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Regional and species variations in metal content of two woodland mosses Pleurozium schreberi and Hylocomium splendens in Finland and northern Norway

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SELOSTE: KERROS- JA SEINÄSAMMALEN METALLIPITOISUUKSISTA SUOMESSA JA POHJOIS-NORJASSA

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The woodland mosses *Pleurozium schreberi* and *Hylocomium splendens* were used in air pollution monitoring. During late summer and autumn 1977, 44 samples of *Pleurozium schreberi* were collected in semi-open coniferous forests from S Finland (60°N) to N Finland and N Norway (70°N). Additionally 26 samples of *Hylocomium splendens* were collected in similar places south of 61°30'N. Analysis of both moss species revealed decreasing concentration gradients from south to north for Cu, Fe, Pb and Zn. Conversely, Mn and Mg levels increased with latitude, while Ca did not change significantly. Some decreasing west to east concentration gradients for Cu, Zn and Pb also were measured in *P. schreberi* and in *Hylocomium splendens* collected from S Finland.

A comparison between these two mosses showed significant differences in Cu content (ave. 22 % higher in *H. splendens*) and Zn content (ave 8 % higher in *P. schreberi*). However, the differences were considered minor in relation to regional differences in Finland.

In local study of emissions from the Koverhar steel works in S Finland, Fe and Zn concentrations in *P. schreberi* and *H. splendens* were found to decrease significantly with increasing distance up to 6 kilometres north and south of the source.

Tutkimuksessa tarkasteltiin kerros- ja seinäsammalen Ca-, Cu-, Fe-, Mg-, Mn-, Pb- ja Zn-pitoisuuksia v. 1977 Suomesta ja Pohjois-Norjasta kerätyissä näytteissä. Keräyspisteistä 7 sijaitsee Koverharin rauta- ja terästehtaan ympäristössä Hankoniemellä, muut 37 tausta-alueilla.

Tutkituista alkuaineista Cu-, Fe-, Pb- ja Zn-pitoisuuden todettiin selvästi alenevan sammalissa etelä–pohjoissuunnassa. Sitävastoin Mn- ja Mg-pitoisuudet lisääntyivät jonkin verran pohjoista kohti. Ca-pitoisuuden muutos ei ollut tilastollisesti merkitsevä. Etelä-Suomessa Cu-, Pb- ja Zn-pitoisuuksien todettiin vähenevän jonkin verran myös länsi-itäsuuntaisesti.

Tutkittujen sammallajien väliset erot olivat vähäisiä. Tämän aineiston perusteella kerrossammalen kuparipitoisuus oli jonkin verran korkeampi ja sinkkipitoisuus alhaisempi kuin seinäsammalen.

Rauta- ja terästehtaan vaikutus sammalten rauta- ja sinkkipitoisuuteen näkyi pohjois–eteläsuunnassa vielä yli 6 kilometrin etäisyydellä tehtaasta. Muista pääilmansuunnista ei ole kerätty riittävästi näytteitä vaikutusalueen rajaamiseksi.

Keywords: Air pollution monitoring, heavy metals, mosses, *Pleurozium*, *Hylocomium*
ODC 173.2+425+181.45+(480)+(481)

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1. Introduction

Woodland mosses, especially *Hylocomium splendens* and *Pleurozium schreberi* have been used in heavy metal monitoring for several years particularly in Scandinavia (Rühling & Tyler 1968, 1969 and 1971, Steinnes 1977, Rühling & Skärby 1979, Gydesen et al. 1983). The moss technique in based on the effective sorption of deposited heavy metals by the moss carpets. Therefore, there is a great correlation between the atmospheric deposition and the concentrations of heavy metals in the moss (Gydesen et al. 1983).

In Finland comprehensive regional surveys are based mainly on bog mosses (Pakarinen 1978, 1981a). In local studies, the woodland mosses, however, have been used in heavy metal monitoring (Pakarinen & Rinne 1979, Folkeson 1981a, 1981b, Mäkinen 1982, 1983).

The main purpose of the study described herein was to examine atmospheric deposition of seven metals in the feather moss, *Pleurozium schreberi* (Brid.) Mitt., in Finland and N Norway, and to compare the results with published material for other mosses and lichens. Additional aims were to compare regional metal concentrations in *P. schreberi* in S Finland with those in another feather moss, *Hylocomium splendens* (Hedw.) Br. et Sch., commonly used in pollution studies, and to employ both of the above species in a small-scale investigation of metallic emissions from a steel works.

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2. Material and methods

Samples of *P. schreberi* were collected during July to November 1977 from 44 sites located on low, forested hills (in dry, semi-open pine forests) throughout the boreal coniferous vegetation zone of Finland and N Norway. 14 southernmost sites were located in the hemiboreal vegetation zone (cf. Ahti et al. 1968). Additionally, samples of *H. splendens* were collected from 26 of the S Finnish sites (Fig. 1, No's 1–7 and 10–29). Sites 1–7 were located at distances ranging from 1.7 to 12 km from a steel works at Koverhar on the Hanko Peninsula in S Finland (Fig. 1, inset). The remaining sites were located more than 1 km from industrial or built up areas. All collections were made at least 200 m from travelled roadways, from microsites having a minimum of overlying vegetation canopy (cf. Pakarinen et al. 1978, Mäkinen 1983).

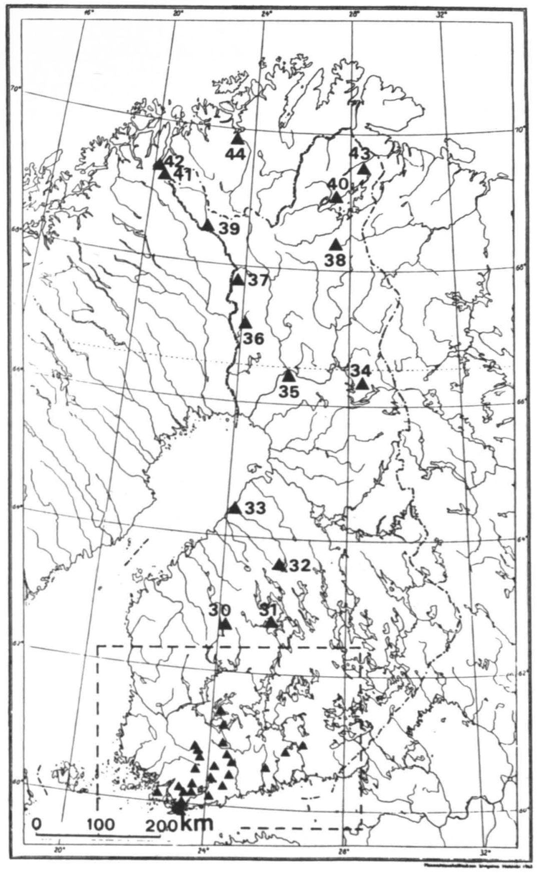
At each site, at least three subsamples of the entire thickness of the intact moss carpet were taken within an area of approximately

400 m^2. The samples were placed in paper bags and stored in a freezer at ca. −18°C.

Melted moss material was then carefully sorted by hand to remove foreign matter. The entire moss plant, approximately 4 years old was utilized in analyses (as in Rühling & Tyler 1973, Rinne & Barclay-Estrup 1980).

Dryed samples (min. 72 h at +20°C) were homogenized in a grinder (stainless steel blades) and ca. 1 g portions were ashed at 450°C for 4 h, followed by dissolution in 10 ml 37 % HCl in a hotplate, filtration, and dilution to 50 ml with distilled, deionized water. Blank solutions were prepared in the same manner. Standard solutions were prepared from commercially available stock concentrates.

Analyses for the metals Ca, Cu, Fe, Mg, Mn, Pb and Zn were conducted using a Varian-Techtron AA- 1200 atomic absorption spectrophotometer (flame method, see Ramirez-Muñoz 1968) at the Department of Botany, University of Helsinki. Lanthanum was added in the Ca and Mg determinations to overcome possible interferences (Allen et al. 1974). All concentrations were calculated as $\mu g\ g^{-1}$ (ppm), air-dry weight, and represent the means of duplicate determinations.



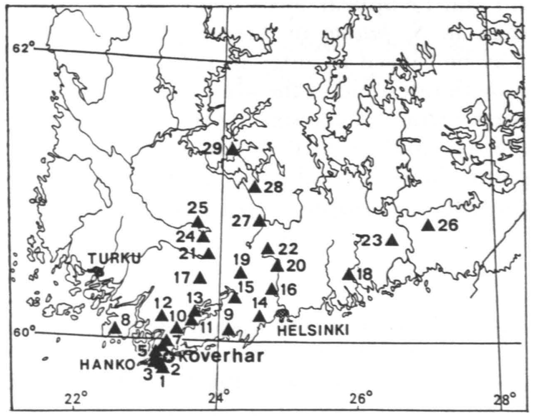


Fig. 1. Study sites in Finland and N Norway. Inset shows moss collection sites south from 62°N and the location of the Koverhar steel works on the Hanko peninsula. *Pleurozium schreberi* was collected in all sites, while *Hylocomium splendens* in sites 1–7 and 10–29 only.

3. Results and discussion

3.1. Regional gradients in metal content of moss

Comparison with other studies

A comparison of *P. schreberi* results from the south and north parts of the study area shows that concentration of Fe, Cu, Zn and Pb decreased from south to north (Table 1 and Fig. 2). Similar distributions for these metals in Finland have been reported for *Sphagnum fuscum* growing in ombrotrophic bogs (Pakarinen & Tolonen 1976, Mäkinen & Pakarinen 1977, Pakarinen 1981a) and for *Cladonia* lichens from both mineral soil (Pakarinen et al. 1978) and bog hummocks (Pakarinen 1981b). The sequence of south/north concentration ratios for the metals analyzed in these studies was generally: Pb > Fe > Cu, Zn > Ca, Mg, Mn. The concentrations of Pb, Zn and Fe appear to be higher in *P. schreberi* than in *S. fuscum* or *Cladonia* lichens. That may be caused by inter-species differences in growth rates and in the ability to retain deposited metals (Folkeson 1979), but certainly the age and vertical depth of the analyzed plants have an influence upon their metal content. For instance the concentrations of Cr, Ni and Pb increase from younger living tops to older dead parts of many mosses (Rühling & Tyler 1970, Pakarinen & Rinne 1979, Mäkinen 1982).

Although the Finnish lichen samples had lower average concentrations of the tested metals than *P. schreberi* or *S. fuscum*, they exhibited the greatest relative decline in concentrations of Pb, Fe, Zn and Cu from south to north. Thus, they can be considered as very sensitive bioindicators in studying regional variation of heavy metal deposition.

In spite of the decrease of Ca and Mg deposition from S to N Finland (Järvinen & Haapala 1980) their levels increase somewhat with latitude in moss and lichen samples (Rinne & Barclay-Estrup 1980, Pakarinen et al. 1978). It has been suggested that these metals are subject to greater competition from the presence of higher amounts of other metals (Pb, Cu, Zn, Fe) or H^+ ions (Rinne & Barclay-Estrup 1980). Corresponding observations concerning Mn have been reported in several regional (Pakarinen et al. 1978, Grodzinska 1978, Rinne & Barclay-Estrup 1980, Pakarinen 1981a) and local studies (Johnsen & Rasmussen 1977, Rasmussen 1977, Folkeson 1981a).

Table 1. Mean metal concentrations (µg/g, air-dry wt.) and standard deviations in regional samples of *Pleurozium schreberi* collected in 1977 from S Finland (60°–65°N) and from N Finland and/or N Norway (65°–70°N) compared with samples collected 1979 from NW Ontario, Canada. S = mean south concentration, N = mean north concentration.

Metal	Finland and N Norway[1] S n = 26	N n = 11	Ratio S/N	Canada, NW Ontario [2] n = 25
Ca	2407 ± 497	2472 ± 648	1.0	. .
Cu	5.9 ± 1.1	4.6 ± 1.4	1.3	6.6 ± 1.4
Fe	702 ± 278	301 ± 126	2.3	692 ± 281
Mg	597 ± 118	782 ± 136	0.8	. .
Mn	305 ± 128	509 ± 258	0.6	290 ± 128
Pb	36 ± 11	16 ± 6	2.2	29 ± 6
Zn	54 ± 13	36 ± 9	1.5	71 ± 41

1) Results of present study (entire plant analyzed including the brown parts).
2) Results from Rinne & Barclay-Estrup 1980. Sites 1–25.

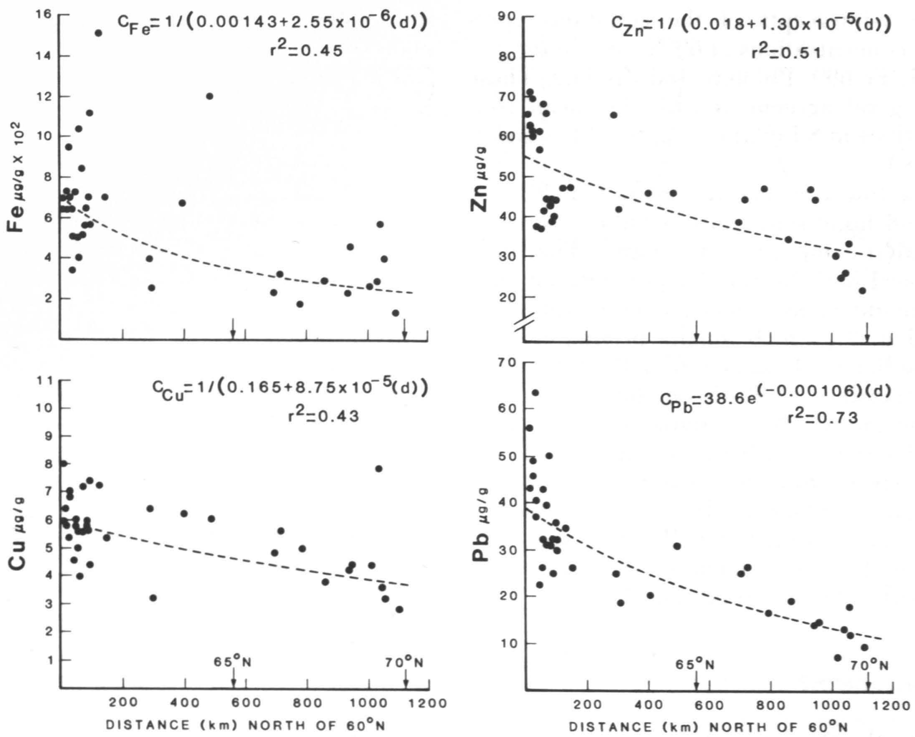


Fig. 2. Variation in Fe, Cu, Zn and Pb concentration (C, in µg/g, air-dry wt.) in *Pleurozium schreberi* with distance (d, in km) north of 60°N latitude in Finland. Best fit relationships (significant at $p < 0.001$) are shown.

Approximate concentrations ($\mu g/g^{-1}$) reported in *H. splendens* from S Finland, for samples collected in 1968–70, were: Cu 9, Fe 1000, Pb 50 and Zn 70 (see Rühling & Tyler 1973, Figures 2–3). Levels measured in the same species in the present study (concentrations for *H. splendens* given in Table 2) were some lower. The same decreasing trend was observed in other studies (Mäkinen 1982, 1983).

This may represent a real decrease in amounts of deposited metals in S Finland from 1968–70 to 1982. Also Pakarinen (1981a) found some decreasing gradient in the Pb, Fe and Zn content of *S. fuscum* in S Finland occurred from the mid 70's to 1980. This he ascribed to several factors, including the introduction of low lead gasoline, decreased industrial output after the oil crisis of 1974, and improved control of industrial emissions. Corresponding decreasing gradient from 1975 to 1980 in metal content of feather mosses was reported in Scandinavia by Gydesen et al. (1983).

"Best fit" equations to describe concentration gradients

In order to determine the relationships which best described the observed decreases in Cu, Fe, Pb and Zn contents of *P. schreberi* in the present study with increasing latitude in Finland and N Norway, 10 forms of curvilinear relationships were tested for "best fit". The main criterion used in selecting the best fit equations were the size of the coefficient of determination (r^2) and the presence or absence of y-intercepts.

The best fit relationships which were arrived at in the present case are shown in Fig. 2. All were curvilinear, and all were significant at $p < 0.001$. Those for Cu, Fe and Zn were of form: $1/y = a + b x$, while the best fit Pb equation was of the form $\ln y = a + b x$.

The y-intercepts of the equations (predicted concentrations at 60°N) are, in $\mu g\ g^{-1}$: Cu 6.1, Fe 699, Pb 38.6, and Zn 55.2. These are in good agreement with the mean concentrations in S Finland samples of *P. schreberi* (Table 1).

Some lower concentrations of Cu, Pb and Zn in offshore island mosses indicate smaller deposition compared with inland. That may be caused both by smaller precipitation and local inland emission sources. One example is lead (Fig. 2), which mainly originates from the gasoline (in Finland 0.65 g Pb/l in 1974). Also Pakarinen (1981a), on the basis of low Pb concentrations in moss samples from sparsely-settled southern coastal areas of Finland, suggests that the greater amount of car traffic in S Finland is chiefly responsible for the observed south–north Pb gradients. We, however, have to remember the long-range transport of lead in small particles.

West–east gradient

When the results for S Finland samples of *P. schreberi* and *H. splendens* were divided according to longitude (24°E), concentrations of Cu and Zn in both mosses, and of Pb in *H. splendens*, were found to be some higher in SW Finland than in SE Finland. The average Pb level in *P. schreberi* also was higher in the SW than in the SE, but the difference was not statistically significant ($p = 0.05$).

In later studies similar west–east gradients were not found except near great local emission sources. The south–north gradients of many heavy metals are distinctly greater in Nordic countries (Rühling & Skärby 1979, Rambæk & Steinnes 1980).

2.2. Comparison between regional levels in *Pleurozium schreberi* and *Hylocomium splendens*

Mean levels of the tested metals in *P. schreberi* and *H. splendens* samples collected from the same sites in S Finland are presented in Table 2. *H. splendens* contained significantly more Cu and significantly less Zn than *P. schreberi*. Pb, Fe and Ca levels tended to be some higher in *P. schreberi*, while average Mg and Mn concentrations were nearly equal in the two species.

Other studies (Le Blanc et al. 1974, Crodzinska 1978, Pakarinen & Rinne 1979, Folkeson 1979) also have reported generally higher Cu levels in *H. splendens* than in *P. schreberi*. Results for the other metals have been less consistent, probably due in part to differing analytical techniques (e.g. analysis of whole plant vs. green parts only) and to differing degrees of pollution in the study area. In an earlier comparison of Pb and Zn content of the two mosses in rural NW Ontario, Canada (Barclay-Estrup & Rinne 1978), in which the sampling and analysis procedures were very similar to those in the present study, the concentration ratios (*P. schreberi/H. splendens*) were 1.09 for Pb and 1.06 for Zn, very comparable to the ratios (1.08 for both Pb and Zn) obtained in the present study.

Table 2. Comparison of the mean metal contents ($\mu g/g$, air-dry wt.) of *Pleurozium schreberi* and *Hylocomium splendens* in S Finland excluding Koverhar sites. Significance of t-values (two-sided paired t-test) for inter-species differences: * = $p < 0.05$, ** = $p < 0.01$, *** = $p < 0.002$.

Metal	*P. schreberi* n = 19 x̄ S.D.	*H. splendens* x̄ S.D.	Ratio of Means P/H	t-value
Ca	2458 ± 499	2307 ± 389	1.07	1.14
Cu	5.8 ± 0.9	7.1 ± 1.5	0.82	–5.16***
Fe	707 ± 272	614 ± 157	1.15	1.86
Mg	598 ± 115	616 ± 96	0.97	–0.56
Mn	295 ± 107	304 ± 113	0.97	–0.32
Pb	35.0 ± 8.1	32.5 ± 6.4	1.08	1.46
Zn	51.7 ± 11.8	47.9 ± 12.5	1.08	2.49*

2.3. Effect of a steel works

An examination and comparison of the data in Figures 1 and 3 indicates that elevated levels of Fe and Zn were present in moss samples collected at sites 1 to 7 located 6.6 and 11.4 km from the Koverhar steel works. Site No 4 (the highest values) was situated 1.7 km west from the smeltery.

The best fit equations for these metals are calculated in the same manner as for the regional moss samples. Those for Fe were all of the form: $y = a + b/x^2$ (reciprocal), and were significant at $p < 0.01$. The best fit equations for Zn were of various forms, and were less significant than those for Fe. The relationships determined by these equations are depicted in Fig. 3.

For Ca, Cu, Mg, Mn and Pb no significant distance relationships were found in both moss species both north and south of the steel works, although trends of decreasing Cu and Pb levels with increasing distance south of the steel works were apparent.

The dependence on the reciprocal square of the distance, as observed for Fe in moss near the Koverhar steel works, has also described with U and Pb contents of mosses and lichens collected near uranium mine-exhaust vents in N Ontario, Canada (Beckett et al. 1982). A very rapid decrease in concentration with increasing distance from the source probably indicates large downward terminal velocities of the emitted particles depending on particle size, wind velocity and/or source height (Beckett et al. 1982). Probably these are the main factors at Koverhar, too. The height of the stack is there 60 m.

In an other study made around Danish steel works (Pilegaard 1979) Fe and Ni levels of transplanted moss (*Dicranoweisia cirrata*) samples also vary with the reciprocal square of the distance (i.e. best fit equations of the form: $y = a + b/x^2$).

This similarity between the variation with distance in metal content of moss provides a further indication of the reliability of moss analysis in determining the degree and extent of heavy metal deposition, on both a local as well as a regional basis. Periodically repeated moss analysis on same places and with same method can also suggest trends in heavy metal deposition.

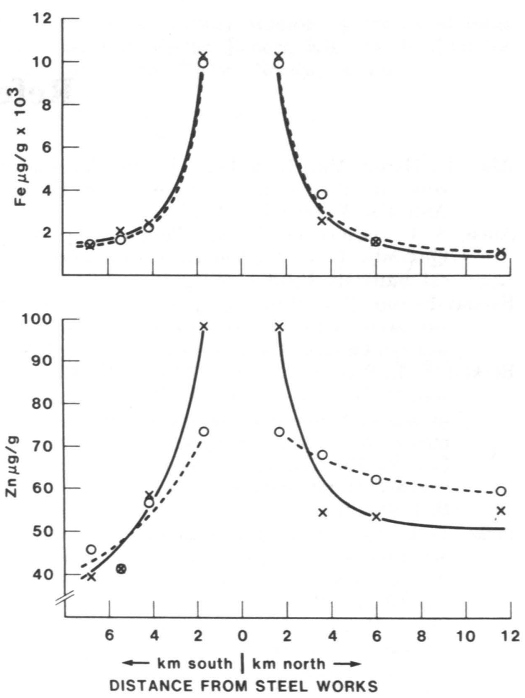


Fig. 3. Variation in Fe and Zn content of *Pleurozium schreberi* (open circles, broken line) and *Hylocomium splendens* (x's, solid line) with distance in both a southerly and a northerly direction from the Koverhar steel works in Finland. Curves represent best fit relationships.

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Total of 33 references

Seloste

Kerros- ja seinäsammalen metallipitoisuuksista Suomessa ja Pohjois-Norjassa

Metsäsammalia on käytetty Pohjoismaissa 1960-luvun lopulta lähtien ilman epäpuhtauksien kartoituksessa sekä paikallisten emissiolähteiden ympäristössä että ns. tausta-alueilla. Ruotsissa koko maan kattava kartoitus on suoritettu neljästi (168/69, 1975, 1980 ja 1985) metsänarvioinnin yhteydessä. Kesällä 1985 toteutettiin vastaava raskasmetallien laskeumatutkimus myöskin Suomessa ILME-projektin yhteydessä. Kartoituksessa käytettiin samoja sammallajeja (kerros- ja seinäsammalta) kuin tässä tutkimuksessa. Niiden kyky pidättää ilmasta laskeutuvia raskasmetalleja on suuri hyvän ioninvaihtokapasiteetin vuoksi. Ne ottavat tarvitsemansa kosteuden ja sen mukana tulevan laskeuman suoraan ilmasta.

Tässä tutkimuksessa on tarkasteltu em. sammalten Ca-, Cu-, Fe-, Mg-, Mn-, Pb- ja Zn-pitoisuuksia v. 1977 Suomesta ja Pohjois-Norjasta kerätyissä näytteissä. Keräyspisteistä 7 sijaitsee Koverharin rauta- ja terästehtaan ympäristössä Hankoniemellä, muut 37 tausta-alueilla.

Tutkituista alkuaineista Cu-, Fe-, Pb- ja Zn- pitoisuuden todettiin selvästi alenevan sammalissa etelä–pohjoissuunnassa. Sitävastoin Mn- ja Mg-pitoisuudet lisääntyivät jonkin verran pohjoista kohti. Ca-pitoisuuden muutos ei ollut tilastollisesti merkitsevä. Etelä-Suomessa Cu-, Pb- ja Zn-pitoisuuksien todettiin vähenevän jonkin verran myös länsi–itäsuuntaisesti.

Tutkittujen sammallajien väliset erot olivat vähäisiä. Tämän aineiston perusteella kerrossammalen kuparipitoisuus oli jonkin verran korkeampi ja sinkkipitoisuus alhaisempi kuin seinäsammalen.

Rauta- ja terästehtaan vaikutus sammalten rauta- ja sinkkipitoisuuteen näkyi pohjois–eteläsuunnassa vielä yli 6 kilometrin etäisyydellä tehtaasta. Muista pääilmansuunnista ei ole kerätty riittävästi näytteitä vaikutusalueen rajaamiseksi.

Kannattajajäsenet – Supporting members

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A. AHLSTRÖM OSAKEYHTIÖ
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OY TAMPELLA AB
KAJAANI OY
MAATALOUSTUOTTAJAIN KESKUSLIITTO
VAKUUTUSOSAKEYHTIÖ POHJOLA
VEITSILUOTO OSAKEYHTIÖ
OSUUSPANKKIEN KESKUSPANKKI OY
SUOMEN SAHANOMISTAJAYHDISTYS
OY HACKMAN AB
YHTYNEET PAPERITEHTAAT OSAKEYHTIÖ
RAUMA REPOLA OY
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KANSALLIS-OSAKE-PANKKI
SOTKA OY
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