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Working Group on Effects
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Item 6 of the provisional agenda

OCURRENCE, MOVEMENT AND EFFECTS OF SELECTED HEAVY METALS

Review of ongoing activities compiled by the Bureau of the Working Group on Effects

1. At its nineteenth session, the Working Group on Effects approved the outline of the substantive report on the occurrence, movement and effects of selected heavy metals. It invited all programmes to actively cooperate in the preparation and requested the Bureau to submit a draft of the report to it at its twentieth session (EB.AIR/WG.1/2000/2, para. 67 (a)).
2. The Bureau and the Extended Bureau of the Working Group on Effects discussed the progress in preparing the report at their meetings in February 2001. It was noted that due to a lack of resources it would not be possible to synthesize the information provided by the programmes into an integrated, well balanced substantive report on the heavy metals problems.

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3. The Bureau therefore agreed to compile a summary report reviewing the activities and the results of the individual International Cooperative Programmes (ICPs) and the Task Force on the Health Aspects of Air Pollution in addressing the occurrence, movement and effects of selected heavy metals.
4. The Bureau of the Working Group welcomed the important work already done by ICPs and the Task Force in summarizing recent data and results and in assessing new knowledge and information on heavy metals and their effects. ICPs and the Task Force were invited, and agreed, to publish their reports separately and to make them available to the Working Group on Effects.
5. The Bureau noted with appreciation the comprehensive reports on heavy metals already prepared by ICP Forests and the Task Force on the Health Aspects of Air Pollution, and decided that they should be presented to the Working Group. The report on “Atmospheric Heavy Metals and Forest Ecosystems” and “Health Risk of Heavy Metals from Long-range Transboundary Air Pollution” will be presented to the Working Group on Effects at its twentieth session under agenda item 7 (d) and (e), respectively.
6. The annexes below present short summaries of the activities and the results prepared by the individual International Cooperative Programmes and the Task Force on the Health Aspects of Air Pollution. It is expected that the presentation of these reviews will encourage Parties to the Convention to further exchange information on the present state of knowledge on the occurrence, movement and effects of heavy metals. Collation and critical assessment of the best available information on the topic would be a valuable contribution of the Working Group on Effects to the envisaged review of the 1998 Protocol on Heavy Metals.

Annexes

- I. Impact of atmospheric heavy metals and forest ecosystems (ICP Forests)
- II. Heavy-metals-related activities of ICP Waters (ICP Waters)
- III. Release of heavy metals due to corrosion of materials (ICP Materials)
- IV. Heavy metal deposition to vegetation (ICP Vegetation)
- V. Heavy metals in forested reference catchments (ICP Integrated Monitoring)
- VI. Progress in deriving critical limits and calculating critical loads for selected heavy metals (ICP Mapping)
- VII. Health risk of heavy metals from long-range transboundary air pollution (Task Force on the Health Aspects of Air Pollution)

Annex I

IMPACT OF ATMOSPHERIC HEAVY METALS ON FOREST ECOSYSTEMS

1. The level I and level II monitoring programmes carried out by ICP Forests in close cooperation with the European Commission are continuously providing data on air pollution in forests and its effects on forest ecosystems. The present review assesses and summarizes the available heavy metal data from needle, leaf and soil analyses, and from atmospheric deposition, as related to the risk assessment.
2. For each of the analysed elements the current database contains the results of between 1,000 and 3,000 needle and leaf analyses from level I monitoring and 200 to 2,000 from level II. There are 2,500 to 4,000 soil analysis results from level I monitoring and 200 to 1,200 additional level II data per element. For some heavy metals, results from over 20,000 deposition measurements are available.
3. The median values of the element concentrations in needles and leaves obtained from level I and level II monitoring vary between tree species and years: 20-28 µg Zn/g dry matter, 600-700 µg Mn/g, 60 µg Fe/g, 3-4 µg Cu/g and 1-2 µg Pb/g. For level I the element concentrations are shown in table 1. These values are within the range considered by the Foliar Expert Panel as harmless (regarding toxicity) and indicate that the nutrient supply of the measured elements is also within safe limits, especially as regards important micro-nutrients such as Cu and Zn. A separate examination of the various tree species (groups), leaf or needle ages and/or sites does, however, in some cases show excessive toxic values and a shortage or surplus of nutrients. For instance, pines, especially for older needles, show particularly high median values of 5 µg/g Pb (figure 1). There is a regional occurrence of higher Pb median values of > 5 µg/g in Denmark, Norway, Bulgaria and others. Very high Cu median values of 7-9 µg/g can be found in Bulgaria and Italy, mainly in pine trees and spruce.
4. The concentration of heavy metals in needles and leaves varies between the different tree types due to the different ways these elements are either filtered out by the tree crowns or taken up by roots. More highly mobile elements such as Mn or Zn are mainly taken up by the root system and are then transported from there to the crowns, high values of less mobile elements such as Pb are the result of direct deposition onto needles and leaves.

Table 1.

Number of analyses (n) and element concentration (µg/g) in leaves and needles of all needle ages and all level I sites

Statistic	Zn	Mn	Fe	Cu	Pb
Minimum	6.0	5.0	0.0	0.1	0.0
25. Percentile	24.0	301.0	39.0	2.4	1.0
50. Percentile	33.0	609.5	63.0	3.2	2.1
75. Percentile	43.0	1087.0	110.0	6.6	4.5
Maximum	369.0	8435.0	947.0	98.5	35.7
n	3146	3146	3081	1761	1128

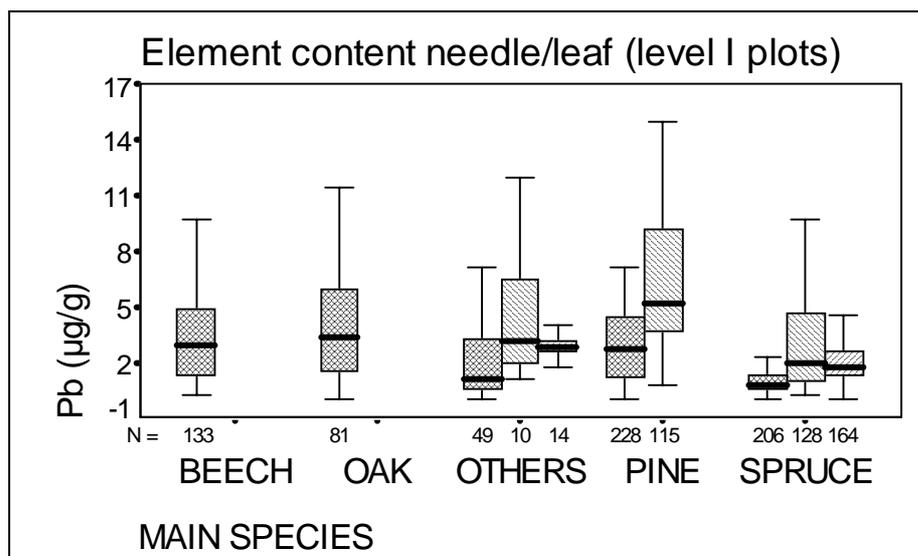


Figure 1.

Element concentration ($\mu\text{g/g}$) and number of analyses (N) in 0- (first bar), 1- (second bar) and 2-year old (third bar) needles or leaves of all level I plots. Outer lines give range of measurements (excluding extreme values); boxes indicate 75th and 25th percentile; bars in bold show median

5. Single extreme values of needle and leaf concentration, at least in the case of less mobile heavy metals, are a clear indicator of regionally high atmospheric pollution. High heavy metal values in the soil reflect pollution levels of past years. As well as the ubiquitous long-distance pollution that has been causing levels to rise for decades over all regions, particular industrial areas have been subjected to short-range pollution for a long time. Apart from such high soil levels caused by atmospheric input, pollution in some places may have natural causes, such as the presence of magma, or may be aggravated by slag tips.

6. The European median values for heavy metals in soils (over all depths) from level I monitoring were around 10000 mg Fe/kg of soil, 400 mg Mn/kg, 50 mg Zn/kg, 27 mg Pb/kg, 17 mg Cr/kg, 14 mg Ni/kg, 12 mg Cu/kg and 0.4 mg Cd/kg (table 2). The median level II results were derived from a larger amount of less polluted material from deeper soil layers. Hence, concentrations of heavy metals were only about half as high. If the soil is subdivided into an organic layer and a mineral layer, low in organic concentration, then the values observed in the organic layer, in particular for Cd, Zn and Pb, would be two to eight times higher than those in the mineral soil.

7. An evaluation framework based on toxicological and field investigations and laboratory analysis can provide threshold limits for estimating the danger posed to micro-organisms by heavy metals in soils (Bååth, E. 1989; Wilson, D.O. 1977; Berg et al. 1989, Atanassov., I., Vassileva, V., Shegunova, P. 1999; Tyler, G. et al. 1989; Bengtsson, G., Tranvik, L. 1989; Tyler, G. 1996; Inman, J.C., Parker, G.R. 1978; Coughtrey, P.J et al. 1979). This enables identification of a number of problem and risk areas. Using threshold values based on the lowest value at which heavy metals show noticeable toxicity, between 5% and 25% of all level I samples, depending on the soil depth, exceed threshold limits. It must be pointed out, however, that such evaluations cannot be generalized for all soil types, and cannot be made when few indicator organisms are available. Using an assessment framework based on a much greater number of studies, solely on mineral soil

that has only a small amount of detoxifying organic material, few stands exceed critical values. High regional values can, however, still occur (figure 2).

Table 2.

Element concentration (mg/kg) and number (n) of heavy metal analyses in all humus and mineral layers of level I plots

Statistic	Fe	Cr	Ni	Mn	Zn	Cu	Pb	Cd
25. Percentile	3607	10	9	180	27	6	12	0.1
50. Percentile	9372	17	14	396	51	12	27	0.4
75. Percentile	20970	30	28	817	75	20	48	0.8
Maximum	111800	567	360	53427	638	438	2114	28.8
n	3583	2508	2455	3806	4082	3695	3656	3145

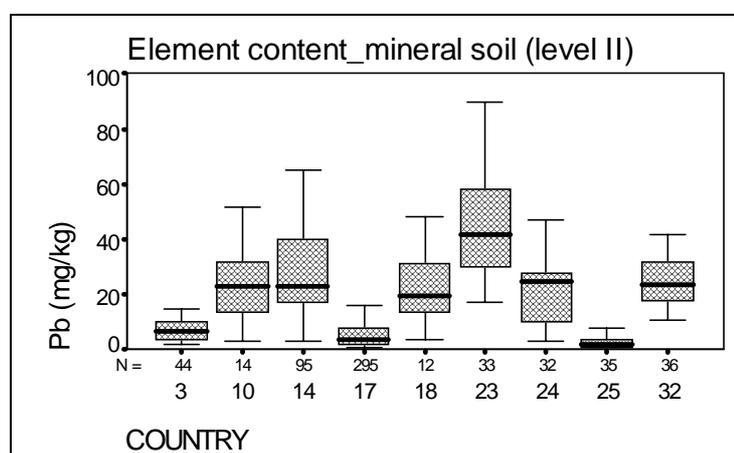


Figure 2.

Element concentration in mineral layers in mg/kg.

(3: Netherlands; 10: Portugal ; 14: Austria ; 17: Poland; 18: Slovakia; 23: Croatia; 24: Czech Republic; 25: Estonia; 32: Russian Federation). Outer lines give range of measurements (excluding extreme values); boxes indicate 75th and 25th percentile; bars in bold show median

8. Concentrations in precipitation samples obtained at level II show variations reflecting the amount of precipitation and local “hot spots”. There is, however, a general temporal trend of the atmospheric heavy metal input measured in participating European countries, as shown in other regions on a local scale. Ignoring meteorological effects and differing sampling intervals between countries, Cd and Pb concentrations continuously decreased between 1996 and 1998 (figure 3). However, the assessed time period is too short for a consolidated trend analysis. No such clear trend is apparent for Mn and Fe, while Zn and Cu concentrations appear to be increasing.

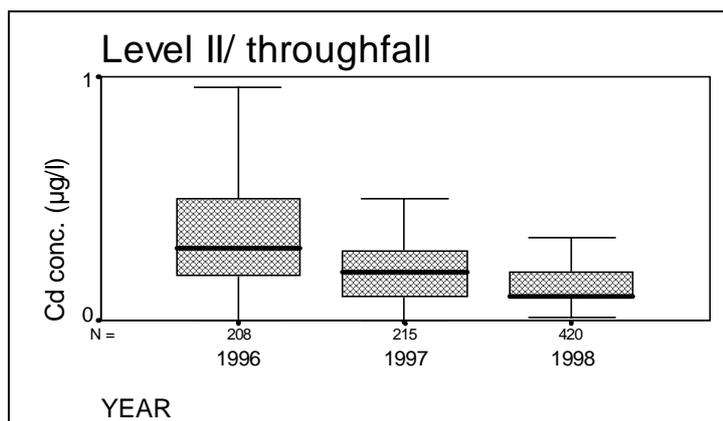


Figure 3.

Time trends of concentrations ($\mu\text{g/l}$) in throughfall samplers of level II monitoring sites. Outer lines give range of measurements (excluding extreme values); boxes indicate 75th and 25th percentile; bars in bold show median

Conclusions

9. In most regions of the countries participating in the programme and at most of the observation plots, forest pollution by heavy metals, particularly by the more toxic elements such as Pb and Cd, is not critical. Nutrient supply, particularly that of micro-nutrients such as Cu and Zn, is on the whole balanced. However, for certain tree species, soils types and in some regions, there are specific conditions for a range of heavy metals that give cause for concern. In particular, soils may show the effects of decades of accumulation of metals stemming from times of much higher atmospheric pollution. In general, however, it may be assumed that atmospheric deposition of heavy metals, especially Cd and Pb, is continuing to decrease.

10. The heavy metal data gained from the level I and level II monitoring programmes on a wide range of European sites constitute a unique database. The continuation of this important activity by ICP Forests and by other regional and national projects/programmes, together with further analyses and assessment of data, will provide better quantification and location of the effects of heavy metals, and improved assessment of related risks to forest ecosystems.

11. In future, due attention should be given to improving the comparability and reliability of results. In addition to careful data quality control, it would require, *inter alia*, the use of compatible monitoring and analytical methods and evaluating procedures. Closer time intervals should be chosen for future surveys. Due to the complexity of ecosystem research, the multiplicity of parameters involved, and the volume of the data, further development and wider application of problem-oriented evaluation models will be paramount for the success of the future work.

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Annex II

HEAVY-METALS-RELATED ACTIVITIES OF ICP WATERS

Heavy metals data within the ICP Waters database

1. The ICP Waters database contains a number of sites providing also heavy metal data. However, these sites are located in relatively few countries, and even in these countries heavy metal data are reported from fewer sites than major solutes (Skjelkvåle et al., 2000). To be able to have a good picture of the general level of heavy metals in surface waters throughout Europe and North America, heavy metal data from more sites with a larger geographical cover are needed. Some National Focal Centres reported that additional data on heavy metals from some rivers existed. Unfortunately, these sites are not likely to be suitable for monitoring the effects of air-borne heavy metals to surface waters.
2. Heavy metal data in the ICP Waters database have been analysed with different analytical methods and analytical precision. Hence, intercalibration of heavy metals analysis is essential for improving data quality and ensuring their comparability within the programme. All laboratories reporting data to ICP Waters participate in national and international intercomparison.
3. Few sites have long time series of data on heavy metals. Furthermore, at the sites with long-term records the analytical methods have changed and the detection limit has generally decreased through the monitoring period.

Chemical intercomparison of heavy metals

4. Determination of heavy metals was included in the intercalibration exercise for the first time in 2000. Fairly good results were achieved for iron and manganese. For lead, nickel and zinc less than 50% of the results were acceptable, maybe due to low concentrations used for these metals which were close to the detection limit for the methods used (Haavind, 2000). It should, therefore, be discussed whether an absolute acceptance limit should be used instead of the general target of $\pm 20\%$ when the concentrations are close to the detection limit of the recommended method.

Long-term trends in heavy metals

5. The methods for analysing heavy metals have substantially changed and improved over the past few years. The Inductively Coupled Plasma Mass Spectrometry (ICP-MS) method has in recent years increasingly become the standard and has resulted in major improvement in detection limits for many metals. However, at many sites both the change in method and the change in detection limit make it difficult to identify time trends for heavy metals. In addition, in many countries monitoring of heavy metals is a relatively new activity.
6. Due to the limited number of sites with heavy metals data and because of the shortcomings in the available data (short time series, changes in analytical methods), it is not yet possible to analyse long-term trends in heavy metals on a regional scale, in a manner similar to that for acidification (Skjelkvåle et al., 2000).

Results from regional surveys

7. Several countries have carried out synoptic surveys of heavy metals in surface waters. Results from the Nordic lakes survey in 1995 (Skjelkvåle et al., 1999) indicated that direct and indirect influence of long-range transported air pollution was the most important factor explaining the distribution of Pb, Cd and Zn in lakes on a regional scale, while bedrock geology and overburden were the major controlling factor for Cu and Ni, except in areas around the smelters at Kola (Russian Federation). The results further indicated that heavy metal pollution in lakes was a minor ecological problem on a regional scale in the Nordic Countries. Certain areas, however, in particular in southern Norway and Sweden, were affected by long-range transport leading to Pb, Cd and Zn concentrations in lakes above the limits set by the national environmental authorities. There are indications that especially in small streams there may be generally higher levels of heavy metals than in lakes, and thus the ecological problem of heavy metals may be bigger for running waters than for lakes. Mercury was not included in this survey.

8. The results of a Czech freshwater survey (Veselý and Majer, 1996; Veselý and Majer, 1998) showed that acid deposition mobilized Mn, Be, Cd and Zn from overburden and bedrock. Direct atmospheric deposition was important for Pb, F, As and Li concentrations in freshwaters. Natural higher concentrations were observed for Cu, As and Be. Local pollution of freshwater was observed for all heavy metals.

Critical limits of heavy metals in surface waters

9. In general, the concentrations of heavy metals at ICP Waters sites not influenced by local pollution sources are not very high (Skjelkvåle et al., 2000). There are at present no internationally agreed limits for toxic levels of heavy metals in surface waters. However, by applying for instance the Swedish limits, which are generally the most stringent and have the lowest critical limits for Pb and Cd, it would appear that a number of the ICP Waters sites have a concentration level of heavy metals above the critical limit. For a more complete assessment of actual levels and trends in heavy metals in surface waters throughout Europe and North America, more data in longer time series for more sites with a larger and balanced geographical coverage would be needed.

Workshop on monitoring methods for heavy metals in surface waters

10. A workshop is scheduled to take place in spring 2002 in Oslo, aimed at presenting and discussing different methods for assessing the anthropogenic contribution to the level of heavy metals in surface waters. Methods to be considered include heavy metals in sediments (both top and reference sediments), use of aquatic mosses as bioindicator (in cooperation with ICP Vegetation) and heavy metals in fish and other aquatic organisms. Analytical methods and the use of diffusion gradient thinfilm (DGT) will also be discussed.

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Annex III

RELEASE OF HEAVY METALS DUE TO CORROSION OF MATERIALS

1. Certain heavy metals such as mercury, cadmium and lead have long been known to be toxic to living organisms. In recent years there has been increased interest also in the effects of other heavy metals such as copper, zinc, chromium and nickel. Large amounts of metals are used in constructions and products which are essential to modern society. As a result of the weathering of roofs, facades and other constructions, accelerated due to acidifying pollutants, a significant part of the metals are emitted to the biosphere. The main accumulation of metals occurs in urban areas, where their influx is the greatest. Metals released from surfaces are washed away by rain and eventually end up in the sludge from waste-water treatment plants or directly in lakes, rivers and oceans. High levels of heavy metals in sludge used as fertilizer, in bottom sediments or in drinking water may in the long run have adverse effects on biological systems and human health. The present annex summarizes the work conducted within ICP Materials which can be used to assess the release of heavy metals due to corrosion of materials.

Basic concepts

2. For direct determination of the release of heavy metals due to corrosion, precipitation that has been in contact with material specimens (run-off) must be collected and analysed for metal content. These types of measurements are costly and are not being undertaken in the network of ICP Materials test sites. It is possible, however, to assess the release of heavy metals (MR) indirectly, with less accuracy, by using results from gravimetric measurements and simple mass-balance arguments:

$$MR = ML - z \cdot MCP \quad (1)$$

where ML is the total amount of corroded metal, z is a constant and MCP is the total mass of corrosion products. ML can be measured as the difference in mass between the unexposed and exposed sample after removal of corrosion products by pickling, and MCP can be measured as the difference in mass between the exposed and pickled sample. The constant, z, can be calculated by measuring or assuming the chemical composition of the corrosion products. In the case of copper, for example, if the corrosion product consists entirely of cuprite, a copper oxide with the chemical composition Cu_2O , z is equal to $2M_{Cu}/(2M_{Cu}+M_O) = 2 \cdot 64 / (2 \cdot 64 + 16) = 0.89$.

Relevant data in the ICP Materials database

3. The results of corrosion attack (ML) of zinc, copper and bronze are available for all exposure periods, since this is the most important and reliable parameter for quantifying corrosion attack. The results of the total mass of corrosion products (MCP) are, however, only generally available for copper and bronze. For zinc they have been available since 1997. Detailed analyses of corrosion products have been carried out for copper but not for bronze and zinc. Therefore, the present annex first gives an overview of metal release values for zinc, copper and bronze after 1 year of exposure and then a more detailed analysis of metal release values for copper, including time dependence.

Metal release from zinc, copper and bronze samples

4. The results of metal release are shown in table 1. Both the absolute release and the release relative to the total corrosion attack vary substantially within the network of test sites depending on the different environmental conditions.

Table 1.

Ranges (lower and upper quartile of results from the network of test sites) of metal release from copper, bronze and zinc based on the results from ICP Materials after 1 year of exposure

	Exposure time	Metal release g m⁻²	Metal release %
Copper	1987/88	0.3 – 1.2	3 – 21
Bronze	1987/88	0.6 – 4.8	8 – 61
Zinc	1997/98	2.0 – 6.0	29 – 64

5. The results show that a significant part of the corroded metal remains on the surface as part of the corrosion products, for example as green coloured patina on copper roofs or bronze statues. As will be shown in the next section, both the absolute and the relative release can vary substantially with time and results after only one year of exposure are, therefore, not sufficient for estimating metal release rates.

Detailed analysis of metal release from copper samples

6. The average corrosion rates and metal release rates after 1, 2, 4 and 8 years of exposure are shown in table 2. The metal release rate is always lower than the corrosion rate, and the proportion increases with time due to decreasing corrosion rates and increasing metal release rates. During the exposure period (1987-1995) the SO₂ concentration decreased substantially within the network of test sites. Even so, the trend in metal release rate is obvious and increases with exposure time. The decreasing SO₂ levels, however, accentuate the decrease in corrosion rate.

Table 2.

Ranges (lower and upper quartile of results from the network of test sites) of copper corrosion rates and metal release rates based on results of corrosion attack from ICP Materials during the 1987-1995 period

Exposure time (years)	Corrosion rate^a g m⁻² yr⁻¹	Metal release rate^a g m⁻² yr⁻¹	Metal release %
1	6.7 – 13.4	0.3 – 1.2	3 – 21
2	5.2 – 10.3	0.5 – 1.6	7 – 33
4	5.0 – 9.3	0.7 – 1.8	10 – 33
8	3.8 – 6.8	0.8 – 2.0	20 – 42

^aAverage rate during the measuring period, i.e. ML/t and MR/t.

7. Previous analyses of corrosion attack (ML in g m^{-2}) on unsheltered copper performed by ICP Materials resulted in a dose-response function ($R^2 = 0.73$)

$$\text{ML} = 0.0027[\text{SO}_2]^{0.32}[\text{O}_3]^{0.79}\text{Rh}\cdot\exp\{f_{\text{ML}}(\text{T})\}\cdot t^{0.78} + 0.050\text{Rain}[\text{H}^+]\cdot t^{0.89} \quad (2)$$

where $[\]$ is the concentration in $\mu\text{g m}^{-3}$ of SO_2 and O_3 , Rh is the relative humidity in %, f_{ML} is a temperature function equal to $0.083(\text{T}-10)$ when $\text{T} \leq 10$ °C, otherwise $-0.032(\text{T}-10)$, t is the exposure time in years, Rain is the amount of precipitation in mm yr^{-1} and $[\text{H}^+]$ is the hydrogen ion concentration of precipitation in mg l^{-1} . Based on results of metal release (MR in g m^{-2}), calculated from results of corrosion attack and corrosion product analyses as described in equation 1, a similar function has been obtained ($R^2 = 0.84$)

$$\text{MR} = 0.0038[\text{SO}_2]^{0.47}\text{Rh}\cdot\exp\{f_{\text{MR}}(\text{T})\}\cdot t^{1.13} + 0.0058\text{Rain}[\text{H}^+]\cdot t^{1.41} \quad (3)$$

where f_{MR} is a temperature function equal to $0.10(\text{T}-10)$ when $\text{T} \leq 10$ °C, otherwise $-0.064(\text{T}-10)$. O_3 is important for the total corrosion attack but not for the metal release. The time dependence is also different and agrees qualitatively with the results given in table 2, where the corrosion rate decreases with time and the metal release rate increases with time. It is important to note that the effect of decreasing SO_2 concentrations during the 1987-1995 period is not included in the equations, in contrast to the results in table 2. For constant environmental conditions the corrosion rate and metal release rate eventually reach the same value, corresponding to the so-called steady state, where the composition and amount of corrosion products do not change with time. This is illustrated in figure 1 using typical values of environmental parameters within the network of test sites.

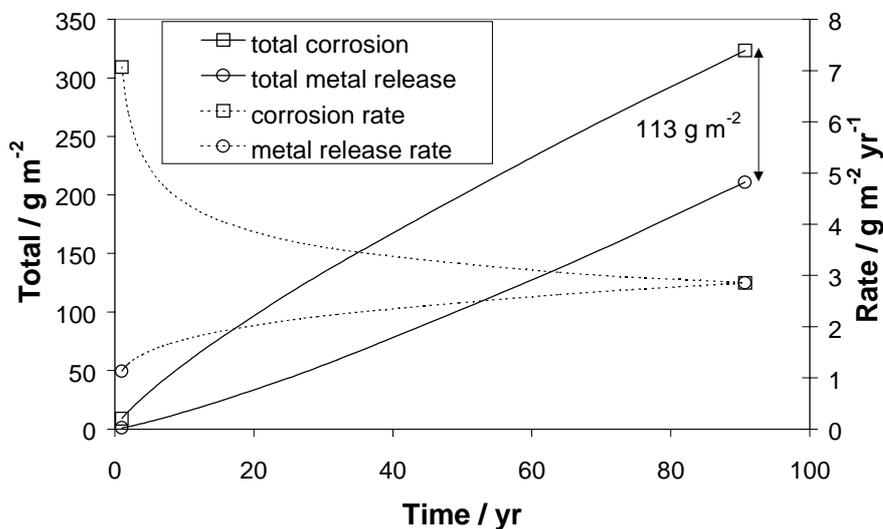


Figure 1.

Calculated copper corrosion and metal release amounts and rates as a function of exposure time based on dose-response functions (Eq. 2 and 3) and constant environmental conditions ($[\text{SO}_2] = 10 \mu\text{g m}^{-3}$, $[\text{O}_3] = 40 \mu\text{g m}^{-3}$, Rh = 75%, $\text{T} = 10$ °C, Rain = 700mm yr^{-1} , and pH = 4.5). The difference between the amounts of corrosion and metal release (113g m^{-2} at steady state) corresponds to the amount of metal retained on the surface in the corrosion products

Conclusions

8. An overview analysis of the results of zinc, copper and bronze after 1 year of exposure and a detailed analysis of copper after 1, 2, 4 and 8 years of exposure in ICP Materials permit the following conclusions:

(a) For all metals both the absolute release of metal and the release relative to the total corrosion attack vary considerably depending on the environmental conditions. SO_2 is the most important parameter and it increases both the total corrosion and the metal release. After one year of exposure the metal releases in the network of test sites are typically 0.3-1.2, 0.6-4.8 and 2.0-6.0 g m^{-2} for copper, bronze and zinc, respectively;

(b) For copper, a dose-response function for the amount of metal release has been obtained where the metal release rate increases with time. By combining this relation with the previously obtained dose-response function for corrosion attack, where the corrosion rate decreases with time, it is possible to estimate rates applicable to "steady state";

(c) The dose-response function for the amount of metal released includes the environmental parameters SO_2 , relative humidity, temperature, amount and acidity of precipitation, while the dose-response function for the corrosion attack includes these parameters and in addition the O_3 concentration;

(d) The decreasing levels of acidifying air pollutants and the decrease in acidity of precipitation have contributed to a reduction in the rate of metals released from surfaces of buildings and other constructions.

Annex IV

HEAVY METAL DEPOSITION TO VEGETATION

Introduction

1. The International Cooperative Programme on Effects of Air Pollution on Natural Vegetation and Crops (ICP Vegetation) is, *inter alia*, documenting the concentrations of heavy metals in vegetation in the ECE region. Three approaches are being taken: (i) the heavy metal content of white clover grown at selected ICP Vegetation sites is being monitored; (ii) information from the literature on the concentrations in food plants and possible uptake from soils is being collated and reviewed; and (iii) the concentrations in the natural environment are being monitored by analysing mosses sampled from over 8000 sites in Europe. These ongoing activities were initiated by ICP Vegetation with the aim of overcoming the deficit of information on the heavy metal content of vegetation that was noted at the Bad Harzburg Workshop in 1997.

Heavy metal content of crops in the ECE region

2. Data on the deposition of heavy metals to growing plants is essential for the validation of heavy metal deposition maps that have been developed from data from direct deposition to rain gauges or their equivalent. The values from such deposition gauges do not necessarily relate to the uptake by vegetation. First, the deposition must be intercepted by the 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. 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 of the Norwegian Institute for Air Research (NILU).

3. The primary contribution of ICP Vegetation on this subject has been to analyse samples of clover and growth media from the 1998 and 2000 ozone experiments for heavy metal content. In these experiments, cuttings of ozone-sensitive (NC-S) and ozone-resistant (NC-R) biotypes of white clover were distributed to participants by the Coordination Centre. The plants were grown according to a standard protocol, and harvested every 28 days by cutting back to a few centimetres above soil level. The regrowth of each biotype is linked to the pollution and climatic conditions during the period of regrowth. By analysing the harvested material of the NC-R biotype for heavy metal content, it has been possible to monitor concentrations at each site over three separate monthly periods. There were practical advantages from using this approach. It was not necessary to set up additional plants for heavy metal analysis, and the clover was already being grown according to a well-standardized experimental protocol that worked well in the climatic conditions experienced at sites in countries as far apart as Spain and Sweden.

4. Heavy metals analysis was conducted at the Veterinary and Agrochemical Research Centre (VAR), Tervuren (Belgium), by Mr. L. De Temmerman, as a contribution in kind to ICP Vegetation. The results from the first survey in 1998 were considered in detail in a technical report presented to the Working Group on Effects (UN/ECE, 2000). 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 unlikely to be 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, 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.

5. Examples of results are shown in table 1 which indicates the seasonal mean lead concentration in clover (averaged over three summer months) at selected ICP Vegetation sites. The lead concentrations in the whole data set (17 sites representing 13 countries) ranged from 0.24 $\mu\text{g g}^{-1}$ to 2 $\mu\text{g g}^{-1}$ dry matter in 1998 and from 0.3 to 1.67 $\mu\text{g g}^{-1}$ dry matter in 2000. Concentrations were the highest at the urban sites, but were also relatively high at sites in rural areas that are influenced by motorways. The 1998 samples were also analysed for cadmium, copper and arsenic (UN/ECE, 2000), and further analysis of the 2000 samples for these metals plus chromium and nickel is planned for 2001/02.

Table 1.

The lead content of clover grown at selected ICP Vegetation sites, presented as the mean of three summer month exposures in $\mu\text{g g}^{-1}$ dry matter

	Remote/rural sites		Rural sites with influence of motorway		Rural/urban fringe sites		Urban sites	
	Bangor (UK)	Östad (S)	Seibersdorf (A)	Isola Serafini (I)	Tervuren (B)	Trier Univ. (D)	Cologne (D)	Rome (I)
1998	0.47	0.70	0.99	0.39	1.85	1.13	1.43	2.06
2000	0.50	0.14	0.70	1.12	0.53	0.91	1.67	0.88

6. These results were presented by Mr. De Temmerman, a member of the ICP Vegetation Steering Committee, at the ad hoc expert group meeting on effects-based critical limits for heavy metals (Bratislava, October 2000), and the meeting on health risks of heavy metals organized by the World Health Organization's (WHO) European Centre for Environment and Health (Bilthoven, October 2000). Two important areas where ICP Vegetation could contribute to the debate on critical limits of heavy metals for crops arose from these meetings. Firstly, there is a need for more information on the relationship between total heavy metal content of soils, the biologically available concentration (in the soil solution), and the uptake by crops. Secondly, more information is needed on the contribution of heavy metals from long-range sources to the contamination of food. These issues will be addressed by ICP Vegetation during the next two years.

Heavy metal content of mosses in Europe

7. A new development for ICP Vegetation was agreed at the 18th session of the Working Group on Effects (August, 1999). Following the success of the study of the deposition of heavy

metals to clover, ICP Vegetation was 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 by Mr. A. Rühling (University of Lund, Sweden) as a joint Danish-Swedish initiative, had grown in size to include 30 European countries in the last survey in 1995. Some 8000 moss samples were collected in the 1995 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).

8. The 2000/2001 sampling survey is being jointly organized by Mr. Rühling, and the ICP Vegetation Coordination Centre at Bangor (United Kingdom). Letters have been sent to each of the participants of the 1995 survey to inform them of the transfer of the programme to ICP Vegetation, and to request their permission to use their data from all surveys for work carried out under the Convention. So far, 22 countries have responded to this request. Without exception, the participants have responded enthusiastically and have given their permission for their data to be used. Close cooperation between the ICP Vegetation Coordination Centre and Mr. Rühling facilitated the transfer of all of the data to Bangor. It also made it possible to consider the data from each country and sampling year individually with regard to data quality issues, heavy metals analysis methods, major sources of metals, and knowledge of the country and participants. All the data from the 1985, 1990 and 1995 surveys has now been transferred to the Coordination Centre in the form of text files. The process of transferring the data into an ORACLE database linked to a geographical information system (GIS) has now started. Methods for transferring the data into an EMEP 50 km x 50 km grid are currently being developed.

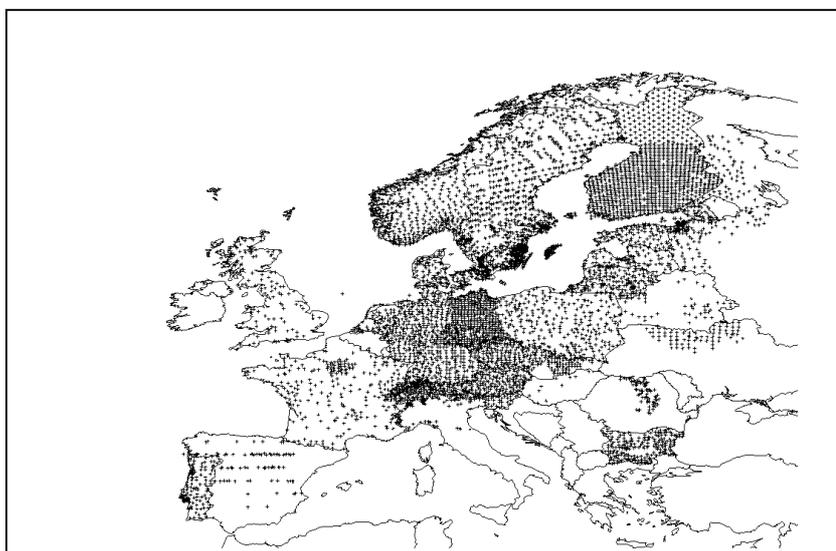


Figure 1. Moss sampling sites in the 1995 survey
The boundaries shown on this map do not imply official endorsement or acceptance by the United Nations.

Further work

9. In view of the expected future review of the current Protocol on Heavy Metals, ICP Vegetation will continue to provide information on the heavy metal content of vegetation in the ECE region. Methods for converting the data from the clover samples into deposition rates are being developed at VAR by considering growth rates and leaf area development during the one-month growth periods. These data could then be used to validate EMEP deposition maps for Pb and Cd. Further assistance in the development of transfer functions to convert soil heavy metal contents into biologically-available heavy metal contents (within the soil solution) will be provided to ICP on Mapping of Critical Levels and Loads and to its Task Force. Information on the heavy metal content of crops, derived from the literature and from the analysis of samples from commercial fields close to selected ICP Vegetation sites will be collated for the Task Force on the Health Aspects of Air Pollution. The heavy metals in mosses data will be transferred into a database for use in mapping. Concentration maps will be produced on an EMEP 50 km x 50 km grid for each metal and year and, where appropriate, trends will be analysed. An advisory committee of experts on the heavy metals in mosses survey will be established to consider methods for calculating heavy metal deposition rates from the concentrations in the mosses.

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Annex V

HEAVY METALS IN FORESTED REFERENCE CATCHMENTS^{1/}

Introduction

1. The International Cooperative Programme on Integrated Monitoring of Air Pollution Effects on Ecosystems (ICP IM) carries out investigations on heavy metals (HM) at integrated monitoring sites in mainly forested catchments. The main focus is on cadmium (Cd) and lead (Pb), but attention is also given to copper (Cu), nickel (Ni) and zinc (Zn) (nine sites) and arsenic (As), vanadium (V) and chromium (Cr) (six sites). However, in a few countries mercury (Hg) is also of considerable interest (data from two sites are reported). It should be noted that the heavy metal measurements have been optional in the integrated monitoring (IM) programme, so not all sites report data.

2. In total, data on heavy metal concentrations were provided from 29 integrated monitoring sites. Information on bulk deposition was available from 19 sites, moss chemistry from 22 sites, throughfall from 17 sites, stem flow, soil, groundwater and run-off from 10 sites, foliar and litter from 12 sites and information on soils from 22 sites. This annex deals mainly with Cd, Pb, Cu, Zn and to some extent with Hg.

3. Heavy metal concentrations in relevant environments are often below detection limit (dl), especially in water. For assuring data quality, the Integrated Monitoring Manual procedures are applied (ICP IM, 1998). The Manual requires that "if the primary data-series contains values below the detection limit, these values are estimated by 0.5 x detection limit value prior to statistical mean calculations". Values are often positively skewed, which means that non-parametric statistical methods should be used. However, in this annex the values rely on ordinary average and median calculations.

4. The degree of heavy metal retention in forest ecosystems is monitored as input and output from small well-defined catchments, according to the IM method. Dry deposition should be included in the input, so that total deposition roughly equals throughfall plus litterfall, with internal circulation in the tree stand as an added term. Additional measurements in soil water and groundwater allocate the accumulation to various soil layers. For proper mass balance calculations transport has to be determined by use of hydrological soil models. A monthly water balance model for forest soils (WATBAL) applied on IM sites is an example of a simple, easy model.

Heavy metal concentrations in water compartments

5. To calculate mean annual deposition concentrations, the amount of monthly precipitation gave the weight deposited each month and the total was added up. This resulted in ranges of bulk deposition concentrations, sometimes agreeing well with EMEP estimations, sometimes less well,

^{1/} Summary of a technical report on the topic by Lage Bringmark, Tuija Ruoho-Airola, Michael Starr, Petri Porvari, Matti Verta, Lars Lundin and Martin Forsius (to be published).

with most deviations observed for Pb. In the years 1996-98 the IM sites reported concentrations of Cd in a range of 0.01-0.8 µg/l, Cu of 0.8-4.4 µg/l, Pb of 0.5-9.5 µg/l, and Zn of 1-50 µg/l.

6. Concentration of heavy metals in collected bulk deposition is influenced by the vegetation cover, especially by trees. When the precipitation passes through the canopy, the concentration increases due to metal leaching of the leaves or needles (Ukonmaanaho et al., 2000). The leached metals originate either from dry deposited pollution, or from inner circulation of elements in the vegetation cover. Fractions that are not leached will reach the ground when leaves or needles are shed. The following median concentrations of metals in throughfall were observed: Cd 0.07-0.7 µg/l, Cu 0.9-7 µg/l, Ni 0.6-8 µg/l, Pb 2-10 µg/l, and Zn 6-68 µg/l.

7. Extensive measurements in soil water performed at the IM sites of Finland, Latvia, Poland and Sweden yielded the following concentration ranges: Cd 0.07-1.3, Cu 0.24-5.4, Ni 6-12, Pb 0.26-27 and Zn 11-138 µg/l, all representing site median concentrations. The very high levels were found in upper soil layers in Latvia and Poland.

8. Ranges for run-off concentrations (site medians) at ten sites were: Cd 0.015-0.36, Cu 0.13-1.4, Ni 0.13-5, Pb 0.05-2 and Zn 0.4-14 µg/l; export of heavy metals from forested catchments differs as a consequence of metal deposition and other factors.

Fluxes and retention

9. The reported input/output balances for IM catchments in Finland and Sweden show the considerable retention of Cd, Cu, Ni, Pb and Zn.: 80 to 95% of the total input (Aastrup et al., 1995; Ukonmaanaho et al., 2000). At some sites retention is somewhat lower for Cd and Zn, but even for these more mobile metals the general picture indicates ongoing accumulation in the system. Finnish plot scale budgets calculated for heavy metal transport in soil water show that storage takes place in lower parts of the catchment, either in deep soil layers or in peatlands. (This observation refers to a low deposition situation in a forest landscape with large peat deposits in wet areas.)

10. Although the hydrological soil model has not yet been applied for transport calculations at all sites, available metal concentration profiles in soil water for a few sites in eastern Europe indicate relocation from upper soil layers to lower (table 1). High metal levels may occur further down in the soil profile and in run-off water in some cases. These sites are subject to larger metal loads than Nordic sites. Soils are of similar podzolic types implicating similar processes at least in upland areas.

Soil stores

11. Soils have a large capacity for heavy metal storage due to adsorption to organic material. The present soil stores have resulted from a long deposition history (Aastrup et al., 1995). Reduced deposition and relocation between soil layers by leaching in recent years have not yet had a full impact. The following concentration ranges were observed in humus layers of IM sites: Cd 0.3-1 µg/g (even up to 3 at one site), Cu 5-23 µg/g, Ni 0.6-8 µg/g, Pb 13-160 µg/g, and Zn 23-100 µg/g. In mineral soil layers in the lower part of the rooting zone at a depth of 30-40 cm, the

following concentrations occurred: Cd 0.01-1 µg/g, Cu 0.7-21 µg/g, Ni 2-24 µg/g, Pb 4-46 µg/g, and Zn 3-85 µg/g. Especially for Pb, a major component of long-range air pollution, there is a pronounced allocation to humus layers. The same is the case for Hg although the IM data are scarce.

Table 1.
Aqueous heavy metal concentration profiles through selected catchments. Site median concentrations (µg/l)

		Cd	Cu	Ni	Pb	Zn	
<u>Lekuk (Poland)</u>	deposition	0.3	2.1	1.0	3.7	16	
	throughfall (spruce)	0.4	4.6	2.7	5.7	68	
	soil water 25 cm		1.3	5.0	9.8	27.0	52
	soil water 50 cm		0.7	3.7	6.3	41.0	52
	run-off water	0.4					
<u>Rucava (Latvia)</u>	deposition	0.2	1.3	0.6	3.7	19	
	throughfall (pine)	0.4	1.8	0.5	3.5	27	
	soil water 10 cm		0.2	2.3		6.4	91
	soil water 20 cm		0.07	0.7		0.8	13
	soil water 40 cm		0.03	0.5		0.2	7
	run-off water	0.06	1.4		0.2	7	
<u>Aneboda (Sweden)</u>	throughfall (spruce)	0.15	5.0	0.8	4.5	39	
	soil water 38 cm		0.3	0.6		0.5	30
	run-off water	0.04	0.8	0.8	1.2	5	
<u>Valkeakotinen (Finland)</u>	deposition	0.04	1.0	0.4	2.0	4	
	throughfall (spruce)	0.4	2.0	3.5	7.3	12	
	soil water 35cm					27	
	run-off water	0.02	0.3	0.5	0.5	4	

Biological effects of heavy metals

12. The increased attention devoted by the Working Group on Effects to the environmental and health effects of heavy metals pollution has stimulated biological research, including mass balance calculations and attempts to define critical limits of selected heavy metals. Consequently, more studies have focused on the topsoil, the organic soil layer where heavy metals are efficiently stored. High heavy metal content inhibits basic microbial activity with decreasing decomposition of the organic material resulting in hampered turnover of nutrients.

13. At its recent meeting on effect-based critical limits for heavy metals (Bratislava, October 2000) the ad hoc expert group compiled preliminary effect-based critical limits for soils and soil solution, based on the "precautionary principle", rather than the "maximum acceptable damage" principle (UN/ECE, 2000). The Meeting proposed, *inter alia*, the following ranges of total soil contents: Hg 0.1-0.25 mg/kg, Pb 10-40 mg/kg and Cd 0.1-0.4 mg/kg. It was noted, however, that

the available data and knowledge would require further elaboration and a comprehensive assessment. The integrated monitoring programme and its sites would be the most suitable for this kind of research.

14. Mercury is of special interest to freshwater biology but information is very limited. From a few catchments there are total Hg data but the most bioactive phase of Hg, that is methylmercury, is rarely monitored. However, data from the literature indicate an input of methylmercury from deposition (0.04-0.46 g/km² per year) that could be sufficient to cause problems in lake fish. But it is more likely that the main source of methylmercury in lakes is the internal formation in wet areas of catchments (Verta et al., 1994; Rudd 1995; Munthe et al., 1998). Observed outflow of methylmercury from catchments to surface water ranged from 0.007 to 0.33 g/km² per year.

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Annex VI

PROGRESS IN DERIVING CRITICAL LIMITS AND CALCUTATING CRITICAL LOADS FOR SELECTED HEAVY METALS

Introduction

1. This annex reviews the progress achieved in deriving critical limits and calculating critical loads for heavy metals in terrestrial ecosystems and outlines the requirements for future work.
2. The workshop on critical limits and effect-based approaches for heavy metals and persistent organic pollutants (Bad Harzburg, November 1997) concluded that applying the critical load approach was feasible for Cd and Pb, while for Hg appropriate databases and models were not available at that time (Gregor et al., 1998). The follow-up workshop on effects-based approaches for heavy metals was held in Schwerin in October 1999 (Gregor et al., 1999). The workshops drew up and agreed on principles for deriving critical limits and on methods for critical load calculations. The use of mass balance models was recommended for calculating critical loads for cadmium (Cd) and lead (Pb). For mercury (Hg), however, several approaches were considered which would require further elaboration and testing. Two manuals for calculating critical loads of heavy metals for terrestrial ecosystems (DeVries and Bakker, 1998) and for aquatic ecosystems (DeVries et al., 1998) were presented and discussed at the workshops.
3. To advance the work on deriving critical limits for terrestrial ecosystems, the Task Force on ICP Mapping at its sixteenth meeting (Edinburgh, April 2000) decided to set up an ad hoc expert group on effect-based critical limits for heavy metals. At its first meeting (Bratislava, October 2000), the expert group evaluated existing knowledge and databases on the effects of Cd, Pb and Hg on soils, took account of soil properties (identified as influencing bio-availability of heavy metals), suggested ranges of values for critical limits of selected heavy metals (based on defined extraction methods), and considered the possibilities for transforming effect-related data (total contents or reactive soil concentrations) into total concentrations of the soil solution.
4. The ad hoc expert group stressed the need to speed up the further development of the effect-based approach for heavy metals so that it could be applied in any future review of the Protocol on Heavy Metals once it enters into force. Given that this review may take place in 2004-2005, the group envisages the following time frame for further work:

2004 - 2005	Possible review/revision of the 1998 Protocol on Heavy Metals;
2002 - 2003	Finalizing regional data sets and mapping critical loads for Cd, Pb and Hg;
2001 - 2002	Developing, testing, and validating tools for critical loads calculations;
2000 - 2002	Preparing critical limits and transfer functions.

Progress in deriving critical limits for heavy metals

5. The ad hoc expert group at its meeting in Bratislava also compiled a set of critical limits for Cd, Pb and Hg, reflecting the present state of knowledge, and characterizing different levels of

risk (as proposed in Gregor et al., 1999). These levels are:

- (a) The precautionary principle; and
- (b) Maximum accepted damage.

The third suggestion, the so-called stand-still approach, does not need critical limits but requires recent concentrations. This approach was not elaborated on at the Bratislava meeting.

6. Most biological effects of metals on soils are more closely related to the soil solution concentrations, or free ion activity of the metal in the soil solution, than to total contents. A critical concentration of the soil solution is also necessary for calculating the term of tolerable leaching in the critical load model. As the critical limits related to such soluble fractions are rarely available, there is a need to transform contents or concentrations of different fractions using transfer functions. The values of limits put forward at the Bratislava meeting (Čurlík et al., 2000) were based on:

- (a) Total content;
- (b) Total reactive content; and
- (c) Soil solution concentration.

7. The values were achieved by a range of different methods of derivation (e.g. epidemiological method or direct derivation for specific receptors from single bioassay experiments). Some values for soil solution were the results of transfer calculations. Safety factors were sometimes included in the values. The known information on used databases and methods were specified in footnotes to the individual values. In some cases, however, the explanations provided for countries' critical limit values would require further completion by the National Focal Centres (NFCs).

8. Following the decision of the expert group, the transfer functions used by some countries for Pb and Cd were collated after the meeting (Čurlík et al., 2000). Full testing of these transfer functions, including the exchange and analysis of the underlying data sets, was identified as an urgent task. Experts from the Netherlands and the United Kingdom agreed to coordinate this activity. Compiling different methods of measurement of heavy metals in soils was also essential. It was noted that the form of the transfer functions for Hg would differ from those for Pb and Cd.

9. The available values of critical limits enable individual countries to start with critical load calculations. However, the ranges of values are still large, especially for soil solution concentrations. Therefore, additional specifications and instructions would be needed to harmonize calculations on a wider European scale.

10. For further improvements of the critical limits more information would be needed on levels of "original" background concentrations of heavy metals in soil and concentrations "added" over large spatial scales by past human activities. It is important to compare current concentrations with critical limits in order to assess the implications of critical load exceedance.

Progress in critical load calculations

11. Since the 1999 Schwerin workshop, considerable progress has been achieved in several countries in applying effect-based approaches for heavy metals. The experience gained has made it possible to propose alternative procedures for practical work at different levels of sophistication.
12. Models to pursue a critical loads approach are available, and most countries possess much of the data required to apply such models in the near future. Some countries have already gained substantial practical experience and also produced national critical load maps for selected heavy metals. This experience should be shared among countries and their NFCs through ICP Mapping.
13. Pursuant to the request of the ad hoc expert group, the “Short Guidance for the Calculation of Critical Loads for Cadmium, Lead and Mercury from Effect-based Critical Limits” (Gregor et al., 2000) was produced shortly after the Bratislava meeting. The guidance should assist the interested countries and NFCs to commence the work without any undue delay. However, adequate funding would be required on both national and international levels to ensure that the necessary tools and methods are available, verified and fully operational on a European scale.
14. The expert group also suggested that ICP Mapping should provide the necessary application tools and encourage the use of relevant models in the whole UN/ECE region. The Task Force on ICP Mapping should initiate and coordinate this activity and ensure effective cooperation with other ICPs. It should also compile national maps to support the further harmonization of the models and databases. It would also be useful to intensify cooperation with projects, programmes or organizations/institutions outside the Convention dealing with problems of heavy metals.

Recommendations for future work

15. The proposed critical limits for heavy metals should be tested and as far as possible applied by countries in their national exercises as soon as possible, with due account taken of their qualifiers and additional specifications. Full use should be made of the instructions provided in the Short Guidance, which collate the minimum requirements for this activity.
16. The necessary experimental work on a national and international level should be supported. Special attention should be given to transfer functions and to effects related directly to soil solution concentrations and free ion activities in the lower concentration ranges. Re-analysis of existing experimental work using appropriate transfer functions to estimate soil solution concentrations and free ion activities can in the short term greatly increase the available data to estimate critical limits.
17. In the course of the work, informal groups of experts should be formed to deal with specific problems and/or subregional workshops organized to harmonize approaches.
18. Existing transfer functions should be compiled and validated. More specifically, an ad hoc expert group should be formed to review the state of science in the field of transfer functions and experts from the United Kingdom and the Netherlands have already volunteered to coordinate it.

19. A follow-up meeting of the ad hoc expert group should be organized in 2002 to review new data and knowledge, inter alia, on the effects of heavy metals and transfer functions, and to consider experience gathered from applying critical limits in critical load calculations.

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Annex VII

HEALTH RISK OF HEAVY METALS FROM LONG-RANGE TRANSBOUNDARY AIR POLLUTION

Introduction

1. Heavy metals such as cadmium, lead and mercury are common air pollutants and are emitted predominantly into air as a result of various industrial activities. This annex summarizes the report to be published soon by the Task Force on the Health Aspects of Air Pollution, reviewing the available information on the sources, chemical properties and spatial distribution of pollution of cadmium, lead and mercury from long-range transboundary air pollution, and assessing the potential health effects in Europe.

Cadmium

2. Both worldwide and in European countries, approximately 85-90% of total airborne cadmium emissions arise from anthropogenic sources, mainly from smelting and refining of non-ferrous metals, fossil fuel combustion and municipal waste incineration.

3. Food is the main source of cadmium exposure in the general population. It is responsible for about 99% of the total intake in non-smokers. Cigarette smoking can double the daily intake of cadmium.

4. Daily intake of cadmium is directly related to the concentration in soil. Long-range transport of air pollution contributes about 0.1 - 0.2% to the actual cadmium content in the topsoil (15 cm). This is less than the contribution by phosphate fertilizers (1%) and much less than can be contributed by application of municipal sludges.

5. Present data on the concentration of cadmium in the air and daily intake of cadmium with food suggest a decreasing trend in environmental exposure to cadmium. The present average concentration of cadmium in urine of non-smokers in Europe is 5 - 13 times lower than 2.5 µg/g creatinine, considered as the critical level in the case of environmental exposure. Particularly for smokers, however, the margin of safety between the present daily intake of cadmium in diet and the intake which can result in early signs of kidney dysfunction, is rather small. Therefore, every effort should be made to further reduce cadmium emissions and the direct input of cadmium to the soil by fertilizers and sludges.

6. There is virtually no risk of any additional cases of lung cancer from inhalation exposure to cadmium present in air as a result of long-range transport of air pollution.

Lead

7. Lead and its compounds may enter the environment at any point during the mining, smelting, processing, use, recycling or disposal. The likelihood of the health effects is referred, both in adults and in children, to the concentration of lead in blood (Pb-B).

8. The geometric mean of Pb-B concentrations in adults is much lower than the Pb-B level associated with the most sensitive effects. Therefore, the present environmental exposure to lead could be considered as rather safe to adults.
9. Children constitute the critical population in environmental lead exposure. Based on current data on environmental exposure, including concentration values of 200 ppm of lead in soil and dust, the model recently published by the United States Environmental Protection Agency (US/ EPA) predicts a relatively small probability (1.5%) that exposed children will have blood lead levels in excess of 100 µg/l. It should be noted, however, that the value of Pb-B 100 µg/l cannot be recognized as the threshold for the possible influence of lead on the cognitive functions.
10. In children, the possible effects of lead on the central nervous system are likely to develop under specific conditions of exposure, such as living in close vicinity to point sources of emission, exposure to lead paint flakes or to lead-contaminated soil.
11. Present data on the concentration of lead in air, daily intake of lead with food and Pb-B suggest a decreasing trend in environmental lead exposure mainly due to the elimination of lead from petrol.
12. It is assumed that long-range transport of air pollution can contribute about 0.03% to the actual lead content in the topsoil (5 cm). It can be concluded that this does not influence to a significant degree the content of lead in food or human exposure to lead.

Mercury

13. Mercury can be present in the air in several physico-chemical forms: elemental, particulate, gaseous oxidized inorganic and gaseous oxidized organic mercury. In the monitoring of mercury content in the atmosphere, the concentration of the so-called total gaseous mercury is measured.
14. Mercury is deposited to the soil mainly as metal and inorganic salts; on arrival this is initially complexed by organic acids. Methylation and demethylation activity takes place, also causing some revolatilization of volatile forms of mercury (metallic and methylated).
15. The critical organ after exposure to mercury vapours is the nervous system, and the critical effects include hand tremor and increased memory impairments. There is also some subjective and objective evidence of autonomic dysfunction. Mercury concentrations in atmospheric air (below 0.01µg/m³) are much lower than the Reference Concentration (RfC) proposed by the US EPA (0.3 µg/m³). It seems therefore that a direct risk from inhalation exposure is negligible.
16. The effects of methylmercury on the adult differ both quantitatively and qualitatively from the effects observed after prenatal or, possibly, postnatal exposure. The critical organ is the nervous system, and the critical effects include developmental neurologic abnormalities in human infants and paraesthesia in adults.
17. The estimation of the risk of dietary exposure to mercury resulting from the deposition of mercury in the soil is at present difficult to quantify due to the very complex dynamics of mercury

in soil and water and the factors that influence the biomagnification of methylmercury concentration in predatory fish.