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## MOSS AND LICHEN AS BIOMONITORS FOR HEAVY METALS

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Concentrations of Zn, Pb and Cd in the mosses Hypnum cupressiforme and Hylocomium splendens were compared with the measurements of these elements in lichen-samples of Hypogymnia physodes at five sampling sites with different pollution situation in Switzerland. From measurements of several sites we found that the ratio of lichen to moss concentrations is a function of the the pollution situation determined in moss concentrations. This finding was controlled by further measurements of mosses and lichen samples from the Simmental region. These results fit well in this functional dependency, this is especially true for zinc and cadmium concentrations.

Keywords: Biomonitor; air pollution; lichens; mosses; zinc; lead; cadmium

#### INTRODUCTION

Both, moss and lichen are used as biomonitors to get information about the magnitude and distribution of important pollutants. Therefore, it is useful to compare moss and lichen as biomonitors for the interpretation of investigations where either mosses or lichens were used as biomonitors.

Mosses and lichens are suitable biomonitors because they obtain most of their nutrient supply directly from atmospheric deposition. As a result, mosses were used in the survey of heavy metal deposition in Europe using bryophytes as biomonitors.

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Lichens, for example, have no roots or structures which have the absorptive function of roots. Thus, lichens depend for their mineral nutrients to a large extent on material deposited on the lichen by wet and dry fallout from the atmosphere. Also, lichens unlike higher plants, do not have a well-developed cuticle and, hence, there is no comparable physical barrier to impede the uptake of mineral elements to levels far greater than their expected physiological needs. Lichens are perennial and this feature, together with the other characteristics, has led to the use of these plants as long-term integrators of deposition from the atmosphere of elements originating from both natural and man-made sources.

The aim of the present paper is to compare moss and lichen as suitable biomonitoring systems for heavy metal pollution.

#### MATERIALS AND METHODS

#### Sampling Areas

The fieldwork was carried out at 5 sites within Switzerland covering different air quality situations. One station is situated in the Swiss midlands at 470m a.s.l. (Burgmoos). Three sites are located in the Bernese Oberland (1000-1500m a.s.l., Eriz, Jaun, Egelsee). The last station is situated on the south side of the Alps at 1000m a.s.l. (Gola di Lago).

Later we did a detailed investigation in the Simmental region in Bernese Oberland. In an area of 20×20 km we collected about 80 samples of moss and lichen.

#### Sampling and Sample Preparation

Samples of the lichen species *Hypogymnia physodes* were collected from branches of spruce. In the laboratory the lichen material was separated from bark material and pine needles, freeze-dried and powdered. Portions of about 0.25 g were digested in nitric acid and perhydrol by microwave heating in PTFE-bombs. The resulting solutions were measured by ICP-OES technique.

Samples of the moss species *Hylocomium splendens* were collected from soil in forest glades or on the edge of the forest. After eliminating of extraneous material, the three upper segments of *Hylocomium splendens* were used, representing the last 3 years of growth. Samples of the moss species *Hypnum cupressiforme* were taken from tree stumps. Only green and yellow-green sprouts were prepared. Then, the moss-samples were freeze-dried, powdered and digested as the lichen samples.

TABLE I Zinc, lead and cadmium concentrations, and standard deviations of the mean ( $1\sigma$ ) in  $\mu g \ g^{-1}$  dry lichen samples from five sampling sites in Switzerland

Locality	$n^a$	Zn ± sd	Pb ± sd	$Cd \pm sd$	
Burgmoos	3	97 ± 24	34 ± 17	1.26 ± 0.69	
Eriz <sup>b</sup>	2	77 ± 6	$22 \pm 3$	$0.39 \pm 0.11$	
Egelsee	4	90 ± 17	$26 \pm 9$	$0.83 \pm 0.13$	
Jaun <sup>b</sup>	10	71 ± 6	22 ± 9	$0.75 \pm 0.15$	
Gola di Lago <sup>c</sup>	1	138	17	1.67	

<sup>&</sup>lt;sup>a</sup>Each sample was collected, prepared and measured separately

#### RESULTS AND DISCUSSION

# Comparison of Moss and Lichen as Biomonitoring Systems for Heavy Metals

The highest concentrations of Zn, Cd and Pb were found in Gola di Lago. Also Burgmoos (Swiss midlands) showed higher concentrations than the rural sites located in the Bernese Oberland (see Table I and Table II). The data of Burgmoos and Gola di Lago are less reliable because of limited amounts of collectable sample material at these places. The lack of moss and lichen species at these sampling sites may depend on the climatic situation as well as on the high pollution.

The results of the samples of the Simmental region showed quite low pollution (see Table III).

TABLE II Zinc, lead and cadmium concentrations, and standard deviations of the mean (1 $\sigma$ ) in  $\mu g \, g^{-1}$  dry moss samples

Locality	n <sup>a</sup>	Zn ± sd	Pb ± sd	$Cd \pm sd$	
Burgmoos <sup>c</sup>	1	44	18.0	0.21	
Eriz <sup>b</sup>	2	$18 \pm 2$	$3.7 \pm 1.4$	$0.20 \pm 0.02$	
Egelsee	7	$26 \pm 14$	$3.5 \pm 2.1$	$0.25 \pm 0.09$	
Jaun <sup>b</sup>	10	27 ± 10	$5.6 \pm 1.7$	$0.33 \pm 0.10$	
Gola di Lago <sup>c</sup>	2	$125 \pm 62$	28 ± 12	1.10 ± 0.61	

<sup>&</sup>lt;sup>a</sup>Each sample was collected, prepared and measured separately

 $<sup>^{\</sup>rm b}$ Each sample was composed of 5-10 subsamples, collected within an area of 50  $\times$  50 m

<sup>&</sup>lt;sup>c</sup>Limited amount of sample material for this sampling site

<sup>&</sup>lt;sup>h</sup>Each sample was composed of 5-10 subsamples collected within an area of 50 × 50 m

<sup>&</sup>lt;sup>c</sup>Limited amount of sample material for this sampling site

TABLE III Zinc, lead and cadmium concentrations, range in µg g <sup>-1</sup> dry material of lichen and moss
samples from Simmentalregion (20 × 20 km) in Bernese Oberland

Simmental	n <sup>a</sup>	Zn	Pb	Cd
Lichen <sup>b</sup>	41	42-93	3.6-49	0.17-0.96
Moss <sup>b</sup>	41	12-66	2.5-28	0.17-0.75

<sup>&</sup>lt;sup>a</sup>Each sample was collected, prepared and measured separately

The comparison of concentrations of heavy metals in moss and lichen shows higher values for lichens (dry material). This is especially true for zinc. For cadmium and lead we found also places where there are higher concentrations in moss than in lichen samples. Concentrations in mosses and lichens show no linear correlation (see Figure 1).

One or several of the following interpretations might be the reasons for the observed difference of the two biomonitors:

Faster growth of mosses over lichens will disperse the deposited heavy metals throughout more mass of dry material.

Different exposure of lichen and moss towards air quality can lead to the observed behaviour. The lichen samples were collected from branches of free standing spruce trees, whereas moss samples were collected from the ground or from tree-stumps. So, it is possible that lichens are skimming out the air more effectively.

The surface structures of the two biomonitors lead to a different trapping behaviour of the two natural systems.

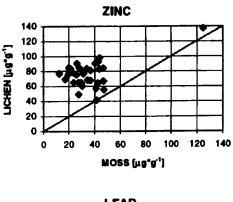
#### Ratio of Lichen to Moss as a Function of Concentrations in Moss Samples

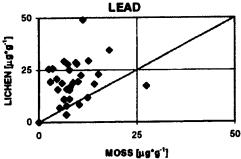
The lichen species *Hypogymnia physodes* changes its accumulation capacity with increasing pollution in a different way than the mosses *Hylocomium splendens* and *Hypnum cupressiforme*.

For high polluted areas the ratio lichen/moss is around one. This result is confirmed by the measurements of Folkeson. For low polluted areas the ratios lichen/moss increase to a factor of up to eight, depending on the measured elements.

At a load of 100  $\mu$ g g<sup>-1</sup> for zinc in moss samples the lichen to moss ratio of concentrations is about one. For lead a ratio of one is reached at a concentration of 30  $\mu$ g g<sup>-1</sup> in the moss samples. For cadmium the ratio reaches unity at about 0.5  $\mu$ g g<sup>-1</sup> in moss samples.

<sup>&</sup>lt;sup>b</sup>Each sample was composed of 5-10 subsamples, collected within an area of 50 × 50 m





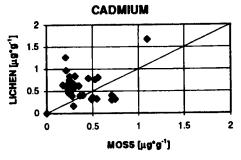


FIGURE 1 Concentrations of zinc, lead and cadmium in lichen and in moss samples (all sampling sites included) do not show a 1:1 correlation

To describe mathematically our datapoints we used the sigmaplot curve fitter to fit our data to equations that are nonlinear functions. The Sigmaplot curve fitter uses the Marquardt-Levenberg algorithm to find the coefficients (parameters) of the independent variable (the x value) that give the best fit between the equation and the data. This algorithm seeks the values of the parameters that mini-

mize the sum of the squared differences between the values of the observed and the predicted values of the dependent variable (the y value). As a function which fulfills the condition of convergence  $f = a^*e^{(c-b^*x)} + d$  was obtained. The calculated parameters are presented in Table IV.

The functional connection of concentrations in moss and lichen allows a calibration: If the concentration of a moss sample is known for one sampling site, one can find out the heavy metal contents in lichens by means of the found correlation and vice versa.

The ratios between concentrations of zinc, lead and cadmium in moss and lichen show a functional connection depending on the pollution situation (see Figure 2). These results demonstrate the difficulties related to interspecies calibration, and also show the completely different accumulation behaviour of moss and lichen. One or several of the following reasons may lead to the observed concentration dependent uptake of pollutants:

The sorption and fixation behaviour of the surfaces of the two biomonitors under discussion vary with contamination. Lichens show more efficient accumulation of heavy metals at low levels of contamination which decreases when the load of contamination increases.

The surfaces of lichens and mosses exhibit different wetting behaviours (faster for lichen). Since the first drops of any precipitation show higher concentrations of solutes compared to later rain. So, lichen take up the existing contamination to a higher degree.

TABLE IV Zinc, lead and cadmium concentrations in moss samples, ratios of lichen (L) to moss (M) concentrations and parameters of the calculated fit function:  $f = a^* e^{(c-b^*x)} + d$  for each element

Locality	Zn		Pb		Cd		
	moss [µg g <sup>-1</sup> ]	ratio L/M	moss [µg g <sup>-1</sup> ]	ratio L/M	moss [µg g <sup>-1</sup> ]	ratio L/M	
Burgmoos	44	$2.2 \pm 0.2$	18.0	1.9 ± 0.5	0.21	$5.9 \pm 0.6$	
Eriz	18 ± 2	$4.4 \pm 0.2$	$3.7 \pm 1.4$	$5.6\pm0.5$	$0.20\pm0.02$	$2.0\pm0.4$	
Egelsee	26 ± 14	$3.5 \pm 0.7$	$3.5 \pm 2.1$	$7.5 \pm 0.9$	$0.25 \pm 0.09$	$3.3 \pm 0.5$	
Jaun	$27 \pm 10$	$2.6\pm0.4$	$5.6 \pm 1.7$	$3.9 \pm 0.7$	$0.33 \pm 0.10$	$2.3\pm0.5$	
Gola di Lago	$125 \pm 62$	$1.1 \pm 0.5$	$28 \pm 12$	$0.6\pm0.5$	$1.10 \pm 0.61$	$1.5\pm0.6$	
Sweden <sup>a</sup>	$208 \pm 18$	$1.1 \pm 0.2$	$105 \pm 7.3$	$0.2 \pm 0.1$	$1.40 \pm 0.07$	$0.8\pm0.1$	
Parameter of fit function	a = 8.88 $b = 0.041$ $c = 0$		<b>a</b> = 1	a = 10.33		a = 13.71	
			b = 0.18 $c = 0$		b = 16.63 c = 2.408		
	d = 0		$\mathbf{d} = 0$		d = 1.25		

a These data are from a Swedish study

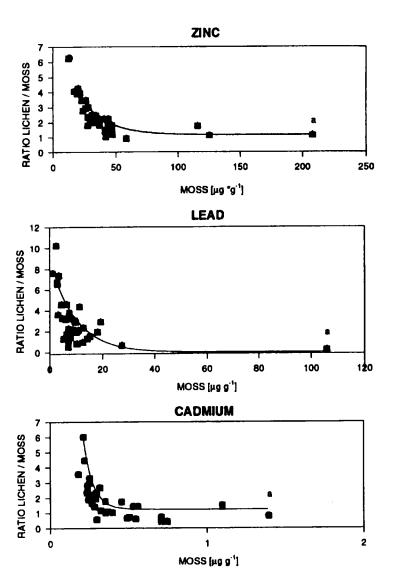


FIGURE 2 Ratios of concentrations of heavy metals in lichen over moss as a function of measured concentrations in moss samples from Simmental region (solid line calculated fit function for 6 sampling sites, see Table IV)

The metabolism of the biomonitors may be affected by heavy metals to such a way that the resulting uptake of contaminants show the measured relation presented in Figure 2.

When beside the correlation factors between moss and lichen, the bulk deposition rates and concentrations in air particulate matter are known, the pollution situation for a certain sampling site can be evaluated.

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