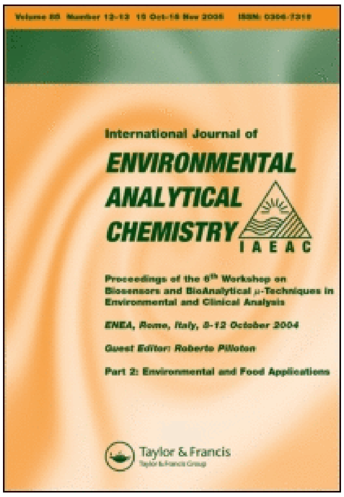

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AN ATTEMPT TO EVALUATE SOME FACTORS AFFECTING THE HEAVY METAL ACCUMULATION IN A FOREST STAND*

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Two sites which differ in their pollutant level were examined. The gravitational deposition was compared to the concentration of Pb, Cu, Cd and Zn in mosses collected inside and outside the forest and also to the heavy metal accumulation in the various litter horizons at the two sites.

The accumulation of heavy metals in the organic layer and in mosses within the forest stand are shown to be dependent on the pollutional level, the type of vegetation as well as on the metal under consideration. Higher accumulation has been found in spruce than in beech stands due to differences in interception. Furthermore, Pb and Cu are more readily accumulated in the forest ecosystem than Cd and Zn.

KEY WORDS: Forest, mosses, biomonitoring, accumulation, heavy metals, deposition, litter, AAS, DPASV, sample handling.

INTRODUCTION

Gravitational deposition, i.e. the deposition of rain, snow, hail, sedimenting dust, etc. is an important mechanism for the input of heavy metals into an ecosystem. However, the deposition via interception, i.e. the impaction of aerosols on the surface of vegetation, may contribute a considerable amount. Especially over rough surfaces as they are found in forests, input via interception may override that from gravitational deposition. It is known that, depending on the metal under consideration, there is a 3–8 times higher input within a stand compared to the freeland deposition.[1] The contribution from interception is governed by the local immission situation as well as the exposition and the type of vegetation in the stand under consideration.

Comparing the accumulation of metals in the biomass with the total deposition in a forest ecosystem shows that the input of Cr, Ni, Mn and Fe from the atmosphere is low compared to the amounts stored per year in the biomass. Uptake of these metals must be supplied partly by weathering of soil minerals. The uptake of Cd, Zn, Pb and Cu, however, is mainly accounted for by atmospheric input.[2]

The accumulation of heavy metals is different in the various compartments of a forest ecosystem. Tyler[3] showed that dead organic matter, such as litter and the underlying horizons, as well as low-level plants (especially lichens and mosses) can

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Table 1 Characteristics of the forest sites

Elevation (m a.s.l.)	*Sites*			
	Oberstammheim 580		*Winterthur* 530	
Tree species	beech	spruce	beech	spruce
Age (years)	*ca.* 90	*ca.* 90	80–90	80–90
Humus form	typical mull	moder-like mull	typical mull	mull-like moder
Soil classification	Cambisol calcic >40 cm gleyic	Cambisol eutric, gleyic	Cambisol gleyic	Cambisol marly
pH A_h (KCl)	6.9	5.6	4.6	4.2

accumulate high amounts of heavy metals. One reason for this accumulation is the stability of the chemical complexes formed between heavy metal ions and negatively-charged organic groups. Furthermore the charges on unprotected plant surfaces (no cuticle) provide ion-exchange facilities which allow the effective adsorption of metal ions to occur. Higher plants, however, accumulate metals less effectively[4] because their cuticle-covered epidermis is not very permeable to metal ions.

Due to the different chemical behavior of the various metals, the accumulation may vary considerably. It is thus the aim of this work to evaluate factors affecting the accumulation of heavy metals in various compartments of a forest ecosystem.

The present study was conducted at two sites with different immission levels. Gravitational deposition outside the forest stands was collected over a one-year period and compared to the heavy-metal content in mosses (*Bryum argenteum* Hedw.). The accumulation of Pb, Cd, Cu and Zn was measured in various litter and mineral horizons as well as in mosses (*Hypnum cupressiforme* Hedw.), both in a beech and a spruce stand at each site.

MATERIALS AND METHODS

Sampling Sites

Two sampling sites were chosen, one lying at "Oberstammheim" in a rural landscape, and the other one at "Winterthur", on the outskirts of a city with about 80000 inhabitants. Within each site an unsheltered position as well as two forest stands were investigated: a beech (*Fagus silvatica*) and a spruce (*Picea abies*) forest situated 0.2–0.5 km from one another.

Table 1 summarizes the characteristics of the forest sites.

Samples

Samples from humus horizons were taken according to the definition given by

Babel.[5] The degree of mineralisation was also examined using thermogravimetric investigations.[6] Samples of the moss *Hypnum cupressiforme* Hedw. were collected from tree stumps. All sampling was done in zones clearly lying between tree crowns. *Bryum argenteum* Hedw. was taken from gravelled roads near the deposition collectors. All samples were collected using polyethylene (PE)-gloves and PE-tweezers, and stored in PE-containers. Wet deposition was collected on an event basis with a wet and dry sampler according to Georgii.[7] Forty-two samples were taken during the 12 month examination period. Bulk sampling was done with a modified Bergerhoff collector. It consisted of two 5-litre PE-flasks connected by their necks, with the base of the upper flask cut off to serve as a collecting funnel. The samples were taken monthly.

Sample Preparation

All bottles and containers used for sampling and storage were subsequently washed with 0.1 M HNO_3 and highly purified water (deionized water purified by ion-exchange filtration through active charcoal and an 0.45 μm filter; Millipore Corp., Milli-Q) to avoid contamination of the samples. Handling of the samples in the laboratory was done in clean benches using PE-gloves.

1. Mosses and organic layers

The organic layers and the moss samples were kept frozen ($-20\,°C$) after collection.

Only the green part of the moss plant was used for analysis. The material was washed with Millipore water and dried at 70 °C for 20 hours.

The organic layers and the soil samples were dried at 50 °C for 24–48 h. In order to get good homogeneity, the organic layers (L, F) were ground in a ball mill (Fritsch pulverisette 5), whereas the mineral horizons (A_h, A_{hh}) were treated by a mechanical mixer (Moulinex, with tantal knife) to avoid damage to the polyamide container and the Teflon grinding spheres of the ball mill.

2. Precipitation

The samples were filtered with 0.45 μm cellulose nitrate filters, acidified by addition of HNO_3 and deep-frozen until analysis. The filters from the bulk samplers were digested with 5 M HNO_3 and analyzed. The results obtained from the filtrate and the filter were added to yield the total deposition. With the wet-only samples only the soluble part was taken into account. The details of the sampling and treatment procedures are described elsewhere.[8]

3. Digestion procedure

Digestion of the organic layers and the mosses was done using a mixture of

$HNO_3/HClO_4$. HNO_3 (predistilled), 1–3 ml c. 70%, and $HClO_4$ (suprapur), 1 ml 70%, were added to a 250–300 mg sample in a 7-ml quartz beaker covered with a watch glass. After overnight hydrolysis, the mixture was gently heated on a hot plate to 80 °C (faster heating rates can cause foaming, which may lead to losses). The temperature was then raised to 120 °C until no more NO_x was produced. The yellow solution was heated afterwards to 160 °C with the watch glass full of water (reflux) until the solution became colorless. Finally the solution was evaporated to near-dryness at 140 °C. The residue was dissolved in 4 times 5 ml 1 M NaAc/HAc (NaAc, p.a.; HAc suprapur) and analyzed within a week (storage at 4 °C). The quality of each digestion series was examined by running BCR No. 62 "olive leaves" (Olea europaea, Community Bureau of Reference, Brussels) as a control digestion. The following metal content ($n=25$) in relation to the certified values was detected: 0.089 μg/g Cd (−11%), 25.3 μg/g Pb (−1%), 17.2 μg/g Zn (+6%) and 43.2 μg/g Cu (−7.2%). Procedural blanks were run with all series and did not contain significant metal concentrations.

The mineral soils (A_h, A_{hh}) were extracted using 2 M HNO_3 (soil/solution 1:10) for 2 h on a boiling water bath[9] in order to compare the detected values with the allowed heavy metal limits in Swiss soils.[10]

4. *Instrumental analysis*

The elements Cd and Pb in the 1 M NaAc/HAc solution were electrochemically detected using differential pulse anodic stripping voltammetry (DPASV) at the hanging mercury drop electrode (Metrohm VA-Processor 646, VA-Stand 647). The elements Cu and Zu as well as Pb in the HNO_3-extract were determined by atomic absorption spectrometry (AAS) using IL Model 451 with D_2 background correction to compensate non-specific absorption. Cd was measured in the extract solution by flameless AAS on an IL 755 graphite furnace mounted on an IL 451 model using $Pd(NO_3)_2$ and $Mg(NO_3)_2$ as the matrix modifier.

RESULTS AND DISCUSSION

1. *Distribution of Heavy Metals Within Different Organic Soil Layers*

Table 2 summarizes the concentrations of Cd, Pb, Cu and Zn in the different horizon layers. For the A_{hh} and A_h only an HNO_3 extract was used, which dissolves c. 60–80% of the total amount of heavy metals.[9] The heavy metal concentrations in these specific horizons are therefore lower estimates.

Heavy metal concentrations in the forest floor reach a maximum in the $L_v/F_m/A_{hh}$ region, whereas the extent of the accumulation depends on the metal under consideration.

As shown in Figure 1 the highest concentrations of Pb occur in the F_m/A_h horizons. The extent of the accumulation is more pronounced in the spruce stand for both sampling sites, which indicates a higher heavy metal burden in the

Table 2 Heavy metal concentrations in the organic soil horizons (L: litter; F: fermentation horizon; A_h, A_{hh}: mineral earth horizon, colored by humus)

	Cd [*mg/kg*]		*Pb* [*mg/kg*]		*Cu* [*mg/kg*]		*Zn* [*mg/kg*]	
	b	*s*	*b*	*s*	*b*	*s*	*b*	*s*
Stammheim								
L_n	0.31	0.26	15.3	25.7	9.1	7.7	53.4	65.5
L_v	0.32	0.34	20.7	45.9	9.7	10.8	51.6	65.5
F_m	–	0.40	–	41.2	–	11.2	–	68.4
A_{hh}	–	0.24	–	44.9	–	9.3	–	37.8
A_h	0.20	0.06	23.6	20.9	7.6	5.8	34.3	24.0
Winterthur								
L_n	0.45	0.24	21.4	42.8	9.1	8.5	52.1	41.0
L_v	0.44	0.38	36.4	126.9	14.0	23.9	71.3	65.1
F_m	–	0.32	–	166.7	–	28.0	–	76.4
A_{hh}	0.31	0.24	44.1	158.5	13.9	24.6	58.3	55.6
A_h	0.23	0.03	28.4	32.9	10.6	7.5	51.4	55.5

b: Beech stand; *s*: Spruce stand. Standard deviation in percent of the mean ($n = 2$): Cd and Pb 1–10%, Cu 1–15%, Zn 1–15%.

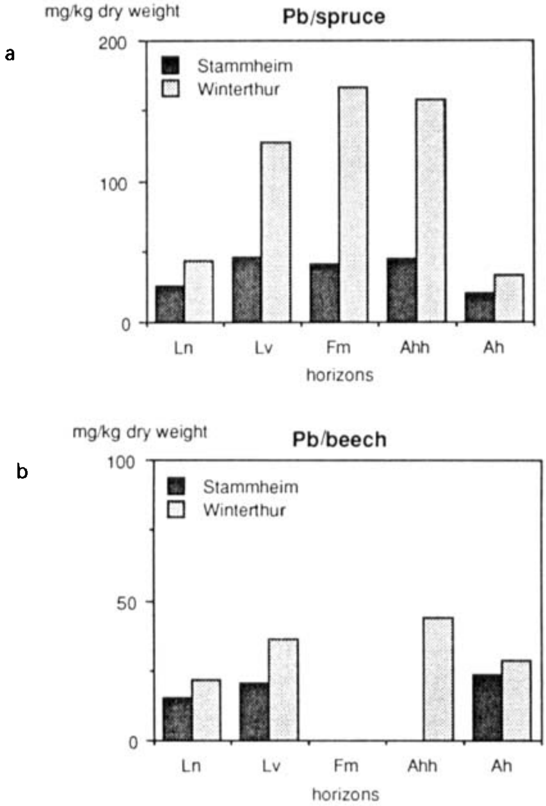

Figure 1 Pb-content in different organic soil horizons.

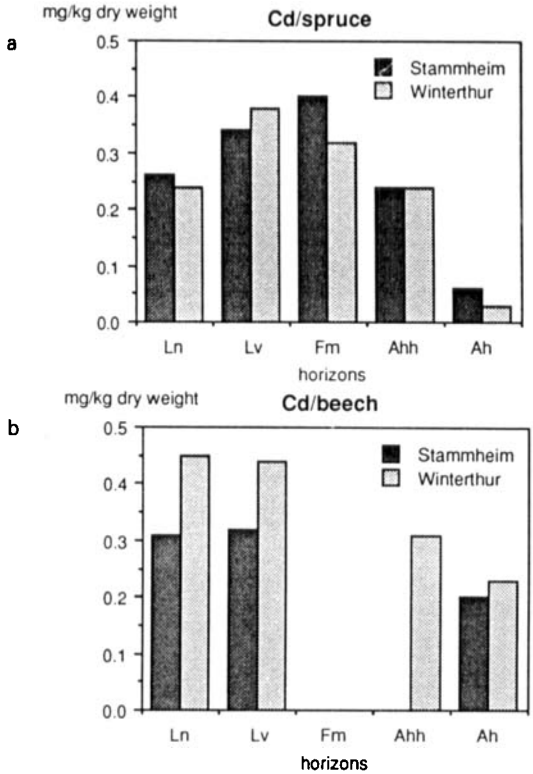

Figure 2 Cd-content in different soil horizons.

organic layers in a spruce forest. This is also true for the A_{hh} horizons (organic matter (OM) 35–40%) but not for the A_h horizons (OM 6–15%), which confirms the high positive correlation of Pb with the organic matter of the mineral horizons mentioned by other authors.[11,12] All organic layers show a higher Pb content at the Winterthur site than at the rural site in Stammheim. The same dependence on the decomposition stage of the horizons and the tree type is observed regarding the Cu concentration. Cu and Pb seem to show a similar pattern of behavior in the organic forest floor.

In Figure 2 the Cd content in the different horizons at the two sampling sites is shown. In the spruce stands the increased Cd concentrations are observed in the L_v/F_m layers, whereas in the beech stands no distinct accumulation was detected at the two specific sampling sites. The affinity of Cd for organic matter in the mineral horizons is also evident; A_{hh} horizons contain generally higher concentrations than A_h layers at the same sampling site. Horizons of the spruce stands show no higher Cd content than in beech forests, although Mayer[2] has reported larger Cd inputs into a spruce stand compared to the beech location at the Solling (FRG). This behavior of Cd can be explained by its high mobility within the forest floor,[13] which increases even in the more acid spruce layers. Zn reacts very similarly, although the affinity for the organic matter in the A horizons is less pronounced.

In order to compare concentrations in the organic floor with the data obtained

Table 3 Comparison of the precipitation concentrations (volume weighted means) at different sites

	Pb ($\mu g\, l^{-1}$)	*Cd* ($\mu g\, l^{-1}$)	*Cu* ($\mu g\, l^{-1}$)	*Zn* ($\mu g\, l^{-1}$)
"Rural"[14]	3–12	0.05–0.25	1–10	5–50
Stammheim	3.4	0.09	1.0	7.5
Winterthur	5.3	0.27	1.6	10.6

from moss and immission analysis, the L_v horizon was chosen because this layer can be found in all four investigated humus forms and the accumulation starts already there.

2. *Behavior of the Four Metals at the Different Sites*

The annual wet deposition of heavy metals at the two sites are found to be in the same order of magnitude as other rural regions in the northern hemisphere. The volume weighted mean in rural precipitation at various sites in the USA, Canada and Europe are given in Table 3 and compared with the values found at Stammheim and Winterthur. Winterthur shows, due to its proximity to a city, elevated mean concentrations of all four metals.

The freights (Figures 3a–d) were calculated from the concentrations and the annual rain amount at the two sites (870 mm for Stammheim; 1100 mm for Winterthur).

The two moss species mainly suitable as biomonitors in Switzerland are *Hypnum cupressiforme*, found in forest ecosystems, and *Bryum argenteum* which is abundant in both agricultural and urban areas. Concentrations in mosses (*Hypnum cupressiforme*) collected outside the forest stands were found to represent rural areas; similar values have been found e.g. by Rasmussen.[15] The data may also be compared to values obtained in earlier studies in Switzerland with *Bryum argenteum* as bioindicator; mosses from a rural area outside the city of Zurich have been found to contain 1, 91, 15 and 68 mg/kg dry weight for Cd, Pb, Cu and Zn respectively.[16]

Comparison of the concentrations in litter from this work with "soil" concentrations from the literature is difficult if no detailed characterisation of the sampled soil horizon is given. Nevertheless the data from this study correspond well with similar studies in rural regions of FRG.[17]

Figure 3 presents the results of the heavy metal concentrations in litter and mosses together with immission data for the sampling sites.

Pb

The deposition of lead is higher in Winterthur than in Stammheim; a fact clearly due to the higher traffic density in the former region. As can be seen from the

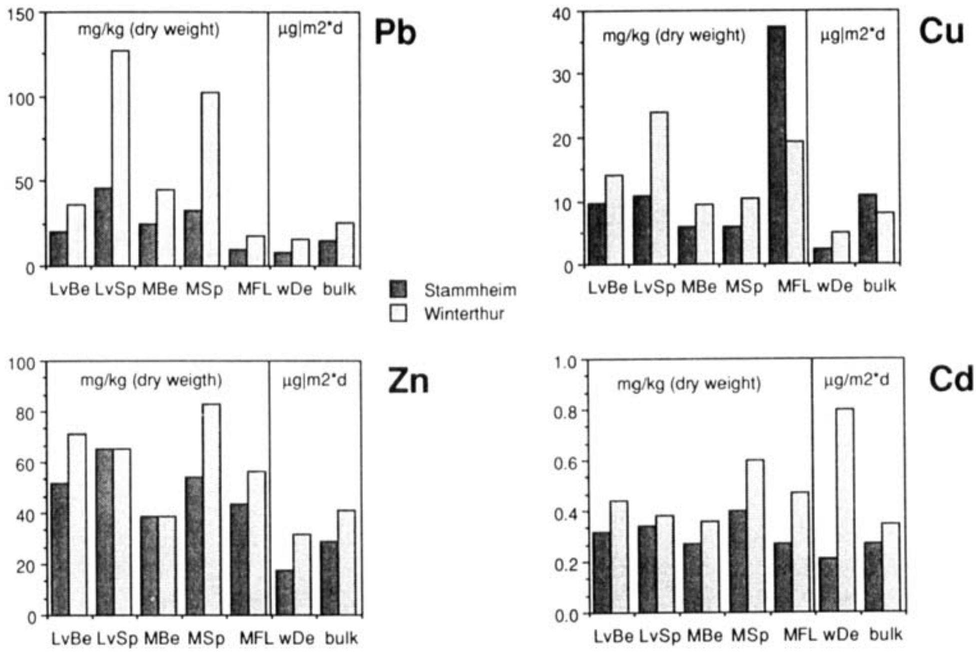

Figure 3 Comparison of heavy metal concentrations in litter and moss with deposition freights at the sampling sites (LvBe: L_v, beech; LvSp: L_v, spruce; MBe: moss, beech; MSp: moss, spruce; MFL: moss, outside the forest; wDe: wet deposition; bulk: bulk deposition).

difference between total and wet deposition, dry deposition contributed appreciably to the total lead deposition. Differences between the two sites can be seen in all moss and litter samples under examination. The Pb-moss concentrations outside the stands and in the mosses as well as the litter horizons in the beech stands are reflected in the gravitational deposition. The concentrations in the spruce stands are remarkably high. This supports the idea that interception is higher in coniferous forests than in deciduous ones.[18] Of all four elements lead shows this effect the clearest. This can be explained by the fact that Pb has a high ability for complexation with insoluble humic substances leading to fixation and immobilisation of this element in the organic soil layer. Mobilisation or wash-out by soil solution or rain water with low pH is of minor importance for this element. The equal accumulation in mosses and L_v-horizon can thus be considered as a means for the input of lead via interception.

Cu

The copper content in wet deposition in Winterthur is higher than in Stammheim. However, enhanced concentrations are found in the total deposition in Stammheim. These high values have also been found in the separately measured dry deposition. This effect is even more pronounced in the moss collected outside the forest. The high Cu concentrations are due to the presence of a vineyard near the sampling site in Stammheim. The frequent treatment of this area with copper-containing solutions leads to increased concentrations especially in the dry deposition. The forest stand in Stammheim is about 1 km away from this vineyard; this distance reduces the effect.

The samples from within the forest stands exhibit roughly the same behavior as with Pb. This seems reasonable because the chemical behavior of the two elements is similar. It is noteworthy that little or no differences are found for the concentrations in spruce and beech stands for Stammheim. This might be due to the relatively low concentration compared to "natural" copper levels in plants. The higher the absolute concentration the larger is the difference between spruce and beech stands.

Cd

The cadmium concentrations in the various sample types show a completely different picture as compared to those of lead and copper.

The concentrations in the deposition are low (0.03–0.3 $\mu g\,l^{-1}$) which leads to a relatively high uncertainty in the determination. It is thus not surprising that differences between wet and total deposition are found. However, from deposition data and the data obtained from mosses outside the forest it is clear that Cd-deposition is higher in Winterthur than in Stammheim. According to the concentrations of Pb and Cu it can be assumed that the input via interception into the spruce stand is higher for Cd as well, knowing that Cd is mainly associated with airborne particulate matter which is especially subjected to interception. This is confirmed by the fact that the Cd-concentrations in mosses in the spruce stands are appreciably higher than in the beech stands.

Considering the Cd-levels in the litter horizons shows that the concentrations in the spruce stands are about the same as in the beech stands. Cadmium tends to form soluble complexes with low molecular weight substances[19] which are mobile and thus can percolate through the organic soil layers. Furthermore, the Cd-complexes are pH-sensitive. Because the soil pH is lower in spruce than in beech stands, leaching of cadmium from the litter is further enhanced.

Zn

Zinc concentrations exhibit a similar pattern to Cd concentrations. No accumulation of Zn in spruce litter can be seen due to the same effects, and Zn concentrations in mosses are again higher in the spruce than in the beech stands. The concentration in the mosses from the beech stand in Winterthur is unexplainably low.

CONCLUSIONS

Following factors have been found to influence the accumulation of heavy metals in a forest ecosystem:

Differences in *atmospheric gravitational deposition* are in many cases reflected by the concentrations in the biological material from the different sites. Depending on the *element* under consideration, site differences may be smeared out due to the different chemical behavior of the heavy metals. Thus, comparing the accumulated concentration with the deposited freight on a relative basis leads to the conclusion that Pb and Cu are the heavy metals that are more readily accumulated than Cd and Zn. One reason for this effect is the fact that Pb and Cu tend to form complexes with insoluble organic components whereas Cd and Zn are likely to form complexes with soluble organic molecules, and furthermore the complexation of these elements is especially pH-sensitive. Cu, as a micro nutrient, is additionally transported within the plants themselves and thus is not a good means for the estimation of atmospheric input into a forest ecosystem. In order to get information about the atmospheric heavy metal burden within a forest, Pb can be used as a "tracer". Considering the differences between different *types of vegetation* shows, especially for Pb, that spruce stands exhibit a higher input than beech stands. This is due to the higher interception in the spruce stands, which itself can be explained by the fact that coniferous vegetation can partake in interception all year long. Because the soil-pH in spruce stands is generally lower than in beech stands, Cd and Zn tend to be mobile and their accumulation does not reflect their atmospheric input.

In order to get information about the burden of a forest ecosystem with heavy metals two types of investigations have to be performed:

The measurement of atmospheric deposition outside the forest enables the classification of the site situation in comparison to other sites. The results do not give any information about the real input into a forest ecosystem because of the above-mentioned points.

The determination of the lead content in mosses within the stand or in well-defined strata of the litter yields relative information about the total input into a forest ecosystem (including atmospheric deposition and interception) compared with other stands.

The accumulation in the forest ecosystem itself has to be evaluated for each stand and each element separately because of the various factors which influence the accumulation as well as the mobilisation of the different elements at the different sites.

References

1. K. D. Höfken, *Ber. Inst. Meteorol. Geophys. Univ. Frankfurt a. M.* **46** (1981).
2. H. G. Heinrichs and R. Mayer, *J. Environ. Qual.* **9,** 111 (1980).
3. G. Tyler, *Ambio* **1,** 52 (1972).
4. J. Hertz, Bioindicators for Monitoring Heavy Metals in the Environment. In: *Heavy Metals in the Environment* (E. Merian, ed.), in press.
5. U. Babel, *Hohenheimer Arbeiten Nr 60* (Verlag Eugen Ulmer, Stuttgart, 1972), p. 120.
6. C. Angehrn-Bettinazzi, P. Lüscher and J. Hertz, *Z. Pflanzenernähr. Bodenkunde* **152,** in press.

7. H. W. Georgii, C. Perseke and E. Rohbock, Abschlussbericht Forschungsprojekt Nr. 1041 02600 im Auftrag des Umweltbundesamtes (Eigenverlag der Universitätsinstitutes für Meteorologie und Geophysik, Frankfurt, 1982).
8. J. Hertz, P. Bucher, G. Furrer, L. Keller, O. Daniel and L. Thöni, *Chimia* **42,** 57 (1988).
9. Bundesamt für Umweltschutz, Eidg. Forschungsanstalt für Agrikultur und Umwelthygiene Wegleitung für die Probenahme und Analyse von Schadstoffen im Boden, EDMZ, Bern (1987).
10. Bundesamt für Umweltschutz, Erläuterungen zur Verordnung vom 9 Juni 1986 über Schadstoffe im Boden (Bundesamt für Umweltschutz, Bern, 1987).
11. A. M. Andresen, A. H. Johnson and T. G. Siccama, *J. Environ. Qual.* **9,** 293 (1980).
12. A. J. Friedland and A. H. Johnson, *J. Environ. Qual.* **14,** 322 (1985).
13. J. Hertz and C. Angehrn-Bettinazzi *Int. Conf. Heavy Metals in the Environment* (T. D. Lekkas, ed.), Athens (1985), p. 503.
14. L. A. Barrie, S. E. Lindberg, W. H. Chan, H. B. Ross, R. Arimoto and T. M. Church, *Atmos. Environ.* 2, 1133 (1987).
15. L. Thöni, J. Schmid-Grob, J. Hertz and E. Urmi, *Staub, Reinhalt. Luft* **46,** 295 (1986).
16. L. Rasmussen, K. Pilegaard and H., Gydesen, *Bot. Tidsskrift* **75,** 93 (1980).
17. H. Koenies, *Berichte des Forschungszentrum Waldökosysteme/Waldsterben* **9** (1985).
18. G. Glatzel, M. Kazda and G. Markart, *Atmospheric Pollution in Forest Areas: Their Deposition and Interception* (Dordrecht, 1986).
19. G. Brümmer und U. Herms, *Bielefelder Oekol. Beitr.* **1,** 117 (1985).