HEAVY METALS IN BULK PRECIPITATION AND TRANSPLANTED *HYPOGYMNIA PHYSODES* AND *DICRANOWEISIA CIRRATA* IN THE VICINITY OF A DANISH STEELWORKS

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Abstract. *Hypogymnia physodes* (L.) Nyl. and *Dicranoweisia cirrata* (Hedw.) Lindb. were transplanted to 12 stations in the vicinity of the steelworks in Frederiksvaerk, Denmark. The transplants were exposed for 7 mo, and samples were taken after 31, 64, 104, 154, 184, and 214 days. Bulk precipitation was collected simultaneously. The concentrations of the metals Cd, Cr, Cu, Fe, Mn, Ni, Pb, V, and Zn were analyzed by atomic absorption spectrophotometry in both transplants and bulk precipitation. The amounts of accumulated metals in the transplants were linearly correlated with fallout from the atmosphere, the bryophytes accumulating the metals slightly faster than the lichens. The metal concentrations in the transplants, as well as the bulk precipitation, followed a decreasing power curve when the distance to the steelworks was increased. It was concluded that transplanted lichens and bryophytes can be applied as monitor organisms of heavy metal pollution from the air.

1. Introduction

The value of biological monitoring of air pollution has been proved in a large number of studies. Lichens and bryophytes have been used for monitoring of SO_2, HF and metals. Species occurring naturally in the area as well as transplanted species have been used as monitor organisms. Transplantation has been used in areas where no suitable monitor organism could be found in the indigenous vegetation, and in cases where the more comparable substrate and exposition conditions of transplants were considered to be superior to the conditions in the natural vegetation.

Transplantation and subsequent correlation of SO_2-pollution with morphological, physiological and chemical changes of the transplanted plants have been performed in several studies with lichens (Brodo, 1961, 1966; Schönbeck *et al.,* 1976; Kirschbaum *et al.,* 1971; Søchting and Johnsen, 1978). Transplantation of mosses, correlating the tolerance of several species with SO_2 levels, has been performed by Frahm (1976).

Goodman and Roberts (1971) used logs covered with the bryophyte *Hypnum cupressiforme* and nylon mesh bags with the same species as indicators and integrators of airborne metal pollution by transplantation for 8 weeks in the Swansea Valley, U.K. The 'mossbag' technique has also been used in studies of heavy metals in the vicinity of the large Zn and Pb smelting complex at Avonmouth, near Bristol, U.K. (Little and Martin, 1974; Cameron and Nickless, 1977), and in the vicinity of a battery factory (Ratcliffe, 1975).

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Similar experiments with transplanted lichens as monitors of metal pollution from the air have only been carried out in a few studies. Krog and Brandt (1975) transplanted *Hypogymnia physodes* growing on bark disks from an unpolluted area to the city of Oslo, and measured the content of S and Pb after 7 weeks of exposure. Kauppi (1976) used transplanted *Cladonia stellaris* for the monitoring of F, S, N, K, and Ca in fertilizer dust in the surroundings of a chemical factory in Finland, and Brown (1976) transplanted saxicolous *Parmelia glabratula subsp. fuliginosa* into a highly polluted area, but found no accumulation of Pb and Zn after an exposure time of 2 mo.

The purpose of the present study was to compare the accumulation of metals in transplanted lichens with that in transplanted bryophytes, and to correlate the amounts of accumulated metal with exposure time and fallout from the atmosphere. *Dicranoweisia cirrata* (Hedw.) Lindb. was chosen as the bryophyte species because it is resistant to desiccation (Barkmann, 1958) and tolerant to SO_2 (Syratt and Wanstall, 1969). *Hypogymnia physodes* (L.) Nyl., which was chosen as the lichen species, is semitolerant to SO_2 (Johnsen and Søchting, 1973) and can withstand long periods of low humidity.

The investigation area was known from a previous study to be heavily polluted with metals from the atmosphere, the major part of which originated from a steelworks (Pilegaard, 1978).

2. Material and Methods

On the basis of the findings of Pilegaard (1978) 11 stations were selected in the Frederiksvaerk area (Figure 1). The stations were placed in three transects (NNW, NE, SE) from the steelworks and the distance between them was chosen so as to cover the whole variation in the fallout. In addition, a background station was placed 7 km N of the steelworks (Figure 1). All stations were placed in open areas without interfering effects of trees and buildings and more than 50 m from automobile roads. A bulk precipitation collection system and a stand with transplants were placed at each station. The sampling of bulk precipitation and exposition of transplants started simultaneously on 4 April, 1977. Samples of transplants and bulk precipitation were collected on 5 May, 7 June, 19 July, 5 September, 5 October, and 4 November.

2.1. BULK PRECIPITATION

The collection system consisted of a polyethylene funnel (diameter 212 mm and vertical board 100 mm) and a polyethylene bottle (5 l). The funnel–bottle system was mounted in a concrete pipe keeping the upper edge of the funnel 1.5 m above ground level, and protecting the bottle from light. Before each sampling period,

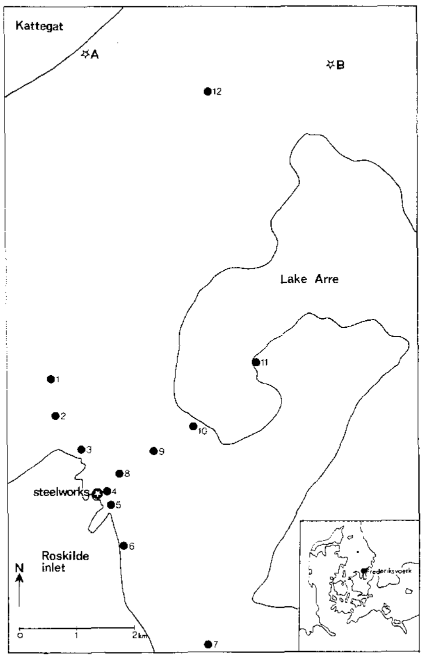

Fig. 1. Map of the Frederiksvaerk area showing the 12 stations and the sampling sites for *Hypogymnia physodes* (A) and *Dicranoweisia cirrata* (B).

10 ml conc. HNO_3 (Merck, *pro analysi*) was added to the bottle to preserve the precipitation collected. After each period the bottle was weighed and the amount of precipitation determined. Extraneous material was removed by filtering through a coarse nylon filter (1 mm mesh). The collected bulk precipitation was then evaporated in beakers by boiling. Twenty ml 7N HNO_3 was added to the empty bottle, and the bottle was shaken to dissolve the material adsorbed to the inner surface of the bottle. The acid was added to the beaker, and the solution evaporated to dryness. One hundred ml 1N HNO_3 was added and the evaporated material brought into solution again by heating. The solutions were stored in 100 ml polyethylene bottle in a refrigerator.

2.2. TRANSPLANTS

Samples of *Hypogymnia physodes* growing on 1 to 2 cm thick branches of *Pinus mugo* Turra were collected by cutting the branches into lengths of 20 cm. The sampling site was 7.6 km N of the steelworks (Figure 1).

Dicranoweisia cirrata was collected as cushions of approximately 25 cm^2 together with the substrate, a dead birch tree (*Betula péndula* Roth) lying horizontally on the ground 8.4 km NE of the steelworks (Figure 1).

The transplants were placed on a wooden stand with the end stuck into the soil so that the transplants were placed 1.5 m above ground level. At each stand 7 branches with *Hypogymnia* and 6 cushions of *Dicranoweisia* were attached horizontally with a nylon thread to the upper part of the stand. On each sampling date one branch and one cushion were collected, dried for 3 days at 50°C, detached from the substrate, and rinsed from extraneous material. The samples were digested to total dissolution in a mixture of 10 ml conc. HNO_3 and 10 ml demineralized H_2O evaporated to dryness followed by addition of 2 ml $HClO_4$ to the residue, evaporation to dryness again and dissolution of the residue in 25 ml 1N HNO_3. The solutions were filtered and stored in polyethylene bottles in a refrigerator.

2.3. ANALYSES

The concentrations of the metals were determined by atomic absorption. Cd, Ni, and V using a Perkin–Elmer 303 spectrometer with graphite furnace HGA–76. Cr, Cu, Fe, Mn, Pb, and Zn using Perkin–Elmer model 403 with an air/acetylene burner.

3. Results

1. BULK PRECIPITATION

The results of the analyses of metals in bulk precipitation during 4 April–4 November are shown in Table I, calculated as mg m^{-2}. As can be seen, the highest values of all the metals are found nearest to the steelworks, except for Cd where there is a second maximum at station 2 (1425 m N of the steelworks).

The regression equations for the natural log of concentration on the natural log of distance ($\log_e y = a + b \log_e x$ or $y = ax^b$, where y = fallout (mg m^{-2}) and x = distance from the steelworks (m)), using the fall-out values from the period 4 April–4 November, are shown in Table IV. This transformation produced regression values of higher

TABLE I

Fallout of heavy metals (mg m^{-2}) in the Frederiksvaerk area during the period 4/4 to 4/11/77

Station	Distance (m)	Cd	Cr	Cu	Fe	Mn	Ni	Pb	V	Zn
1	2000	0.26	1.16	3.92	260	21.0	0.35	20.4	0.58	68.5
2	1425	5.49	2.73	6.59	531	35.1	0.64	33.7	0.87	118.9
3	750	1.65	4.61	9.06	1039	60.0	1.12	65.9	1.12	282.4
4	250	6.60	18.78	63.75	4915	305.2	10.01	493.3	3.20	1579.0
5	425	1.30	5.47	17.50	1391	88.7	2.56	105.8	1.69	300.2
6	1125	0.34	1.85	3.82	510	28.2	0.40	21.5	0.57	75.1
7	3350	0.27	1.05	2.66	399	15.6	0.52	13.7	0.85	52.0
8	650	2.08	8.01	20.38	1817	106.6	3.22	155.5	3.25	567.4
9	1275	0.90	2.70	6.98	486	37.6	0.67	59.1	1.25	206.8
10	2150	0.44	1.43	3.73	272	31.6	0.50	28.7	1.00	106.2
11	3675	0.10	0.65	1.39	146	6.2	0.17	8.8	0.59	22.8
12	7000	0.10	0.48	1.15	90	12.3	0.12	6.0	0.50	25.0

significance than those obtained by using untransformed data or other transformations. In these regressions all of the stations in the three transects are used (except for Cd where station 2 is omitted because of a local source close to this station). Thus, the variations due to differences in wind speed and direction are included. The correlation coefficients are all highly significant ($p < 0.01$ for V and $p < 0.001$ for the other metals). The exponent b in the equation $y = ax^b$ is for all metals except V very close to -1.2 (mean $\pm$ standard deviation: -1.17 ± 0.08). For V it is -0.544, indicating that the gradient is much less steep.

3.2. TRANSPLANTS

Tables II and III show the results of the analyses of heavy metals in transplanted *Dicranoweisia cirrata* and *Hypogymnia physodes* after exposure for 214 days. The general pattern is that the highest values are found close to the steelworks. The only

TABLE II

Heavy metals (ppm d.w.) in transplanted *Dicranoweisia cirrata* after 214 days of exposure

Station	Cd	Cr	Cu	Fe	Mn	Ni	Pb	V	Zn
1	0.38[a]	6.8[a]	17.2[a]	2480[a]	94[a]	6.5[a]	131[a]	13.1[a]	150[a]
2	24.6	21.5	55.1	5700	158	13.6	213	17.7	471
3	1.69	21.8	52.0	6900	202	11.2	266	15.7	716
4	4.28	62.2	237	26200	176	35.2	827	19.3	1941
5	3.09	48.6	148.4	20200	442	23.9	521	16.8	1378
6	0.43	14.0	23.8	3360	96	4.3	119	11.9	140
7	0.35	8.4	14.3	3510	69	5.7	91	13.6	133
8	2.86	51.6	152.4	11870	312	18.6	623	19.0	1599
9	0.97	16.7	40.1	4270	133	8.4	220	15.0	528
10	0.34	3.9	10.1	1320	47	2.0	42	4.8	115
11	0.56[b]	5.0[b]	16.9[b]	2230[b]	83[b]	5.0[b]	107[b]	12.5[b]	144[b]
12	0.39[c]	3.9[c]	10.3[c]	2130[c]	64[c]	1.0[c]	96[c]	3.9[c]	84[c]

[a]exposure time 64 days: [b]exposure time 106 days: [c]exposure time 154 days.

TABLE III

Heavy metals (ppm d.w.) in transplanted *Hypogymnia physodes* after 214 days of exposure

Station	Cd	Cr	Cu	Fe	Mn	Ni	Pb	V	Zn
1	1.00[b]	4.7[b]	11.6[b]	1620[b]	45[b]	0.9[b]	100[b]	5.2[b]	190[b]
2	21.7	17.8	35.7	4530	140	6.4	226	7.1	469
3	3.46	22.9	71.6	7330	238	12.5	445	10.1	1072
4	7.10	47.2	172.3	19000	400	27.5	1018	10.7	2208
5	1.52	19.4	64.6	8260	176	11.4	373	9.9	559
6	1.34	16.1	23.0	4120	237	7.3	207	9.4	369
7	0.85	5.8	10.3	2430	61	3.7	83	7.3	139
8	3.50	34.0	105.5	8530	232	14.7	765	10.5	1623
9	0.87	10.4	28.8	3730	79	5.3	253	7.8	421
10	0.70	8.4	15.7	2490	58	3.7	138	6.5	247
11	0.84	8.1	15.1	2340	53	4.5	123	7.8	192
12	0.73	4.3	8.3	1640	33	3.0	75	4.7	100

[b]exposure time 106 days.

exception is Cd where the highest values are found at station 2 (1425 m N of the steelworks), which is in agreement with the fallout data.

As for the fallout data, a power curve ($y = ax^b$) produced the highest significant regression values of the concentrations of metals in lichens and mosses on the

TABLE IV

Values of regression equations ($y = ax^b$) and correlation coefficients of distance from the steelworks (x) and concentrations (y) of metals in transplants, bulk precipitation and *in situ* lichens[1]. (* = $0.05 > p > 0.01$, ** = $0.01 > p > 0.001$, *** = $p < 0.001$).

		Bulk precipitation	*Dicranoweisia cirrata*	*Hypogymnia physodes*	*Lecanora conizaeoides*[1]
Cd	r	−0.939***	−0.926***	−0.831**	−0.880***
	b	−1.247	−1.141	−0.644	−1.260
	a	4650	2790	151.3	20600
	n	11	8	10	16
Cr	r	−0.966***	−0.880**	−0.935***	−0.858***
	b	−1.086	−0.993	−0.702	−1.140
	a	5950	18670	2140	118900
	n	12	9	11	17
Cu	r	−0.960***	−0.913***	−0.947***	−0.886***
	b	−1.158	−1.244	−0.940	−1.127
	a	25600	263000	27600	196400
	n	12	9	11	17
Fe	r	−0.958***	−0.886**	−0.969***	−0.899***
	b	−1.121	−1.040	−0.712	−1.080
	a	1754000	8040000	749000	14730000
	n	12	9	11	17
Mn	r	−0.931***	−0.760*	−0.920***	−0.843***
	b	−1.025	−0.667	−0.747	−1.014
	a	59100	14470	25200	222000
	n	12	9	11	17
Ni	r	−0.933***	−0.819**	−0.939***	−0.829***
	b	−1.229	−0.918	−0.656	−0.716
	a	5290	5500	796	2110
	n	12	9	11	16
Pb	r	−0.952***	−0.882**	−0.934***	−0.818***
	b	−1.259	−1.064	−0.807	−1.155
	a	335000	339000	79000	913000
	n	12	9	11	17
V	r	−0.815**	−0.558$^{n.s.}$	−0.875***	−0.705**
	b	−0.544	−0.299	−0.222	−0.390
	a	53.3	108.7	39.9	190.9
	n	12	9	11	14
Zn	r	−0.933***	−0.874**	−0.922***	−0.867***
	b	−1.220	−1.210	−0.917	−1.165
	a	876000	2010000	313000	2460000
	n	12	9	11	17

[1] Data from Pilegaard (1978).

distance from the steelworks. The regression equations for the data from 4 November are shown in Table IV. In the equations for Cd station no. 2 is excluded. The correlation coefficients of the regressions for *Hypogymnia* are all highly significant ($p < 0.01$ for Cd and $p < 0.001$ for the other metals). The regressions for *Dicranoweisia* produced correlation coefficients of somewhat lower significance ($p < 0.20$ for V, $p < 0.05$ for Mn, $p < 0.01$ for Cr, Fe, Ni, Pb, and Zn, and $p < 0.001$ for Cd and Cu).

The exponent b in the regression equations for *Hypogymnia* are, for V -0.222, and for the other metals as an average -0.8 ± 0.1 (mean $\pm$ standard deviation). For *Dicranoweisia* the values are -0.299 for V and -1.0 ± 0.2 for the other metals.

The general trend for the concentration in the transplants during the exposure period is that the longest exposure (7 months) gave the highest values. The rises in concentrations, however, are not constant during the period but depend on exposure time, the actual fallout and probably the season of the year. These problems will be further dealt with in the discussion.

In Table V are shown the concentrations of heavy metals in *Dicranoweisia* and *Hypogymnia* in the original material before transplantation. These values are all

TABLE V

Concentrations of metals (ppm d.w. $\pm$ standard deviations ($n = 5$)) in *Dicranoweisia cirrata* and *Hypogymnia physodes* before transplantation

	Dicranoweisia cirrata	*Hypogymnia physodes*
Cd	0.51 ± 0.03	0.58 ± 0.08
Cr	6.2 ± 0.3	5.0 ± 0.5
Cu	11.4 ± 0.6	8.4 ± 0.3
Fe	2120 ± 120	1710 ± 180
Mn	114 ± 14	24 ± 3
Ni	5.8 ± 1.0	2.8 ± 0.3
Pb	96 ± 3	76 ± 9
V	9.6 ± 0.6	5.6 ± 0.2
Zn	123 ± 15	85 ± 3

very close to the values obtained from the transplants at station no. 12, which is assumed to be background station.

In Figure 2 is shown the relationship between Cu concentration in transplants after 7 mo of exposure and Cu concentration in bulk precipitation. It will be seen that the relationship is linear, which is also true for the other metals, except V. The values of fall-out at station no. 4 are much higher than the fallout at the other stations, and the concentrations of the metals in transplants are not as high as expected according to the data from the other stations.

In Table VI are shown the values of the regression equations and the correlation coefficients. In the calculation of these regressions the values from station no. 4 are not included, and values from station no. 2 are not included in the regressions for Cd.

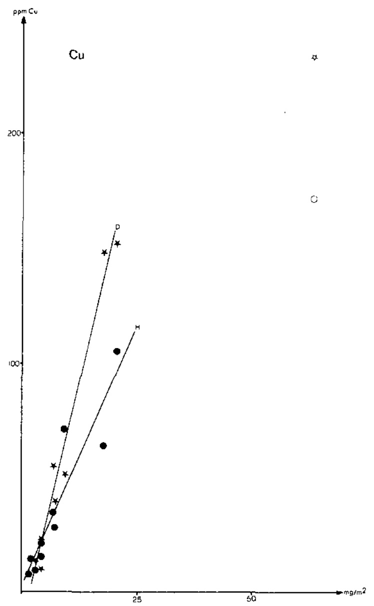

Fig. 2. Concentration of Cu (ppm d.w.) in *Dicranoweisia cirrata* (∗) and *Hypogymnia physodes* (●) in relation to fallout (mg m^{-2}) during the period 4 April to 4 November, 1977. The open signs represent values not included in the regression lines (see text).

Except for V the correlation coefficients are significant in both *Dicranoweisia* and *Hypogymnia*. Generally, the slope of the lines is steeper for *Dicranoweisia* than for *Hypogymnia,* indicating that *Dicranoweisia* accumulated the metals to a higher degree than *Hypogymnia.* The sequence of the values of the slope is for *Dicranoweisia*: Fe > Cu > Cr > Ni > Pb > Mn > Zn > Cd and for *Hypogymnia*: Cu > Fe > Pb > Cr > Ni > Zn > Mn > Cd.

It will be seen, that although these orders are not exactly the same, there is a very high degree of similarity between them.

4. Discussion

The total fallout of material from the atmosphere consists of wet deposition, dry fallout, adsorption and impaction. The bulk precipitation collected in this study includes wet deposition and dry fallout, whereas adsorbed and impacted material is represented in smaller amounts. The digestion procedure used is believed to dissolve the water-soluble material and a part of the particlebound. Thus, these analyses are assumed to represent the wet deposition of soluble material and a fraction of the metals in the particlebound material in both wet and dry fallout.

Station no. 12, which was placed 7 km NNE of the steelworks, was believed to represent the regional background level of metal fallout. The values from this

TABLE VI

Values of linear regression equations ($y = a + bx$) and correlation coefficients of the concentrations of metals in bulk precipitation and transplanted *Dicranoweisia cirrata* and *Hypogymnia physodes* after 7 mo of exposure. (* = $0.005 > p > 0.01$, ** = $0.01 > p > 0.001$, *** = $p < 0.001$).

		Dicranoweisia cirrata	*Hypogymnia physodes*
Cd	r	0.863*	0.889**
	b	1.453	1.390
	a	−0.058	0.43
	n	7	9
Cr	r	0.934**	0.939***
	b	6.92	3.55
	a	−0.761	4.43
	n	8	10
Cu	r	0.985***	0.930***
	b	8.48	4.51
	a	−12.95	4.79
	n	8	10
Fe	r	0.816*	0.964***
	b	9.07	4.40
	a	−169	1600
	n	8	10
Mn	r	0.892**	0.700*
	b	3.74	1.77
	a	−6.24	58.9
	n	8	10
Ni	r	0.852**	0.867**
	b	5.92	3.44
	a	3.84	3.84
	n	8	10
Pb	r	0.966***	0.946***
	b	4.11	4.15
	a	13.34	62.0
	n	8	10
V	r	$0.322^{n.s.}$	$0.523^{n.s.}$
	b	3.94	2.39
	a	9.51	5.60
	n	7	9
Zn	r	0.931***	0.913***
	b	3.17	2.62
	a	−18.18	75.3
	n	8	10

station were very close to those obtained in a survey of atmospheric deposition at 15 stations throughout Denmark in 1975–76 (Hovmand, 1977).

The concentrations of metals in the transplants were shown to be dependent on both exposure time and fallout. The concentrations were linearly correlated with the fallout. The values from station no. 4 were not as high as expected from the correlation, however. The two probable explanations of this could be: (1) That the exposure period was not long enough to establish equilibrium between the high fallout and the tissue of the cryptogams, and (2) That the measured fallout, due to the digestion procedure, includes a part of the metals in the dust fraction which might be unavailable to the cryptogams.

In Figure 3 the relation of distance from the steelworks and Cu concentration of *Hypogymnia* after 7 mo of exposure is shown together with data on *in situ Lecanora conizaeoides* (Pilegaard, 1978). In background areas the metal contents of *Hypogymnia* are slightly higher than those of *Lecanora* (Pilegaard and Rasmussen,

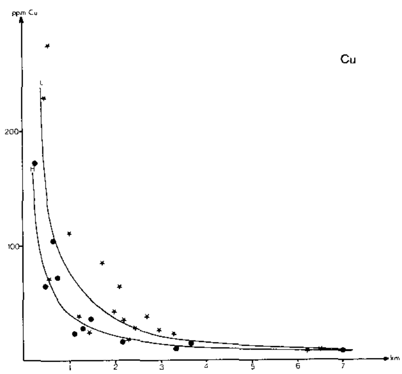

Fig. 3. Concentration of Cu (ppm d.w.) in *Lecanora conizaeoides* (*) and transplanted *Hypogymnia physodes* (●) in relation to distance from the steelworks.

1979), so it was expected that *Hypogymnia* would reach at least the same values as *Lecanora.* As can be seen from the figure, the concentration in *Hypogymnia* closest to the steelworks is lower than in *in situ Lecanora.* This is not only the case at the station closest to the steelworks (no. 4) but generally at all stations closer than 3 km. At greater distances the values in the two lichens are very close to each other. These relations obtain also for the other metals investigated.

It is known that the *in situ* lichens can reach very high values close to the steelworks, so the most probable explanation for the lower values in *Hypogymnia* is that the exposure time has not been long enough for the lichens to achieve equilibrium with the high fallout close to the steelworks.

The concentrations of the metals in *in situ* lichens also follow a power curve when correlated with the distance from the steelworks. The values of the correlation are

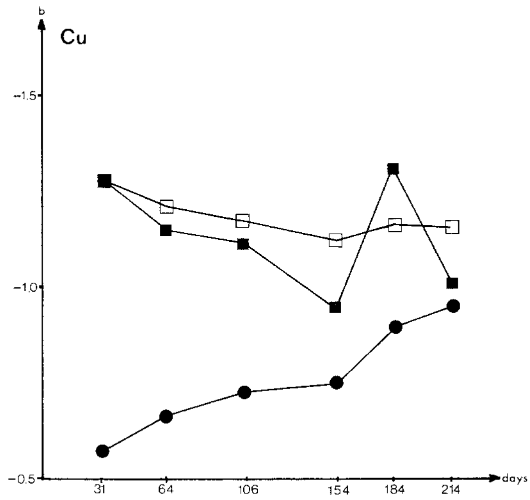

Fig. 4. Values of the exponent b of the regression lines for Cu ($y = ax^b$, see text) in relation to exposure time. ■ = fallout calculated for the periods separately, □ = accumulated fallout, ● = *Hypogymnia physodes*.

shown in Table IV. The exponent b is as an average −1.1 (when V is excluded), which is closer to the bulk precipitation than both transplanted *Hypogymnia* (−0.8) and *Dicranoweisia* (−1.0). It is therefore concluded that 7 mo of exposure, at fallout values as high as those within 3 km from the steelworks, is not long enough to achieve equilibrium.

According to the value of b for *Dicranoweisia* this species seems to achieve equilibrium faster than the lichens, but unfortunately no values of *in situ* mosses are available.

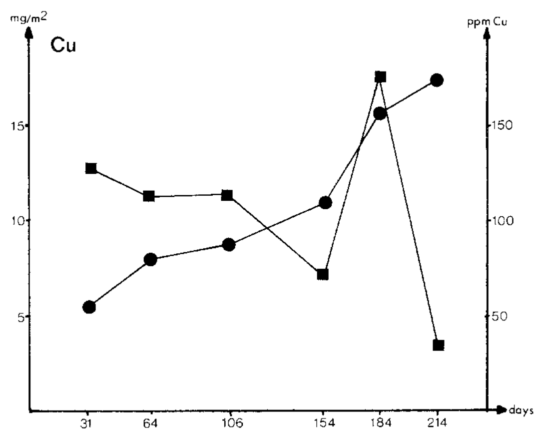

Fig. 5. Concentrations of Cu (ppm d.w.) in *Hypogymnia physodes* (●) and periodical fallout mg m^{-2} (■) at station no. 4 in relation to exposure time.

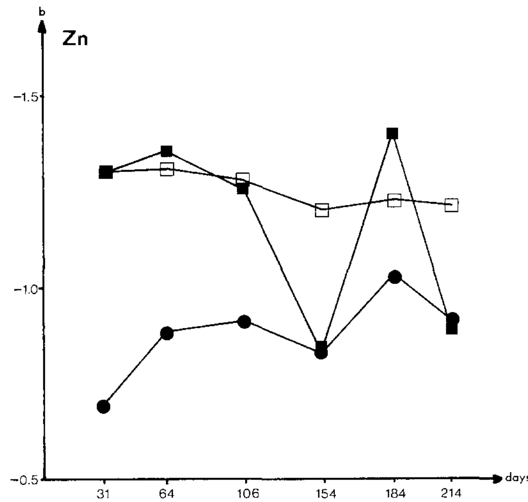

Fig. 6. Values of the exponent b of the regression lines for Zn ($y = ax^b$, see text) in relation to exposure time. ■ = fallout calculated for the periods separately, □ = accumulated fallout, ● = *Hypogymnia physodes.*

The relations of metal concentration in *Hypogymnia,* exposure time and fallout of metals are exemplified by data of Cu and Zn in Figures 4 to 7. Copper is the metal which *Hypogymnia* accumulated best from the fallout (Table VI) and Zn is among the least accumulated metals.

In Figure 4, the exponent b of the regression equations of concentration, fallout in the 6 periods, and accumulated fallout on distance from the steelworks are shown in relation to exposure time. It will be seen that the exponent of the regression equation of concentration in *Hypogymnia* is decreasing constantly during the periods, indicating an increasing gradient and a continuous accumulation. This happens in spite of the fluctuations in the fallout, and indicates that the concentrations in *Hypogymnia* have not yet achieved an equilibrium with the fallout, as also concluded above.

In Figures 6 and 7 the same is shown for Zn. During the first 3 periods the lichens accumulate Zn but they are not able to retain the high amounts of Zn when the fallout decreases. The great decrease in the fallout in the period 19 July to 5 September is due to lower concentrations of metals in the precipitation, whereas the decrease in the period 10 October to 4 November is mainly due to lower precipitation. It is therefore suggested that the reason for the concentration decrease at 5 September is due to a weak retention of Zn combined with the high precipitation, which then is able to wash out the metal from the lichen tissue.

The tendency outlined here for Cu obtains also for Cr, Fe, Mn, Ni and Pb, whereas Cd and V follow the tendency shown for Zn.

These results are in accordance with Puckett *et al.* (1973), who found that those metal ions binding most tightly to the lichen thallus are taken up most quickly and in

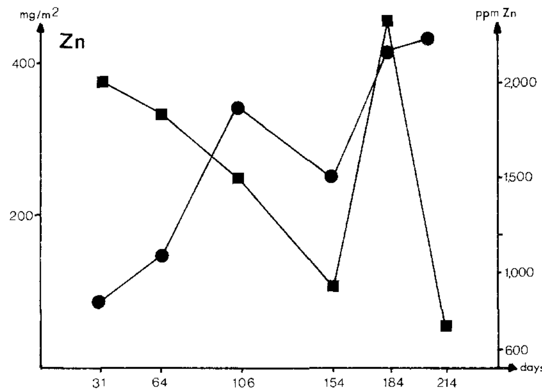

Fig. 7. Concentrations of Zn (ppm d.w.) in *Hypogymnia physodes* (●) and periodical fallout mg m^{-2} (■) at station no. 4 in relation to exposure time.

larger quantities. For *Umbilicaria muhlenbergii* they found the preference sequence: Fe ⩾ Pb ⩾ Cu ⩾ Ni, Zn ⩾ Co, which is in accordance with the sequence found in this study.

It was calculated, that if only the exposure time is considered (fallout assumed to be constant), the time required to obtain the same values in *Hypogymnia* as in the *in situ Lecanora* would be approximately 450 days. This calculation was based on a linear correlation between the exponent *b* and the exposure time (significant for Cr ($p < 0.001$), Cu and Fe ($p < 0.01$), and Mn ($p < 0.05$)), assuming that the exponent should reach the same value as for the accumulated bulk precipitation and the *in situ* lichens.

The time of year probably also has an influence on the uptake of metals in the cryptogams. Lang *et al.* (1976) showed that the loss rate of elements from lichen tissue increased when the temperature was raised. Therefore the fall in accumulation for some of the metals during 19 July to 5 September could be a combination of this and the decrease in fallout. The best periods for transplantation experiments are probably the autumn and the spring, where the humidity is high and the growth rate of cryptogams higher than during the summer and the winter.

In a transplantation experiment (Brown, 1976) with the saxicolous lichen *Parmelia glabratula subsp. fuliginosa,* the lichens transplanted to a highly polluted area for 2 mo showed no change in the quantities of K, Pb, and Zn. The author suggested that the shiny upper surface of the thallus represented a poor surface for particles to become attached to, and may also have acted as a barrier to penetrations of cations in solution. High rainfall during the test period probably washed off particles from the surface. The author also mentioned that the time of year may be an important consideration as, following a dry spell, dew formation or the first rain may be responsible for dissolving cations from the particles which have rested on the thallus for a much longer period than is possible during wet conditions. In Brown's experiment the short exposure time (2 mo) may also be a reason for the failure of the transplanted material to accumulate Pb and Zn.

In the present study it was found that concentrations of metals in bulk precipitation as well as transplanted cryptogams follow a decreasing power curve ($y = ax^b$) when the distance from the pollution center is increased. This was also found to be true for the metal concentrations in the *in situ* lichen *Lecanora conizaeoides* in an earlier study (Pilegaard, 1978). The exponent b was found to be -1.2 and -1.1 in bulk precipitation and *Lecanora conizaeoides,* respectively. In the transplants the exponent was somewhat lower, probably due to too short an exposure period. Nieboer *et al.* (1972) and LeBlanc *et al.* (1974) have found that the concentrations of metals in several lichens were correlated with the inverse distance from the pollution source ($y = ax^{-1}$). Campbell (1976) proposed a generalized treatment and discussed the reciprocal-distance linearity dependence of parameters such as prevailing wind velocity, the downward flux of the particles, the height of the chimney and coefficient of eddy diffusion. He concludes that concentrations which decrease notably faster than inversely with distance from a source are still fully consistent with ordinary atmospheric dispersion. This may happen, for example, in cases with high terminal velocity of the particles (e.g. greater particle size and/or density), or in situations in which a high prevailing wind velocity and a high chimney are combined. In Frederiksvaerk the chimneys have a height of 40 m, and the wind velocity at this height is as an average 6.5 m s^{-1}. It is thus more likely, that the faster decrease of the concentrations in this case is due to the particle size.

5. Conclusions

Lichens and bryophytes transplanted to the vicinity of a Danish steelworks in Frederiksvaerk and exposed during 7 mo showed the same qualitative picture of heavy metal pollution as indigenous lichens in the area.

It was found that the amount of accumulated metal ions in the transplanted cryptogams were linearly correlated with fallout from the atmosphere, measured as bulk precipitation. The bryophytes, however, accumulated the metals slightly faster than the lichens.

The exposure time of 7 mo was too short to achieve equilibrium between the fallout of metals from the atmosphere and the metal content in the cryptogams transplanted to stations within 3 km from the pollution source.

The metal concentrations in the transplanted cryptogams as well as in the bulk precipitation followed a decreasing power curve when the distance to the pollution source was increased.

It is concluded therefore that transplanted lichens and bryophytes can be applied as monitor organisms of air pollution with heavy metals, but care should be taken regarding the length of exposure and the season of the year.

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