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Ecology of Heavy Metals — a Regional and Historical Study

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ABSTRACT

Samples of *Hypnum cupressiforme*, collected during 1968—69 in north-eastern Götaland, the low-land areas and the ridge areas of Skåne (southern Sweden) have been analysed for Pb, Zn, Cu, Ni, and Cr. The concentration of these metals were significantly lower in the north-eastern area than in the areas of Skåne, particularly in Pb, Ni, and Cr. Between the two areas in Skåne differences were only established for Pb and Cu, with the largest concentrations in the humid ridge areas. The differences in the concentrations of these heavy metals between north-eastern Götaland and Skåne will be explained by the geographical position with respect to the large industrial regions of Europe.

Samples of the same species, collected in Skåne 1870—1943 have also been analysed. Significant increases during the decades around 1900 were demonstrated for Cu and Zn. In the concentrations of Ni a rapid rise has occurred since about 1920, when this metal was introduced in the world production. The content of Ni in the samples from 1969 is more than twice as large as in the samples collected before 1920. The historical trends in the concentrations of Pb have earlier been demonstrated (RÜHLING & TYLER 1968 a). There is little doubt that the rise in the concentrations of these metals is an effect of a larger air-borne supply, originating from human activity.

INTRODUCTION

The present paper is a continuation of a previous study (RÜHLING & TYLER 1968 a, in the following abbreviated RT). In this study a distinct regional decrease towards the north-east in southern and central Sweden was established as to lead concentration of three different mosses. Particularly large concentrations were measured in the most humid parts of south-western Götaland, indicating that a considerable part of the lead which is brought down by the rain, at least in this area, originates from areas outside Sweden.

The aims of the present paper is to measure the local, regional and

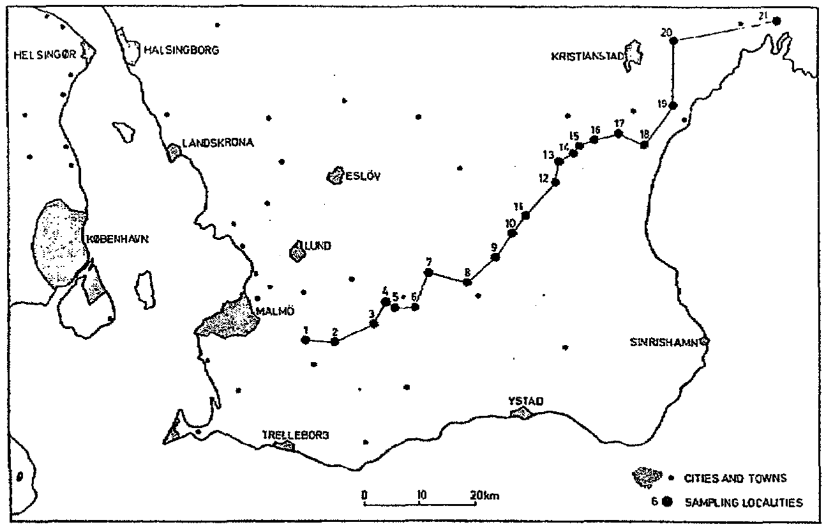

Fig. 1. Sampling localities in the transect across Skåne.

historical differences in the concentrations of certain heavy metals, as they are reflected in a common moss species.

MATERIALS AND METHODS

As the material of this study the moss *Hypnum cupressiforme* was chosen. In 21 localities, situated more than 300 m from roads along a SW—NE transect across Skåne (cf. Fig. 1), three separate samples were collected on each locality in February 1969 and analysed. For comparison samples from Östergötland and adjacent areas, as well as from Denmark (Sjælland) and the very humid south-western slopes of Sydsvenska Höglandet, collected in 1968 and previously analysed for lead (cf. RT) were analysed for other heavy metals (Zn, Cu, Ni, Cr, and Co). The same elements were also determined in a historical material from Skåne, collected in 1870—1943. The analyses were performed by atomic absorption spectrophotometry (cf. RT). The metal concentrations of the samples are always calculated as ppm dry matter. Statistical calculations have been performed according to SNEDECOR (1961).

THE TRANSECT ACROSS SKÅNE

The position of the 21 localities along the transect line is illustrated in Figs. 1 and 2, cf. also Table 1. The transect is drawn from the low-land plain

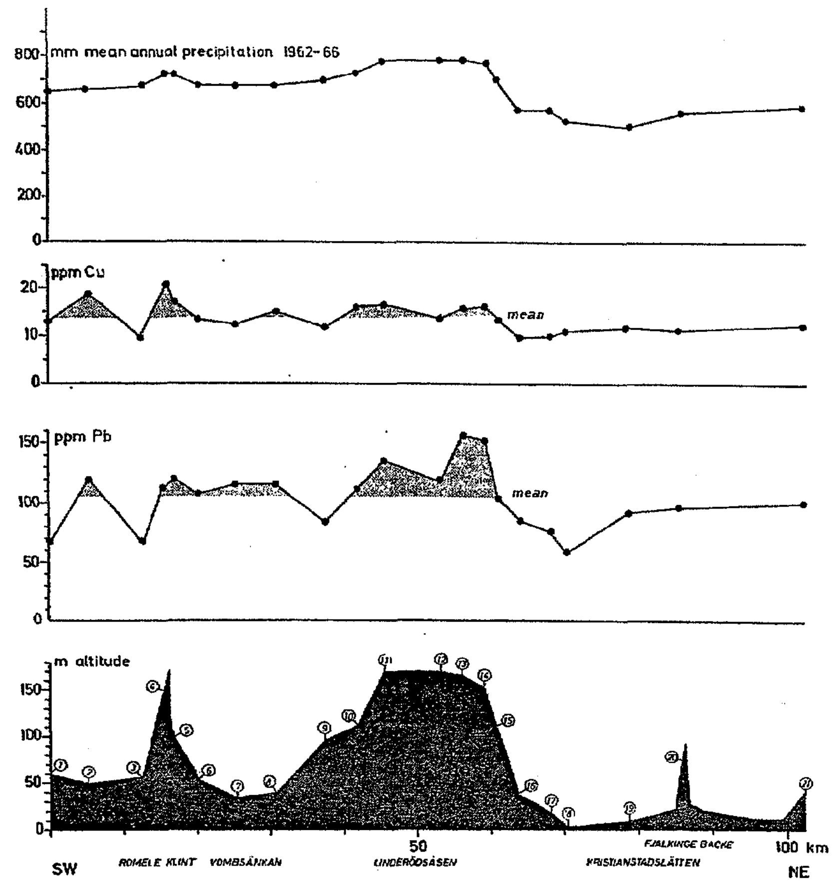

Fig. 2. The transect across Skåne. Mean annual precipitation, concentration of Cu and Pb in *Hypnum cupressiforme* and elevation above sea-level of the sampling points (1—21).

E Malmö (localities 1—3), across the ridge of Romeleåsen (4—5), the plain of Vombsänkan (6—9), the ridge of Linderödsåsen (10—15) and the plain of Kristianstadslätten (16—21). Consequently, widely different soils are represented, and the humidity is considerably higher on the ridges than in the low-land areas. The bedrock of the ridges (localities 4—5, 10—15), is predominantly igneous Archaean gneiss and the soils are more or less podzolised Archaean moraines poor in calcium. The mean annual precipitation is distinctly higher than on the adjacent plains. The plains are developed on

Table 1. The concentration of heavy metals in *Hypnum cupressiforme* from the southwest—northeastern transect across Skåne. Median values (n=3), calculated as ppm dry matter.

Locality \ Element	Pb	Cu	Zn	Ni	Cr	Co
1. Torup, 4.5 km S Bara ch.	68	12.7	99	11.3	6.5	1.5
2. Ekholmssjön, 4.5 km SE Hyby ch.	120	19.2	126	13.3	9.5	1.3
3. Häckeberga, 2 km SSE Genarp	67	9.8	102	8.6	5.5	1.7
4. 300 m SW Romeleklint, 3.5 km SW Veberöd	112	21.2	149	12.5	9.7	1.2
5. 0.5 km SSW Husagård, 3 km SSW Veberöd	120	17.0	112	8.8	7.5	1.3
6. Skogmöllan, 3.5 km SE Veberöd	107	13.5	135	10.2	7.5	2.7
7. 1 km ESE Vomb ch.	116	12.5	93	7.8	5.8	1.3
8. 1.3 km NW S Åsum ch.	116	15.0	102	8.6	9.8	2.5
9. 0.5 km W Vollsjö ch.	83	11.8	115	9.2	14.0	3.0
10. 1.5 km N Fränninge ch.	112	16.3	107	7.6	6.5	1.6
11. 2.5 km SSE Långaröd ch.	136	16.6	148	7.7	5.6	1.5
12. 3.0 km SW Huaröd ch.	117	13.9	98	9.8	8.0	2.8
13. 2.5 km NW Huaröd ch.	156	15.8	101	9.4	7.7	1.9
14. 2.2 km SW Ö. Sönnarslöv ch.	151	16.4	100	11.8	6.2	1.4
15. 1.1 km SW Ö. Sönnarslöv ch.	103	13.7	100	8.3	8.2	1.6
16. 2 km SW Everöd ch.	85	9.8	93	8.6	8.6	1.2
17. 2.5 km E Everöd ch.	76	10.1	88	6.5	5.5	1.0
18. 4 km NNE Vittskövle ch.	57	11.2	90	9.9	8.9	2.4
19. Horna, 3 km NNW Åhus	92	11.7	99	7.4	7.5	1.3
20. Fjälkinge backe, 2 km N Fjälkinge ch.	95	11.4	108	6.8	8.1	1.0
21. 2.5 km NNE Valje	100	12.5	119	6.7	5.3	1.3

Cretaceous rocks, chiefly limestone (localities 1—3, 6—8, 16—19), Silurian slate (9) or Archaean rocks (20—21). The low-land soils are variable, in the south-west (localities 1—3) rather clayey moraines but otherwise mostly glacio-fluvial sands, on Kristianstadslätten partly very calcareous.

The mean annual precipitation for the period 1962—66, calculated from SMHI (1964—1968) is between 700—800 mm on the ridges, 600—700 mm on the south-western plain and in Vombsänkan, and 500—550 mm on Kristianstadslätten (cf. Fig. 2, where the altitude of the localities is also given).

The results of the analyses are compiled in Table 1 as the medians from each locality. Any significant differences between the ridges and the low-land areas have only been established with Pb and Cu. The lead concentration ranges between 103—156 ppm (mean 124) on the ridges, and 57—100 ppm (mean 87) on Kristianstadslätten, corresponding to the precipitation of 725—775 mm and 500—590 mm, respectively. The values for the south-western plain and Vombsänkan are intermediate both in lead and in mean annual precipitation. A quite similar trend may be demonstrated for Cu (cf. Fig. 2). The copper concentration on the ridges averages 16.3 ppm, on the plains 12.4 ppm.

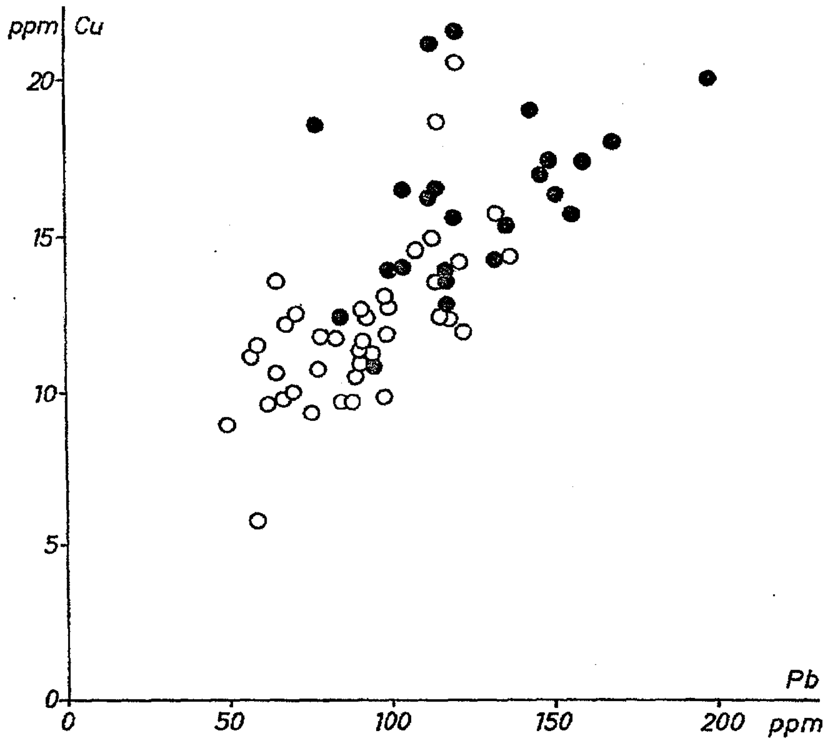

Fig. 3. Correlation between Pb and Cu in the samples of the transect across Skåne. Open circles=low-land areas, filled circles=ridge areas.

The correlation between Pb and Cu is evident from Fig. 2 and illustrated in Fig. 3. The coefficients of correlation between the concentrations of the metals have been compiled in the following table.

	Pb	Zn	Cu	Ni
Zn	0.29	—	—	—
Cu	0.49	0.56	—	—
Ni	0.29	0.33	0.61	—
Cr	0.29	0.16	0.24	0.45

Rather good positive correlations were obtained between Cu and Ni, Cu and Zn, as well as between Cu and Pb.

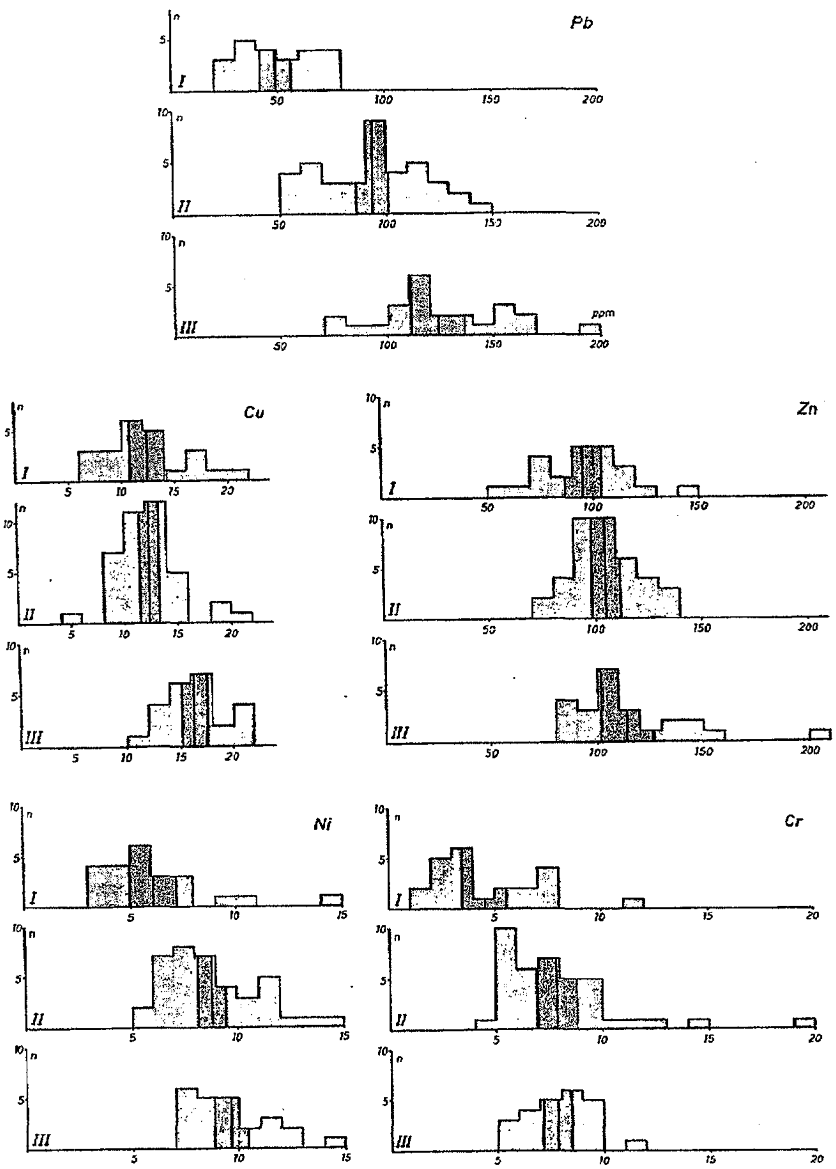

Fig. 4. The distribution of metal concentrations (ppm dry matter) in samples from 1968—69. I=Östergötland and adjacent areas, II=Skåne, low-land areas, III=Skåne, ridge areas. Means and limits of means, probability 95 %, are indicated.

Table 2. Statistical calculations on the regional differences in 1968—69. Means (ppm) and significance of the differences between the means. Area I=Östergötland and adjacent areas, II=Skåne, low-land areas, III=Skåne, ridge areas. Level of significance: *=$p < 0.05$, **=$p < 0.01$, ***=$p < 0.001$.

Area	Means, ppm			t-values and levels of significance		
	I	II	III	I—II	I—III	II—III
Pb	49	93	124	*** 8.49	*** 10.4	*** 4.10
Cu	12.4	12.4	16.3	0.00	*** 3.94	*** 5.36
Zn	95	105	114	* 2.21	* 2.64	1.38
Ni	6.1	8.8	9.6	*** 4.33	*** 5.40	0.17
Cr	4.5	7.9	7.9	*** 4.74	*** 5.30	0.00

REGIONAL COMPARISONS

23 samples of *Hypnum cupressiforme* from different parts of Östergötland and adjacent areas have also been analysed for heavy metals. This group is designated I in Fig. 4. For comparison the samples from the transect across Skåne have been divided into two groups, one group (II) comprising the low-land plains (localities 1—3, 6—9, 16—21) and one group (III) comprising the ridge areas (localities 4—5, 10—15). Statistical calculations have been compiled in Table 2.

Significant differences (***) between the means of lead were recorded for all areas, with the lowest mean (49 ppm) from the north-eastern area, the highest mean from the humid ridge areas in Skåne (124 ppm) and with the mean of the low-land areas of Skåne in an intermediate position (93 ppm). Also for Ni and Cr the means of the north-eastern area are significantly lower than the corresponding means of the two areas in Skåne but no differences exist between the latter. The copper means of the north-eastern area and the low-land area are identical (12.4 ppm), whereas the mean of the ridge area is significantly higher (16.3 ppm). The observed differences in the means of Zn are not fully secured.

In general the concentrations of these metals are highest on the ridges in Skåne, lowest in the north-eastern area. In this area Zn takes the largest share of the metals analysed, but on the humid ridges Zn is surpassed by Pb. As a comparison, a few samples from Denmark (Sjælland) and Halland have also been analysed. The samples from Sjælland are higher in Pb and Cu than the samples from the corre-

Table 3. Statistical calculations on the historical changes. Means (ppm) and significance of the differences between the means (cf. Table 2).

	Means, ppm				t-values and levels of significance			
	1870/99	1900/19	1920/43	1969	1870/99—1900/19	1900/19—1920/43	1920/43—1969	1870/99—1969
Cu	10.2	13.0	13.5	13.9	1.73	0.30	0.30	* 2.74
Zn	66	94	103	109	* 2.23	0.70	0.71	*** 5.49
Ni	4.0	3.7	5.5	9.1	0.55	** 4.12	*** 10.2	*** 10.7
Cr	5.8	5.5	6.5	7.7	0.27	1.15	1.36	1.74

sponding low-land areas in Skåne, but no differences were measured in Zn, Ni and Cr. The four samples from the very humid Halland area are very high in Pb (mean 164 ppm), rather high in Cu (15.7 ppm), but the concentrations of Zn, Ni and Cr are similar to the north-eastern area.

MEASUREMENTS OF HISTORICAL CHANGES

In previous papers (Rühling & Tyler 1968 a, 1968 b, 1969) changes in the lead concentrations of mosses during the last 100 years have been recorded and discussed. In order to establish if any changes in other heavy metals have occurred during this period, we have also analysed samples of *Hypnum cupressiforme*, collected in Skåne 1870—1943. This historical material has arbitrarily been divided into three groups: 1870—99 (n=15), 1900—19 (n=15) and 1920—43 (n=13). As a fourth group the figures in Table 1 from the transect across Skåne in 1969 (n=21) have been used. The means and the significance of the differences between the means of the periods have been compiled in Table 3.

The copper concentrations increase between the periods 1870—99 and 1900—19, whereas no changes have been measured in the 20th century (Fig. 5). A large increase in the concentrations of Zn has occurred since the 19th century, chiefly confined to the decades around 1900. For Ni and Cr any corresponding change between the first and the second period has not been measured. Between 1900—19 and 1920—43 there is a rise in the concentrations of Ni and the figures from 1969 indicate that this rise has continued and accelerated. In the case of Cr the apparent increase of the means and the medians is not statistically significant, partly owing to two aberrant values in period 1870—99

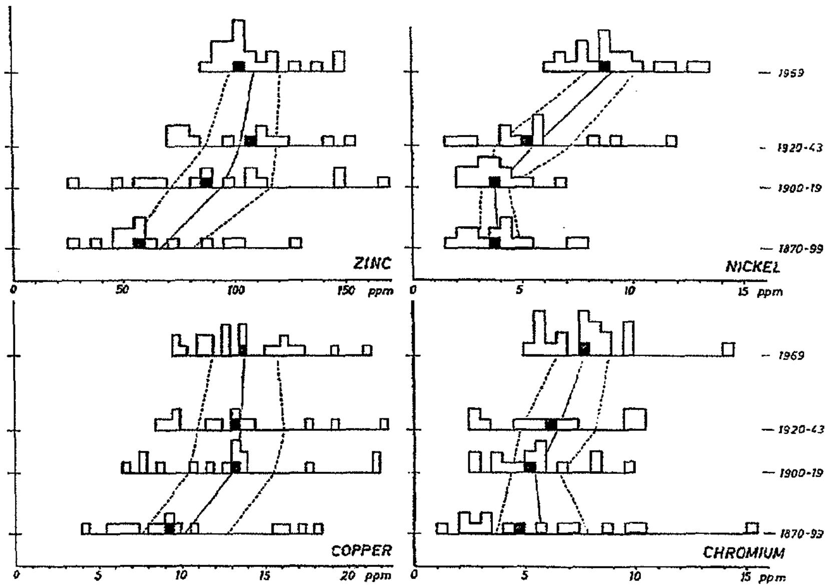

Fig. 5. Changes in the concentrations of Zn, Cu, Ni, and Cr in samples from Skåne during the last century. The entire curve connects the means and the broken curve the limits of the means, probability 95 %. The position of the medians are indicated by the black symbols, the number of samples in each class by the height of the columns.

and 1969, respectively. But half of the values from 1870—99 are below the lowest value from 1969 (cf. Fig. 5).

DISCUSSION

As distinguished from vascular plants, mosses have little or no possibilities to utilize minerals directly from the ground. The minerals must be collected either through a concentration of the minerals in the precipitation or supplied as dust (cf., e.g., TAMM 1953, SVENSSON & LIDÉN 1965). Through the action of mineral or organic acids the elementary constituents of the dust particles may be released and absorbed by the moss carpet. The share of metals supplied as dust or as dry deposition will be larger in the vicinity of the source. The indirect influence of the substrate cannot be neglected, because the main part of the dust originates from the close vicinity. However, the local mineral substrate seems to be less important as a source of the metals included in this study than the supply from the atmosphere. The deposition of dust particles, originating from eolic erosion, must be larger in the low-land areas than on the ridges in Skåne. If this deposition were of any importance to the supply and accumulation of these minor metals by the mosses, the low-land areas would exhibit the largest concentrations, but this is not the case with any of the metals.

The recent acidification of the precipitation (cf. ERIKSSON & ODÉN in Miljövårdsforskning 1967, ODÉN 1968) could theoretically have increased the weathering and the release of minerals from the dust particles, deposited in the moss carpets. But as no change in the concentrations of Cu and Zn has been demonstrated during the 20th century, the large recent increases in Pb and Ni cannot be due to increased weathering. A substantial increment in the supply of Ni and Pb from the atmosphere, originating from human activities must be the obvious reason.

The soils of north-eastern Götaland and the ridge areas of Skåne are both predominantly Archaean moraines. Nevertheless, the concentrations of all minor metals are considerably lower in the north-eastern area (cf. Fig. 4). The single probable reason for these differences must be a corresponding difference in the atmospheric supply of these metals.

The very considerable rise in the lead concentrations, recorded since about 1950, can be connected to a very special source of pollution — the lead petrol — which does not apply to other metals. But a recent increase has been established for Ni, first recognized as the difference in the means of the periods 1900—19 and 1920—43, and the increase has accelerated between 1920—43 and 1969. This trend is correlated with the world production of Ni, which was negligible before 1920 — less than 0.01 million tons a year, corresponding to 0.36 million tons in 1966 (Statistisk Årsbok för Sverige 1920—1968).

The rise observed in the nickel concentration of mosses will be the effect of industrial losses. The differences in the contents of Ni between north-eastern Götaland and the low-land areas of Skåne (cf. Fig. 4) will be explained by the geographical position with respect to the large industrial regions of Europe. But unlike lead, no difference in Ni between the low-land and the ridge areas of Skåne has been observed. Evidently, a larger precipitation will not achieve any increase in the case of Ni. Will this indicate that a large share of this metal, transported as atmospheric pollution, is supplied as dry deposition and therefore more uniformly distributed between the ridge and the low-land areas?

For Zn and Cu an increase has been established between the periods 1870—99 and 1900—19, but not later. However, it is very probable that this rise may have started already before the first period (as previously demonstrated for Pb; cf. Fig. 8 in RT), but sufficient material from earlier days was not available. The rise in zinc concentration is considerable, amounting to about 30 ppm between the first two periods, whereas the corresponding figures for Cu is only about 3 ppm. The production of these metals did not differ substantially, but the probable reason for this much larger supply of Zn will be the greater volatility of this metal. Metallurgic processes as well as the increased combustion of coal may both have been of importance as sources of pollution. During the 20th century more refined processes may have reduced the relative emission, balancing the increases in the production of the metals and keeping the total emission on a more constant level.

CONCLUSIONS

Significant differences in the recent concentrations of Pb, Cu, Zn, Ni, and Cr in *Hypnum cupressiforme* have been established between north-eastern Götaland and the ridge areas as well as the low-land areas of Skåne, the only exception being Cu between the north-eastern area and the low-land areas. Between the two areas in Skåne significant differences exist in Pb and Cu, but not in the other metals. Where differences have been demonstrated, the highest means occur in the ridge areas of Skåne, the lowest means in north-eastern Götaland.

Significant increases during the last century have been established for Cu, Zn and Ni, as previously for Pb. The rise in the concentrations of Ni has been very marked during the last decades and corresponds to the introduction of this metal in the world production. For Zn and Cu there has also been an increase in the concentrations, considerable in the case of Zn, but chiefly confined to the decades around 1900. There is little doubt that the rise in the concentrations of these metals is an effect of a larger air-borne supply, originating from industrial activity.

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