis.

6. The analysis was carried out at VAR using a technique based on the CII method (Comité Inter-Instituts d'études des techniques analytiques) of ashing the dried material, dissolution in HNO_3, and measurement with graphite furnace atomic absorption spectrometry (GF-AAS). The same method was used for peat-based organic soils. Mineral soils were extracted with HNO_3/HCl 1:3 (aqua regia) and measured with GF-AAS. The detection limits were 0.08, 0.025, 1.0 and 0.009 $\mu g\ g^{-1}$ dry matter for lead, arsenic, copper and cadmium respectively.

7. From the analysis of the duplicate samples (two containers per clone), it appeared that the reproducibility of the measurements was satisfactory for the different elements. In spite of a different growth rate for the NC-S and NC-R clones at some of the sites, there was no clear difference in bioaccumulation of arsenic, cadmium, copper and lead between the clones (e.g. lead, fig. I). When comparing concentrations of heavy metals in clover plants, the amount of growth is not of major importance, as an increase in biomass is related to an increase in leaf surface and a better interception of the dust fallout. As a precaution though, the data presented in this report are only from the NC-R clone.

8. A further consideration was the influence of root uptake on the content of the foliage given that different substrates were used at each site. Organic and mineral substrates were considered separately (table 1). No clear relationships were found between the lead and cadmium contents in the growth media and the clover forage, indicating that the cadmium and lead content in the soil is not the predominant source of those elements in the above-ground biomass. For copper, there was a relationship between the content in mineral soil and the forage (fig. II), but no such relationship existed for the organic soils. Thus, with the possible exception of measurements of the copper content of clover grown in mineral soils, there was little input from the soil substrate and the measured heavy metal contents can be considered to have been mainly deposited on to the foliage from the atmosphere.

IV. PATTERNS IN THE HEAVY METAL CONTENT OF CLOVER

9. The mean heavy metal content of the forage at the participating sites is presented in fig. III. The natural heavy metal contents, originating from root uptake, were low in the clover foliage,

and in a few cases were below the detection limit of 0.08, 0.025 and 0.009 µg g^{-1} dry matter for lead, arsenic and cadmium respectively. Copper, an essential element for plants, was present at higher concentrations in the forage.

Table 1: Regression of the heavy metal content of the soil substrate against that of the clover forage

	r^2 from linear regression	
	Organic substrates	Mineral substrates
Lead content	0.04	0.01
Cadmium content	-0.2	0.01
Copper content	0.32	0.60

Note: This relationship could not be investigated for arsenic because the levels were below the detection limit at most sites.

10. The seasonal mean lead concentration in clover ranged from 0.24 µg g^{-1} dry matter in the coastal areas of France, Wales and Germany to 2 µg g^{-1} dry matter in central Europe. The highest lead depositions were found in Germany-Cologne, Belgium-Tervuren, Switzerland-Cadenazzo and Italy-Rome and can, to some extent, be linked to the high traffic density in those areas. For cadmium, the concentrations ranged from 0.019 to 0.12 µg g^{-1} dry matter. The highest cadmium concentrations in clover were found in Belgium-Tervuren, Germany-Cologne and Germany-Trier and their surrounding areas. Emission maps for cadmium also indicate high levels in these areas. The natural arsenic content of clover is very low, and was below or very close to the detection limit of 0.025 µg g^{-1} dry matter at over half of the sites. The seasonal mean values were only clearly above the natural content expected from root uptake at the following sites: Italy-Isola Serafini (0.074 µg g^{-1}), Spain-Madrid (0.090 µg g^{-1}), Spain-Navarra (0.081 µg g^{-1}), and Italy-Rome (0.114 µg g^{-1}). It was difficult to draw conclusions from the copper contents of the clover samples because root uptake could have markedly influenced the cooper content. Nevertheless, the highest values were found at sites near to large cities or affected by major roads.

11. For most of the experimental sites, the heavy metal accumulation can be attributed to dust deposits on the leaves from long- or mid-range transport of heavy metals, as there were no known large local sources. A contribution from short-distance transport was likely at the sites in large towns or in the neighbourhood of areas with high traffic density.

V. THE HEAVY METALS IN MOSSES PROJECT

12. A new development for the ICP Vegetation was agreed at the eighteenth session of the Working Group on Effects (EB.AIR/WG.1/1999/2, paras. 28 and 30). Following on from the success of the above pilot study on the deposition of heavy metals to clover, ICP Vegetation has

been asked to take over the coordination of a well-established programme that monitors the deposition of heavy metals to mosses. The programme, originally established in 1980 as a joint Danish-Swedish initiative, has grown in size to include 30 European countries in the last survey in 1995. Some 64,000 measurements were made in the latest survey, thus providing a comprehensive picture of metal deposition across Europe (Rühling and Steinnes, 1998). Use of mosses for this type of survey has several advantages over conventional precipitation analysis, as sampling is easier without the need for expensive equipment and the higher trace element concentrations in mosses make analysis more straightforward and less prone to contamination. Several regression approaches have been used to relate the results from moss surveys to precipitation monitoring data (Berg and Steinnes, 1997). Whilst the Nordic Council of Ministers via the Nordic Working Group on Monitoring and Data is currently supporting the early phases of the year 2000 survey, its initial remit of supporting the development and harmonization of methodologies has now been fulfilled, especially as the programme has considerably outgrown its original framework as an entirely Nordic project. ICP Vegetation has therefore been invited to incorporate the programme within its remit in order to use this important source of data for the Protocol on Heavy Metals. This will be in collaboration with EMEP, the Coordination Centre for Effects, ICP Mapping and ICP Integrated Monitoring, and will take place officially on 1 April 2001. In the meantime, the year 2000 sampling survey will be conducted by Professor Rühling (Lund University, Sweden), and ICP Vegetation will begin to collate the data.

VI. CONCLUSIONS

13. The results presented have shown that the clover clone system for detecting the effects of ozone can have the dual purpose of being used to monitor heavy metal deposition to crops. Concerns over the contribution from root uptake were largely unsubstantiated for arsenic and lead because these elements are not readily taken up by the plant and thus there was no relationship between soil and forage content. However, the soil type and acidity were important for the uptake of copper and to a lesser extent cadmium. It would be preferable to have a standard soil mixture at all sites to increase the comparability. Unfortunately, this was not found to be feasible in earlier ICP Vegetation experiments as it was not possible to grow plants equally well in a standard substrate at all sites in the different climates experienced in the network. Furthermore, the basic substances for the substrate were not found to be identical in the different countries.

14. Some patterns have emerged in the data. For example, the site at Italy-Rome had the highest detected content of lead, copper, and arsenic. Since this site is close to the centre of Rome, it seems likely that dust deposition from local sources might be responsible for these high values. Other sites close to city centres, e.g. Spain-Madrid, Germany-Trier City, and Germany-Cologne, also feature in the group of sites with the highest levels of each heavy metal. It is more appropriate to consider the metal content of the rural sites that are away from local sources, such as motorways, in order to gain an impression of the input from long-range transport. Sites such as Austria-Seibersdorf and Netherlands-Wageningen fall into this category and had similar mid-range heavy metal contents for all four metals. However, a similarly rural site at Germany-

Deuselbach had comparable contents for three of the metals, but had the highest cadmium content of all sites with no obvious root uptake. This suggests that emissions from a local cadmium source might be being deposited on the clover at this site.

15. Excluding inputs from local sources, the broad patterns of lead and cadmium content at ICP Vegetation sites largely reflected those predicted by ESQUAD (1994). For example, the lead content was “high” at sites in the Benelux countries, Switzerland and northern Germany where there were predicted high deposition rates. Similarly, patterns in the concentrations of heavy metals in mosses in the Nordic Council-funded project (Ruhling and Steinnes, 1998) broadly reflected those determined by ICP Vegetation. However, the concentrations in the mosses of the Nordic Council project were approximately 10 times higher than in the clover clones. This could reflect the time period of exposure (28 days compared to an undefined period covering the age of the moss), physiological differences between the receptors, chemical differences in the substrate used (growing media versus forest soils) or the location sampled (open field versus forest clearing).

16. This provisional study has indicated that the clover clone system can be used to monitor heavy metal deposition at ICP Vegetation sites. The next stage is to repeat the sampling in 2000 using a revised experimental protocol. Additional measurements will be made such as leaf area index to allow deposition rates to be calculated. The results, together with those from the 2000 mosses survey, will ultimately be used to validate EMEP and ESQUAD deposition maps.

VII. FURTHER WORK

17. ICP Vegetation will continue to investigate heavy metal deposition to clover and will incorporate the mosses project into the programme in the following ways:

(a) Deposition of heavy metals to clover:

(i) A new sampling programme will be conducted in the summer of 2000, followed by analysis of lead, cadmium, arsenic and copper content;
(ii) Deposition rates to clover will be calculated by including the total area of the clover foliage;
(iii) The deposition to clover at ICP Vegetation sites will be compared with ESQUAD deposition maps and maps of heavy metal content of mosses;

(b) Deposition of heavy metals to mosses:

(i) Professor Rühling (Lund University, Sweden) will be assisted with the administration for the year 2000 survey for heavy metals content, and this will facilitate the transfer of the programme to ICP Vegetation on 1 April 2001;
(ii) Data from the year 2000 survey will be collated, analysed and presented in a colour report illustrating the main results;

(iii) Existing data from the previous four surveys will be converted into a usable format for mapping and for analysing trends in the data;

(iv) Ways of estimating actual deposition of heavy metals to terrestrial surfaces from the moss survey data will be investigated allowing deposition maps to be produced.

VIII. REFERENCES

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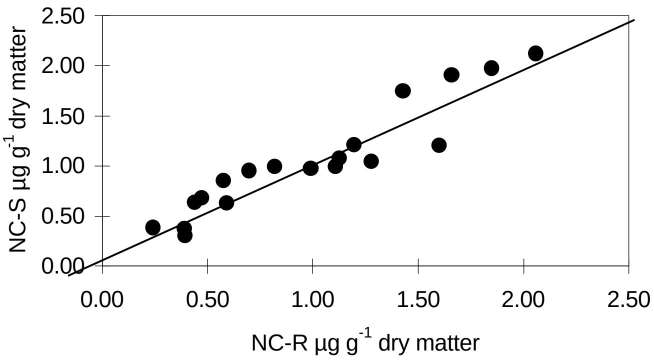

Figure I: The lead content of the NC-R clone versus that of the NC-S clone

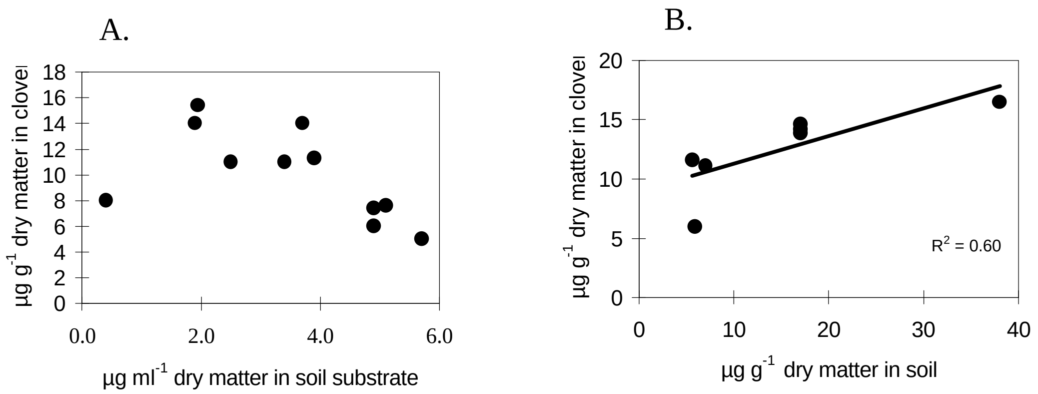

Figure II: The relationship between the copper content of the clover forage and that of the (A) organic and (B) mineral soil substrates used at the sites

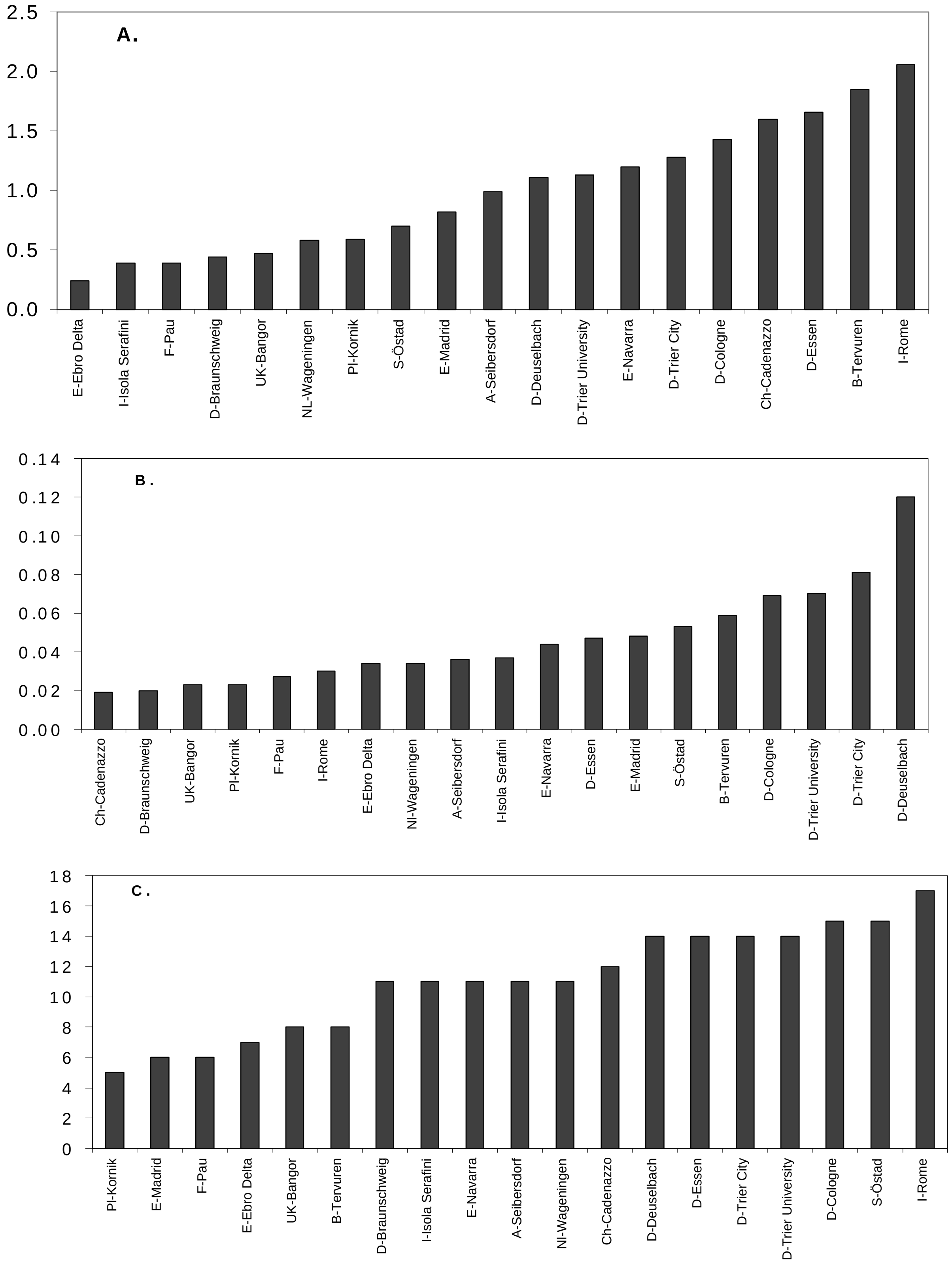

Figure III: The content of (A) lead, (B) cadmium, and (C) copper in the forage of the NC-R clone of white clover. Each value represents the mean content per 28-day harvest interval in µg g^{-1} dry matter. The sites are ordered by increasing content.