**Convention on Long-Range Transboundary Air Pollution**
**International Co-operative Programme on Assessment and Monitoring of Air Pollution Effects on Forests**

United Nations
Economic Commission
for Europe

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**PETER RADEMACHER**

# Atmospheric Heavy Metals and Forest Ecosystems


**Federal Research Centre**
**for Forestry and Forest Products (BFH)**

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Current implementation of ICP monitoring systems and contribution to risk assessment

***Report by: Dr. P. Rademacher***
***Commissioned by: ICP Forests - Programme Coordinating Centre-***

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## 1. Introduction.

Forest ecosystems, especially those of central Europe and other regions, have been exposed to pollution for decades, in the case of some stands for centuries. Thus, at the end of the Seventies, foliar damage first became visible (Tyler, 1972; Mayer & Ulrich, 1982; Burgess et al., 1984). At the beginning, coniferous forest stands appeared to be the most severely affected. Later on, damage also became evident in deciduous forests. Both forest types showed signs of discolouration as well as sporting necrotic alterations to the leaves. Furthermore, impaired root-growth (flattening-out of the root system, dying-off of the fine roots) was observed (Persson, 1978), as well as changes to the stem, such as a decreasing growth-rate and an increase in damage caused by insects or fungi (Lepp, 1975; Symeonides, 1979; Bauch et al., 1985).

Following a controversial initial discussion about the causes of this damage, atmospheric pollution increasingly came to be held responsible. Acid forming gasses such as $SO_2$ and $NO_x$ were thought to be the main culprits, for they not only adversely affected the crowns of the trees, but also led to increasing soil acidity (van Breemen et al., 1983; Ulrich & Summer, 1991). Buffering leakage of basic nutrient cations and the acidifying or eutrophying effects of sulphur, and later above all nitrogen compounds, caused important mineral micro and macro nutrients to be in short supply (v.d. Burgh, 1985; Oren et al., 1988; Hüttl, 1991). At the same time the acid soil began to cause the mobilisation of heavy metals which had accumulated in the soil due to atmospheric input (Tyler, 1978; Verry & Vermette, 1992; Brümmer & Herms, 1983). Particularly in acidic stands the more mobile heavy metals such as zinc, manganese and cadmium were increasingly taken up by plant (Steinnes, 1984; Balsberg-Påhlsson, 1989) and animal organisms of the forest ecosystems (Tyler et al., 1989; Alberti et al., 1996) and also led to increasing surface and ground water pollution (Norton & Kahl, 1992; de Vries et al., 1998). Less mobile heavy metals such as lead and, partly, copper, have been accumulating for a long time in the organic soil layer, particularly in the top soil (Siccama & Smith, 1978; Friedland, 1992; Schulte, 1994; Steinnes & Njåstad, 1995; v. Zezschwitz; Bund/Länder AG Bodenschutz, 1995) and, even in regions with decreasing atmospheric input (Nriagu, 1992; Norton & Kahl, 1992; Schulte et al., 1996), still present a potential danger in the case of their release (DVWK, 1988; Friedland, 1992).

While at the beginning the individual European countries tried to counter the problem of forest damage on a regional or at most national basis, it was not until the Eighties and Nineties that the research projects became increasingly coordinated on an international level. Thus, in 1986 the Extensive Large Scale Network, the so-called Level I programme, was put in action, followed in 1994 by the Intensive Monitoring Programme, the so-called Level II programme (European Commission, 1995; UN/ECE, 2000; Haußmann & Kennel, 2000). For this, mainly single inventory and nutrient parameters (soil chemistry, needle and leaf chemistry) were assessed and crown condition was checked regularly in forests on a monitoring-grid, the size of which was determined by each participating country. In addition, in Level II time courses of element fluxes (atmospheric input, soil solution chemistry) and meteorological observations were made and tree-growth as well as ground vegetation were investigated.

While the most important questions regarding the stress factors, extent and causes of forest damage are already dealt with in a number of reports (European Commission, 1995; UN/ECE, 1996; Müller-Edzards et al., 1997; Lorenz et al., 2000; Fischer et al., 2000), the intentions and extensive survey data of the Level I and II programmes regarding heavy metal pollution has so far only been analysed in a few publications (de Vries & Bakker, 1996; 1998; Andreae, 1996; Vanmechelen et al., 1997; Stefan et al, 1997; Augustin & Andreae, 1998; Bartels et al., 1998; UBA; 1999). The present short paper is intended as a contribution towards extending the knowledge about the available heavy metal data. In an exemplary fashion some assessment and risk calculation of present heavy metal pollution will be made. Therefore some exemplary heavy metal data sets of Level I and II have been evaluated in this report.

## 2. Current state of knowledge.

Over a number of years atmospheric input of heavy metals caused by air pollution was very high and until quite recently actually was on the increase (Nriagu, 1979; Bergkvist et al., 1989). During the last decade or two this input decreased in certain areas because of the use of improved filters in industrial installations and also because of more stringent environmental laws (Schultz, 1987; Church & Scudlark, 1992; Schulte et al., 1996). Bergkvist et al. (1989) present a comprehensive survey of input and output seepage measurements as well as ecosystem assessments from Europe and North America. Depending on the distance from high population areas, higher or lower input was measured. Most surveys investigate open-field deposition. These are situated in the five affected areas shown in table 2-1. According to 4-17 investigations per region and element, in the past a median atmospheric input of 70-375 g Pb/ha/a, 1-17 g Cd/ha/a, 100-2000 g Zn/ha/a and 10-80 g Cu/ha/a was registered. In forests, particularly in coniferous stands with greater filtering strength, depositions can be much higher (Schmidt, 1987). Depending on the mobility of the individual heavy metals, depth displacement of zinc and cadmium into the middle and lower mineral soil layer was observed well as their being taken up by plants in soils with pH-values below 5,5-6,0, while copper and particularly lead accumulated in the organic soil and upper mineral soil layer when the pH-value was above 4,0-4,5 (Hall et al., 1975; Brümmer & Herms, 1983; DVWK, 1989). Thus, in the course of time, an accumulation of diverse heavy metals in the soil occured, ranging from a few kilos to several hundred kilos per hectare (Schultz, 1987; Friedland 1992; Schütze & Nagel, 1997).

A large number of investigations are concerned with the increasing soil contamination in areas with very high atmospheric deposition loads and the resulting potential danger for the forest ecosystem and peripheral areas (Rühling & Tyler, Friedmann & Hutchinson, 1980; 1971; Nürnberg et al., 1983; Tyler, 1984; Steinnes 1984; Favretto et al., 1986; Wittig & Neite, 1989; Landolt et al., 1989; Bengtsson & Tranvik, 1989; Steinnes & Njåstad, 1994). The following effects and standard values, which are described in detail in a number of studies, were discussed because they are relevant to the present survey:

1- Accumulation of large amounts of heavy metals over a long period in the organic layer and top soil and contamination of soil organisms, especially those that play a role in the formation of the soil. Heavy metal accumulations of 1 mg Cd/kg soil, 150 mg Pb, 100 mg Zn and 20 mg Cu/kg are, according to Wilson (1979), Berg et al. (in: Bååth ,1989), Bååth (1989), Atanassov et al. (1999) and Sloof et al. (1999), not yet harmful to soil organisms. On the other hand, a 4 to 10 times higher content can lead to clear reduction of, or damage to biomass production, litter decomposition, enzyme activity or of the C and N metabolism (Inman & Parker (1978); Coughtrey et al. (1979), Berg et al. (cite in Bååth,1989), Tyler et al. (1989), Bååth (1989); Bengtsson & Tranvik (1989) [tab. 2-2]). Tyler et al. (1989) and Bååth (1989) however, call to attention that the toxicity of heavy metals depends largely on the pH-value and the clay and organic C-content of the soil. Thus mineral soils with a Pb content of several hundred milligrammes, but with a $C_{org}$-content of >10% remained unaffected (Bååth, 1989). At a $C_{org}$-content of about 5% only Pb-contents of < 150 mg/kg and at a $C_{org}$-content of 1-2% only < 10 mg Pb/kg remained unaffected. The amount of micorrhiza with which forest trees are affected, also influences the effects of heavy metals by preventing the ingress into the roots and the inner parts of the trees or by reacting more sensitively to the heavy metals than the trees themselves (Godbold et al., 1987). Other authors also report on the negative effects on soil organisms when soil content of Zn is greater than 500mg/kg, Cu content is greater than 20-100mg/kg, Pb greater than 50-250mg/kg and Cd greater than 2-10mg/kg (Tyler et al., 1989; Bååth, 1989; Alberti et al., 1996; Augustin & Andreae, 1998). This causes rain worms to contain the noxious amount of 250-2000 µg Zn/g dry matter, 10-60 µg Cd/g and 100-150 µg Pb/g, ditto. Soil mites sport a contamination thrice the amount in the case of cadmium and thirty times the amount in the case of lead.

2- Using this data as critical limits, a number of national or international bodies issued limiting or threshold values for various soils and their usage. Thus the value for mercury usually is 0,3-1,0 mg/kg, for cadmium 0,8-1,5 mg/kg, lead has 50-100, zinc 100-200, copper and nickel both have 30-60 and chromium has a value of 50-100 mg per kg (Leitfaden Bodensanierung [NL], Verordnung über Schadstoffe [CH], Eikamnn-Kloke-Werte [D], Klärschlamm- und Kompostverordnung [D], see tab. 2-3 [Landesanst. f. Umweltschutz Bad.-Württ. & Roth, 1997]).

3- Increased mobilisation of heavy metals and their absorption into the plant. According to published works and own research Balsberg-Påhlsson (1989) contends that concentrations in soil solutions of cadmium from (10-)20 µg/l and > 200 µg Zn/l, > 25 µg Cu/l and > (50-)200 µg Pb/l have a negative effect on plants and trees (see also Tyler et al, 1989; Andreae, 1996). Apart from direct damage to enzymes or cellular metabolism, heavy metals can find their way into the plant cells and can thus damage the organism. When plant tissues, particularly of leaves and roots, have a higher heavy metal content than around 5-10 µg Cd/g, 20-35 µg Pb/g, 200-300 µg Zn/g and 15-20 µg Cu/g, the whole plant can be shown to be damaged, as various investigations have shown (Balsberg-Påhlsson, 1989; Dosskey & Adriano, 1992 [tab. 2-4]). There are many more investigations regarding agricultural land and the effects of certain heavy metals on plant growth than on sylvan ecosystems (e.g. Sauerbeck, 1982; Köster & Merkel, 1985).

4- Besides having a measurable damaging effect, heavy metal contents can be used as indicators for pollution in certain leading organisms such as grasses, mosses, lichens or fungi as well as in needles and leaves of forest trees (Tyler, 1972; Lee & Tallis, 1973). Extreme values such as around 70 µg Pb, 50 µg Cu and 175 µg Zn per g needle dry matter (Göbl & Mutsch, 1985) can be measured in the vicinity of foundries and mines (Nürnberg et al., 1983; Tyler, 1984; Trüby, 1994). The Foliar Expert Panel of ICP Forests (EC-UN/ECE, 1995) drew up an evaluation guide for macro and micro nutrients as well as for heavy metals. Guide values were subdivided according to nourishment deficiency, critical shortage, a lower, median and upper optimum as well as a critical transgression of element content in beech, oak, Scots pine (Pinus sylvestris) and spruce (Picea abies). According to this guide, values of Zn >50-100 µg/g, Mn >1000-4000 µg/g, Fe >200-500 µg/g, Cu >7-20 µg/g, Pb >4-30 µg/g and Cd >1-3 µg/g, depending on the trees in question, are regarded as excessive. For micronutrients the following minimum amounts have been suggested : <15 µg Zn, <40-60 µg Mn, <20-70 µg Fe and <2,5-3,0 µg Cu per gramme needle dry matter (tab. 2-5).

5-Increasing mobility of heavy metals and their resultant release into surface and ground waters. As this may affect the quality of drinking-water, EU governments have issued laws regarding limiting values of heavy metals in seepage or drinking-water. In Germany, for example, the limits are 1 µg Hg/l soil solution, 5 µg Cd/l, 10 µg Pb/l, 50 µg each for Cu, Cr and Ni/l and 500 µg Zn/l (BMU, 1997).

## 3. Availability of heavy metal data.

ICP Forests launched the monitoring of forest condition at the large scale (Level I) in 1986. In cooperation with the European Union, this led to the establishment of a uniform 16x16 km transnational grid of more than 5700 permanent observation plots in 30 European countries. Besides the annual assessment of crown condition on the plots, the additional element content of needles and leaves from 1444 plots as well as the soil chemical state of 5289 plots was analysed so far once only. At Level II, which is carried out on 864 plots in 30 countries, it is additionally intended to investigate the causes and ecosystematic coherencies of the effects of atmospheric pollution on forests.

Thus annual atmospheric deposition, soil seepage and a number of meteorological data is being painstakingly recorded on Level II plots. The nutritional state of the trees and their growth rate as well as vegetation surveys are also being conducted regularly. Statements, which would be representative for the whole area, can not be made on the basis of these case studies.

The present paper concerns itself only with the data on heavy metals in soil, leaves and needles supplied by the Level I and Level II programmes with a view to risk assessment. Additionally, concentration values obtained from deposition data supplied by Level II are also used. As a first step in the evaluation of these results some data sets are calculated in chapter 3.

### 3.1 Foliar data.

#### 3.1.1 Level I foliar data.

*Assessment scale:* in all, the Level I programme has around 1000-3000 data sets that yield measurements on the element content of needles and leaves of several tree species and needle ages. The number of data sets for all sites and each tree species differs according to the analysed metal. Thus the zinc (Zn) and manganese (Mn) content of the needles and leaves is measured in 2091 cases, Iron (Fe) in 2030, copper (Cu) in 1035 and lead (Pb) in 697 cases (fig. 3-1.1-1 and tab. 3.1.1-1). The content of cadmium (Cd), chromium (Cr), nickel (Ni) and mercury (Hg) in the soil are analysed in the Level I and II programmes, but there is no data available for needles and leaves.

The coniferous stands, in particular, provide more than one mixed or median sample in this present year because of diverse needle ages. There are therefore more heavy metal analyses than observation plots: 3146 each for Zn and Mn, 3081 for Fe, 1761 for Cu and 1128 for Pb.

The data derives from needle and leaf analyses of 41 kinds of tree. For practical reasons, these were classed by the Foliar Expert Panel into five tree groups, namely 'BEECH', 'OAK', 'PINE', 'SPRUCE' and 'OTHERS'. While for the BEECH, OAK and OTHERS group there are only about 50 to 250 heavy metal analyses per element, there are 340 (Pb) to 870 (Zn, Mn, Fe) for PINE and 500 (Pb) to 1500 (Zn, Mn, Fe) for SPRUCE for all needle ages. There are about 700 to 800 Cu analyses for PINE and SPRUCE (fig. A.3.1.1-1 and 2).

Because the number of observation plots for PINE and SPRUCE is so much higher than for the other groups, analyses could be differentiated according to single trees and countries of origin (cf. below, and tab. A.3.1.1-3).

As already mentioned, heavy metal data of European deciduous trees was mainly supplied by the current year's leaves. This compares to 70-80% for OTHERS, no more than around 60-70% for PINE and only 40-60% for SPRUCE (tab. A.3.1.1-1 and -2). Thus quite a number of measurements come from older, pluriannual needles. This subdivision appears of some importance bearing in mind that heavy metal in the needles and leaves accumulate over a longer period. Also for the analyses of element contents that are of nutritional relevance, such as Zn and Cu, the investigation of the youngest, i.e. the current year's needles and leaves is important

*Heavy metal contents:* taking into consideration all tree species and needle and leaf ages, the median heavy metal content (50% percentile) value for Zn is 33 µg/g dry matter, for Mn is 610, Fe 63, Cu 3.2 and Pb is 2.1 µg/g (tab. 3.1.1-2, fig. 3.1.1-2). The mean values, which as a rule are not considered here, as they are too high because of extreme and runaway data, lie for most heavy metals about 30% above the median values. The standard deviation can be found in the average values, which means that, with the exception of Zn, they can vary by 100% or more. The maximum values established in Level I were, for Zn, 369 µg/g, for Mn 8435, for Fe 947, for Cu 99 and for Pb 36 µg/g. This data was obtained from measurements taken from coniferous stands.

If only the values of the current year's needles and leaves are considered, there is a clear reduction in the median values in tree species OTHERS, PINE and SPRUCE (fig. 3.1.1-3). This is particularly true for Pb, but also for Mn, while the values for Zn, Fe, and Cu hardly change. The current year's PINE needles have values of 40 µg/g for Zn, 336 for Mn, 70 for Fe, for Cu 3.5 and for Pb 2.7 µg/g dry matter. SPRUCE needles in comparison have 32 µg/g Zn, 597 µg/g Mn, 39 Fe, 2.6 Cu and 0.8 µg Pb per gramme dry matter (tab. 3.1.1-3 and tab. A.3.1.1-1 and -2).

The distribution of heavy metal median values gathered from the current year's pine and spruce needles according to the countries participating in the Level I Programme results in particularly low Zn values for forest stands in Croatia, ditto Mn for Spain, Croatia and Lithuania, but higher values for Germany, UK, the Slovak Republic, Norway, the Czech Republic, Austria and Slovenia. The Fe values for Austria, Finland, Slovenia, Russia and Norway on the whole lie lower than the median values of all other sites, while it is higher in Germany, Spain, UK, Croatia, the Czech Republic and Bulgaria. Cu is rather low in Lithuania, but markedly higher in Italy, the Slovak Republic and in Bulgaria. Lower Pb-contents were measured in Lithuania, Slovenia and Russia, high values exist in the Slovak Republic, Norway and Bulgaria (tab. 3.1.1-4, tab. A.3.1.1-4 and -5).

Such regional or national comparisons are, however, of limited worth, because the tree types gathered together in the main groups vary depending on region and country. The accumulation rate of heavy metals in leaves and needles varies a lot among the different species ~~kinds~~ of one group. Thus there is an overlay of biological effects that can obscurate regional differences in pollutant levels. For example, Pb values for Quercus robur are markedly lower than for Quercus petrea, while Mn contents in Quercus robur are far above the median values for the OAK group. The Mn values in Pinus halepensis and Pinus nigra are clearly lower than the median value for PINE, whereas the Cu values for Pinus nigra are markedly higher. In the SPRUCE group, particularly Picea sitchensis possesses higher Mn values.

Deviations in the Mn values of needles and leaves, besides the ~~type~~-species-specific influence, are surely dependent on the availability and presence of this metal in the soil. This is largely influenced by the buffering capacities and pH values of the soil, because increased soil acidity often can cause increased mobility of heavy metals.

The correlation of the element content of Zn, Cu and Pb with the help of scatter plots does not lead to an apparent dependence of these heavy metals (fig. A.3.1.1-1).

### 3.1.2 Level II foliar data.

*Assessment scale:* since 1990 the Level II programme has yielded data on element content in needles and leaves from an ever increasing number of observation plots in 19 countries. There are 2000 analyses of the elements Zn, Mn and Fe available, 1200 for Cu but only 178 for Pb (cf. fig. 3.1.1-1 and tab. 3.1.2-1). Compared to the number of heavy metal analyses of needle and leaf samples of the Level I programme, the amount of analyses of Level II is smaller, that is to say 60-70% for Zn, Mn, Fe and Cu, and only 16% for Pb. In Level II repeated sampling takes place on a regular time scale. However, the amount of data which is also provided by other assessment parameters in Level II, permits a much more differentiated evaluation of the data mass - but this can unfortunately only be touched on in this present short report.

*Heavy metal contents:* the median value of the Zn contents in all needle and leaf samples (the current year's and other years) is 28 µg/g dry matter. The other median values are 715 µg Mn, 64 µg Fe, 3.7 µg Cu and 1.2 µg Pb per gramme dry matter (tab. 3.1.2-1). Thus the values are similar to those of the Level I Programme, with the exception of the value for Pb, which is around 80% higher in Level I.

If one distributes the median values of the heavy metal contents of all needle and leaf samples equally among the main tree groups BEECH, OAK, PINE, SPRUCE and OTHERS, the following situation is apparent: pines have 41 µg Zn/g dry matter, which is markedly more than the median values for all tree species, while oak is lower, having only 20 µg Zn/g. Beech and oak have more than the median values for Mn, Fe and Cu, pine trees and spruce often have less. With Pb it is the other way around (tab. 3.1.2.-1).

Taking all tree species and needle and leaf ages into consideration, the lowest Zn median values of about 25 µg/g are to be found in France, Belgium, UK, Portugal and the Czech Republic, while the highest values of >40 µg Zn/g occur on observation plots in Finland and Poland. Other countries on the whole have middle values of between 25 and 40 µg Zn/g (fig. 3.1.2-1). Higher values for Mn (>1500µg/g) are found in Luxembourg and the Slovak Republic, lower ones (<500 µg/g) in the Netherlands, Poland and Croatia. The highest median values for Fe (>150 µg/g) are found in Greece and Spain, the lowest (<50 µg/g) in Sweden, Austria and Finland (fig. A.3.1.2-1). The wide variation of the median values among different countries is particularly apparent in the case of Cu and Pb. Finland and the Czech Republic have, with <3 µg Cu/g, a rather low value, Portugal and Luxembourg have higher values with 7 µg Cu/g, while the Slovak Republic sports 9 µg Cu/g. Particularly Germany has a relatively low lead value with about 1 µg Pb/g, while Denmark has more than 6 µg/g (cf. fig. 3.1.2-1).

In contrast to the – up to now - once-only recording of the needle and leaf contents in Level I the annually recurring analyses of the Level II programme enable conclusions to be drawn on the temporal development of the nutritional state and of pollution. The data gathered over the years shows, however, that a trend towards decrease in the content of heavy metals is not apparent (fig. 3.1.2-2 and fig. A.3.1.2-2). The same is true when all values for the current year's needles of Picea abies only are considered (fig. A.3.1.2-3). On the other hand, the current year's needles of Pinus sylvestris do show a slight decline in their Zn and Cu contents. For while at the beginning of the last decade the values for Zn were 60 µg/g and for Cu 4 µg/g, towards the middle and end of the Nineties median values of around 40 µg Zn/g and 3-3.5 µg Cu/g were recorded (fig. A.3.1.2-4). It must be remembered though, that particularly at the beginning of assessment, but also right through the whole period, the amount of data available, particularly that on Pb, was rather too small as to permit more differentiated assertions. Moreover, last year's samples seem to show higher heavy metal contents again, although not all the data appears to have been processed so far.

## 3.2 Soil.

### 3.2.1 Level I soil data.

*Assessment scale:* In addition to investigating the situation of nutrients and strain imposed by heavy metal pollution of needles and leaves from the monitoring plots, the nutrient supply and pollutant stress potential of the forest soil was also examined. During the late Eighties and throughout the Nineties soil sampling plots of Level I yielded around 4000 single heavy metal samples each for the elements Zn and Mn, 3500 each for Fe, Cu and Pb, about 3000 for Cd and about 2500 each for Cr and Ni. Sampling took place at various depths, in the humus (O and H layers) as well as in the mineral soil. Slightly more than half of the analyses come from the humus, slightly less than half from the mineral soil (fig. 3.2.1-1 and tab. 3.2.1-1).

*Heavy metal contents:* :throughout the humus and mineral soil of all observation plots the heavy metal content median value is 9372 mg Fe/kg, 17 mg Cr, 14 mg Ni, 396 mg Mn, 51 mg Zn, 12 mg Cu, 27 mg Pb and 0.4 mg Cd per kilogramme dry soil. Yet the contents vary widely and the minimum values for all heavy metals lie beneath the detection limit. In all the plots printed here, 'zero' signifies a value below the detection limit, which however varies according to the laboratory and to which method was being used (on this vid. Vanmechelen et al, 1997). Maximum values for Fe lie above 100000 mg/kg, for Cr around 567, for Ni 360, for Mn the figure is 53427, for Zn 638, for Cu 438, for Pb 2114 and for Cd 29 mg/kg (tab. 3.2.1-1).

The partially large differences in the pH-values, the amount of organic carbon and clay as well as the exchange capacity of humus and mineral soil has a strong effect on the dissolving capacity of heavy metals. It is the latter that enables them to be taken up by plants. For a proper element content and risk assessment it is therefore advantageous to carry out a separate investigation of the organic and mineral soil, which are often analysed using a diverse number of techniques.

The quotient 'median value for heavy metals in humus' to 'median value in mineral soil' enables conclusions to be drawn about the intensity of heavy metal movement from the upper humus layer to the lower mineral soil. For Fe, Cr and Ni this value is about 0.3-0.4. This means that the Cr, Ni and particularly the Fe contents in humus are markedly lower than in the mineral soil. Mn and Cu contents are about the same for both soils (factor =1.1-1.2). Zn and Pb values for humus are much higher (factor= 1.5-1.9), while Cd values are very much higher (factor = 5.0 [tab. 3.2.1-2]).

For risk assessment it is not so much the median values that are important, but above all, the occurrence of higher heavy metal contents. Thus, for example, 25 % of the Cd contents in the humus lie within 0,8-6,6 mg/kg (= 75% Percentil), 10% lie above 1,5 mg/kg (= 90% Perc.), 5% above 1,7 (= 95% Perc.) and 1% above 2,6 mg/g (= 99% Perc.). Pb values are: 25% lie above 77 mg/kg, 10% > 132, 5% > 180 and 1% is higher than > 374 mg/kg (fig. 3.2.1-2; fig.

A.3.2.1-1). 25 % of all measurements for Cr lie between 17-567, for Ni between 15-233, for Zn between 83-638 and for Cu between 19-438 mg/kg (tab. 3.2.1-2).

The question of whether the occurrence of heavy metals correlate with one another could not be answered satisfactorily, though scatter plots for both soils were made for the elements Zn, Cu, Pb and Cd (fig. A.3.2.1-2 and -3). Further statistical research is clearly required.

Table A.3.2.1-1and -2 shows the Level I heavy metal contents from the depth ranges 0-5, 5-10, 0-10, 10-20, 20-30, 10-30 and 30-50cm in the mineral soil. To provide an easier overview and to increase the assessment scale of each observation class the 0-10, 10-30 and 30-50cm depth ranges were pooled together. Pb and Cd show an even median distribution across the three depth ranges, with values of 19-25 mg/kg for Pb and 0.1-0.2 mg/kg Cd, with its lowest values in the medium depth range. In contrast, the values of the other heavy metals increase more or less strongly towards the lowest depth range. The median value for Fe rises from 14000 mg/kg to 30000 mg/kg at the bottom. The figures for Cr are from 25 to 29, for Ni from 21 to 32, for Mn from 283 to 450, for Zn from 34 to 66 and for Cu from 9 to 21 mg/kg soil (tab. 3.2.1-3).

**3.2.2 Level II soil data.**

*Assessment scale:* For all depths of each humus layer and all mineral soils slightly more than 1000 heavy metal analyses for Fe, Mn, Zn and Cu are available. 770 soil samples were analysed for Pb and about 350 for Cd. There are only about 200 analyses for Cr and Ni, for Hg merely eight from the humus layer. The Cr and Ni samples are evenly distributed among the two soil types, the others stem mainly from the mineral soil (fig. 3.2.2-1 and tab. 3.2.2-1).

*Heavy metal contents:* the median values of all sample types and soil depth ranges are 4480 mg Fe/kg, 12 mg Cr, 7 mg Ni, 191 mg Mn and 14 mg Pb per kg soil. They are thus only about half as high as the values derived in Level I. Indeed, Zn and Cu are merely a quarter the size, measuring 12 and 3 mg/kg respectively. Only the median value of 0.3 mg/kg for Cd is comparable to the Level I value (tab. 3.2.2-1). The maximum values of the Level II programme are, with the exception of Fe, Zn and Cu, also markedly lower. But here it has to be born in mind, that in Level II lower depth ranges are sampled and so, when all depth are considered together, less contaminated material - from depths below 50 cm - may have had a bearing on the median values. If only the values from the humus layer are taken into consideration, the median values of both Level I and II become similar. Indeed, the Pb value for Level II is actually markedly higher. Comparison of the values from mineral soil samples gives the same results as obtained for both soil types, the Level II percentiles of the heavy metal contents are, with the exception of Cd, markedly lower (tab. 3.2.2-2).

In Level II, the quotient 'median value for heavy metals in humus' to 'median value in mineral soil' is also lowest for Fe, Cr and Mn, though they here have values ranging from 0.8 - 1.8. Markedly higher values are obtained for Cd, Ni, and Cu in the humus layer (factor 2.0-4.0), where the highest accumulation, also in Level II, was reached by Zn and Pb with factors from 5.1 to 7.6 (tab. 3.2.2-2).

The frequency distribution of heavy metals, which sheds light on higher or lower contents, is comparable for Pb and Cd: the vast majority of analyses show a low content, only few measurements give high or very high values (fig. 3.2.2-2).

The median values for lead content in the humus layer are higher in Belgium, Germany and the Czech Republic with >100mg/kg. Median Cd values of > 1.0 mg/kg are found in the humus layers of Portugal and the Slovak Republic. Finland has a conspicuously wide range of values. The lowest median values for Pb and Cu are found in Portugal (Pb) and in France, Germany, the Czech Republic, Estonia and Russia (Cd). The mineral soil has particularly higher Pb median values of > 40 mg/kg in Croatia, low values are found in the Netherlands, Poland and Estonia. Higher Cd median values of >1.5 mg/kg in the mineral soil are found in Croatia, lower values (<0.1 mg/kg) are found particularly in the Netherlands, Austria, Estonia and Russia (fig. 3.2.2-3 and fig. A.3.2.2-1).

**3.3 Level II flux data.**

*Assessment scale:* between 1991 and 1999 eleven countries participated in the analysis of heavy metal pollution through atmospheric input. Taking all collectors in consideration, this provided 20000 measurements for Mn, 10000 for Fe, around 4000-5500 each for Cu, Zn and Cd, 2500 for Pb and about 200-400 each for Hg, Co (cobalt) and Mo (molybdenum [tab. 3.3-1]). Around 18000 water quantity measurements exist. Thus most - but not all - concentration measurements permit flux calculation. Most heavy metal measurements were gained by the collector types 'throughfall' (1) and 'bulk' (2), only a small percentage was obtained by 'wet-only' (3), 'stemflow' (4), 'fog' (5+6) and 'air concentration samplers' (7 [tab. A.3.3-1]).

*Heavy metal contents:* within the limited scale of this short report it was not possible to calculate comparable time courses of element fluxes (such as annual fluxes). The concentrations, however, do allow some overview regarding the pollutant levels of heavy metal depositions. The median concentration values of all precipitation collectors are 50 µg Mn/l, 38 µg Fe, 8,4 µg Cu, 25 µg Zn, 0,1 µg Hg, 2,7 µg Pb, 0,5 µg Co, 0,3 µg Mo and 0,9 µg Cd/l (tab. 3.3-1). 50% of all concentration values (25% to 75% percentile) are in the region of around 17-90 µg Mn/l, 17-115 µg Fe, 4-20 µg Cu, 14-50 µg Zn, 0,1 µg Hg, 1-5 µg Pb, 0,2-0,5 µg Co, 0,1-1 µg Mo and 0,1-5 µg Cd/l. Maximum values reach 15000-23300 µg/l for Mn and Fe, more than 4000 µg/l for Zn, more than 500 µg/l for Cu, 155 µg/l for Pb, around 47-66 µg/l for Mo and Cd, 3 µg/l for Co and 0,4 µg/l for Hg.

The temporal development of the Cd and Pb concentrations shows a decrease since the measurements began towards the middle of the Nineties. Zn and Cu seem to increase during the same time, while Fe and Mn do not have a clear trend (fig 3.3-1 and fig. A.3.3-1)

## 4. Evaluation

Experience has shown that the estimation and evaluation of the risk of heavy metal concentrations and fluxes in the living world is fraught with difficulties. This is particularly true when large variation occurs in the sampling collective with respect to the sample materials, environmental conditions, experimental sites and the analytic methods. In particular cases this problem occurs in the Level I and II programs. Thus, this makes a comparative interpretation of the results of the plants difficult, and in particular the soils due to the number of analytical methods used.

Some methods determine specifically the easily mobilised or plant available heavy metal fractions, or even metal species (ionic, chelate bound or complex fractions). Other less specific methods determine not only the physiologically active, but also additional or total heavy metal contents. These fractions which are not the plant available fractions, for example extraction methods used for plant and soil investigations such as, in increasing order "water extract" < EDTA-extract < $HNO_3$ digestion ≅ Aqua regia < HF-digestion, are at best of interest in the long-term. Of similar importance are the differences in sample preparation (e.g. without washing of leaf or needle materials, with water or chloroform) or cleaning of the analytical vessels. For predicting the toxic load on organisms or ecosystems the value of these methods decreases as listed above (Krivan et al., 1987; Dietze & König, 1988; Neite, 1989; König & Wolff, 1993; Raitio, 1995; Riek & Wolff, 1997; Bartels et al., 1998; UN/ECE, 1998).

The problems of interpretation of the heavy metal data are increased by synergistic effects of heavy metals, and also by additional stress factors (e.g. acids, organic pollutants, water stress etc.). But also, a decrease or increase in the toxicity of heavy metals for example due to environmentally mediated changes in the mobility or plant availability (dependence on for example pH-value or complexing substances), the binding strength to soils or plant materials (clay content, organic material, carboxylate groups) as well as the solubility in soil water or cells, have a strong influence on the damaging effect of heavy metals on lower life forms, higher plants or animals. (Tyler, 1978; Brümmer & Herms, 1983, Mayer, 1984; Schulte, 1994).

However, irrespective of these problems, it should be seen that the data collected with the forestry monitory program Level I and II are possibly the most complete data set worldwide. The data set has an impressive depth, both spatially and temporally, from a high number of investigations. For this reason, an evaluation of the data of heavy metal contamination of ecosystems within the European monitoring program, above and beyond the methodological differences between the countries taking part is important. The evaluation should lead to a progressive development in the methodology. This can only occur if the current state of knowledge about the effect of heavy metals on organisms or ecosystems within the frame work of the discussion of critical loads and critical limits is included. In the medium term, an effort should be made to increase commonality of the analytical methods. For example agreement about the experimental design, as well as identical methods for collecting samples, sampling times, treatment of samples, preparation methods, and also similar analytic methods and calculations.

### 4.1 Evaluation of heavy metal data in foliage samples

The interpretation of the needle and leaf element contents of the Level I data is made difficult by the long sampling period over several years. This is as for the different years, the element levels in the leaves has been strongly influenced by meteorological factors in particular the water supply to the soil and stand (van den Driessche, 1974; Riek & Dietrich, 2000). This has had a greater influence on the nutrient contents compared to the heavy metal levels. There are differences also in the element level for different sampling areas within the crown, and for the different methods for combining the original or ground material.

The median heavy metal content of the current leaves and needles of beech, oak, pine and spruce at all the Level I sites (compare tab. 3.1.1-3) lie, compared to the evaluation frame work of the Foliar Expert Panel (1995 compare chap. 2 and tab. 2-5), in the middle level of the supply or load. The micro nutrients Zn, Mn, Fe and Cu are mostly at optimal levels. The Zn levels in pine are in the upper optimum range, as are the Cu levels in beech and Fe levels in oak. In contrast, the Fe levels in pine and spruce are in the lower level of the optimum range, as are the Cu levels in spruce. The only non-essential potentially toxic trace element determined in the leaf and needle analysis was Pb. In this case also most of the values determined were in the middle of the load range. In oak and spruce the Pb levels were clearly below the middle of the load range.

The load situation does not change greatly if instead of the median (50 % percentile), the 25 % and 75 % percentiles are considered. The tree species or species groups and elements that stood out if the median was used, are even more noticeable. Thus in 25 % of the oaks examined, based on the 75 % percentile, are clearly above the values for over or luxury Fe nutrition. In beech the levels of Cu are clearly above the optimum (compare tab. A.3.1.1-2). In 25 % of the beech and pine investigated, the Pb levels are above the maximum tolerable levels for beech and pine. In oaks and spruce the Pb levels are mostly below the critical values, which for oak however must be considered very high if based on the toxic effects on plants discussed in chapter 2 (30 µg/g in comparison to 4 g/g for pine and spruce, and 10 µg/g for beech leaves.). For the other elements and tree groups the physiological toxicity values in plant tissues are mainly in agreement with the assessment values of the Foliar Expert Panel (tab. 2-5).

The regional distributions given in chapter 3.1.1, show that Cu and Pb in Bulgarian pine and spruce stands are above the critical levels of 7 µg Cu/g and 4 µg Pb/g (compare tab. 3.1.1-4 and A.3.1.1-4 to -5). In Norwegian forests the levels of Pb in spruce stands are clearly above the critical levels. In Italy the critical levels for Cu are exceeded in many cases.

At the Level II sites no differentiation was made between current and older needles in this report (compare tab. 3.1.2-1), however, as was shown in the Level I sites, this does not strongly affect the results (compare tab. 3.1.1-3). Except in the case of Mn, for which older needles had a 20 – 30 % higher content, it was not important to differentiate into different needle ages to estimate micro nutrient supply. In general for all Level II sites, the levels of micro nutrients are within the optimal range (tab. 2-5). The Pb load which is primarily due to direct atmospheric input, and increases in older needles due to the longer exposure time, are mostly in pine and spruce with several needle years, as well as broad leaves at the Level II sites with values of 0.8 – 1.8 µg/g (median of all data) below the critical level < 2 µg/g (< 5 µg/g for oak) of the Foliar Expert Panel.

**4.2 Evaluation of heavy metal data in soil samples**

Table 2-2 shows a number of critical values from different experiments for estimations of the effects of heavy metals in soils. Shown are values of heavy metals in the humus layer or the mineral soil at which damage can be expected to values at which no load or damage to soil organisms can be expected. The organisms which comprise the micro and meso fauna in soils are assumed to be the most sensitive indicators for ecosystem loading by heavy metals. Different research groups have estimated the maximum tolerable level to be (7-25) 70 – 150 mg Pb/kg (values in parenthesis give some minimum or maximum values), 0.3-2.0 mg Cd/kg, (30) 70-200 (250) mg Zn/kg, (6) 30-70 (140) mg Cu/kg, 20-130 mg Cr/kg, 20-50 mg Co/kg, 10-85 mg Ni/kg, and 0.1-1 mg Hg/kg. These values are mostly in agreement with numerous European compulsory and advisory critical levels (tab. 2 –3). At values above these levels damage to the litter degrading organisms can be expected. This would show itself as a decrease in microbial biomass, $CO_2$ exhalation, C and N metabolism or enzyme activity (Bååth, 1989; compare literature Chapter 2.).

As discussed in chapter 3.2 the median values of heavy metals in the humus layer and mineral soil at the Level I sites are about 10000 mg Fe/kg, 17 mg Cr/kg, 14 mg Ni/kg, 400 mg Mn/kg, 50 mg Zn/kg, 12 mg Cu/kg, 27 mg Pb/kg and 0.4 mg Cd/kg (tab. 3.2.1-1). The Level II program shows 50 % lower median values for heavy metals (tab. 3.2.2 –1).

Thus most of the soil samples investigated have heavy metal levels below the numerous national or European critical levels, determined in the toxicological investigations. However, a number of laboratory investigations have shown physiological – toxicological effects at heavy metal levels similar to or below median values for heavy metal contents in soils in Europe. Between 5 – 25 % of the Level I site soil heavy metal contents (representing the 95 to 75 % percentile) are above the discussed critical values which are shown in table 2-2 and 2-3. Thus it can be expected that this could result in the negative effects on biological processes in soil as described in chapter 2.

If the humus layer and mineral soil are considered separately, the mean heavy metal contents and the number of times the critical levels are exceeded for Zn, Pb and Cd are increased only slightly (tab. 2.2.1-2). However, the toxicity in the organic complex rich humus layer decreases strongly (compare chapter 2). In the mineral soil the median values of 65 mg Zn/kg, 30 mg Cr and Ni/kg, 20-25 mg Cu and Pb/kg and 0.2 mg Cd/kg are mostly higher in the deeper organic poor layers (30 – 50 cm) than in the upper soil (tab 3.2.1-3). Depending on the heavy metal, between 5 – 25 % of the soil samples have values above the critical limit in table 2.2.

As discussed in chapter 3.2.1 grave excesses of critical values was shown in a number of countries, whereas in other countries based on the above assessment framework do not have such heavy metal contamination in forests.

### 4.3 Evaluation of heavy metal data in precipitation samples

A final assessment of heavy metals in precipitation can not be carried out until calculations with the precipitation amounts to give flux values have been finished. The heavy metal concentrations show large fluctuations dependent upon the precipitation amount and regional pollution sources (tab 3.3-1). However, the temporal patterns in the heavy metal loads, show clear decreasing trends for the concentrations of Cd and Pb. The trace elements Zn and Cu in contrast appear to be increasing, whereas Mn and Fe show no clear trend (fig. 3.3-1 and fig. A.3-1).

### 4.4 Final evaluation of Level I and Level II heavy metal data

In conclusion, it must be stated that despite the decrease in atmospheric heavy metal loads shown in many regions of Europe, the heavy metal loads which have accumulated over several decades in sites to ”heavy metal legacies”, still today result in high levels of heavy metals. Dependent upon the element considered and the assessment framework, in an average of 5 – 25 % of the soils investigated it can not be ruled out that these levels have resulted in a decrease in biological activity, and in some cases to a decrease in vitality of higher plants and trees, as has been shown in laboratory and field experiments. In general, the heavy metal load on trees is clearly lower than the load on soil organisms. Tree fine roots and mycorrhizas are likely to be most strongly affected by heavy metals, but are not sampled in the European monitoring program.

As discussed above, specific mechanisms which increase or decrease the toxic effects of heavy metals due to different environmental effects make an assessment of the risk of heavy metals difficult. This is especially true if the results of a long-term monitoring program are to be assessed within an assessment framework based on stationary, critical values. As the monitoring program is based on non-independent values, an interpretation and final assessment of the research results can only really be carried out using an integrated model and cartography of all relevant parameters. This emphasises the importance of development and routine use of applied problem solving models (de Vries, 1991; de Vries & Bakker, 1996; 1998; Becker et al., 2000).

## 5. Summary

The Level I and II monitoring programmes for the protection of the forests from atmospheric pollution were started at the instigation of the European Commission during the mid Eighties and Nineties. These programmes provide a continuous flow of data on air pollution in forests and its effects on forest ecosystems. This present study, which has been commissioned by the ICP Forests Programme Coordinating Centre, assembles the available heavy metal data from needle, leaf and soil analyses as well as from deposition by atmospheric pollutants. For the first time, a pan European assessment has been carried out regarding possible stress and risks through pollution by heavy metals.

There were approximately 1000 to 3000 needle and leaf analyses per element available from Level I and about 200 to 2000 from Level II. The soil analyses programme contains about 2500 to 4000 measurements from Level I and 200 to 1200 additional data from Level II. The deposition measurement programme in some cases has over 20000 measurements per heavy metal.

The Level I programme concerns itself mainly with a continuous surveillance of crown condition on the monitoring plots as well as a, up to now, singular sampling and analysis of needles, leaves and soil at pre-determined grid points in all participating European countries. Level II additionally yields a continuous assessment of the needle and leaf chemistry of the forest stands, a complete analysis of atmospheric depositions, seepage water chemistry as well as the monitoring of meteorological and increment data and soil vegetation.

The median values of the *element contents in needles and leaves* obtained in Level I and Level II fluctuate over all tree species and years. This can be observed at the rate of 28-20 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 (tab. 5-1). Thus the values lie within the pollution limits which the Foliar Expert Panel regards as being harmless (such as toxicity caused by Pb), and which show that the nutrient supply is also within safe limits, especially as regards important micro nutrients such as Cu and Zn. A differentiated examination of the various

tree species (groups), leaf or needle ages and sites, does, however, in some cases show excessive toxic threshold values and a shortage or surplus of nutrients. Thus pines, especially the older needle years, show particularly high median values of 5 µg/g Pb (fig. 5-1). There is a regional occurrence of higher Pb median values of > 5 µg/g in Denmark, Norway, Bulgaria and others. Exceedingly high Cu median values of 7-9 µg/g can be found in Bulgaria and Italy, mainly in pine trees and spruce.
The measured contents of heavy metals in needles and leaves vary so much between the different tree types because of the different ways these elements are either filtered out or taken up by the trees' crown or by the 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 content values of less mobile elements such as Pb are the result of direct deposition on needles and leaves.
Single extreme values of the needle and leaf contents, 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 deposition levels caused by atmospheric input, pollution in some places either has natural causes, such as the presence of magma, or is additionally aggravated by slag tips.

Level I has yielded European median values for heavy metals *in soils* over all depth ranges of around 10000 mg Fe/kg 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 (tab. 5-2). The median Level II values comprise a larger amount of less polluted material from lower ground levels, and are thus only about half as high. If one subdivides the soil into an organic layer and a mineral layer poor in organic contents, one may observe between two to eight times higher values particularly for Cd, Zn and Pb in the organic layer as compared to the less polluted mineral soil.
If an evaluation framework for heavy metals is used, that is based on toxicological and field investigations and laboratory analysis, and which enables one to arrive at threshold limits based on the danger which heavy metals in the soil pose to micro-organisms, a number of problem and risk areas can be determined. Thus, when threshold values are used that are based on the lowest value at which heavy metals show any 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 generalised for all soil types, and can not be made with few indicator organisms. Using an assessment framework, which is based on a much larger amount of investigations, exclusively on mineral soil which merely has a small amount of detoxifying organic material, only few stands show excessive critical values. Higher regional values can, however, still occur (fig. 5-2).

As yet, there are no *deposition flux* calculations available for the assessment of heavy metal input through atmospheric pollution on a comparable time scale. The *concentration values in precipitation samples* obtained in Level II undergo a fluctuation depending on the amount of precipitation and local stress peaks. There is, however, a general temporal trend of the atmospheric heavy metal input measured in participating European countries, as has been shown in other regions on a local scale. According to this observation, leaving aside meteorological influences, concentrations above all of Cd and Pb are on a continual decrease (fig. 5-3). No such clear trend is apparent for Mn and Fe, while Zn and Cu concentrations rather appear to be on the increase.

In conclusion, it can be said that heavy metal pollution, particularly with the more toxic elements such as Pb and Cd, is uncritical in most regions of the participating countries. This is true for most observation plots. Nutrient supply, particularly micro nutrients such as Cu and Zn, is on the whole balanced. For certain tree species, soils and regions, however, there exist conditions encompassing the whole range of heavy metals, that give rise to concern. Soils here particularly show the effects of decades of accumulation of recalcitrant compounds stemming from times of much higher atmospheric pollution. On the whole, however, it may be assumed that atmospheric pollutant input, especially as far as Cd and Pb are concerned, is further on the decline.

The heavy metal data gained through the Level I and Level II programmes on European monitoring plots is surely unique in the world, as it encompasses such a wide analytical spectrum gathered from such a wide-spread number of sites. The continuation of this work, further analyses and further assessment of data, will give rise to better and improved means of risk assessment of the effects of heavy metals on the living environment and forest ecosystems. By this means it would be possible to create the means for a quantitative recognition and localisation of risks through heavy metals and to lessen these risks through aimed and pertinent regional or international counter-measures. Even today a decrease in atmospheric pollution can be observed which is due to improved environmental control and less use of toxic heavy metal compounds. Important background information on this has been gained by the activities of the Level I and II programmes as well as other regional and national projects.

Based on a closely co-ordinated approach towards determining suitable analytical techniques as well as choosing the monitoring plots, an enormous amount of high-quality data has been gathered, which is an ideal basis for further work. Despite the success so far, further efforts should, however, concentrate on improving comparability of analytical techniques and of the results. A closer time-scale should be chosen for further once only samplings, analytical methods should become even more compatible and for evaluations a maximum degree of standardisation should be aspired. Because of the complexity of ecosystem research, the multiplicity of parameters and the volume of the data, further complementation and application of problem-oriented evaluation models will be of paramount importance for the further success of the programme.

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