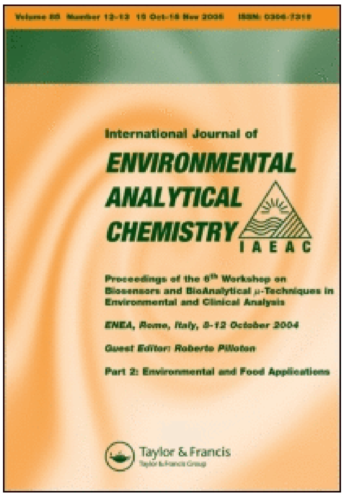

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Monitoring of Heavy Metals in Airborne Particles by Using Mosses Collected from the City of Zurich[†]

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The suitability of the moss Bryum argenteum as indicator plant of airborne heavy metals in urban environment has been examined. After extraction of the metals with 2N nitric acid, copper, cadmium, lead and zinc have been simultaneously determined by differential pulse anodic stripping voltammetry at the hanging mercury drop electrode.

The method has been applied to determine the distribution of the respective metals in the Zurich city area. We have collected about 200 samples, uniformly spread over the area of Zurich, for this investigation. The results show clearly that the metals are considerably accumulated in the city compared to an uncontaminated region outside Zurich. Low correlation coefficients between metal concentrations indicate different emission sources for the various metals.

KEY WORDS: Heavy metals, airborne particles, Mosses, anodic stripping voltammetry.

INTRODUCTION

There are numerous sources of heavy metal emission to the atmosphere. Natural sources are terrestrial and cosmic dust and salt

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spray from the oceans. Heavy metals are emitted in a great variety of technical and industrial processes, but refuse combustion, fossil fuel in domestic heating and motor traffic are the predominant emission sources in many inhabited parts of the world. The emission rate of heavy metals varies with time due to meteorological conditions and variabilities in emission processes. To get information about the mean immission situation at a certain place, continuous registration for an extended period of time is necessary. Nevertheless quite a low deposition rate may, in course of time, give rise to considerable metal concentration in certain organisms of the ecosystem because most metal ions are able to form stable complexes with organic matter. It is thus possible to use such organisms as integrating systems for the observation of heavy metal deposition.[1] Mosses and lichens are known as efficient accumulators of heavy metals. Since they lack roots, these lifeforms largely depend on atmospheric deposition for their supply of mineral elements. The occurrence of many lichens is limited to uncontaminated or slightly contaminated areas; they are missing in industrialized areas as well as in bigger towns.[2] In contrast to these lichens as well as to other mosses, the moss Bryum argenteum is able to tolerate high air contamination levels and so found a new ecological niche in the cities. Bryum argenteum is a small moss forming dense cushions. It occurs commonly and frequently in areas affected by human activities, where it grows in cracks, at the bottom of walls or on open sandy sites.[3]

The earlier applications of moss analysis to regional surveying of atmospheric metal deposition over northern Europe[4,5,6] has been followed by many studies in other European countries and in the USA.[7] Most investigations are concerned with only slightly contaminated regions outside towns and industrial areas. It was therefore the aim of the present work to investigate the possibility of using the moss Bryum argenteum to evaluate the immission situation in a larger city.

EXPERIMENTAL

Apparatus

A polarographic analyser (Princeton Applied Research PAR 174A) equipped with a Metrohm type quartz cell and a Houston Omnigraphic 2000 recorder was used. A hanging mercury drop electrode (HMDE, Metrohm E 410) served as working electrode. The saturated calomel reference electrode (SCE) was connected with the solution via a double junction filled with buffer solution pH 4.6. A platinum coil was used as counter electrode. Dissolved oxygen was removed by passing highly purified nitrogen through the solution for 10 minutes. During measurement nitrogen was passed over the solution. The capillary was treated with dichlorodimethylsilane at regular intervals.

A microcomputer Apple II plus was connected to the system to semiautomate the procedure and to allow screen display, storage and plotting of curves.

Reagents

All chemicals were analytical grade (Merck, p.a.). Standard solutions were prepared daily by dilution from acidified stock solutions. Deionized water was purified by filtration through activated carbon, followed by ion exchange and ultrafiltration (Millipore-system).

PROCEDURE

Sample Collection

200 samples of about 10 g were collected during a six week period between October 26 and December 4, 1982. The moss was sampled from 200 sites uniformly spread over the Zurich city area. (2 to 3 samples per square kilometer at built over areas, as many as possible in the forest). Most of the sites were located in smaller streets, gardens, churchyards and sportsgrounds, i.e. not directly in main streets in order to diminish local effects of traffic. During sampling, transport and storage, metal contact of the moss was avoided.

The material was dried under vacuum at 75°C for 8 hours to prevent from biological degradation during storage.

Sample Preparation

Bryum argenteum is a small moss forming dense cushions. It thus accumulates much particulate matter, which has to be removed prior to analysis. For this reason the material was thoroughly washed and cleaned from adhering soil and dust by treatment in an ultrasonic bath followed by mechanical disintegration and separation. The metal concentration in the ultimate washing water was below the determination level under the given conditions. The cleaned matter was dried again and part of it was taken for extraction.

Extraction

Digestion of moss is a tedious and time consuming task and requires the use of hazardous chemicals.[8] Because of the ion exchange properties of the leaves, metal ions mainly accumulate at their surface and therefore extraction is supposed to remove the main part of the metals. Several successive extractions of the same sample have shown that more than 90% of the totally extractable amount is removed with the first extraction. Therefore the following procedure has been applied: 0.2 g of the dried and washed moss were stirred during 60 minutes at room temperature together with 25 ml 2 M HNO_3. The slurry was treated in a centrifuge (4000 rpm, 10 min) to separate the residual material from the extraction solution. The solution was filtered (0.25 um) and analysed immediately.

Instrumental Analysis

The high potentialities of the voltammetric approach in environmental trace metal chemistry have been established for a wide range of environmental sample types. Especially differential pulse anodic stripping voltammetry (DPASV) exhibits high sensitivity combined with good precision and the possibility of simultaneous determination of several trace metals.[9] The selection of the chemical and electrochemical parameters of the voltammetric determination step is based on the results of various exploratory studies. Adjusting only a slightly acidic pH (4 to 5) enables the determination of Zn, Cd, Pb and Cu without interferences with hydrogen evolution or mercury dissolution of the HMDE. The problems of adsorption of metal ions at the wall of the measuring cell, which can be important in non acidic media,[10] has been overcome by using a home made quartz cell. Highly reproducible stirring was achieved with a rotating shaft dipping into the solution (Metrohm model 628 at 1500 rpm) rather than with magnetic stirrer. Cleaning of the cell and the electrodes was performed mainly by thorough washing with purified water; a blank curve was recorded daily to establish sufficiently low contamination level.

5 ml of the extract was mixed with 20 ml 1.06 M Na-acetate to get a buffered solution pH 4.6 and analysed using the parameters listed in table I.

The determination was performed using the standard addition method. The comparably low Cd concentrations were usually measured in a separate step using a deposition potential of −900 mV (SCE) for up to 240 seconds. This step was followed by simultaneous determination of Zn, Pb and Cu.

TABLE I
Typical measuring parameters for DPASV

Deareation	10 min
Deposition	60 sec at −1250 mV (SCE)
Quiescent Interval	30 sec without stirring
Potential Range	1500 mV
Scan Rate	5 mV/sec
Pulse Time	0.5 sec
Pulse Amplitude	50 mV
Current Range	0.5 to 50 uA full scale

RESULTS AND DISCUSSION

Figure 1 shows a typical voltammogram of an extract recorded with the parameters from table I. The small peak for cadmium can easily be enlarged by using a higher sensitivity of the instrument. The peak potentials for Zn, Cd, Pb and Cu are −1025, −575, −430 and +25 mV (SCE) respectively. In some cases the copper peak is overlapped by another peak which is presumably due to organic impurities in the solution. Reproducibilities have been determined by analysing two sample lots several times at regular intervals. The obtained values (table II) include inhomogeneities in the biological material itself.

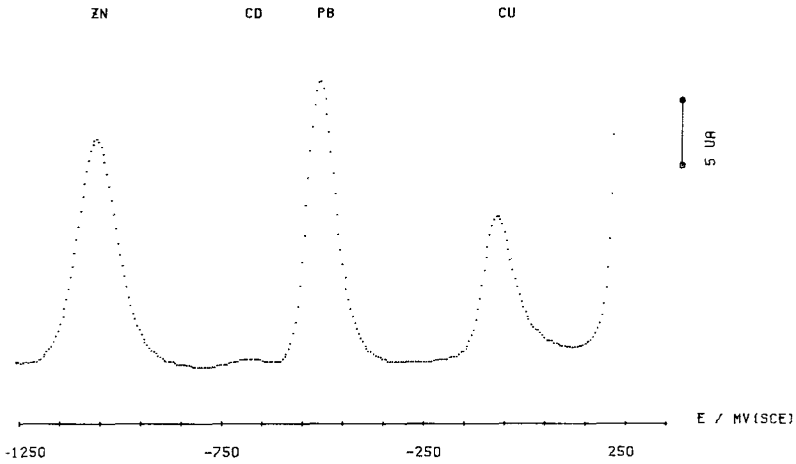

FIGURE 1 Voltammogram of an extract; parameters as in Table I.

TABLE II
Reproducibilities for two samples (Concentrations in ppm)

		Zn	Cd	Pb	Cu
1)	n	17	11	17	18
	$\bar{x}$	828.8	3.56	357.9	312.8
	s	49.0	0.25	31.9	48.7
2)	n	15	11	14	15
	$\bar{x}$	2188.9	2.56	436.8	87.3
	s	181.5	0.15	25.4	14.3

The blank values usually have been smaller than 1% of the data obtained from the samples for Zn, Pb and Cu (10% for Cd) although only analytical grade chemicals have been used for the preparation of extraction solution and buffer.

The results of the determinations are shown in figure 2a–d. Pb, Cu and Cd are clearly accumulated in the center of the town whereas Zn concentrations are somewhat higher in the suburbs. Within the built over area, lead concentrations depend strongly on distance from and traffic frequency in the nearest street. The two refuse

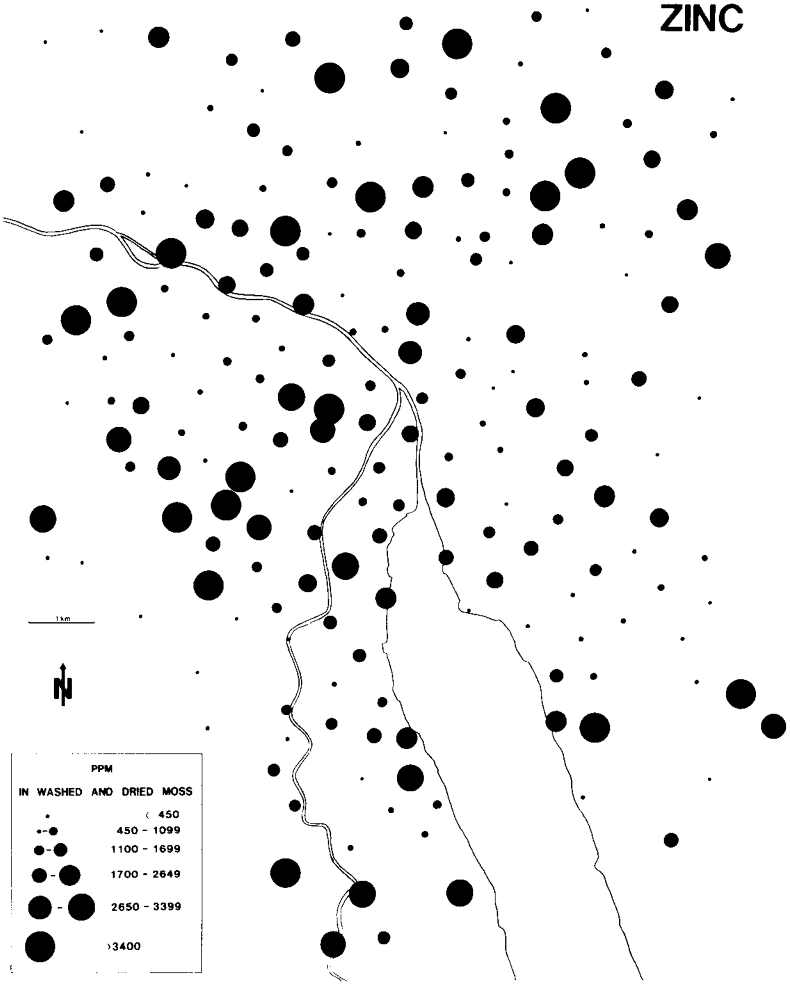

FIGURE 2a Zn concentration in dry moss.

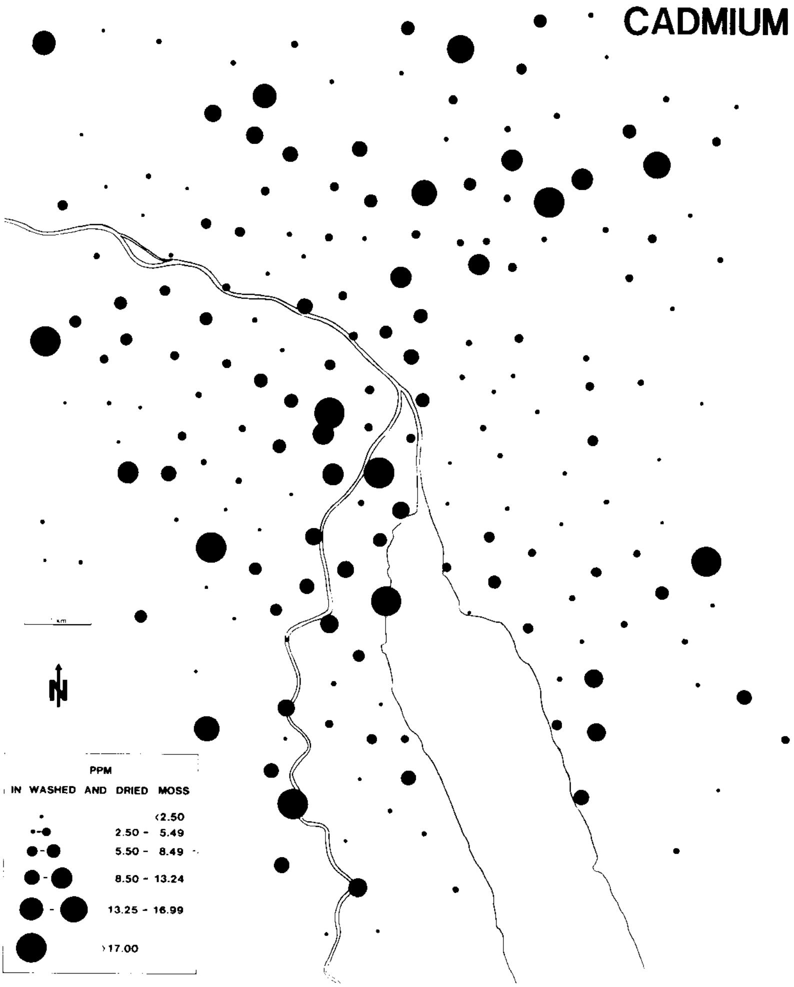

FIGURE 2b Cd concentration in dry moss.

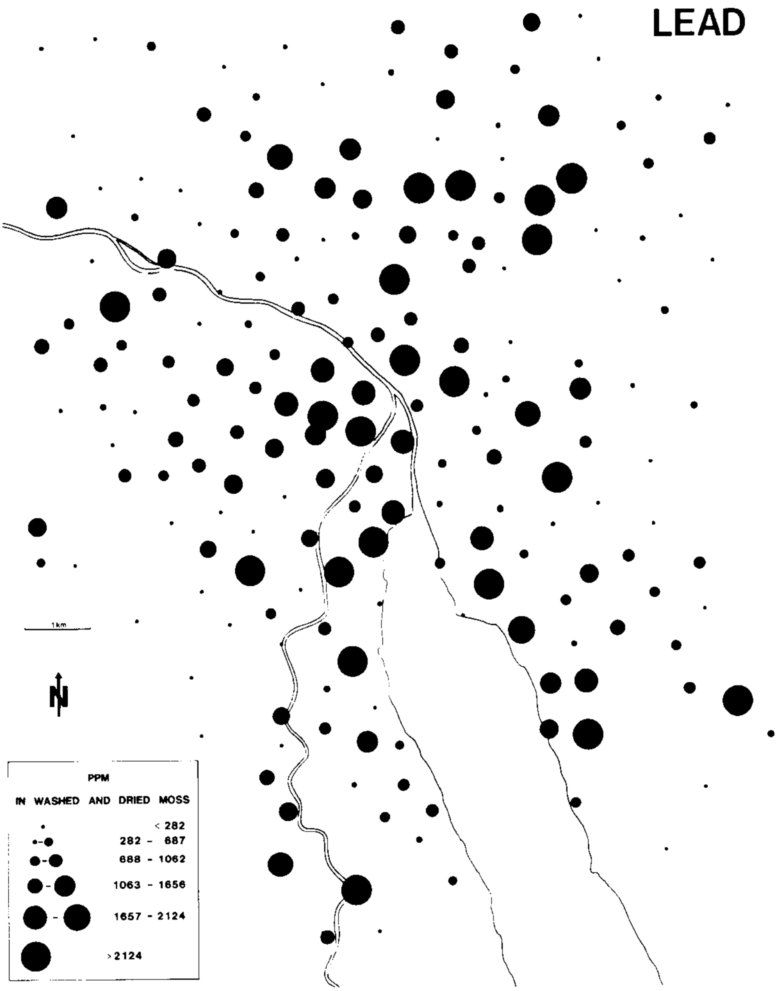

FIGURE 2c Pb concentration in dry moss.

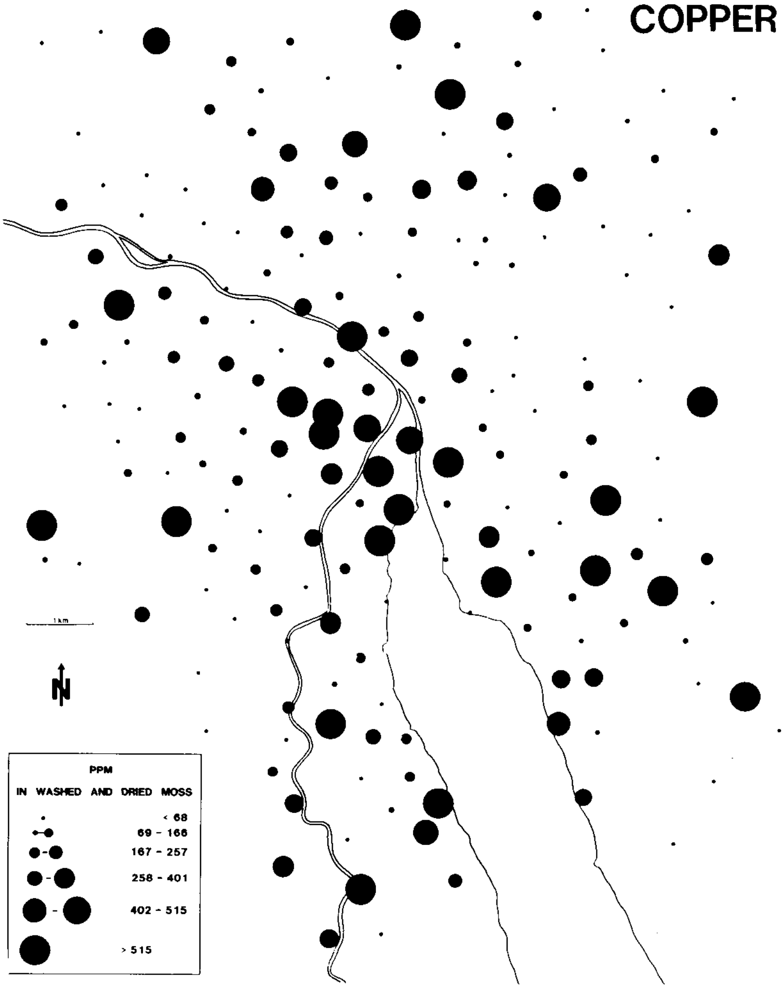

FIGURE 2d Cu concentration in dry moss.

incinerators in Zurich are equipped with highly efficient electrofilters; it may therefore be difficult to find a clear relationship between cadmium distribution and incinerator location.

More than 90% of the metal contents found within the city area are much higher than separately measured concentrations in moss collected from relatively uncontaminated sites outside Zurich (table III).

Correlation coefficients between the various metals are all below 0.15, leading to the conclusion that various emission sources are responsible for the different metal contaminations; the correlations are much higher in the uncontaminated regions (Table IV).

TABLE III
Average concentrations in dry moss from the city and an uncontaminated region outside Zurich (Bachs; Distance 20 km)

	Zn	Cd	Pb	Cu
City *n* = 200	1606.7	6.12	969.3	286.2
Bachs *n* = 7	369.6	0.72	90.0	12.9

TABLE IV
Correlation coefficients between metal concentrations (r^2)

	Zn/Cd	Zn/Pb	Zn/Cu	Cd/Pb	Cd/Cu	Pb/Cu
City *n* = 200	0.035	0.154	0.021	0.113	0.012	0.054
Bachs *n* = 7	0.327	0.215	0.282	0.971	0.810	0.728

CONCLUSIONS

The presented method is well suited to obtain information about the differences in the heavy metal burden in various regions compared to one another. Nevertheless there are some uncertainties in the given concentration for two reasons:

I. Local contamination sources, leading to exceptionally high concentrations cannot be avoided.

II. The age of the moss and hence the accumulation period is largely unknown.

Both problems can partly be solved by analysing a great number of samples in order to enable averaging and discarding of outliers.

References

1. H. Bick, *Decheniana Beihefte* **26,** 2 (1982).
2. S. Zuest, *Ber. Geobot. Inst. ETH, Stiftung Ruebel* **62,** (1977).
3. K. and K. von der Dunk, *Mikrokosmos* **64,** 227 (1975).
4. A. Reuhling and G. Tyler, *Botaniska notiser* **121,** 321 (1968).
5. A. Ruehling and G. Tyler, *J. Appl. Ecol.* **8,** 497 (1971).
6. P. Pakarinen and K. Tolonen, *ambio* **5,** 38 (1976).
7. J. Maschke, "Moose als Bioindikatoren von Schwermetall Immissionen", *Bryophytorum Bibliotheca, No. 22* (1981).
8. K. Grodzinska, *Water Air and Soil Pollution* **9,** 83 (1978).
9. H. W. Nuernberg, *The Science of the Total Environment* **12,** 151 (1979).
10. A. D. Shendrikar, V. Dhamarajau, H. Walker-Merrick and P. W. West, *Anal. Chim. Acta* **84,** 409 (1976).