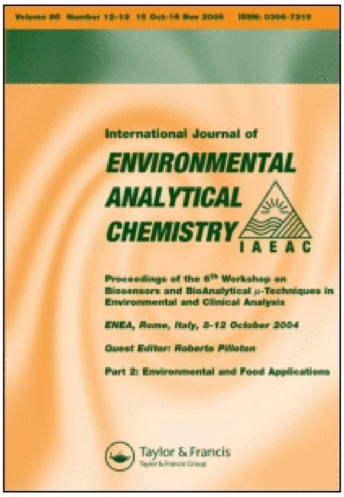

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Distribution of Heavy Metals in Various Litter Horizons and Forest Soils

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DISTRIBUTION OF HEAVY METALS IN VARIOUS LITTER HORIZONS AND FOREST SOILS

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In order to evaluate a procedure for estimating differences in the total input into a forest ecosystem, heavy metal concentrations in various litter and soil compartments within two stands were considered. As a basis for the investigation of differences between various stands, the variability within the different horizons in a stand had to be evaluated.

The variance within a stand is lowest for sampling locations which are midway between two stems, and thus these sampling locations were chosen for monitoring studies.

The concentrations of heavy metals in the L-horizon depends to a great extent on the immission situation. For the other horizons, additional factors are important as well, for example Cd and Zn concentrations in the A_h-horizons depend mainly on pH. In the case of Pb, the local immission situation is the predominant factor for all horizons. Because pH is an intrinsic parameter of a stand, only to a minor extent influenced by the immission situation, it appeared logical to choose the Pb content in the L-horizon in order to gain information about the local immission.

On the basis of this knowledge, it is possible to perform monitoring programs which enable different stands to be classified according to their heavy metal burden, including interception.

INTRODUCTION

The total input of airborne contaminants into a forest ecosystem is difficult to measure. As far as heavy metals are concerned, two pathways play major roles as input mechanisms:

1. gravitational deposition, and
2. interception of airborne particulate matter containing heavy metals.

The input via gravitational deposition, for example, rain, snow, hail and sedimenting dust, can be estimated by respective measurements outside a forest stand. Other inputs, such as those due to interception of particles and droplets (fog, mist) or to gaseous dry deposition may contribute to a great extent,[1] but to date no reliable methods exist for their evaluation. The relative contribution from interception depends on intrinsic parameters of the forest stand under consideration. Not only the local immission situation but also the exposure of the stand (orographic situation, height a.s.e.) and its vegetation play important roles.[2]

Heavy metals are accumulated in different compartments of a forest ecosystem. High accumulation occurs in lower plants such as mosses and lichens and in "dead" material, for example litter and, to some extent, soil.[3] The forest soil and the litter layer provide a long-term sink for airborne contaminants and may thus be considered to be the "ecosystem's memory".[4] From the concentration in these compartments, information about the total input can be gained. In order to estimate the total heavy-metal burden in a forest via "litter-monitoring", it is important to know the factors influencing the accumulation of these elements.

In a previous study,[5] these factors were roughly estimated. It was found that Pb and Cu were more readily accumulated than Zn and Cd owing to the higher complexing ability of the former two elements with the insoluble organic soil matrix, leading to a fixation in the organic soil horizons. The higher accumulation in spruce compared to beech stands and in stands at higher altitudes compared to lower ones[4] was assumed to be due to the increased interception under these circumstances. In order to establish differences between different stands, the variance within a stand had to be evaluated as well.

Because interception occurs mainly during dry periods, metal-containing dust accumulates on the leaf surfaces. This dust is washed off during a rain event and reaches the soil via stem flow. The heavy metal content in the infiltration area of the stemflow thus usually exhibits elevated values. Owing to the physical shape of their branches, coniferous trees do not exhibit stemflow. For this reason, a hardwood forest was chosen for the present study.

In addition to these horizontally distributed micro-stands, a vertical distinction through the soil horizons had also to be made. The most important factor over all was the degree of humification of the litter, which had to be taken into consideration in order to obtain reliable results;[6] heavy metal concentrations in the litter horizons have been shown to be drastically affected by the degree of humification.[5]

On the basis of this work, it should be possible to carry out a monitoring program to gain information about the total input of heavy metals in various ecosystems in relation to the gravitational deposition. Such a program should enable a relative estimate of the contribution from interception to be made. In the present study, two beech stands were examined with the aim of carefully evaluating the variance within a particular stand and quantitatively detecting the contributions of the different influencing factors.

MATERIALS AND METHODS

The two sampling sites chosen were situated in "Oberstammheim", in a rural landscape and in "Winterthur", on the outskirts of a city with about 80000 inhabitants. They were both at about 550m a.s.l. and did not differ considerably in their orographic situation; they were stocked with about 80 to 90 year old beech trees (*Fagus silvatica*). Both humus forms are of the mull type; Winterthur has a lower soil pH than Stammheim. Further details have been published previously.[5]

About 160 samples were taken over the time period between May and September 1986. Within each stand, 3 different locations were considered: one midway between two stems, one at the base of the stem but not influenced by stemflow, and the third in the infiltration zone of the stemflow.

The morphological characterization of the organic layers was done according to Babel;[7] the resulting nomenclature is used throughout. The percentage of organic material was determined by thermal analysis. This method allowed a detailed, reliable characterization of the degree of humification.[5]

Deposition data and concentrations of heavy metals in airborne particulate matter were taken as mean values from a monitoring study which was performed at the same locations during the time period 1984–87.[8]

Litter samples were digested using an $HClO_4/HNO_3$-mixture, whereas soil samples were extracted using 2M HNO_3 (soil:solution 1:10). The analysis was performed by anodic stripping voltammetry and graphite furnace AAS. The details of the procedures can be found in a previous paper.[5]

Soil and litter pH were determined according to DIN (No. 19684) by using 0.01 M $CaCl_2$. The soil:solution ratio was 1:2.5 for mineral horizons and 1:10 for litter layers.

Analysis of variance was performed on the mainframe computer at the computing center, University of Zurich, Switzerland, using the procedures "MEAN" and "General Linear Model (GLM)" from "Statistical Analysis System" - Package (SAS); in addition "Statview 512+" on an Apple MacIntosh SE was used.

RESULTS AND DISCUSSION

Litter Horizons

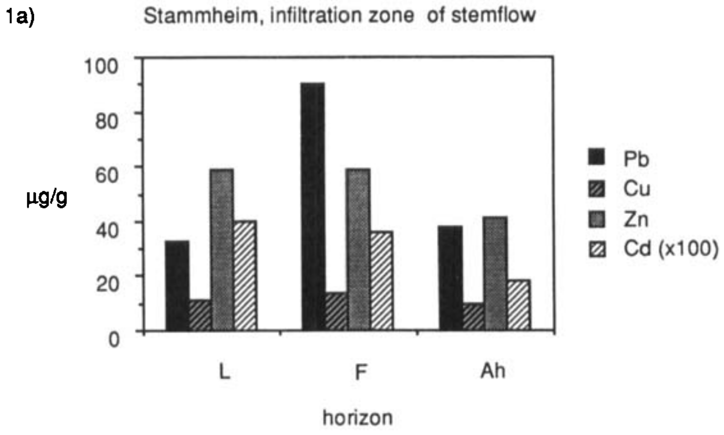
Figure 1 shows the heavy metal content as a mean value in the various litter horizons studied at the different locations at Stammheim.

Lead concentrations were generally highest in the F-horizon, a result which has also been found for spruce stands.[5] The same behavior was shown for Cu, but to a lesser extent. However quite a different picture emerged for Cd and Zn; the concentrations in the L- and F-horizons were similar but decreased sharply in the A_h-horizon.

These findings are in agreement with the chemical behavior of the metals under consideration as found in model studies[9] and can be explained as follows:

Pb readily forms complexes with high molecular weight compounds (e.g., humic acids) which are firmly bound to the soil matrix. Thus the mobility of Pb complexes under these conditions is low, leading to an accumulation in the organic layers.

Cu exhibits similar behavior but it tends to form soluble complexes as well. Therefore, the accumulation in the F-horizon was less pronounced.



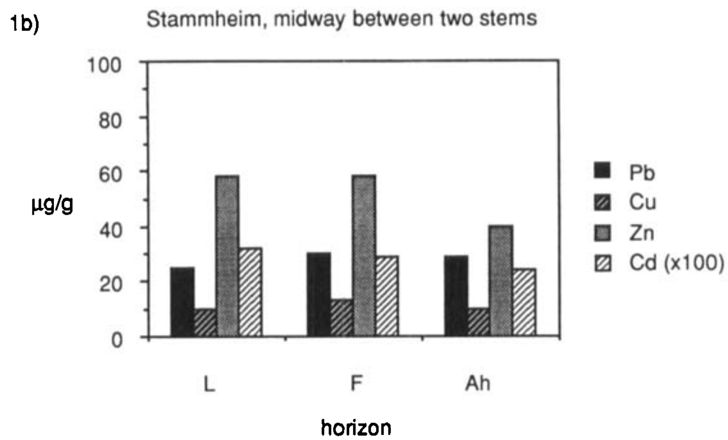


Figure 1 Concentrations of heavy metals in various litter horizons at Stammheim (the F horizons consist of an F/A_h mixture, OM c. 40–60%).

The mobility of Cd in the litter layers is high compared to Pb and Cu[10]; therefore, no accumulation in the F-horizons could be seen. The mobility of this element is governed by the mobility of the ligand in the complexes formed and by the fact that the degree of complexation is strongly pH dependent. Thus, with decreasing pH, increased mobility was found. The pH differences at the three micro-sites were the highest in the A_h-horizons owing to the long-term exposure of the A_h-horizon in the stem-flow region (see Table 1). This explains the lower Cd concentrations in the A_h-horizons of the infiltration zone of the stemflow compared to the A_h midway between stems (Figure 1).

Zn displays a lower complexing ability; thus, the pH dependence of its concentrations in the litter was less pronounced.

All the effects described above became more pronounced if only the infiltration zone of the stemflow is considered (Figure 1a), but are reduced in the region lying between tree crowns (Figure 1b).

Table 1 Mean values for all microsituations (12 observations in each)

	Ah-1		*Ah-2*		*Ah-3*		*L-1*		*L-2*		*L-3*	
Stammheim	*X*	S_x(%)	*X*	S_x(%)	*X*	S_x(%)	*X*	S_x(%)	*X*	S_x(%)	*X*	S_x(%)
OM	14.10	12.6	10.07	7.4	14.43	10.6	89.71	1.5	88.42	3.3	81.23	6.3
Cd	0.18	28.1	0.17	17.2	0.24	11.5	0.40	7.0	0.42	7.1	0.32	6.3
Pb	38.25	10.8	26.45	5.7	28.87	6.5	33.29	10.7	29.81	6.5	25.23	5.8
Cu	9.99	9.9	8.58	7.3	10.70	7.8	10.95	9.7	10.49	9.0	9.80	5.6
Zn	41.21	9.8	35.04	7.4	40.27	5.4	59.28	3.5	62.66	7.9	58.47	4.9
pH	3.86	25.5	4.32	29.4	4.48	31.4	4.59	9.2	4.64	11.9	4.69	10.0
Winterthur												
OM	19.94	12.4	15.24	17.9	15.31	17.4	89.80	2.2	87.7	3.3	83.50	4.1
Cd	0.15	20.0	0.19	15.8	0.23	4.3	0.51	5.9	0.56	5.4	0.53	5.7
Pb	72.18	12.9	44.34	12.2	34.98	6.2	67.38	12.7	51.6	9.3	39.52	4.4
Cu	16.26	13.5	11.07	9.3	15.02	22.4	16.17	11.3	14.05	7.5	13.03	3.8
Zn	43.28	12.1	49.78	10.1	49.22	6.6	72.31	3.8	73.74	3.3	71.87	3.6
pH	3.38	20.4	3.87	24.1	4.24	44.4	4.20	21.1	4.26	28.3	4.53	30.0

Ah, L: horizons; -1: infiltration zone of stemflow; -2: near stem but not influenced by stemflow; -3: between crowns; X: mean values; S_x(%): relative standard deviation of mean; OM: organic material given in % weight loss in thermal analysis; Cd, Pb, Cu, Zn: ppm (dry weight); pH: -log of mean value of H^+-concentration (S(%) of H^+-concentration)

Metal concentrations in F-horizons were highest thoughout, a fact which would make this horizon the preferable choice for studying differences in heavy metal input. However, in many stands, the F-horizon is missing. In order to provide best comparability between the various sampling sites, A_h- and L-horizons were chosen since these were present in all situations.

Variability of Heavy Metals in the Organic Horizons within a Forest Stand

Table 1 shows the mean values for all sites together with their relative standard deviations ($S_{x(mean)}$). The content of organic material (OM) is below 20% in all A_h-horizons and above 80% in all L-horizons. In most cases, the OM content was higher in the infiltration zone of the stemflow compared to the other situations. In the infiltration zone, there exists a different microclimate which leads to increased stratification (e.g., the formation of additional humus horizons). A_h samples in the infiltration zone are therefore a mixture of A_{hh} and A_h with a correspondingly higher content of organic material.

In Winterthur, Pb, Cu and Zn contents were higher than in Stammheim. For Cd this was true only for the L-layers, whereas in A_h-horizons, only small differences between the stands were seen. These differences were mainly due to the lower soil pH in Winterthur leading to a mobilization of Cd in these A_h-horizons and, therefore, to lower Cd content despite higher Cd inputs.

The standard deviations of pH were obtained by averaging H^+-concentrations and calculating corresponding standard deviations of the mean. The given mean values are the negative logarithms of the mean H^+-concentrations, but the standard deviations are given without calculating the logarithms. The standard deviations of pH itself are asymmetric and have to be calculated separately.

The standard deviations are generally highest in the stemflow regions. This is mainly due to the differences between individual trees with respect to age, crown diameter and orographic situation, and precludes this microsite from application in site-differentiating studies. The micro-site which is best defined is the zone clearly lying between tree crowns.

Analysis of the Heavy Metal Variances in the Organic Layers of Two Forest Stands

In order to quantify the contribution of the various factors (immission situation, pH, organic matter content) to the total variance of the heavy metals in the different horizons of the two forest stands, a variance analysis was run using different data-sets. Following subgroups were chosen from the collected data:

data-set 1: all L-horizons (including L-horizons of Winterthur and Stammheim at all microsites, 68 observations)

data-set 2: all A_h-horizons (including A_h-horizons of Winterthur and Stammheim at all microsites, 72 observations)

data-set 3: L-horizons midway between stems (12 observations)

data-set 4: A_h-horizons midway between stems (12 observations)

The model that was applied to explain the variance within the four data-sets included different parameters of the stands. The model was optimized in order to eliminate self-dependent variables. For example, a high correlation was found between the concentrations of heavy metals in airborne particulate matter and the gravitational deposition. This led to the definition of a variable "immission", which consisted of wet and dry deposition. Further variables which proved to be of little influence in the statistical analysis were withdrawn from the model. The following variables were included in the final model:

immission: gravitational deposition

month: sampling time

pH: pH of the horizon ($CaCl_2$)

organic matter: organic matter determined by thermal analysis

stem: microsites (midway between stems; infiltration zone of the stem; at the base of the stem, but not in the infiltration zone)

Because results of chemical trace analysis do not usually exhibit normal distribution, the analysis of variance was run using different mathematical transformations. Based on the frequency distribution of the residues and the plot of the predicted values against the residues, a logarithmic transformation was chosen for Cd, Pb and Cu concentrations whereas no transformation was applied for Zn.

Figure 2 shows the results of the analysis of variance; "100%" refers to the total

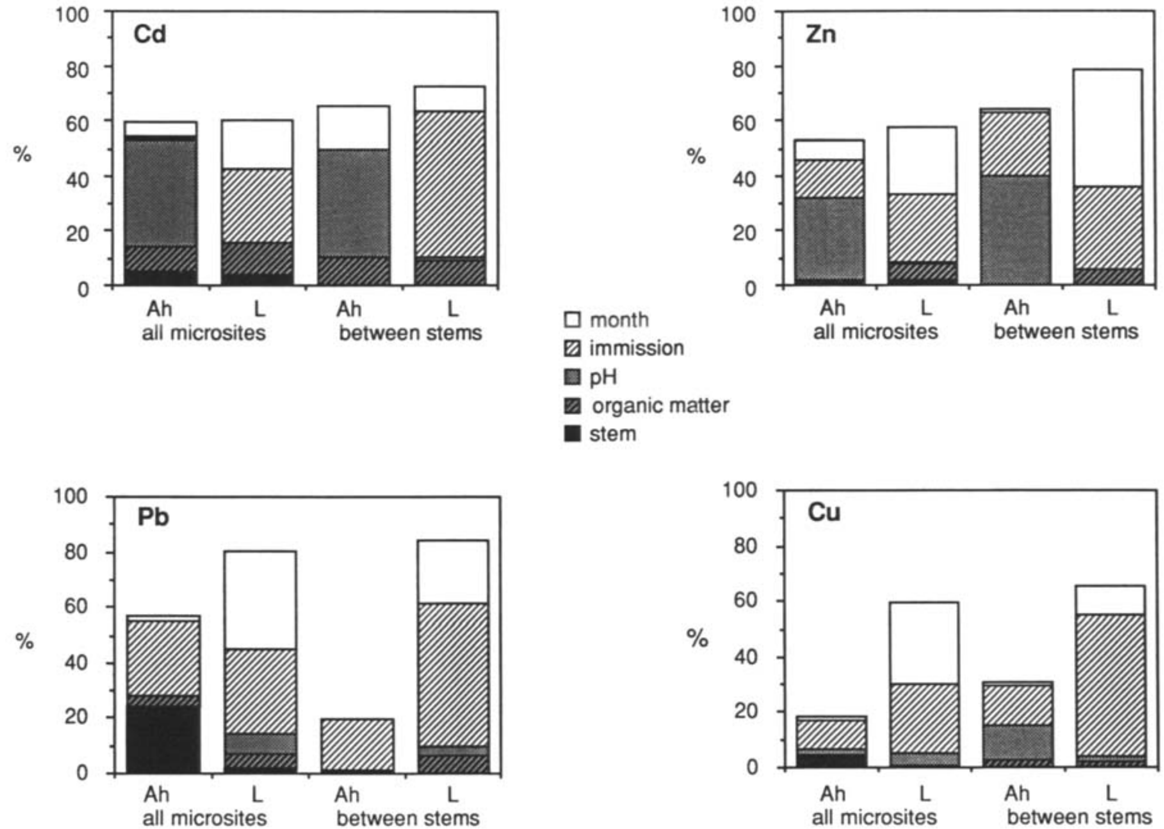


Figure 2 Variance of heavy metal concentrations which can be explained by the model (the model includes the variables: immission (immission situation), pH, organic matter, month (sampling time), stem (microsituation)).

variance of the data-set, whereas, the height of the bar represents the variance which can be explained by the model. The explainable part of the variance has been further subdivided to show the contributions from the individual variables.

A high proportion of the variance in all data-sets can be explained by the month of sample collection, especially for the L-horizon. This is due to the increased accumulation with increasing time on one hand and gradual changes in the decomposition of the material on the other. For example, the Pb concentration in Winterthur increased from May to September by 16%, whereas, the increase in the same period in Stammheim was 38%. However, this factor can be eliminated by an appropriate choice of the sampling month.

High r^2 values (i.e., the part of the variance which can be explained by the model) are found for Cd, Pb (except A_h w/o stem) and Zn. With Cd and Zn there is exceptionally high dependence on pH for the whole data set, except in the L-horizons where the pH-dependence is reduced to an arbitrary value. Owing to the physical distance between L- and A_h-horizons, the influence of the soil pH on heavy-metal concentrations in L was reduced, and pH measurements in the L-horizons showed only small differences between the micro-sites. Only in late autumn higher acidity in the stemflow region of L-horizons was observed.

In the L-horizon, immission proved to be the driving force for the metal content in the litter; this was especially the case when the variance due to the sampling time was not taken into consideration. For Pb, all cases gave the immission situation as the predominant factor for the explanation of the variance, and little, if no, dependence on pH was found. In the A_h-horizons midway between stems, only 20% of the total variance can be explained by the model indicating that the model is not adequate. The influence of other important factors for the fixation of Pb (and other heavy metals) in the mineral horizons, such as the presence of metal oxides and hydroxides as well as clay fractions, has to be taken into account when modelling A_h-horizons.

Cu showed somewhat erratic behavior. Its concentrations are assumed to be determined mainly by the natural content of this element in leaves and soil.

It is interesting to note that the micro-situation with respect to stemflow only plays a major role for Pb. For Cd and Zn, the pH changes due to the higher input of acids in the infiltration zone of stemflow seem to override the equally higher input of these heavy metals, thus reducing the importance of the statistical factor "stemflow".

CONCLUSION

The heavy metal concentrations in different compartments of the forest floor are dependent on various factors. The most important factor as far as Cd and Zn concentrations in A_h are concerned is soil pH, whereas, for Pb the immission situation plays the predominant role.

In order to evaluate a procedure which is capable of estimating the relative total input of heavy metals into a forest ecosystem, Pb is the element of choice. To obtain the smallest possible standard deviation, and thus to be able to differentiate between different stands, the Pb content in the L-horizon, which is present in all humus forms at sites lying between tree crowns, should be considered.

In this study, two stands were chosen with roughly the same orographic situation and with the difference in atmospheric input mainly due to differences in the gravitational deposition. To evaluate the importance of other input mechanisms such as interception, a monitoring study incorporating 40 sites throughout Switzerland is being performed. The results of this study will be published in a future paper.

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References

1. B. Ulrich, R. Mayer and P. K. Khanna, *Schr. Forstl. Fak. Univ. Göttingen u. Nieders. Forstl. VA* **58,** 291 (1979).
2. G. Glatzel, E. Sonderegger, M. Kazda and H. Puxbaum, *Allg. Forstzeitschrift* **26** (7), 693 (1983).
3. G. Tyler, *Ambio* **1,** 52 (1972).
4. V. Glavac, H. Koenis, H. Jochheim and R. Heimerich, *Proceedings of "Air Pollution and Ecosystems", Grenoble*, 1987 (P. Mathy, ed.), D. Reidel Publishing Company, Dordrecht (1988).
5. C. Angehrn-Bettinazzi, L. Thöni and J. Hertz, *Intern. J. Env. Anal. Chem.* **35,** 69 (1989).
6. C. Angehrn-Bettinazzi, P. Lüscher and J. Hertz, *Z. Pflanzenernähr. Bodenk.* **151,** 177 (1988).
7. U. Babel, *Hohenheimer Arbeiten* **Nr. 60** (Verlag Eugen Ulmer, Stuttgart, 1972), 120 pp.
8. J. Hertz, P. Bucher, G. Furrer, O. Daniel and L. Thöni, *Chimia* **42** (2), 57 (1988).
9. G. Brümmer and U. Herms, *Bielefelder Oekol. Beitr.* **1,** 117 (1985).
10. J. Hertz and C. Angehrn-Bettinazzi, *Int. Conf. Heavy Metal in the Environment* (T. D. Lekkas, ed.) (Athens, 1985), p. 503.