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Sources and reduction of metal-content variation in biogeochemical prospecting

by Alf Björklund

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SOURCES AND REDUCTION OF METAL-CONTENT VARIATION IN BIOGEOCHEMICAL PROSPECTING

BY
ALF BJÖRKLUND

WITH 20 FIGURES AND 3 TABLES IN THE TEXT

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Organic topsoil and birch twigs were sampled on 4 196 sites in the vicinity of the Korsnäs lead-ore deposit in western Finland. Characteristics of the samples and of their environment were recorded. Vegetation type, pH and type of underlying material affect the Zn, Pb, Co and Cu contents in the organic topsoil. The Pb, Co and Cu contents in birch twigs are correlated with vegetation type, height of sampled trees and length of sampled shoots. To reduce the variability of the Pb content, which is related to these parameters, the contents were transformed by a standardization procedure. The transformation changed the anomaly patterns and made the one of lead in birch twigs agree better with other indicators of mineralizations in the bedrock.

The samples were grouped according to characteristics, which were measured on a qualitative scale, and an R-mode factor analysis was applied to each subgroup of the birch-twig samples. The anomaly pattern of scores on a supposed lead mineralization factor agrees with other indicators of mineralizations in the bedrock.

Helsinki 1971. Valtion painatuskeskus

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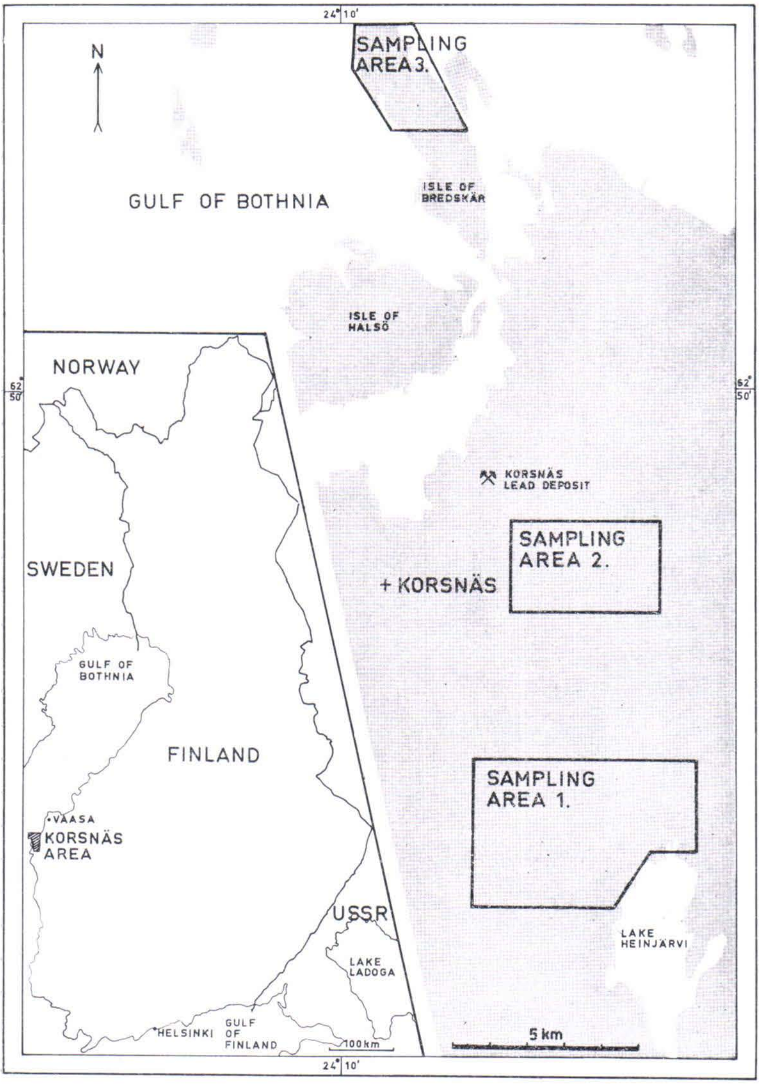

FIG. 1. The Korsnäs area and its location in Finland.

INTRODUCTION

In the Korsnäs area (Fig. 1) PbS- and rare-earth-bearing erratics are abundant in a zone, about 5 km broad, which runs northwest from the southern end of lake Heinjärvi over the isles of Halsö and Bredskär. This fact indicates that there probably exist several lead-ore deposits besides the one known. A regional prospecting method to reveal areas where deposits of economic importance may be situated is needed. The known type of ore deposit cannot be located by aerogeophysical methods. As the relief is very low, a stream-sediment study would appear to be unsuitable, as indicated by Wennervirta (1968). The rare occurrence of exposures renders geological mapping of the bedrock difficult. Hence, since conventional regional prospecting methods seemed to be unsuitable, the idea of performing a biogeochemical investigation arose.

The Korsnäs lead-ore deposit is situated in a fractured and sheared zone, about 20 m broad, which is strongly weathered in its uppermost parts. The zone is eroded to a lower level than the surrounding bedrock and this depression is filled with thick clay and till layers, which are difficult for the roots of the vegetation to penetrate. Accordingly, biogeochemical anomalies above ore deposits of this type cannot be expected. On the other hand, Hyvärinen (1967) has proved that clastic dispersion of galena has taken place in the glacial drift in the Korsnäs area. Anomalies in the drift, caused by this dispersion, may be located by biogeochemistry. During the last four decades, biogeochemistry has been used in ore prospecting. Investigations in different countries (in Finland: Rankama, 1940; Marmo, 1953, 1958; Salmi, 1956; Lounamaa, 1967) have shown that anomalous metal contents in the vegetation usually reflect anomalies in the underlying ground. Malyuga (1964, p. 188) concludes: »The experience of our studies has revealed that without exception all plants growing over ore deposits have an increased metal content.»

Anomaly patterns in organic materials are usually very subtle and have low contrasts. A successful interpretation of such patterns is extremely difficult, especially since the secondary environment in which the plants grow affects the absorption of elements in a very complex manner, giving anomalies with no obvious relation to mineralizations in the underlying bedrock. In most biogeochemical investigations, the metal content is determined in per cent or ppm of dry ash. The main components of plant ash are oxides of the elements Si, Mg, P, S, K, Ca, Na, Al, Fe and Mn. These consequently may be considered to be a solid medium in which trace elements form a dilute solid solution. A change in the content of a trace element in the plant ash is caused by a changing ratio between the uptake rate of the main elements and the uptake rate of the trace element. Hence, when trying to find reasons for fluctuating trace-element contents in ash, the varying uptake rate of main elements should not be forgotten. An increase in the amount of a trace element in the soil may lead to an increased amount of it in plants. Above a toxic level, a further increase of the element in the soil may cause a collapse of the metabolic processes and hence a decreasing uptake of the macronutrients. The net effect is a sharp increase of the trace-element content in the plant ash. Among geologists, this toxic level, perhaps wrongly, has sometimes been referred to as the point where the plants' capacity of withstanding toxic elements breaks down.

According to Malyuga (1964), the sampling of the organic layer of the soil profile is to be considered a biogeochemical method. He stresses the importance of sampling plants and the organic layer of the soil simultaneously in order to achieve maximum efficiency for the biogeochemical method.

In Finland, Salmi (1955, 1956, 1959) has demonstrated that ore bodies are usually revealed by anomalous metal contents in overlying peat. After investigation of the organic layer of the soil in several localities in Finland, Kauranne (1967, p. 268) states: »The likelihood of finding distinct anomalies in humus is rather good if mineralizations contain copper, lead or zinc.» During surveys at Cobalt, Ontario, Boyle and Dass (1967) found that the organic horizon gives the best results in soil sampling over ore deposits, especially in areas where there is a deciduous-tree cover. Presant (1966) demonstrated the usefulness of the uppermost part of the organic layer in ore prospecting and states that major concentrations of lead and silver occur in this horizon, while arsenic, copper and zinc give the best anomaly contrasts above sulphide mineralizations.

The purpose of the present investigation was; (1) to find out whether lead anomalies in the organic layer of the topsoil, called A_0 below, and in birch twigs reflect lead anomalies in the transported overburden; (2) to determine the magnitude of the influence of external and internal conditions on the metal content in the organic topsoil and in birch twigs; and (3) to find a technique by which »undesirable» variability could be decreased in order to clarify the interpretation of the anomalies.

ABSORPTION OF MINERAL SALTS IN PLANTS

The carbon, hydrogen and oxygen combined in photosynthetic reactions are obtained from air and water and comprise 90 % or more of the dry matter of plants. The remaining 13 elements currently considered essential to growing plants are obtained largely from the soil. These elements are:

1) The macronutrients N, K, Ca, Mg, P and S.
2) The micronutrients Fe, Cl, Mn, B, Zn, Cu and Mo.

In addition Na, Si, V and Co are essential for some groups of plants (Price, 1970). For the other elements which occur in plants, no essential function has been found.

According to Malyuga (1964) the mean contents of the most abundant elements in the dry ash of plants are: Si 15 %, Mg 7 %, P 7 %, S 5 %, K 3 %, Ca 3 %, Na 2 %, Al 1.4 %, Fe 1 % and Mn 0.8 %.

Plant physiologists have carried out extensive research to learn about the element absorption mechanisms in plant roots and about the external and internal conditions affecting this absorption. Most attention has been paid to cultivated plants and their absorption of essential macronutrients, whereas trace elements, which are important in ore prospecting, have been little studied.

The absorption of elements by plants can be represented as a three-step process; (1) the movement of the elements in the soil to the root surface; (2) the movement of the elements from the exterior to the interior of the root; and (3) translocation of the elements from the roots to other parts of the plant. These steps determine the uptake rate of available elements.

Availability and movement of elements in the soil

An adequate supply of elements for the vegetation implies; (1) an adequate concentration of elements in the soil; (2) the presence of soluble compounds of the elements; and (3) adequate mobility of the elements in the soil. If one of these conditions is unsatisfied for an element, the element is more or less unavailable.

Eh, pH, micro-organisms and the contents of organic matter and organic acids are the main regulators of availability. Generally, increasing acidity renders compounds soluble and increases mobility of elements, which promotes availability. For example, Lakanen and Paasikallio (1968) demonstrated in pot experiments that the uptake of Sr-89 by timothy grass may increase with decreasing pH. However, leaching effects increase with increasing mobility. This may cause a deficiency of macronutrients at low pH. Hoyert and Axley (1952) conclude that base saturation decreases about 30 % per unit decrease in the pH of Maryland soils. In addition, decreasing pH may render some elements less available. At low pH, for example, molybdenum exists as poorly mobile Mo^{5+}. Lakanen and Vuorinen (1963) demonstrated that below pH 7.5 decreasing pH increases the phosphorus-fixing capacity of iron and aluminium very sharply. They conclude that this capacity probably reaches a maximum at about pH 5.8.

Ong *et al.* (1970) found that the mobility of copper, lead and zinc, among others, increases with an increasing amount of naturally occurring organic acids. They suggest that this may be due to; (1) reduction of some ions to a lower and more mobile valence state; (2) formation of a soluble chemical complex with the organic acids; or (3) colloidal suspensions formed between the metals and the organic acids. Furthermore, they found that the dependence between pH and mobility may be very complex when organic acids are present. Increasing amounts of organic acids may facilitate the availability of some elements by mobilizing them, but other elements (Cu) may be too strongly bound in organic complexes to be available, as indicated by Lees (1965).

The role of aerobic micro-organisms is very important in plant nutrition. They decompose organic matter and convert elements into soluble forms that plants can reuse. Furthermore, biological activity promotes the weathering of mineral compounds in the soil.

According to Moodie (1965), there are three mechanisms by which a root may come into contact with elements: (1) The roots may extend to the site of the elements. This mechanism may play an important role in the absorption of very immobile elements. (2) Elements are transported by the mass-flow of water to the root. Transpiration, which maintains the potential gradient, governs the rate of flow. This mechanism is thought to be able to supply all the highly mobile elements like Ca and Mg. (3) Diffusion down existing concentration gradients. The rate of this migration is determined by physico-chemical conditions in the soil. Elements which have limited mobility are apparently transported by this mechanism.

Uptake of elements by roots

It is evident that elements are absorbed from solutions and absorption sites in ionic form. There is no sharp contact between the root surface and the medium. Jenny and Grossenbacher (1963) have demonstrated that roots are surrounded by a gel-like material which makes intimate contact with the soil. The volume of the medium close to the roots is currently called the rhizosphere. The rhizosphere is the zone of intense microbial activity which is maintained greatly by root exudates. In this zone, pH, partly as a result of carbon dioxide released in respiration, is lower than in the surrounding soil; this may, in combination with micro-organisms, dissolve solid compounds. Thus plants themselves may convert elements into available forms.

The most conspicuous features of the absorption of elements by plants are strong selectivity and a capacity for absorbing some elements against steep concentration gradients. Plant physiologists have conducted numerous experiments to explain the mechanisms which are involved in absorption. All the same, there are very few proved facts concerning this absorption process. The different hypotheses are largely based on assumptions.

Ions are said to be absorbed passively when physico-chemical reversible processes are involved. Sutcliffe (1962) proposed among other mechanisms; (1) diffusion down a concentration gradient; (2) ion exchange, which may proceed against a concentration gradient; and (3) Donnan equilibria, which may transport ions against concentration gradients to maintain electric equilibrium.

The entrance of ions through coupling with metabolic reactions is called active transport. Energy for active transport, which may proceed against steep concentration gradients, is partly released in respiration. Different components of the membrane between the outer space and the cytoplasm are suggested to be acting as carriers. The carriers are thought to expose their binding sites alternately to the two membrane sides. They bind ions selectively and have a different affinity to them at each side of the membrane, generally lower inside. Several types of carriers may operate simultaneously and combine with different groups of ions. Ions which have a common carrier compete with each other. A high level of one ion may cause deficiency in another.

The absorption rate of ions is affected by several internal and external conditions. Competition and other inter-ion effects apparently play an important role. Millar *et al.* (1965) state, for example, that high levels of available P may cause a deficiency of zinc. Jackson and Williams (1968) found that a large amount of nitrate in the soil promotes uptake of, among others, Sr, Cs, K, Mn and Na. Active absorption is decreased at low temperatures. At 1—2 °C the absorption is mainly passive, according to Sutcliffe (1962). An adequate supply of oxygen is essential for active absorption. Remezov and Payrebryak (1965) state that negative effects appear if the content of oxygen in the soil air falls below 12 %. Furthermore, in an anaerobic condition, active absorption is prevented by toxic compounds like methane, nitrites and hydrogen sulphide. For most plants, a pH between 6 and 8 is the optimal for absorption. At low pH, toxic levels of aluminium compounds may be formed.

Transport of ions in plants

Once an ion has penetrated the root wall (epidermis) it may be; (1) accumulated in the cell walls or in the cytoplasm; (2) translocated and accumulated in the vacoule sap; or (3) transported through the symplasm, and possibly also the cell walls, into the stele xylem.

According to Sutcliffe (1962), it has been clearly demonstrated that ions are carried upwards from the roots to aerial parts by the transpiration stream in the stele. As ions may also be carried downwards, it is apparent that other translocation mechanisms operate too. Both active and passive mechanisms have been proposed. Factors such as temperature, light, nitrate and Ca contents in the soil, and the presence of certain micro-organisms within the plant, may affect the translocation rate of ions.

Nitrate, phosphate, alkali metals, Mg and S are highly mobile in plants (Price, 1970). These may be translocated from one part to another and are partly withdrawn from leaves before defoliation. Ca, B, Fe, Mn, Zn and Cu are considered relatively immobile (Price, 1970; Millar *et al.* 1965). These elements, and apparently most heavy metals, once accumulated in the tissues of leaves are not withdrawn before defoliation and may accordingly be concentrated in the organic layer of the soil.

BIOGEOCHEMICAL INVESTIGATION IN THE KORSNÄS AREA

Description of the exploration area

Physiography

The Korsnäs area is situated on the shore of the Gulf of Bothnia (Fig. 1). It can be found on map sheet 1242.

According to Okko (1967), the temperature is on the average —3 to —6 °C in January and +12 to +16 °C in July. The annual precipitation (about 500 mm) is some two times the evaporation. The area has a very low relief, with altitudes of 0 to 25 meters. The forests are mainly spruce-dominant coniferous. Pine is associated with dry hills and bogs. Birch is uniformly dispersed in the forests and occurs in cultivated areas, too. Alder grows mainly on the seashore.

The bedrock is covered with superficial deposits composed of Pleistocene glacial drift, 2 to 4 meters thick on the average. In low-lying areas, this is overlain with Holocene clay and silt sediments . In basins with impeded drainage, peat bogs have developed. The soil types are podzol and swamp. The epeirogenetic land uplift is about 9 mm/year in the area. Thus, the podzol profile is recent and weakly developed near the shore, whereas it is 2 000—2 500 years old and mature at altitudes of 25 meters.

In a recent till-sampling program in the Korsnäs area, bedrock was exposed in pits. According to measurements made by Sinikka Ristiluoma (1970, in press), striation observations reveal that one direction of ice movement, apparently the most recent one, has been southward, 150—170°. Some observations indicate that there also have been two older southward glacial movements, one 0—20° and the other 140—145°. Till-fabric analyses indicate that the till has mainly been transported southward, 150—160° (Sinikka Ristiluoma, 1970, in press).

Bedrock

The bedrock, which is poorly exposed, belongs to the Svecofennian schist zone. The dominate rock type is mica gneiss, which is usually strongly migmatic and in many places intercalated by pyroxene-bearing calcareous gneisses and amphibolites. Conformable lenses of gneissose granites and pegmatites are common. Younger granite and pegmatite dykes intersect the schistosity. Basic and ultrabasic igneous rocks are rare.

The schistosity strikes roughly NNW and dips usually 20—50° E. In the vicinity of the lead-ore deposit, the bedrock is fairly well known from drill holes. Here several north-trending fractured and sheared zones, which usually dip 40—50° E, occur. Differential movement of adjacent bedrock blocks has apparently opened the zones, allowing crystallization of epigenetic minerals. Gangues are mostly coarse-grained frequently with barium- and strontium-rich potash feldspar, calcite, diopside, apatite and scapolite. Galena occurs very randomly in the mineralizations and constitutes an economic body in only one of the known zones. Rare-earths, usually associated with apatite, are abundant in the deposit and are, at present, being extracted from the quarried material.

The mineralizations in the sheared zones are partly strongly disintegrated, especially in the outcrops, where galena is very fine-grained. They are eroded into deep depressions, which are accentuated in the terrain by overlying bogs. Narrow mineralized cracks are very frequent in the solid bedrock blocks of the area. These mineralizations are not disintegrated and they may be the source of most of the ore boulders.

Previous prospecting

In the early fifties an amateur geologist found the first galena-bearing erratics; this started exploration in the Korsnäs area. In the late fifties, the Geological Survey of Finland located the lead deposit, which contained about one million tons of 4 % lead. Numerous lead- and rare-earth-bearing erratics have been found, mainly by amateur geologists, in an area of about 100 square kilometers. From these erratics, it is evident that such mineralizations are common in the area. However, distinct ore-boulder fans do not occur, perhaps because the broad mineralizations are strongly disintegrated in their outcrops and may not have produced solid boulders.

The Geological Survey of Finland (Hyvärinen, 1967) carried out a geochemical survey over an area of 17 km^2 sampling till at different depths in pits. Distinct glaciogenic lead-anomaly fans were found in connection with mineralizations. Near the outcrops they are close to the bedrock but rise gradually to the topsoil at distances of one to two kilometers.

As radioactive minerals occur in the ore deposit, radon measurements of soil air have been carried out. This method did not satisfactorily reveal the deposit.

Several geophysical prospecting methods have been tested and used in the area. Gravity and seismic refraction surveys satisfactorily indicate the sheared zones, which cause negative gravity anomalies and slow wave velocities.

Initial biogeochemical survey

The program was started in 1967 when different plants were sampled to find out which plant would give the best anomaly contrasts over known glaciogenic Pb anomalies in the soil. However, no plant or part of a plant was found to be superior to the others (Seppo Väisänen, unpublished data).

As a suitable plant for biogeochemical lead prospecting in the Korsnäs area, birch (*Betula verrucosa* and *Betula pubescens*) was selected for the following reasons: (1) Birch is quite uniformly distributed throughout all the vegetation types. (2) It has a well-developed and deep root system which may reach deep-seated Pb anomalies in the till. (3) According to Lounamaa (1967), who studied the ability of different plants to reflect metal contents in the bedrock in Finland, the Pb content in birch twigs is very striking in richly PbS-mineralized areas.

Twigs were sampled since; (1) their Pb content is considerable (Lounamaa, 1967); (2) their metal content can be assumed to be rather stable; and (3) they can be obtained in winter as well as in summer.

To determine metal-content differences between annuals of different ages, these were separated on a tree and several samples of each age were analyzed. This test indicated that possible differences were too small to be detected by the analytical method (spectrograph). Accordingly, no particular shoot generation was selected, but the outermost 20—30 centimeters of the twigs were sampled.

In the summer of 1968, 5 483 twig samples were collected, mainly over the known mineralized areas. They were analyzed for Cu, Ni, Co, Zn, Pb and Ba with a Hilger large automatic quartz spectrograph. The following characteristics were recorded for every sample: Length of shoots, height of tree, sampling height on the tree, vegetation density, type of vegetation, type and moisture content of the underlying material, cloudcover, precipitation, temperature, and wind velocity and direction. The samples were grouped according to different characteristics and correlations between the metal contents and one characteristic at a time, with the others kept constant, were studied. It was found that length of shoots, height of trees, type of vegetation, and type and moisture content of underlying material affect the metal contents in birch twigs. Over the known lead-ore body, the lead content of the twigs was several-fold higher than in background areas, exceeding 1 % in some samples. It is evident that this prominent anomaly is largely due to contamination. Over weak Pb anomalies in the till, subtle patterns of low anomalies in the birch twigs were obtained.

The investigation described above was performed by Raimo Rahkonen, Seppo Väisänen and the present author (unpublished data). The program was continued by the author in the summer of 1969, taking advantage of the experience gained in the previous research. In the following, this survey (1969) is considered in more detail.

Sampling

Three sampling areas (Fig. 1) were selected for the survey. In these areas conspicuous clusters of lead-bearing erratics occur. 4 196 samples of birch twigs (the outermost 20—30 cm) were collected. The sampling was carried out along lines bearing east-west and spaced at 200 meters, with sampling sites at 50-meter intervals along the lines. On 108 sites, alder twigs were sampled as birch was absent. A_0, the uppermost, partly undecomposed, organic soil horizon, was sampled on every site. In bogs, these samples were taken from some 20 cm depth and are accordingly peat (mainly sphagnum) samples. The characteristics of the samples and of their environment were recorded and coded according to Table 1.

TABLE 1

Coded characteristics of birch twigs and A_0 and of their environment:

Type of vegetation:
1) Forested, spruce-dominant, wet type.
2) Forested, pine-dominant, dry type.
3) Cultivated area.
4) Bog or marshland.

Altitude above sea level:
1) 0— 5 m.
2) 5—10 m.
and so on with 5 m intervals.

Height of sampled tree:
1) < 2 m.
2) > 2 m.

Type of underlying material:
1) Bedrock.
2) Till.
3) Sand and gravel.
4) Clay.
5) Peat.

pH of A_0:
Measured in laboratory with potentiometer in a 2.5 (water): 1 suspension which was prepared 24 hours before the measurement.

Length of sampled shoots:
1) < 5 cm.
2) 5—10 cm.
3) 10—20 cm.
4) >20 cm.

Preparation of the samples

The samples of twigs and A_0 were ashed in a two-step procedure in beakers made of electrolytically refined nickel. For an initial period of 12 hours at 370 °C, they were allowed to char; then the temperature was raised and kept at 500 °C for a second period of 12 hours. In this manner, twig-ash samples of about 100 mg and A_0-ash samples of about 200 mg were obtained.

Chemical analysis

Spectrochemical analysis was carried out on the ash samples. A relative error of ± 30 % was expected not to affect the results of the investigation seriously. Thus, as a rather large analytical error was tolerated, the ash was not buffered and no internal standards were used.

The ash of twig samples was thoroughly pulverized and analyzed for Cu, Ni, Co, Zn, Pb and Ba with a tape-fed direct-reading multichannel optical emission-spectrometer (quantometer). As the ash of the A_0 samples sometimes contained considerable amounts of mineral grains, problems with homogenization were encountered. For this reason, the tape-fed quantometer was not used for these samples but, rather, a Hilger large automatic quartz spectrograph. Carbon powder was added to the A_0 ash and Mo and La were analyzed in addition to the aforementioned metals.

There are divergent opinions about whether metal contents should be calculated using an oven-dry or dry-ash basis. Fortescue and Hornbrook (1967) stress that an oven-dry basis is to be preferred in biogeochemical ore prospecting, whereas Warren (1962) found contents on dry-ash basis more reliable. At Korsnäs the metal contents were calculated on a dry-ash basis.

The metal contents were rounded to the nearest; 10 ppm for Co and Mo; 100 ppm for Cu, Pb and La_2O_3; 100 ppm in A_0 and 1 000 ppm in twigs for Zn; and 500 ppm for Ba. At high concentrations, the rounding was even greater. However, at the lowest concentrations the greatest relative rounding was done and this rendered the statistical analysis of contents close to the detection limits (the above mentioned numbers) unreliable.

Statistical analysis

According to the statistical definition, a total set of potential observations is called a population, and the set of actual observations in hand is called a sample of this population (Koch and Link, 1970). In the present paper, one piece of the sampled target medium, is called a sample. A set of samples or observations is called a population.

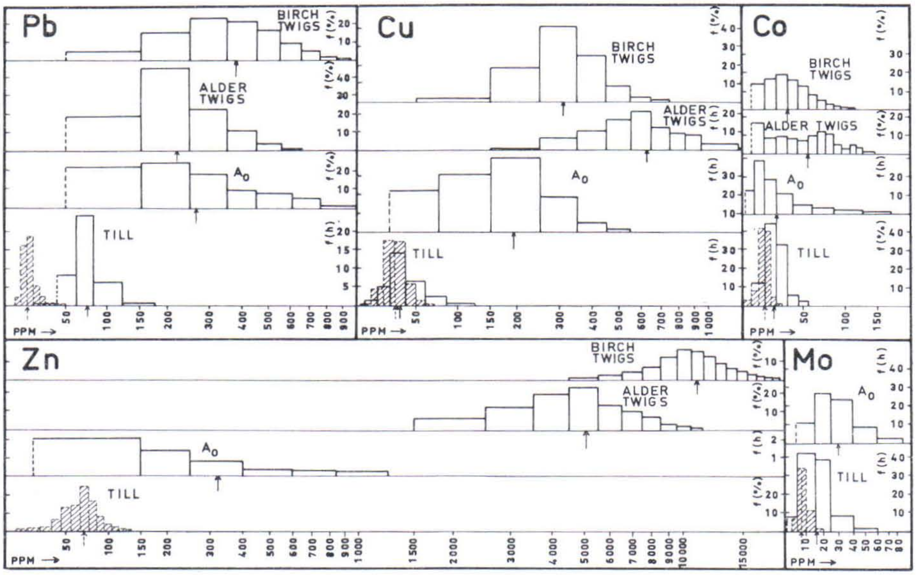

FIG 2. Histograms of lead, copper, cobalt, zinc and molybdenum contents in the minus 0.074 mm fraction of 618 till samples and in the ash of; 1 871 samples of the organic topsoil (A_0); 106 samples of alder twigs; and 4 196 samples of birch twigs. Till was analyzed with a spectrograph and by the atomic absorption method (shaded histograms), the organic topsoil with a spectrograph, and the twig samples with a quantometer. The arrows indicate the medians. In histograms with varying class widths, the relative frequency (%) in each class is:

$$\frac{f(h)\,Q}{10}$$

where Q is the width (ppm) of the class.

To demonstrate the variability of metal contents in different sampling media, histograms are presented in Fig. 2. Nickel was not considered, since contamination from the beakers is apparent. Till, which was sampled in sampling areas 1 and 2 in 1970, was included. Barium was excluded as it was not determined in till and because the contents in A_0 are close to the detection limit, which leads to large analytical error as a result of the great rounding. The A_0 samples are from wet spruce forest, since the organic horizon is thickest and contamination with mineral matter is most easy to avoid in this type of vegetation.

The till samples were sieved and the minus 0.074 mm fraction was divided into two subsamples, one of which was analyzed with the quantometer and the other by the atomic absorption method described by Wennervirta (1968). A very severe discrepancy between the amounts detected by the two methods is apparent for lead and molybdenum (Fig. 2). It is evident that the quantometer gave biased results because the amounts are close to the detection limits of this method.

In Table 2, estimates of the central tendency and spread of the contents, and also the enrichment ratio of metals in A_0 and in twigs as compared to till, are presented. Alder was excluded since it has not been considered in the following treatments. The content of Co in part of the A_0 samples was below the detection limit of the quantometer, which made calculation of the arithmetic mean and standard deviation impossible.

TABLE 2

Median (Q_2), arithmetic mean ($\bar{x}$), standard deviation (s) and coefficient of variation (C) of copper, cobalt, zinc, lead, barium and lanthanum oxide contents; in the ash of birch twigs; in the ash of the organic topsoil (A_0); and in the minus 0.074 mm fraction of till. In the two columns on the right, the ratios; between the median content in twigs and the median content in till; and between the median content in A_0 and the median content in till, indicate the enrichment of metals in twigs and in A_0 respectively.

	Birch twigs, 4 196 samples				A_0, wet spruce forest, 1 871 samples				Till, 618 samples				$\frac{Q_2 \text{ (twigs)}}{Q_2 \text{ (till)}}$	$\frac{Q_2 (A_0)}{Q_2 \text{ (till)}}$
	Q_2	$\bar{x}$	s	C	Q_2	$\bar{x}$	s	C	Q_2	$\bar{x}$	s	C		
Cu	320	330	107	0.32	191	201	130	0.65	34	42	29	0.69	9.4	5.6
Co	35	41	26	0.63	25				23	25	12	0.43	1.4	1.1
Zn	10 905	11 208	3 111	0.28	322	571	644	1.13	73	73	24	0.33	150.0	4.4
Pb	378	400	236	0.59	268	364	338	0.98	73	79	26	0.33	5.2	3.7
Ba	3 330	3 374	1 364	0.40	541	678	414	0.61						
La_2O_3					199	249	111	0.44						

Some general features of the information in Table 2 are: (1) The zinc content is conspicuously high in twigs. (2) As concluded from the difference between the arithmetic mean and the median, the distributions of the contents are usually more strongly skewed (positively) in A_0 than in till and twigs. (3) With one exception (Cu in till), the coefficient of variation is higher in A_0 than in till and twigs. (4) As compared to the contents in till, Cu, Zn and Pb are several-fold enriched in A_0 and in twigs. The enrichment is stronger in twigs.

The sources of variability of the metal contents may be analytical, preparation, sampling and natural causes, in addition to random fluctuation. That part of the natural variability which is caused by uneven distribution of metals in the underlying ground is of particular interest in ore prospecting. To be able to distinguish it, a knowledge of the other sources of variability is necessary.

Analytical variability

To determine the analytical error, a large sample of birch-twig ash was thoroughly homogenized and divided into 100 subsamples. These were periodically included in the »normal» sample set without the knowledge of the chemist. In the uppermost part of Fig. 3 the frequency distribution of the metal contents of the subsamples are presented. The high coefficients of variation (C), especially those for Co and Ba, indicate that the analytical method (quantometer) is only semiquantitative.

Preparation variability

Biogeochemical samples are generally ashed by gradually increasing the temperature to 450—500 °C over a period of several hours in order to prevent them from bursting into flame. Some heavy metals are thought to escape because of high temperature if the samples are allowed to glow or burn. To discover how to keep the samples from catching fire, a micro-thermoelement, which was connected with an x—y recorder, was inserted in small twigs. The twigs were ashed in a gradually increasing temperature. From this it appeared that, however slowly the temperature

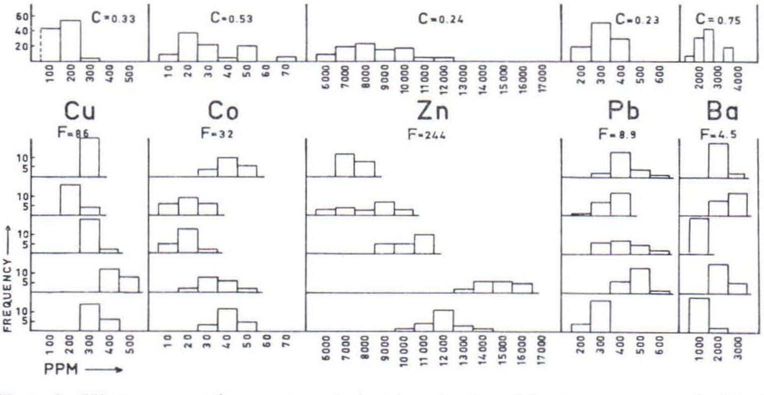

FIG. 3. Histograms of copper, cobalt, zinc, lead and barium contents in birch twigs. The upper part: 100 subsamples of a homogenized gross sample. The lower part: 20 samples from each of five grouped trees. F is the F-distribution of the mean contents in the five trees. $F_{5\,\%} = 3.06$ for 4 and 15 degrees of freedom (Koch and Link, 1970, Table A. 4). C is the coefficient of variation.

was increased, at an oven temperature of about 395 °C the temperature in the twigs increased to some 800 °C for a few seconds. By observing a sample at 395 °C it was found that one twig or several at a time glowed, but not the whole sample simultaneously.

A large sample was ashed at 450 °C over a 24 hr. period and then homogenized and divided into two sets of subsamples. One set was kept for a further 16 hr. period at 800 °C. This experiment revealed that the contents of the measured metals increased relatively about 25 % under the period of 16 hr. at 800 °C.

It seemed evident that; (1) glowing could not be avoided at temperatures exceeding 400 °C; and (2) to restrict preparation variability, care should be taken to ash all samples in a similar manner.

Natural variability and its relation to some parameters

When sampling a medium, a small part is taken. The metal contents of this sample can be used to predict those of a larger part of the medium with an accuracy which depends on the size of the sample and on the variability of contents in the medium. To check the accuracy with which a small twig sample predicts the metal contents of the twigs of the whole tree, 20 samples were collected from each of five adjacent birches. The trees grow 10 meters apart in similar environments and their morphology seemed to be similar. In the lower part of Fig. 3, the frequency distributions of the metal contents in each of the trees are presented. These reveal that the metal-content variability in the samples from the same tree is not larger than the variability resulting from the analytical method (see, the upper part of Fig. 3). It can be concluded that the samples are large enough to predict the metal contents of the twigs of a tree within the accuracy limits set by the analytical method.

In geochemical ore prospecting, variability of metal contents caused by mineralizations is searched for but is often obscured by variability caused by secondary environmental processes. Kauranne *et al.* (1961) demonstrated the effect of different terrain types on the contents of heavy metals in humus. It is evident that the variability is further magnified in vegetation, where physiological processes operate.

To find out whether the mean metal contents are different in twigs from the five trees presented in Fig. 3, a one-way analysis of variance, described by Koch and Link (1970, pp. 131—144), was applied. $F_{5\%} = 3.06$ for 4 and 15 degrees of freedom is obtained from Table of Upper Percentage Points of the Studentized Range (Pachares, 1959). Using the calculated F-values, and with a 5 % error risk, the conclusion can be drawn that for every metal the mean content in twigs is different in different trees. A conspicuous feature is the fact that the F-values are large for Cu, Co and Zn, which metals are essential for or promote plant growth, whereas they are small for Pb and Ba, for which no function in the living plants has been found. This test indicates that there are discrete processes which affect the contents.

In the present survey, correlations between the recorded characteristics, presented in Table 1, and the metal contents in A_0 and in birch twigs were studied. As only a classificatory scale of measurement can be assigned to the type of vegetation and the type of underlying material, the significance of these characteristics cannot be checked either by factor analysis or by correlation calculations. The very rough classification of the height of trees is also inexpedient for these methods.

To test the efficiency of factor analysis in determining different sources of variability in the data, samples of birch twigs from sampling area 1 were grouped according to height of tree, type of vegetation, and type of underlying material. A calculation of the correlation coefficients and an R-mode factor analysis were applied to each of the subpopulations. In the sampling area in question, pH was determined also in the B horizon of the soil (pH_B) and has accordingly been included in the treatments. The results of the treatments of one subpopulation are presented in Table 3. The weak correlations between the metal contents are surprising (Table 3 a). Furthermore, length of shoots, altitude, and pH are very weakly correlated with the metal contents, the highest coefficient being —0.30 between Pb and length of shoots. The coefficient is conspicuously low (0.23) between pH_{A_0} and pH_B, although the latter was measured only 20—30 cm lower than the former.

By factor analysis, no factor or group of factors was found which could account for a considerable part of the variability. This is indicated by the pattern of decreasing eigenvalues, where no distinct break appears (Table 3 b). After computing the loadings of the elements on the orthogonal factor axes, a rotation about the origin was carried out to achieve a minimum of variance in the loadings on each factor. The result is presented in Table 3 c. The weak correlations between the elements (Table 3 a) are reflected in this matrix, where a heavy loading of only one element appears on each factor. Pb, which is of special interest in the present study, has a heavy loading on factor 10, where it accounts for 81 % ($0.90^2 \times 100$) of the variance. This factor is accordingly named the lead-mineralization factor and the source of the variability is suggested to be variable lead content in the soil.

Factor analysis does reveal relations between metal contents and characteristics measured on a quantitative scale. However, if the contents are low in samples with a certain combination of characteristics and high in samples with another combination, it fails to show the magnitude of content difference. Furthermore, it cannot be applied to classify measured qualitative characteristics (e.g. type of vegetation and type of underlying material). For these reasons, a time-consuming method was used to find out whether there are combinations of characteristics which are related to extreme metal contents. The samples of A_0 and birch twigs were grouped according to type of vegetation, type of underlying material, altitude above sea level, and pH in A_0. In addition, samples of twigs were grouped according to height of sampled trees and length of shoots.

The frequency distributions of the metal contents were calculated for each subpopulation. The arithmetic mean is more than 94 % efficient as a point estimate of

TABLE 3

651 samples of twigs from birches exceeding 2 m in height and growing in wet spruce forest on till ground. Ls = length of shoots, Alt = altitude.

a) Matrix of correlation coefficients between elements.

	Ls	Alt	pH_{A_0}	pH_B	Cu	Ni	Co	Zn	Pb	Ba
Ls	1.00	—0.02	0.03	0.02	—0.04	0.04	—0.17	—0.06	—0.30	—0.15
Alt		1.00	—0.08	—0.13	—0.12	—0.06	—0.12	0.06	0.07	0.04
pH_{A_0}			1.00	0.23	0.00	—0.07	0.05	0.09	—0.02	0.14
pH_B				1.00	—0.05	—0.06	0.05	—0.10	—0.11	0.12
Cu					1.00	0.15	0.33	0.36	0.40	0.19
Ni						1.00	0.12	0.02	0.02	0.08
Co							1.00	0.35	0.45	0.38
Zn								1.00	0.47	0.38
Pb									1.00	0.42
Ba										1.00

b) The proportion of data variability contained in each factor received in factor analysis.

Factor	Eigenvalue	Eigenvalues as percentage %	Cum. %
1 ..	2.60	26.0	26.0
2 ..	1.38	13.8	39.8
3 ..	1.18	11.8	51.6
4 ..	1.00	10.0	61.6
5 ..	0.90	9.1	70.7
6 ..	0.76	7.6	78.4
7 ..	0.67	6.7	85.1
8 ..	0.57	5.7	90.8
9 ..	0.50	5.0	95.8
10 ..	0.42	4.2	100.0

c) Varimax matrix of factor analysis accounting for 100 % of total variance.

Factor	1	2	3	4	5	6	7	8	9	10
Ls	0.06	—0.01	—0.01	—0.99	0.02	0.02	0.01	0.07	0.01	0.12
Alt	—0.02	0.06	0.99	0.01	—0.03	—0.04	0.06	0.06	—0.03	—0.03
pH_{A_0}	—0.06	—0.11	—0.04	—0.02	—0.04	0.99	0.00	—0.02	—0.04	0.01
pH_B	—0.06	—0.99	—0.06	—0.01	—0.03	0.11	0.02	—0.03	0.05	0.05
Cu	—0.06	0.02	—0.07	0.01	0.07	0.00	—0.96	—0.13	—0.16	—0.16
Ni	—0.04	0.03	—0.03	—0.02	0.99	—0.04	—0.07	—0.05	0.00	0.00
Co	—0.17	—0.03	—0.07	0.08	0.06	0.02	—0.14	—0.94	—0.14	—0.18
Zn	—0.17	0.06	0.04	0.01	0.00	0.05	—0.17	—0.14	—0.94	—0.19
Pb	—0.19	0.07	0.05	0.16	—0.01	—0.02	—0.19	—0.10	—0.22	—0.90
Ba	—0.95	—0.07	0.03	0.07	0.04	0.07	—0.06	—0.16	—0.17	—0.17

the mean content, provided the coefficient of variation is below 1.0 (Finney, 1941). This condition is fulfilled regarding contents in twigs but the arithmetic mean may be a strongly biased estimate of mean contents in A_0, where the coefficient of variation is considerable. Accordingly, the median was selected as a measure of central tendency for all the subpopulations. By holding all but one characteristic at a time constant, the relation between the median content of the metals and each characteristic was estimated. All the subpopulations below size 10 were excluded. To demonstrate the variability of contents in the subpopulations, frequency polygons are presented for twigs. Concerning A_0, the third quartile was used since high variability of contents and strong rounding rendered construction of polygons difficult. The results of these treatments are presented below.

Altitude above sea level

With increasing altitude, the maturity and hence the thickness of A_0 increases. This need not be true of peat. Contamination with mineral matter in the A_0 samples, which would depress metal contents, was thought to be stronger at low altitudes. As indicated by Fig. 4, no such influence could be detected.

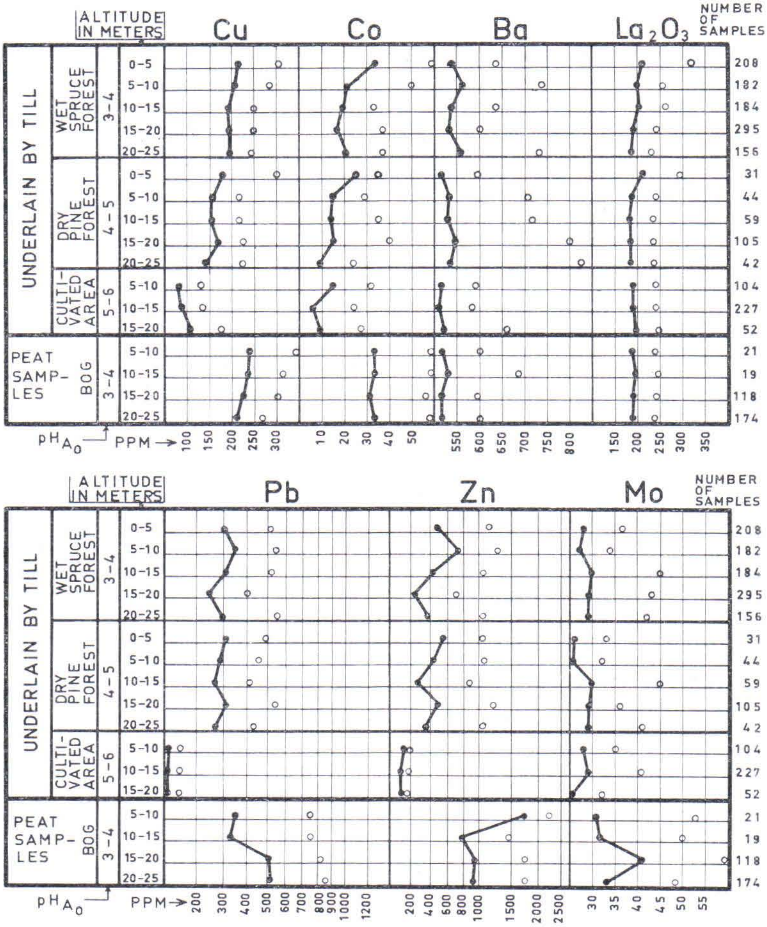

FIG. 4. Medians (filled circles) and third quartiles (open circles) of copper, cobalt, barium, lanthanum oxide, lead, zinc and molybdenum contents in the ash of the organic topsoil (A_0) at different altitudes.

According to Millar *et al.* (1965), mature soils support plant growth better than immature soils. This may be reflected in the metal contents of twigs. However, only Zn and Ba contents were found to depend on the altitude (Fig. 5), being generally higher at high altitudes. To get subpopulations of greater size, the altitude is neglected in the subsequent treatments, although this may introduce a small error in the interpretation of Zn and Ba.

Acidity of the organic topsoil

Decreasing pH in A_0 may render metals more mobile. This effect may be stronger on bases than on heavy metals. Thus, a relative enrichment of heavy metals may be expected with decreasing pH. Such an effect is indeed revealed in Fig. 6 for Cu, Pb and Zn. In peats, this influence is very strong for Pb and Zn, whereas Cu shows an inverse behavior. High content of organic acids may affect the dependence between pH and mobility of metals, as indicated by Ong *et al.* (1970), and may accordingly

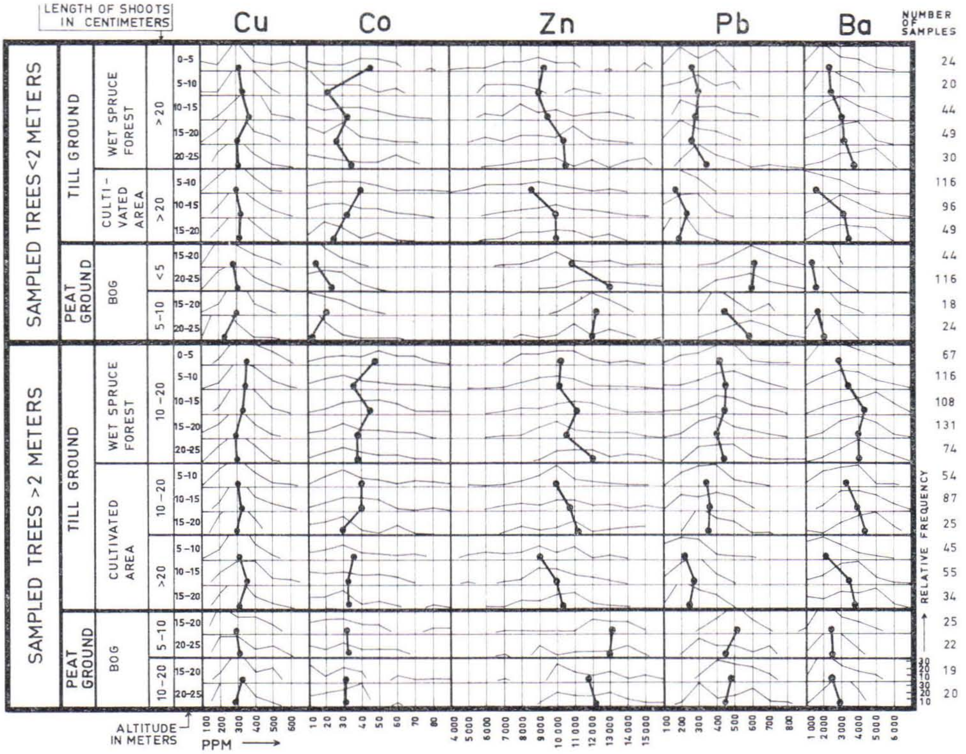

FIG. 5. Medians (filled circles) and frequency polygons of copper, cobalt, zinc, lead and barium contents in the ash of birch twigs at different altitudes.

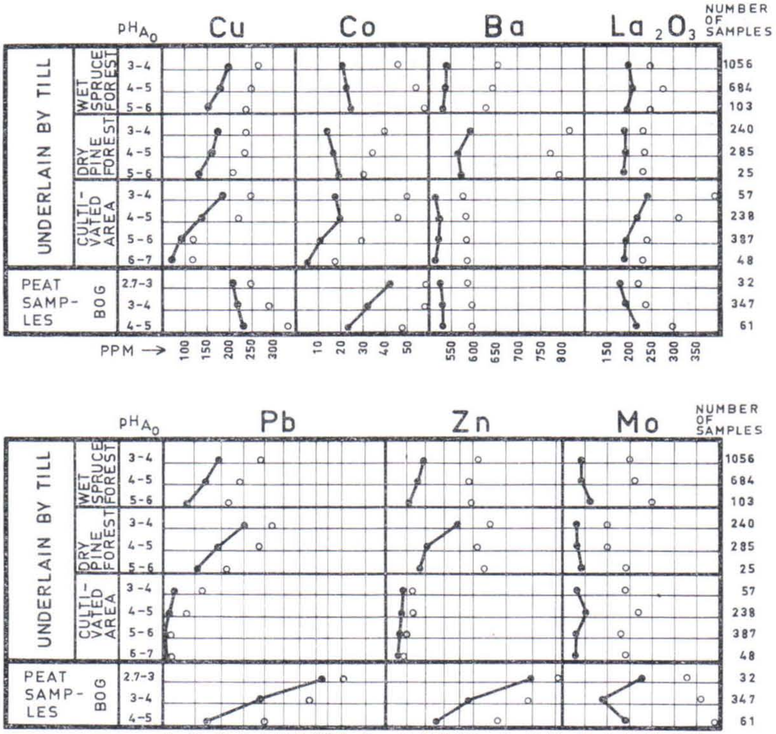

FIG. 6. Medians (filled circles) and third quartiles (open circles) of copper, cobalt, barium, lanthanum oxide, lead, zinc and molybdenum contents in the ash of the organic topsoil (A_0) from different pH (of A_0) classes.

cause the differing behavior of metals in peat. In cultivated areas, the samples were usually seriously contaminated with mineral matter, which may be the reason why the influence of pH on the contents of Pb and Zn in A_0 is weak in this type of vegetation. The median patterns of Co, Ba, La_2O_3 and Mo in Fig. 6 are somewhat random.

Since increasing pH promotes the uptake of macronutrients in plants (Truog, 1953; Millar *et al.*, 1965) and generally decreases the mobility, and hence the availability of heavy metals (Russel, 1961; Sutcliffe, 1962), a relative decrease in the heavy-metal content of the twigs was expected with increasing pH. In Fig. 7 no such relation appears. On the contrary, a positive correlation between the Ba content and pH appears in twigs of trees exceeding 2 meters in height. The great differences between the median values in some vegetation types are apparently due to conditions which have not been noticed in the present study.

pH is neglected in the subsequent treatments of data concerning twigs.

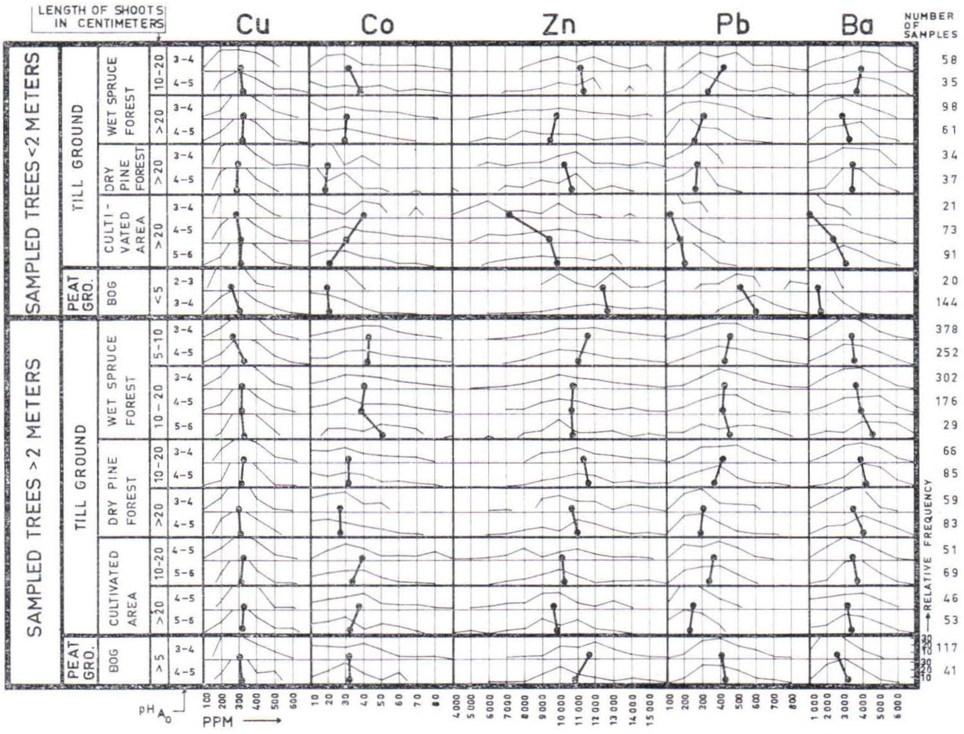

FIG. 7. Medians (filled circles) and frequency polygons of copper, cobalt, zinc, lead and barium contents in the ash of birch twigs from different pH (of A_0) classes.

Type of underlying material

Clay was too infrequent in the sampling area to be considered, and only one subpopulation of twigs over outcrops included more than 10 samples. Peat samples are included to demonstrate the enrichment of Cu, Pb, Zn and Mo in bogs.

Strong leaching of A_0 underlain by sand can be expected to carry bases away more rapidly than heavy metals, thus causing a stronger relative enrichment of the latter over sand than over fine-grained sediments. Such an enrichment over coarse sediments was observed in Kolima, Finland by Kauranne *et al.* (1961). In the present study, the opposite behavior was found for Cu, Pb, Zn and Mo (Fig. 8). It is possible that the organic layer is flushed down by percolating rain water and is contamined with mineral matter more strongly over coarse sediments, resulting in lower metal contents. The difference between the Cu, Pb and Zn contents over different materials disappears at low pH. Regarding Co, Ba and La_2O_3, no systematic difference appears. In these cases the contents are close to the detection limits of the analytical method and the medians are apparently biased.

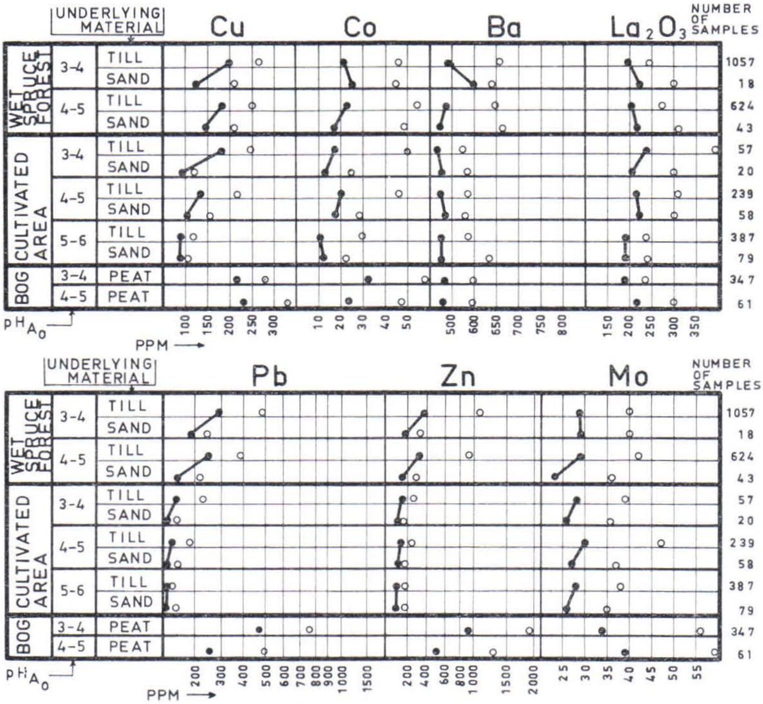

FIG. 8. Medians (filled circles) and third quartiles (open circles) of copper, cobalt, barium, lanthanum oxide, lead, zinc and molybdenum contents in the ash of the organic topsoil (A_0) overlying different material.

In Fig. 9, no systematic relation between type of underlying material and the metal contents of twigs is revealed, but the pattern differs in different environments. As a matter of fact, the sand sediments in the sampling areas are thin, allowing plant roots to penetrate into the underlying till.

Type of vegetation

The subdivision of the environments into four classes is very coarse and is mainly based on the water regime and topography in the area. Forested low-lying areas, where the moisture content of the soil is considerable, are termed wet spruce forests. Environments, where the drainage is impeded, causing waterlogged soils, weak vegetation and the accumulation of peat, are called bogs. Waterlogged areas, where no peat appears, have been included in this class as well. Elevated areas, where the soil is dry and pine usually appears, are termed dry pine forests. Cultivated areas, the fourth class, are used for farming and are therefore usually completely drained.

FIG. 9. Medians (filled circles) and frequency polygons of copper, cobalt, zinc, lead and barium contents in the ash of birch twigs sampled above different types of material.

In Fig. 10, waterlogged areas with no accumulation of peat have been called marshland and are treated separately. Cu, Co and Mo in A_0 have a mutually similar dependence on type of vegetation, being most enriched in peats. Pb and Zn contents are strongly influenced by the type of vegetation, being especially high in bogs (peat) at low pH. A surprising feature is the high Pb, Zn and Ba contents of A_0 in pine forests. Strong leaching, which may carry highly mobile bases away more rapidly than weakly mobile metals, may cause this enrichment. However, this explanation is contradicted by the fact that the other metals do not behave in a similar manner though some of them, for example La, are apparently less mobile than Zn. In cultivated areas, where the topsoil is tilted, A_0 has been mixed with mineral matter and as a consequence the metal contents are low. In marshland, Co, Pb and Zn contents are, for some reason, conspicuously low.

In twigs (Fig. 11), the Zn and Pb contents are usually high in bogs and low in cultivated areas, whereas the Co and Ba contents are low in bogs. The pattern of Co is opposite to that of Zn. The type of vegetation seems to have no appreciable influence on the Cu content.

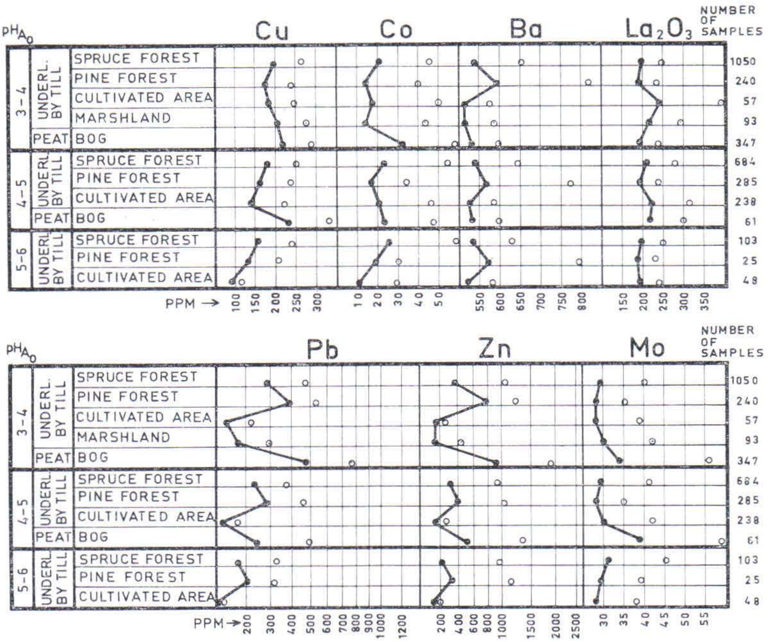

FIG. 10. Medians (filled circles) and third quartiles (open circles) of copper, cobalt, barium, lanthanum oxide, lead, zinc and molybdenum contents in the ash of the organic topsoil (A_0) from different types of vegetation.

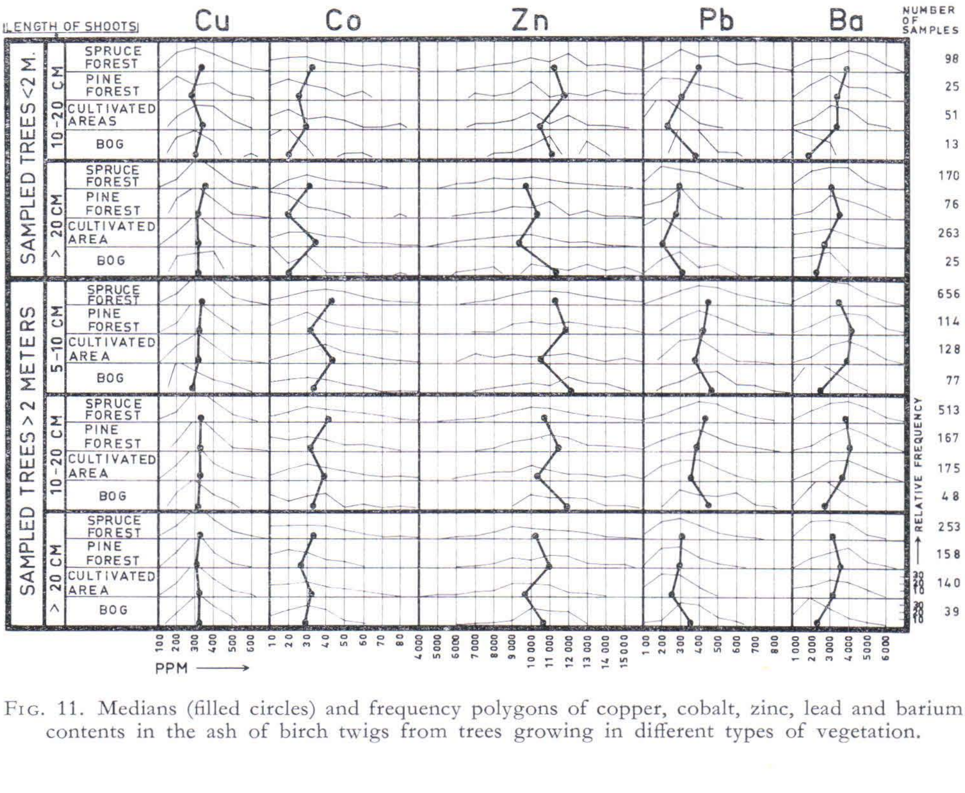

FIG. 11. Medians (filled circles) and frequency polygons of copper, cobalt, zinc, lead and barium contents in the ash of birch twigs from trees growing in different types of vegetation.

Length of sampled shoots

The metals show a very irregular dependence of the length of shoots in short trees (Fig. 12). Nevertheless, the Zn and Pb contents generally decrease with increasing length of shoots.

In trees exceeding 2 m in height the metal contents decrease with increasing length of shoots. This effect is especially noticable for Co, Zn and Pb. Long shoots on a tree apparently indicate a high consumption of macronutrients, which may depress the relative contents of passively absorbed heavy metals.

The slight difference in metal contents between the two intermediate classes is evidently caused by measurement errors. The length of shoots differs considerably on a tree and also on a branch. This is why it is sometimes difficult to decide whether the length of the shoots should be recorded as 5—10 or 10—20 cm.

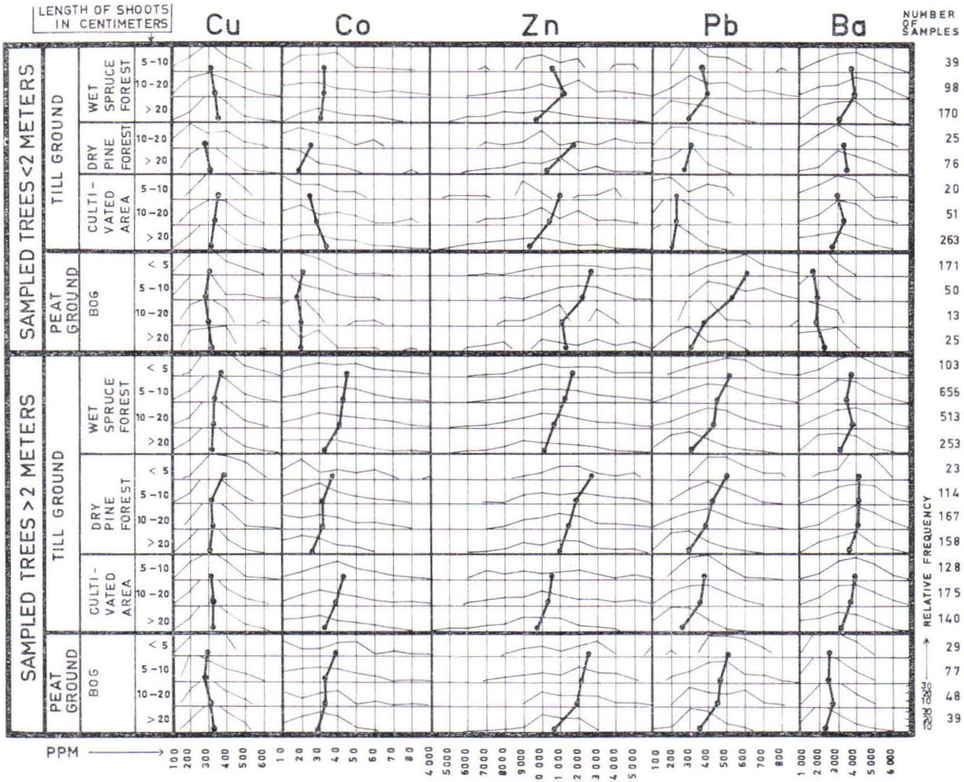

FIG. 12. Medians (filled circles) and frequency polygons of copper, cobalt, zinc, lead and barium contents in the ash of birch twigs with different shoot lengths.

Height of sampled trees

In Fig. 13, Zn has a very random pattern. The Cu content does not vary with varying height of the trees. Co, Pb and Ba occur in higher concentrations in tall trees than in short ones. Pb in twigs with short shoots from bogs makes the most conspicuous exception to this behavior, occurring in lower concentrations in tall trees.

Discussion

The variability of the subpopulation medians in Figs. 4—13 is mostly large. This indicates that there are factors which govern the metal contents in A_0 and in birch twigs. Lack of a systematic correlation between the subpopulation medians and the characteristics examined is more a rule than an exception. Moreover, each metal behaves mainly in an individual manner. However, there are some obvious correlations between the median contents and the characteristics studied.

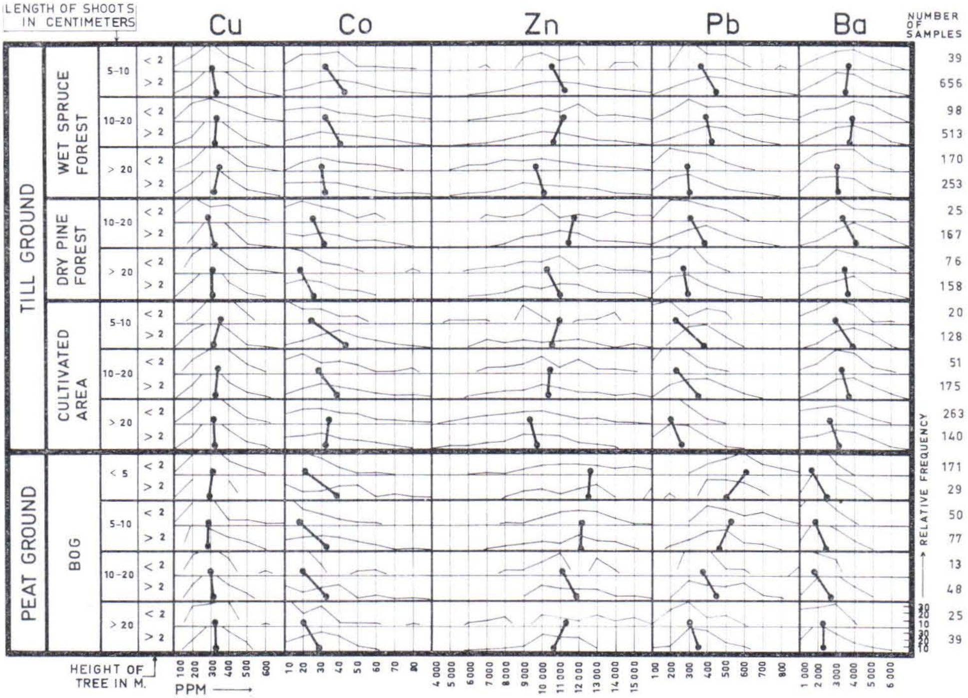

FIG. 13. Medians (filled circles) and frequency polygons of copper, cobalt, zinc, lead and barium contents in the ash of birch twigs from trees of different height.

A_0: The median Ba and La_2O_3 contents have a very slight variability. This is probably due to the fact that the contents are close to the detection limits of the analytical method, which causes large analytical errors and apparently bias as well. The metal contents in A_0, especially of Pb and Zn, are different for different types of vegetation. The Cu, Pb, Zn and Mo contents in A_0 overlying sand are lower than in A_0 overlying till. This fact is probably due to serious contamination with mineral matter in A_0 overlying sand.

When pH decreases two units, the Pb and Zn contents may be doubled in the A_0 of forests and raised three to four times in peat. With decreasing pH, the Cu content increases in forests and cultivated areas but decreases in peat. The ratios between the highest and the lowest median contents of the subpopulations studied are: Zn 19, Pb 8, Co 8, Cu 6, Mo 1.8, Ba 1.4 and La_2O_3 1.4.

Birch twigs: The variability of the median Cu content is very slight. The median contents of all the other metals studied are partly controlled by the type of vegetation. Furthermore, they have a negative correlation with the length of the shoots. The median Co content is considerably lower in short trees than in tall ones. This is valid also for Pb and Ba in most environment. The ratios between the highest and the lowest median contents of the subpopulations studied are: Pb 5, Co 5, Ba 4, Zn 1.8 and Cu 1.7.

APPLICATION OF THE BIOGEOCHEMICAL METHOD IN LEAD PROSPECTING

Transformation of contents

In geochemical mapping of a metal, points on the cumulative frequency distribution of the contents are generally selected as anomaly thresholds. Contents exceeding, for instance, the 90th percentile may be plotted as anomalous.

The 90th percentile of the Pb contents in birch twigs (Fig. 2) is 630 ppm. In Fig. 12, this point is the 52th percentile of the subpopulation in line 9 from the top, but it is above the 100th percentile of the subpopulations in lines 5, 6, 7 and 8 from the top. It is evident that plotting the 90th percentile of the total population would reveal areas with short and slowly growing birches in forests and especially in bogs. Weak anomalies, caused by mineralizations, would be masked by the great natural variability.

The anomaly maps would be more meaningful if the natural variability could be depressed. To decrease the influence of Fe—Mn oxide precipitates on the anomaly patterns of heavy metals in drainage sediments, Horsnail *et al.* (1969) proposed the application of variable threshold levels. In the present case, an analogous treatment could be applied by selecting a threshold percentile and plotting contents exceeding this in each subpopulation. There are, however, two weaknesses in such a procedure:

(1) Plotting would be difficult as the threshold is different in different subpopulations. (2) An equal number of anomalous values would be plotted for each subpopulation although it is evident that a strongly positively skewed distribution is more likely to contain values which are increased by mineralizations.

In the present study, a transformation procedure was applied. The contents in each subpopulation were linearly transformed to give frequency distributions with a common median and a stated mean of the third quartiles. The treatment can be divided into the following steps:

1) In each subpopulation the median is substracted from each of the content values. New subpopulations result, all of which have the median value 0.

2) The difference between the third quartile and the median is calculated for each subpopulation. This value is called the quartile deviation below. The mean of the quartile deviations of all the treated subpopulations is calculated. All the values received in step 1 are divided by the mean of the quartile deviations. This gives populations with a median value of 0 and a quartile deviation of, on average, 1.

3) The values resulting from step 2 are multipled by 100 and added to 400. This gives populations with a median value of 400 and a third quartile of, on average, 500, the latter being greater in populations which have a large quartile deviation before the transformation.

The third step is not necessary but was carried out to get values of the same magnitude as the untransformed contents, making application of a common computer-plotting programme possible. In Fig. 14 (a) and (b), the quartile deviations are plotted against the medians of the original subpopulations. From (a) it is apparent that the quartile deviation in A_0 increases with increasing median. A modification of step 2 which takes this into account was necessary. The median and third quartile were plotted against the midpoint of each pH class in each environment (type of underlying material, type of vegetation). Fig. 14 (c) for A_0 overlying till in wet spruce forests is presented to illustrate the procedure. The lines $Q_2 = 510 - 61\text{pH}$ and $Q_3 = 730 - 74\text{pH}$ are approximated through the medians and third quartiles, respectively. The transformation is performed according to the formula:

$$T_i = \frac{(x_i - 510 + 61\text{pH}_i)\ 100}{(730 - 74\text{pH}_i) - (510 - 61\text{pH}_i)} + 400$$

where x_i is the Pb content of the i:th sample, T_i is the transformed value of x_i, and pH_i is the pH of the i:th sample.

In Fig. 14 (b), the quartile deviation of the Pb content in birch twigs does not increase with increasing median. This fact simplifies the transformation, which is performed according to the formula:

$$T_{ij} = \frac{(x_{ij} - Q_{2i})\ 100}{\bar{Q}} + 400$$

where x_{ij} is the Pb content of the *j*:th sample in the *i*:th subpopulation, T_{ij} is the transformed value of x_{ij}, Q_{2i} is the median (Q_2) of the *i*:th subpopulation, and $\bar{Q}$ is the mean of the quartile deviations of all the subpopulations.

When presenting the transformed values as anomaly maps, each subpopulation contributes to the anomaly pattern with approximately the same weight.

Compilation of anomaly maps

To test the efficiency of the biogeochemical method and the influence of the transformation on the anomaly patterns, sampling area 1 was selected since it is the largest one. Furthermore, the likelihood of finding galena mineralizations in this area seemed to be great. As the variability of the contents (of the transformed ones also) is great, procedures with a smoothing effect were selected when preparing the anomaly maps. Two different methods were used:

1) A computer applied method, where line smoothing was performed with a moving mean over five adjacent sampling sites. To get a denser grid, values were interpolated between the sampling sites. Isovalue contours were then drawn with an on-line x—y plotter. Figs. 16, 18 and 19 were compiled by this method.

2) When compiling Figs. 17 and 20, anomalous contents were plotted with symbols which indicated the degree of anomality. Of the total sampling area, 2—4 % were contoured as high-anomaly areas and 10—20 % as low-anomaly areas, according to the density of highly anomalous (> the median + three quartile deviations) and moderately anomalous (> the third quartile) values, respectively. To avoid a subjective interpretation by the author, persons who were unfamiliar with other facts about the sampling area (location of galena-bearing erratics, etc.) contoured the anomalies.

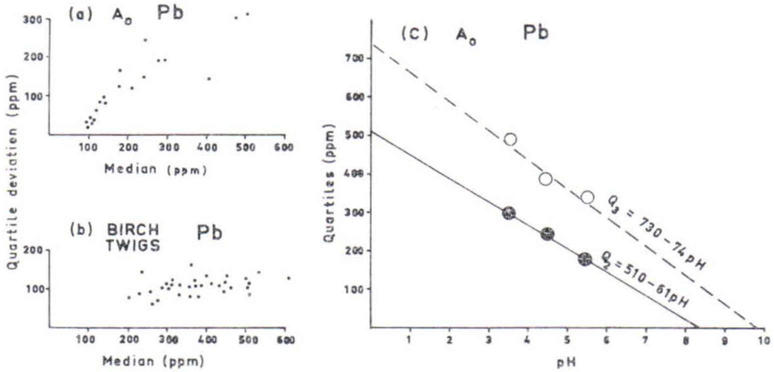

FIG. 14. (a), (b) Relation between the quartile deviation (the difference between the third quartile and the median) and the median of lead contents in subpopulations of the organic topsoil (A_0) and birch twigs, respectively. (c) The influence of pH on the median (filled circles) and the third quartile (open circles) of lead contents in the organic topsoil (A_0).

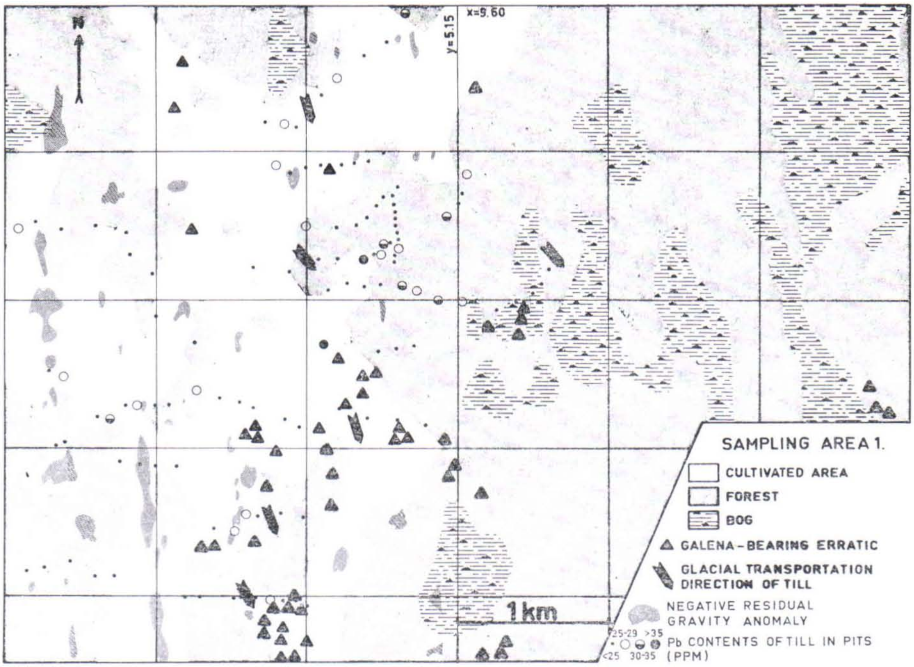

FIG. 15. Vegetation types; ore erratics; negative residual gravity anomalies (to the west of the line y = 5.15); till sampling pits; and anomalous contents of lead in the minus 0.074 mm fraction of the till samples.

Evaluation of anomaly maps

The cluster of galena-bearing erratics located southwest of the center of sampling area 1 (Fig. 15) indicates that there are PbS mineralizations in the vicinity. As the main glacial transportation direction of the till was southward 140—160°, the source of the erratics may be situated west of the center of the area. To the west of line y = 5.15 a gravity survey was carried out. Along the western border of the area, north-trending negative residual anomalies evidently indicate depressions over sheared zones where PbS mineralizations may be situated. In 1970 about 400 till samples were taken from 110 pits in the area. As to the Pb contents of the samples the result was anything but encouraging. However, a slight clustering of samples with weakly anomalous contents occurs in the middle of the area and also in the southwestern part.

Lead anomalies in the organic topsoil

The computer-compiled Pb anomalies in A_0 (Fig. 16) are mainly situated in bogs. This fact could be expected as the Pb content in peat is high, especially where pH

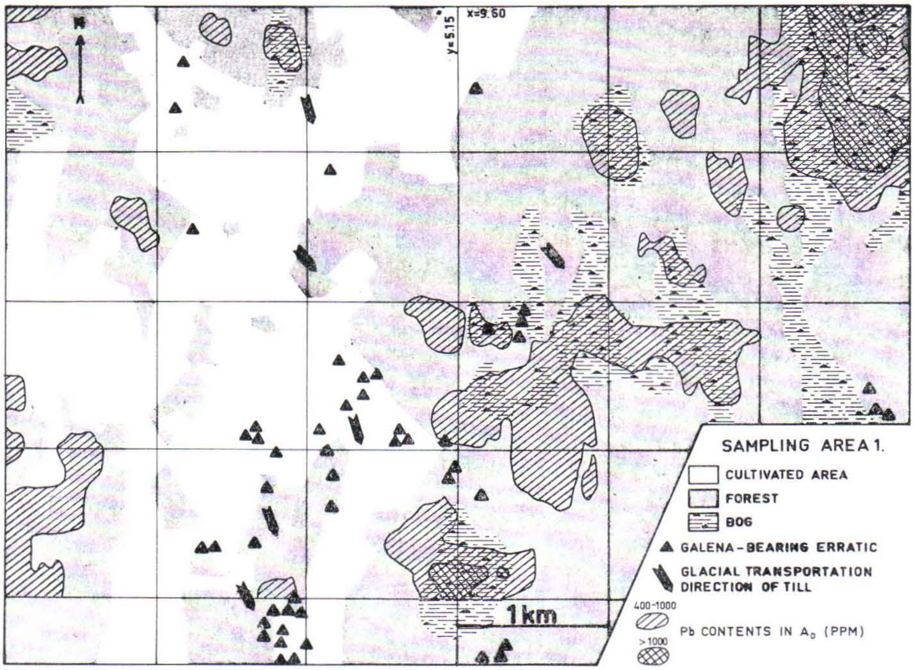

FIG. 16. Lead anomalies in the ash of the organic topsoil (A_0), compiled with moving averages over 50 × 200 m spaced sampling sites and contoured with an on-line x—y plotter. The median is some 220 ppm.

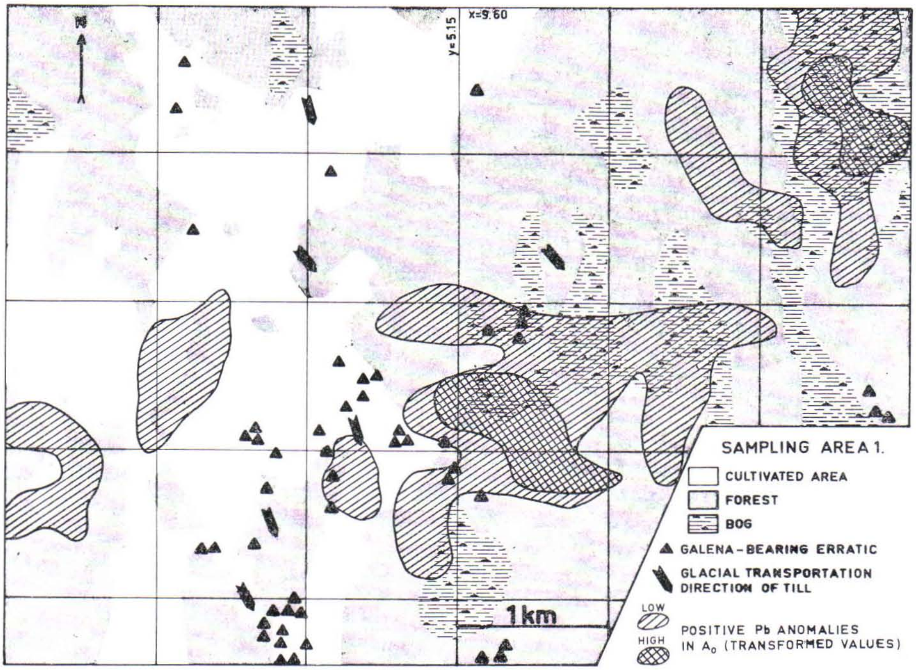

FIG. 17. Anomalies of transformed lead contents in the ash of the organic topsoil (A_0). Clusters of highly anomalous (700) and moderately anomalous (500) values were contoured by hand. The median is 400.

is low (see Fig. 6). However, there are two extensive anomalies, one in the southwest corner and the other just to the southeast of the center of the area, which are situated mainly in forest. The former is partly located on a north-trending line of negative residual gravity anomalies (see Fig. 15). These two anomalies were not eliminated by a transformation of the Pb contents, the result of which is presented in Fig. 17. That one southwest of the center of the area is even strengthened. Yet, this coincidence of the two maps should be regarded with reservations as the anomalies are contoured with different techniques.

The transformation had two considerable effects on the anomaly pattern; (1) several anomalies over bog areas disappeared; and (2) an anomaly appeared in the area where the PbS-bearing erratics are situated and another northwest of it. The strong anomaly in the northeast corner of the area did not change much. A conspicuous feature of the two maps is a zone of anomalies trending northeast from the cluster of ore erratics.

Lead anomalies in birch twigs

An extensive north-trending anomaly in the eastern part of Fig. 18 coincides with the anomaly zone in A_0. About 1.5 km west of the eastern border of the area this anomaly is intersected by a northwest-trending pattern.

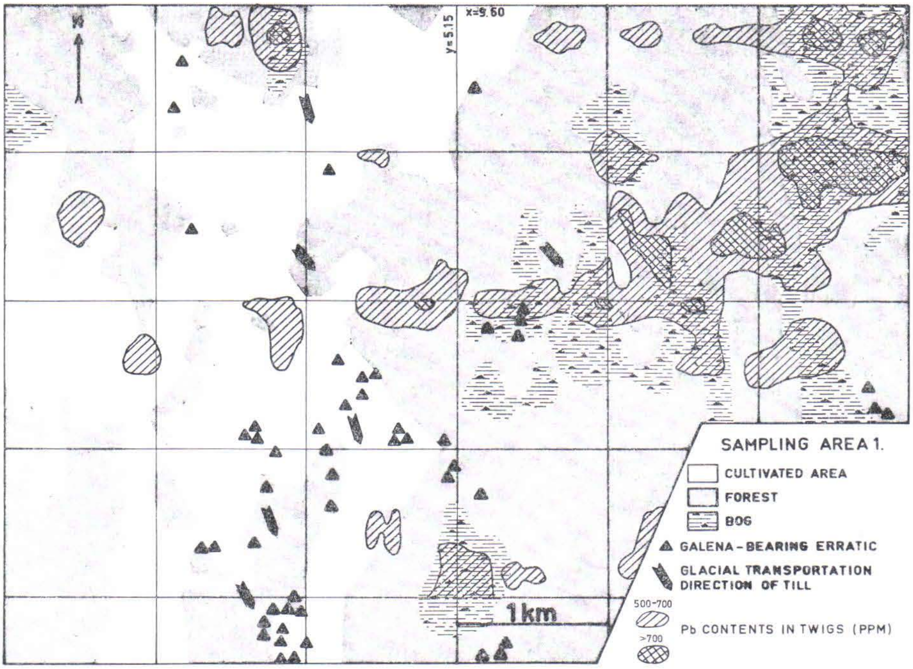

FIG. 18. Lead anomalies in the ash of birch twigs, compiled with moving averages over 50 × 200 m spaced sampling sites and contoured with an on-line x—y plotter. The median content is some 380 ppm.

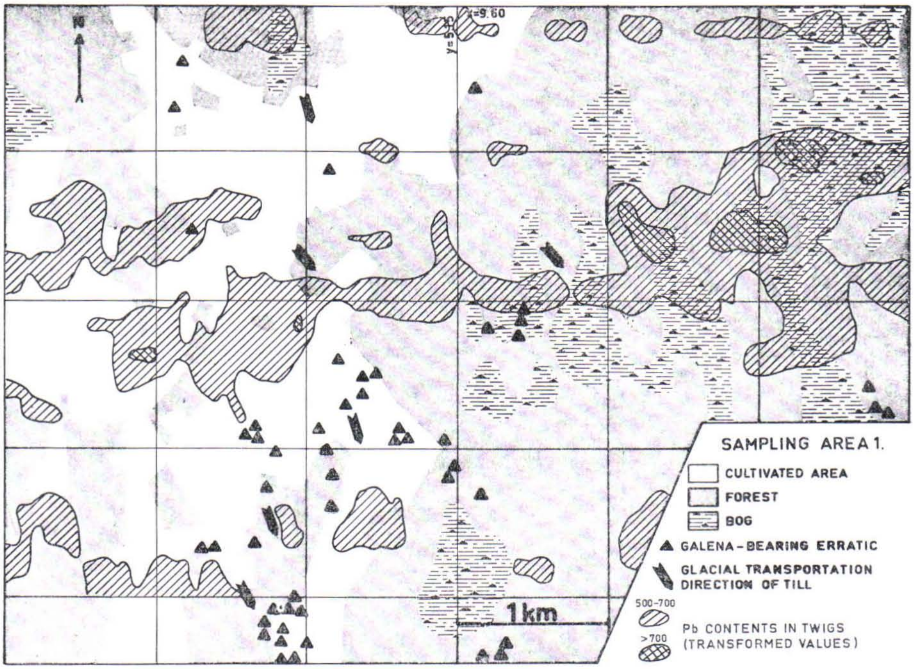

FIG. 19. Anomalies of transformed lead contents in the ash of birch twigs, compiled with moving averages over 50 × 200 m spaced sampling sites and contoured with an on-line x—y plotter. The median value is 400.

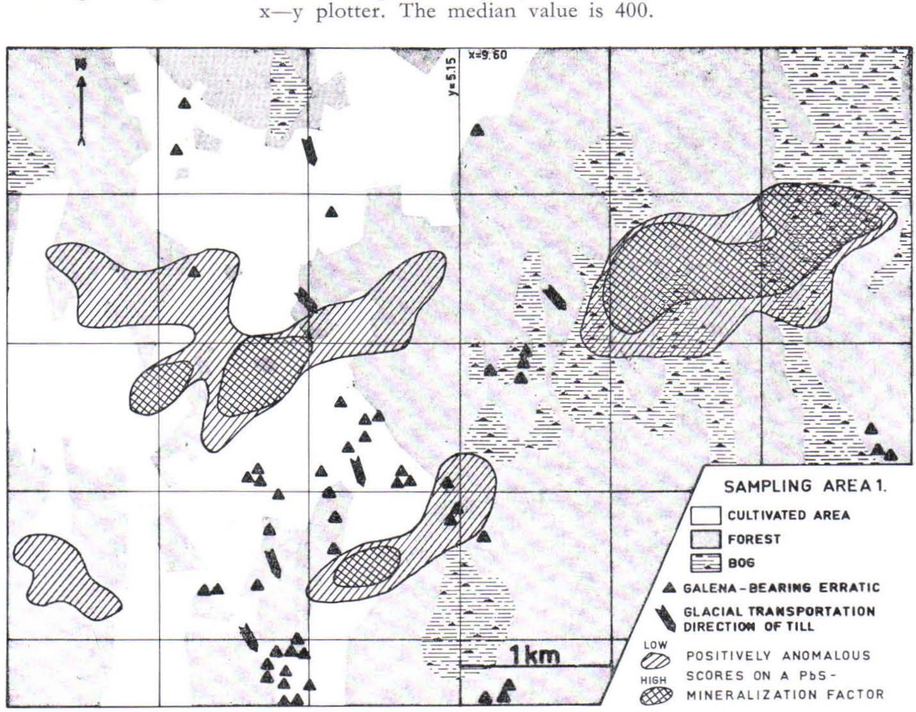

FIG. 20. Ash of birch twigs. Anomalous scores on a supposed PbS-mineralization factor. Clusters of highly anomalous and moderately anomalous scores were contoured by hand.

A remarkable parallelism with the sampling lines occurs near the top of the area and in the central region. Treatment or analytical bias does not satisfactorily explain the phenomenon; a check revealed that samples in the anomalous parts of each of the lines were collected and treated in interrupted series. This parallelism with the sampling lines appears in the anomaly pattern of the transformed contents even more clearly (Fig. 19).

The most visible change in the anomaly pattern caused by the transformation is the appearance of two extensive anomalies northwest of the cluster of ore erratics. This area is where the parent bedrock of the erratics may be situated. In the southwest corner of the sampling area subtle anomalies appeared which partly coincide with anomalies in A_0 (cf. Figs. 16 and 17). About one kilometer west of the eastern border of the area a northwest-trending pattern was more extensive after the transformation, and the anomaly over the bog in the northeast corner partly disappeared.

To check the efficiency of factor analysis in transforming the original anomaly pattern, a probable PbS-mineralization factor (factor 10 in Table 3 c) was selected in each subpopulation (explained on p. 19). After a promax oblique rotation, scores on this factor were calculated and plotted as an anomaly map. A line coincidence similar to that in Figs. 18 and 19 appeared but has been deleted in Fig. 20 by the subjective manual contouring procedure described on p. 27 (method 2). An obvious congruity with Fig. 19 exists despite a considerable difference in the treatment technique. Those anomalies which are situated in the vicinity of the clusters of ore erratics are even more conspicuous in Fig. 20.

Discussion

The anomalies in A_0 partly coincide with those in birch twigs. The most conspicuous identity is a zone of anomalies which trends northeast through the cluster of ore erratics. In this zone, somewhat north-trending bogs are frequent. These may indicate sheared zones in the bedrock. Very few ore erratics have been found in the forested part of this zone but, on the other hand, they are extremely hard to discover in forested areas. A strong anomaly in A_0 southeast of the center of the area does not exist in the birch twigs.

Transformation of the Pb contents did not affect the anomaly pattern in A_0 very much. The effect of the transformation on the anomaly pattern in birch twigs is more obvious. The extensive anomaly in the eastern region of the area shrank and new extensive anomalies appeared northwest of the cluster of ore erratics. The correlation between the anomaly pattern of the transformed contents in Fig. 19 and that of the factor scores in Fig. 20 is striking.

SUMMARY AND CONCLUSIONS

In three areas, covering some 40 km^2, samples of birch twigs and of the organic part of the topsoil (A_0) were collected in a 200 × 50 m grid.

The sampling areas are extensive in comparison to expected mineralizations in the bedrock and anomalies in the glacial drift. Hence, the great majority of the samples obviously reflects background contents. The bedrock is monotonous and therefore the geological control of the variability is evidently slight. Despite large analytical variability of the metal contents it was possible to detect a considerable natural variability. Several characteristics of the samples which are correlated with this variability have been interpreted.

The natural variability of metal contents is greater in A_0 than in twigs. This may be due to varying amounts of mineral matter and varying degrees of decomposition of the organic matter in A_0 in different environments. The Cu, Pb and Zn contents in A_0 and the Pb content in twigs showed the most regular dependence of the characteristics studied. As the biogeochemical method was applied to lead-ore prospecting, the anomaly pattern of lead was studied more thoroughly in sampling area 1. To eliminate that variability of Pb contents which is correlated with the studied characteristics the contents were transformed. This was carried out by; (1) grouping the samples according to combinations of characteristics; (2) calculating medians and third quartiles of the Pb contents in the subpopulations; and (3) standardizing the medians to 400 and the third quartiles to an average of 500. It is evident that the Pb contents were partly transformed in the »wrong» direction, but on average the transformation obviously decreased that natural variability, which is unrelated to mineralizations.

When applying an R-mode factor analysis to the data of birch twigs, a grouping of the samples according to characteristics, measured on a classificatory scale, was necessary before the treatment. For each subgroup, the analysis was performed, an obvious mineralization factor was selected, and the scores on this factor were calculated. The likelihood of selecting an incorrect factor in several of the subgroups is rather great. Scores on erroneously selected factors may have an undesirable effect on the anomaly pattern of plotted factor scores.

The transformation of Pb contents reduced the effect of bogs on the anomaly pattern in A_0, but only weak anomalies appeared in connection with the cluster of ore erratics. After transformation of the contents in birch twigs, conspicuous anomalies appeared northwest of the cluster of ore erratics. In the eastern region of the sampling area, there are anomalies in A_0 and in twigs which partly coincide and which did not disappear in the transformation. Only three PbS-mineralized erratics have been found southeast of these anomalies, but erratics are very hard to find in this part of the area. The north-trending bogs in this part of the area may indicate sheared zones in the bedrock and, hence, lead mineralizations as well.

The pattern of anomalous factor scores is very similar to that of the anomalous transformed Pb contents in birch twigs.

Some general speculations about the biogeochemical method are:

1) In Finland an occurrence containing 100 000 tons of ore with an average content of, for instance, 1 % Cu, 1 % Ni or 5 % Pb may be of economic importance. It is evident that such a deposit gives very weak anomalies in the soil and the anomalies are usually further weakened in the vegetation. Significantly anomalous contents may be 2—3 times the background content.

2) According to Malyuga (1964), Soviet scientists have found that coniferous forests annually return to the soil some 30 tons of ash matter per km^2. This means 1.5 kg of Pb, if the content is 50 ppm. It is evident that the vegetation may transport considerable amounts of a metal over thousands of years. Metals may spread in the vegetation and in the topsoil, thus making the biogeochemical anomalies more extensive.

3) The biogeochemical spread may make the biogeochemical method unsuitable for detailed mapping of weak anomalies in the soil, but it may be an efficient regional ore-prospecting method in areas where other regional methods are unsuitable.

4) The combined analytical, preparation and natural variability may be great as compared to the mineralization variability. Consequently, an anomaly should consist of several samples, until a reliable interpretation can be made.

5) Cluster sampling may be efficient in biogeochemical prospecting. Anomalies are probably sufficiently extensive to be detected with a 500 × 500 meter cluster grid.

6) From the present study it is evident that there are environmental processes which strongly affect the contents of metals in organic matter. Therefore, some form of transformation of contents is necessary when interpreting low-contrast anomalies.

7) In the present study the transformation of the Pb contents seemed to change the anomaly pattern in birch twigs in the »correct» direction, but no definitive conclusions can be made until drilling has been carried out in the area.

8) It would be desirable to find easily measurable characteristics of the samples which are related to the natural variability of the metal contents in a simple manner. According to Warren (1962), the contents of Mn and Fe in plants are more determined by climate and soil pH than by their contents in the underlying soil. Lakanen (1963) stated that available Ca and K usually exist in great excess in Finnish soils. Accordingly, variations in the contents of these elements in plants may reflect external and internal conditions of the plants more than content variations in the underlying soil. Thus, the amount of certain elements in plants may be an indirect measure of different processes. John Ek at the Geological Survey of Sweden has found strong correlations between Pb and several nutrients in birch bark. Transformation of the Pb contents according to these nutrients gave encouraging results (Ek, in preparation).

9) Standardization of the central tendency and spread of contents may be necessary in making samples from different environments comparable. There are also other reasons for using a standardization procedure. In regional prospecting, sampling of different media in different parts of the area may be necessary. Means and standard deviations of the contents in the different media may differ. A standardization procedure may permit plotting on a common map. Furthermore, contents of different metals may be standardized to a common mean and standard deviation, which may make summation and plotting of several metals on a multi-metal map meaningful.

10) Plants may be preferable over the organic layer as a sampling medium in areas where the organic layer is too thin to be sampled without contamination by mineral matter.

11) The variability of contents of passively absorbed metals (e.g. Pb, As, Ti, Ag, Au, Hg and U) in plants may be more easy to interprete than that of actively absorbed metals. Accordingly, passively absorbed metals may be preferable in biogeochemical surveys.

12) The content ratios of certain pairs of metals are often considered to depict ore deposits better than either of the metals separately. Application of content ratios in biogeochemistry implies that the two metals in question are affected by different natural processes in an analogous manner. No pair of metals studied in the present investigation fulfils this condition. Accordingly, a knowledge of the behavior of the metals and a transformation of the contents for both would be necessary, which compounds the problem.

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The ash samples were analyzed by the staff of chemists in the Central Laboratory of the Outokumpu Co. in Pori, with the permission of the head of the laboratory, Mr. Jorma Kinnunen, Ph. M. The data was statistically processed in the Computer Centre of the Outokumpu Co. under the guidance of Mr. Vilho Suokonautio, Ph. M. The factor analysis was carried out in the Ore Prospecting Division of the Geological Survey of Sweden with the permission of the head geochemist, Mr. Charlie Nilsson, Ph. Lic. Mrs. Britt Nairis, Ph. Lic. and Mr. John Ek, Ph. Lic. aided me in the performance and interpretation of the factor analysis.

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