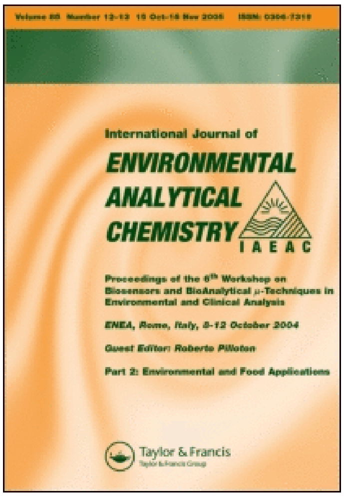

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Pollution of Lakes in a Former Mining and Smeltering Area: Evidence from Successive Extraction and Pollen Analysis of Lake Sediments Part 1. Lake Lissjön

A. Vuorinen[a]; I. Vuorela[b]; S. Welinder[c]
[a] Department of Geology, University of Helsinki, Helsinki, Finland [b] Geological Survey of Finland, Espoo, Finland [c] Department of Archaeology, University of Uppsala, Uppsala, Sweden

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Pollution of Lakes in a Former Mining and Smeltering Area: Evidence from Successive Extraction and Pollen Analysis of Lake Sediments
Part 1. Lake Lissjön

A. VUORINEN,[1] I. VUORELA[2] and S. WELINDER[3]
[1] *University of Helsinki, Department of Geology, Snellmaninkatu 5, SF-00170 Helsinki, Finland*
[2] *Geological Survey of Finland, Betonimiehenkuja 4, SF-02150 Espoo, Finland*
[3] *University of Uppsala, Department of Archaeology, S-75220 Uppsala, Sweden*

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Pollution of lake sediments by heavy metals was studied in a previous mining and smeltering area at Nyberget, Central Sweden. Samples of a lake sediment core were subjected to successive extraction and dissolution kinetics study techniques using 1 M ammonium acetate at pH 7.3 for exchangeable and at pH 4.8 for sorbed and loosely bound elements, and 1 M hydroxylammonium chloride plus 2 M acetic acid for reducible loosely and moderately bound elements. The pollution was studied in connection with environmental history reflected by vegetational changes (pollen analysis) and distribution of charcoal dust particles.

The amounts of loosely and moderately bound metals (especially of Pb, Cd, Ag and Cu) were particularly high in three distinct horizons in the sediments of the Lake Lissjön, which is situated downstream from the pre-existing smeltering site. The input of eroded carbonate-bearing mineral matter into the lake seemed to have neutralized

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acidity of the lake sediments. The anthropogenic pollen data and the amount of charcoal dust correlate well with the metal pollution reflecting environmental history in the area. Besides, the heavy metals were strongly scavenged by Mn oxides on small stones on a streambed nearby the smeltery. The heavy metals, however, had relatively low content and were in rather tightly bound forms in slag fragments sampled from the streambed.

KEY WORDS: Lake sediments, mining and smeltery, heavy metal pollution, successive extraction, pollen analysis, palaeoecology, anthropogenic indicators.

INTRODUCTION

Thousands of small mines have been in use and considerable amounts of metals have been recovered by a number of smelting furnaces in the Bergslagen region in southern Central Sweden.

Environmental effects of the mines have been studied, e.g., by Håkansson[1,2] and Qvarfort.[3,4]

The site of this study is situated in the village of Nyberget in the Bergslagen region (60°29′N, 15°54′E, Figure 1). The onset of settlement at Nyberget followed by agriculture has been documented since about AD 1450. The mine at Nyberget, named Lövåsgruva, has probably been established in the 15th century and referred to in documents since 1549.

The bedrock of the mine area comprises a limestone complex surrounded by porphyric leptite and quartzite. The main ore minerals were argentiferous galena, sphalerite, chalcopyrite and magnetite.[5,6]

Iron smeltery activity adjacent to a stream flowing from Lake Dammsjön to Lake Lissjön has been reported from 1489 to the first half of 17th century.[7,8] In the first decade of 17th century the mine was reorganized, construction works adjacent to Lake Dammsjön for rising the water level about 3 m were carried out and a channel between the two lakes was dug. Thereafter, Pb and Ag were produced by the Lövå mine until the mining was ceased in 1878[5,5] (Fig. 2). Still later, e.g., during 1944–1954, heavy metals were infrequently produced.[6]

The purpose of this study is to assess historical pollution of lake sediments by means of successive extraction and dissolution kinetics study techniques. Sedimentary cores from two lakes, Lake Lissjön and Lake Dammsjön, and fragments of slag and Mn oxides on small stones

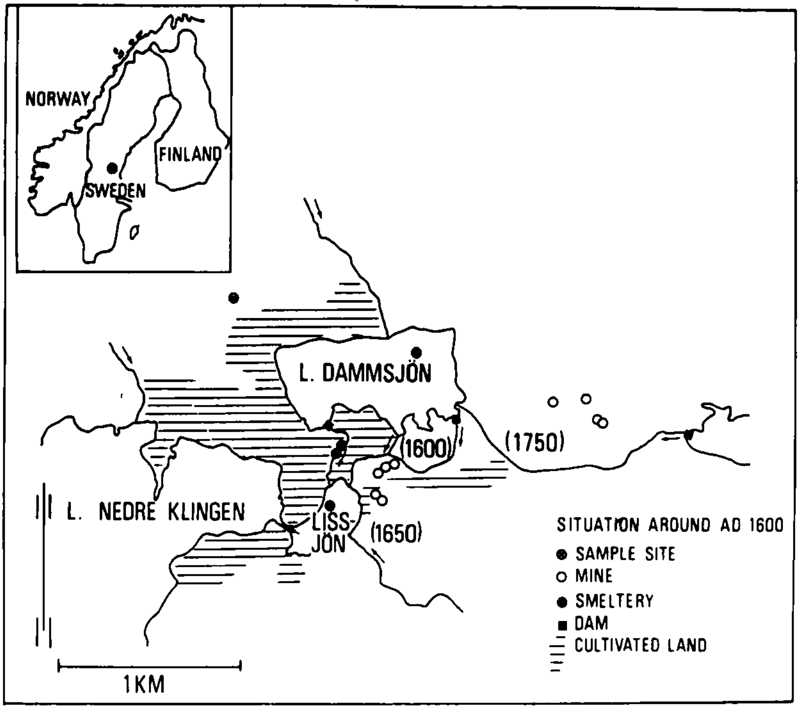


Figure 1 Situation at the village of Nyberget around AD 1600 and the location of sampling sites of the lake sediment cores, the Mn oxide precipitates and the slag fragments.

sampled on a streambed in the vicinity of the pre-existing smeltery were investigated. Besides the chemical evidence, environmental vegetational changes, reflected by pollen and spore data and fire, indicated by microscopical charcoal dust particles are manifested. The results of the investigations of Lake Lissjön, Mn oxides and slag fragments are presented in this paper.

Among the authors, Stig Welinder, familiar with the local circumstances at the village of Nyberget, has given notice to the historical background and is responsible for sampling. Antti Vuorinen is responsible for the geochemical and Irmeli Vuorela for the pollen analytical and charcoal dust investigations.

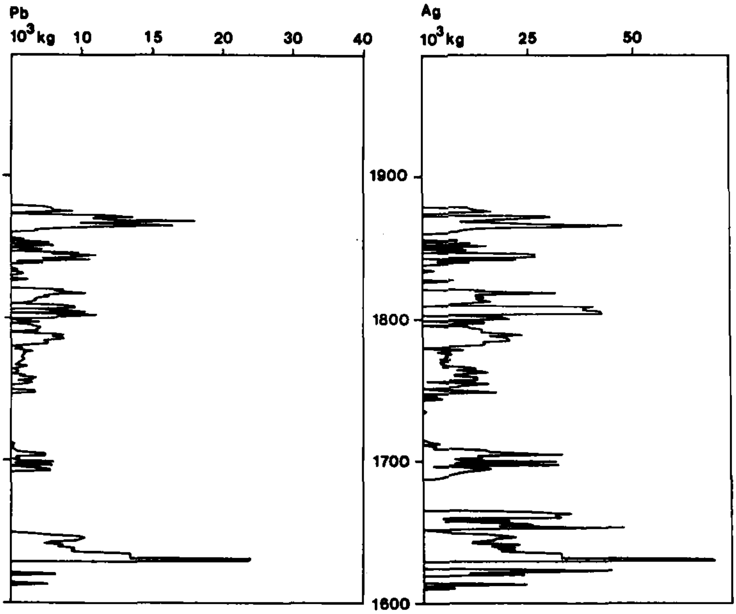


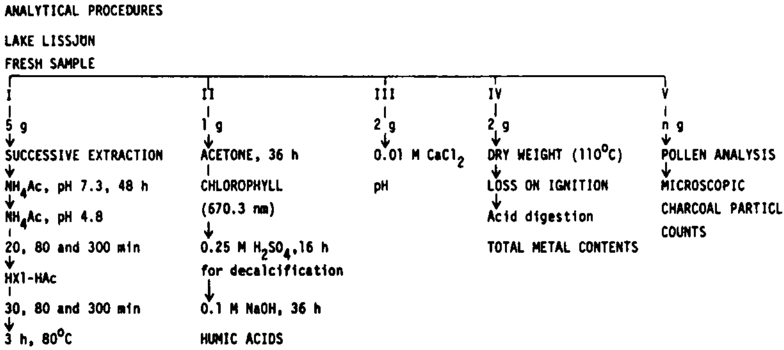
Figure 2 Annual lead and silver production from 1610's to 1878 in Lövås mine (drawn after Tegengren 1924).

MATERIAL AND METHODS

Lake sediments

The lake sediment core was taken using a smaller Russian peat borer. The sediment core was stored frozen after sampling for 4 months. Subsamples were taken at 2 cm intervals from the cores after melting and these were stored further at 4°C and under argon atmosphere before analysis. The sediment material in Lake Lissjön core consists of clay-gyttja. The samples were subjected to analytical procedures presented in Fig. 3.

The samples were extracted in steps I–III in the pre-purified polyethylene test tubes (13 ml; 4–10 ml of extractant) fitted with caps. The tubes were agitated during extraction, centrifuged (15 min, 4000 r min^{-1}), and the extractants were taken for analysis. Thereafter the samples were washed with purified water, and the extraction was continued with a fresh portion of extractant which effectively diminishes



Fe, Mn, Pb, Cd, Cu, Zn, Co, Ni, Cr, Ag, Ca and Mg were analyzed by flame-AAS methods.

NH_4Ac: 1 M ammonium acetate

HXl-HAc: 1 M hydroxylammonium chloride plus 2 M acetic acid

Figure 3 Analytical procedures.

sample acid influence and readsorption of the liberated elements by the sample constituents. pH was measured in the tubes using combined pH electrode. The extractions were performed under argon atmosphere to inhibit O_2 and CO_2 sorption by solutions during the experiments. Distilled and ion-exchanged water (Milli-Q) was used in the experiments. Standard element and buffer pH solutions (Titrisol^R, Merck) were used as reference solutions together with appropriate leachate matrixes. The elements were analyzed by flame-AAS methods.[9,10] Optical density of the humic acid extractants was measured at 422.7, 460.7 and 589 nm using a flow-trough cell, and Ca-, Sr- and Na-hollow cathode lamps, respectively, in modified AAS instrument.[10]

The metal contents leached by the 0.25 M H_2SO_4 from Lake Lissjön sediments were also determined and they correlated well with the concentrations obtained by the successive extraction analysis.

In general, contents of heavy metals (Pb, Cd, Ag, Cu, Zn, Co and Ni) which were dissolved from the lake sediments by the successive extraction corresponded to total metal contents within the analytical accuracy. The relative standard deviation of the determinations was, in all analyses <5%.

For pollen and spore analysis the material was treated with KOH, HF and acetolysis.[13] The concentration values 14 for pollen and charcoal particles ($>20\,\mu m$) were also determined. The relative pollen frequencies are based on 600 AP + NAP.

HYDROUS MANGANESE OXIDES

The Mn oxides on the small stones (85 g) from the streambed were dissolved by a rapid extraction with 10 ml of HX1-HAc to release into solution readsorbed metals. The amount of Mn oxides used in calculations of metal concentrations was obtained by calculating the sum of Mn and Fe (mg/l, Mn 230 000 and Fe 1520) to correspond oxides MnO_2 and FeOOH because of these oxide species (vernadite, -MnO_2 and feroxyhyte, -FeOOH) are the principal Mn and Fe oxide minerals in environments analogous to this study area.[11]

SLAG FRAGMENTS

The slag fragments were purified from Fe and Mn oxide coatings by dissolving with hot HX1-HAc. The fragments were then crushed and extracted with NH_4Ac at pH 7.3 (48 h at 15°C) for exchangeable metals, at pH 4.8 (5, 20, 80 and 160 min) for sorbed and loosely bound elements, with HX1-HAc (5, 20, 40, 80, 160 and 300 min at 15°C and 3 h at 80°C) for reducible loosely and moderately bound metals, with 5% NH_4Cl (10 h at 80°C, followed by HXl-HAc at 80°C, 2 h) for metals in metallic phase, with 1 M NaClO at pH 8.5 (10 h at 80°C, followed by HXl-HAc at 80°C, 2 h) for sulphidic metals, digested with HF for silicate-bound metals, and extracted with acid ammonium oxalate (Tamm's solution) (20 h at 80°C in light) for magnetite which is preferentially dissolved by this reagent.[12] All magnetite, however, was not solubilized.

PALAEOEVENTS IN THE SURROUNDINGS OF LAKE LISSJÖN

The period reflected in the diagrams (Figs 4–6) can be divided into three local pollen assemblage zones (a–c).

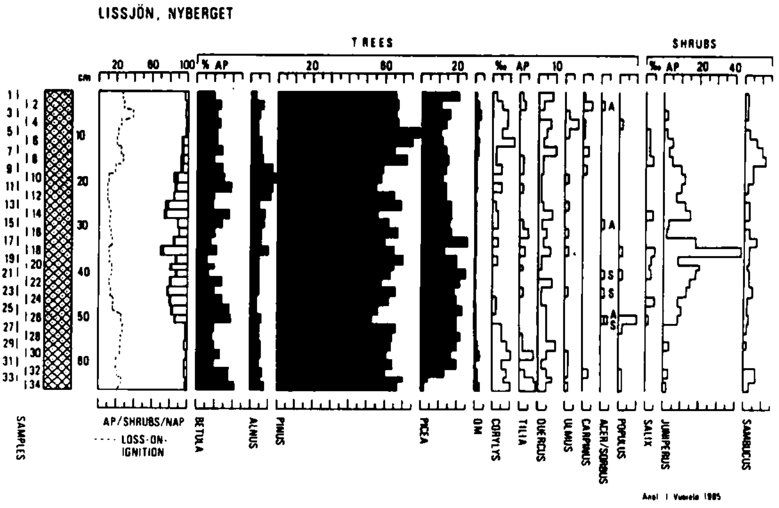


Figure 4 The relative data of tree and shrub pollen and loss-on-ignition values in the sediment core.

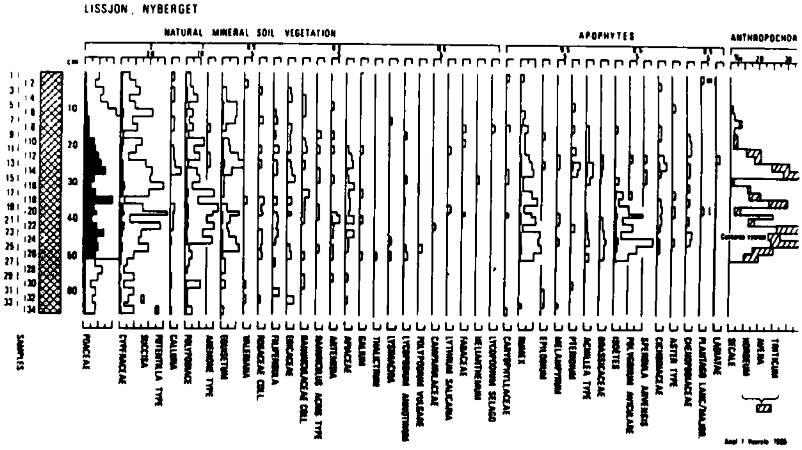


Figure 5 The relative herb pollen data of natural mineral soil vegetation, apophytes and anthropochores.

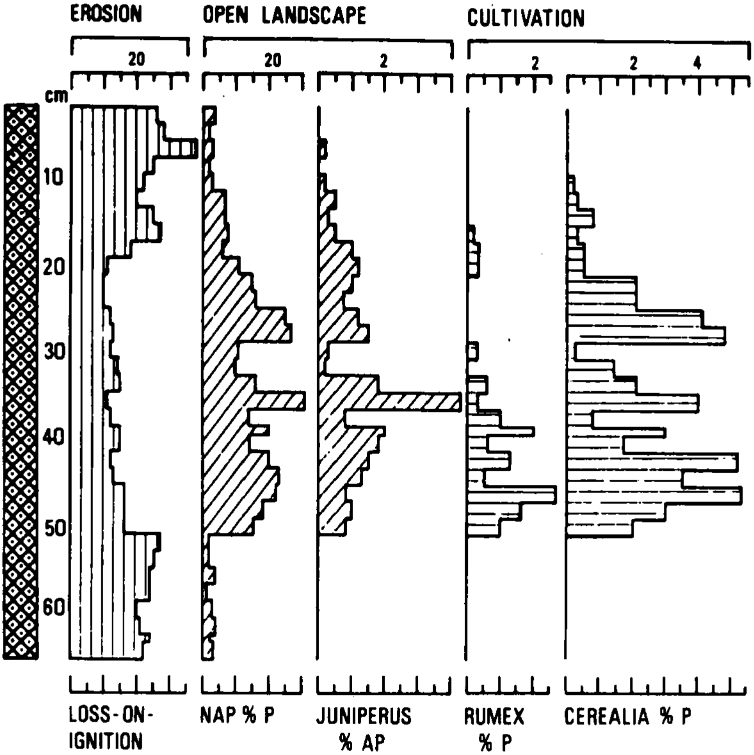


Figure 6 Environmental events reflected by loss-on-ignition values and selected pollen data.

Local p.a.z. (a) (65–51 cm)

The C14-datings of the profile being not available the indication of the invasion of spruce (*Picea abies* L.) to the study area at the depth of 64 cm can be used as a dating event of the profile of Lissjön. According to Pearsson,[15] Moe,[16] Tallantire[17] and Huntley & Birks[18] this event took place around 2500 B.P., in the Late Sub-Boreal/Early Sub-Atlantic chronozone boundary.

For the depths up to ca. 50 cm maximal pollen content (400 000/cm^3) and very scanty herb pollen content are typical (Figs 4–6) and reflect very slow rate of sedimentation (about 0.04 mm/y) and the prevalence of natural shore and forest vegetation in the lake surroundings. The

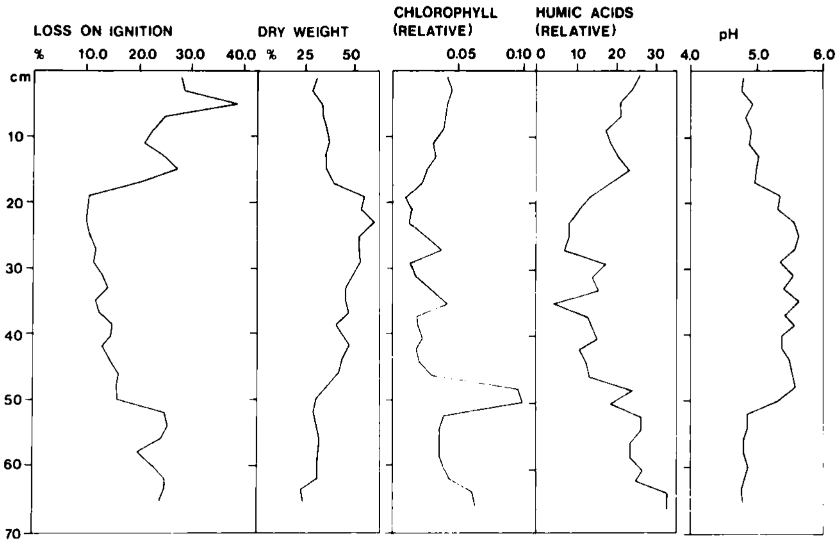


Figure 7 Distribution of loss-on-ignition values, relative chlorophyll and humic acid contents (optical densities at 460.7 and 670.3 nm, respectively, for 1 g of dry sample) and pH (0.01 M $CaCl_2$).

occurrence of charcoal dust and apophyte pollen in this part of the core supposedly reflects natural forest fires.

The QM (broad-leaved deciduous forest) pollen content is highest in the lower parts of the core and decreases upwards indicating climatological degrade which is associated with a decrease in relative chlorophyll and loosely bound Fe, Mn and Mg contents (Figs 7 and 8).

The decrease in the QM (Quercetum Mixtum) species (*Corylus*, *Tilia*, *Quercus* and *Ulmus*) in this pollen assemblage zone thus reflects both climatic deterioration and invasion of *Picea* mainly on the nutrient rich soils previously occupied by broad-leaved deciduous trees. The low herb pollen data (3 %) shows sporadic evidence of man's activity in the area. No anthropochores[19] and only few apophytes (*Rumex*, *Epilobium*, *Melampyrum* and *Pteridium*) were found which all indicate variation in the forest structure probably by fire.[20,21,22,23,24,25]

As regards the simultaneously low frequencies of pollen of natural mineral soil vegetation these pollen types cannot be interpreted as

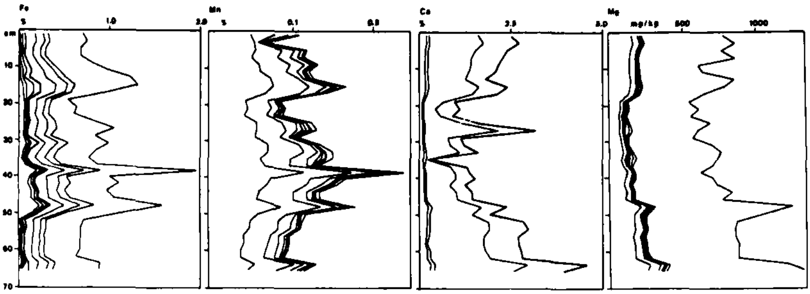


Figure 8 Distribution of the amount of Fe, Mn, Ca and Mg (per dry weight) solubilized in the successive extraction from the sediment core.

settlement indicators but preferably as a reflection of local forest fires, probably also influencing the loss-on-ignition values.

Local p.a.z. (b) (51–18 cm)

Strong human activity in the vicinity of Lake Lissjön is reflected by most of the pollen taxa. Even though the pollen production of surrounding huge forests prevents major anthropogenic fluctuations in the main types of the arboreal pollen data (AP) from being seen, pollen of *Acer*, *Sorbus* and *Populus*, for instance, together with increasing frequencies of *Salix* and *Juniperus* indicate open landscape.[20] A slow decrease of *Picea* together with increasing *Alnus* frequencies towards the late p.a.z. (b) should also be mentioned (Figs 4, 5). The slight increase in *Betula* and *Alnus* pollen is most evidently caused by more intense blooming due to improvement in light conditions (Fig. 4).

The main feature in this pollen assemblage zone is the rapid increase of herb pollen (NAP) at the 51 cm level simultaneously with the chemical evidence of strong human activity in the vicinity of the lake. Among the natural mineral soil vegetation human activity is reflected especially by increasing pollen frequencies of Poaceae, Cyperaceae and Apiaceae and spores of Polypodiaceae and *Equisetum* (Fig. 5). These are accompanied by a rich pollen taxa consisting of Rosaceae coll., *Filipendula*, *Calluna*, Ericaceae, Ranunculaceae coll., *Ranunculus acris* type and *Artemisia*. All these indicate certain grade of deforestation or natural meadows.

Among the apophytes *Rumex* and *Isoëtes* reflect bare mineral soil and erosion of cultivated fields,[26,27,24] indicated also by relatively high Cerealia pollen data. Brassicaceae, Cichoriaceae and Chenopodiaceae are also well represented.

The high proportion of *Secale* (up to 3% P) among the Cerealia refer to the late medieval times.[28,29] The pollen grain of *Centaurea cyanus*, an important weed of rye fields, at the 45 cm level confirms that rye cultivation was done by permanent settlement.[30]

The onset of settlement, land use and agriculture seem to be reflected by carbonate-bearing aluminosilicate matter impact into the lake indicated yy the decrease in biogenic matter (humic acids and loss-on-ignition values), increase in pH (the impact matter has neutralized natural acidity), and by a decrease in exchangeable and loosely bound Mg and Ca contents (Figs 7 and 8). The mineral matter impact is associated with an increase in heavy metal contents (i.e. Fe, Mn, Pb, Cd, Ag, Cu, Zn, Co and Ni; Figs 8–10) released by mining and smeltery activity. The impact is accompanied by an acute increase in the relative chlorophyll content (Fig. 7) which evidently suggests intense eutrophication of the lake (e.g., by an algal bloom) caused by the increased mineral nutrient input into the lake.

The occurrence of charcoal dust in the column influencing the loss-on-ignition values reflects use of fire and wood burning (Figs 4, 6).

The impact of Pb, Cd, Ag and Cu is most intensive at depths of 48–50, 35 and 25 cm, although lesser for Pb and Ag at the depth of 48–50 cm (Fig. 9). The relative chlorophyll content has also maxima at the depths of 35 and 27 cm. The Cerealia and apophyte pollen and charcoal particle

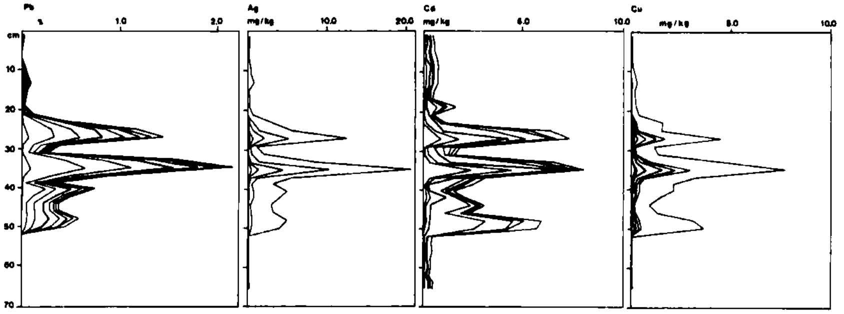


Figure 9 Distribution of the amount of Pb, Ag, Cd and Cu solubilized in the successive extraction from the sediment core

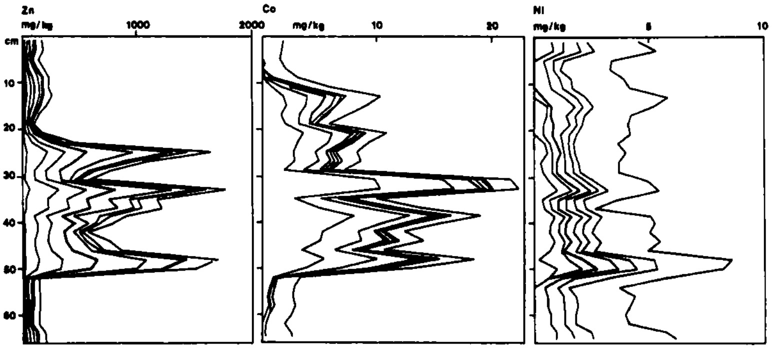


Figure 10 Distribution of the amount of Zn, Co and Ni solubilized in the successive extraction from the sediment core.

contents have distinct maxima at these depths (48–50, 35 and 27 cm), too (cf. Fig. 5 and 6). Maximal contents of Zn, Co and Ni (Figs 17–19) occur in the column later than those for Pb, Ag, Cd and Cu at the depth of 33 cm (for Zn also at the depth of 25 cm). This may indicate different source of these metals or most evidently differences in residence time and transportation mechanisms of the metals into the lake.

The maximum in the amount of loosely bound Ca (NH_4Ac soluble, pH 4.8) at the depth of 27 cm (Fig. 8) seems to reflect carbonate matter impact on Lake Lissjön due to construction works upstream adjacent to the Lake Dammsjön.

Besides mining activities, agricultural practices are also reflected in the ash residue (loss-on-ignition) values of the sediment as well as in considerable frequencies of charcoal dust (Fig. 6). Even though the source area of these components cannot be separated, it is evident that these indicators partly result from the local settlement and agricultural activity.

Local p.a.z. (c) (18–0 cm)

From the depth of 23–21 cm upwards pH is increased and biogenic matter content (loss-on-ignition, humic acids and chlorophyll, Fig. 7) are increased and the heavy metal contents are decreased. These and a decrease in herb pollen taxa suggest reduction in human activity around the lake (Fig. 5).

In this part of the diagram the rapid decrease of cultural indicators is associated with the period following the closing of mining activites and the set-back of agriculture.

This is clearly seen both in the indicator pollen data, in the increasing loss-on-ignition values and in the declining concentration values of charcoal particles. Decreasing rate of sedimentation as a result of minor erosion is also reflected in the pollen concentration values.

Minor changes are also recorded in the relative tree pollen frequencies. The most distinctive of these is the reoccupation of broad-leaved deciduous trees (Fig. 4), a phenomenon which shows that climatic factors do not prevent this group of tree species from still being established in the area. This group seems to have reinvaded the nutrient-rich abandonned areas in the first place while *Picea* being ecologically slower[31] and still suffering from the local human activities maintained its former position only along with a longer period.

These events are also associated with an appearance of carbonate-bearing Fe oxides in sediments with increased contents of Mg, Mn, Co, and to a lesser extent of Pb and Zn (Figs 8–10). The appearance of Fe oxides is supposedly caused by seasonal and biogeochemical processes leading to dissolution of Fe oxides in the lake surroundings and migration of Fe into the lake.[32,33,34]

Manganese oxides

The amounts of heavy metals scavenged by the MnO_2-oxides on stones from the streambed (mg/kg: Ag 8.1, Cd 45, Cu 21.8, Pb 7550 and Zn 26950) (Table I; the stream flows from Lake Dammsjön into Lake Lissjön through the pre-existing smeltery area) seem to be too high to be

Table I The contents of Zn, Pb, Cd, Ag and Cu in Mn oxides on small stones from streambed nearby the previous smeltery.

MG/KG	*Zn*	*Pb*	*Cd*	*Ag*	*Cu*
HX1	23410	640	15	1.6	4.0
HX1-HAc	3540	6910	30	6.5	17.8
Total	26950	7550	45	8.1	21.8

originated simply from the mining activity, and seem thus mainly to be released by the smeltery as a consequence of a secondary enrichment of the metals by the Mn-oxides. The extraordinary high enrichment of Zn by the Mn-oxides seems to be due to a short-distance transport of the metal released by the smeltery which suggests the difference in transportation mechanisms of Zn and the delay of its impact into Lake Lissjön sediments as compared with Pb, Ag, Cd and Cu (Figs 9, 10). A maximal Pb content of ca. 100 mg/kg was found in the peat profile which was sampled to the north-west from the Lake Dammsjön (Fig. 1).

Smeltery slag fragments

In spite of the lack of documented Pb, Ag and Cu production at Nyberget, the former primitive iron smeltery must have caused considerable pollution because the ores of the Lövå mine contained besides Fe oxides (e.g., magnetite) remarkable amount of As-bearing Fe-, Pb- and Zn-sulphides.[5,6] The distribution and mode of occurrence of the heavy metals in slag fragments from Nyberget suggest that the sméltering processes resembled modern (sulphide-bearing) oxidic iron ore smelting. The Fe content and, especially the Cu, Pb, Zn, Co and Cd contents are rather low in the slag. This seems to be due to vaporization of the volatile metals (e.g., Pb, Cd and Zn) and to dissolution of the metals into generated iron smelt as they do in modern processes. The metallic Fe of the magnetite smelt may have reduced ZnO into metallic Zn which was driven off from the smelt.[35] If the sulphidic ores were roasted before smelting, still higher amounts of heavy metals were vaporized into the smeltery surroundings. The vaporized Zn is readily oxidized and the observed delay in Zn migration into Lake Lissjön as compared with Pb, Cd, Ag and Cu might partly be due to the rather low solubility of ZnO in natural waters as well as to the behaviour of Zn in the smelting process. According to the metal specification in the slags, Fe is still in sulphidic phase in the greenish silicate slag (Fig. 11), and in silicate and magnetite phases in the magnetite-bearing slag. Plenty of Cu, Co, Cd and Pb occur in sulphidic phase and in metallic or oxidic phase in the silicate slag (Zn and, to a lesser extent Pb are in sorbed and metallic or oxidic phase and part of Cd occurs in silicate phase). A lot of Cu, Co, Cd and Pb is still in sulphidic phase and Zn, Pb, Co and Cd

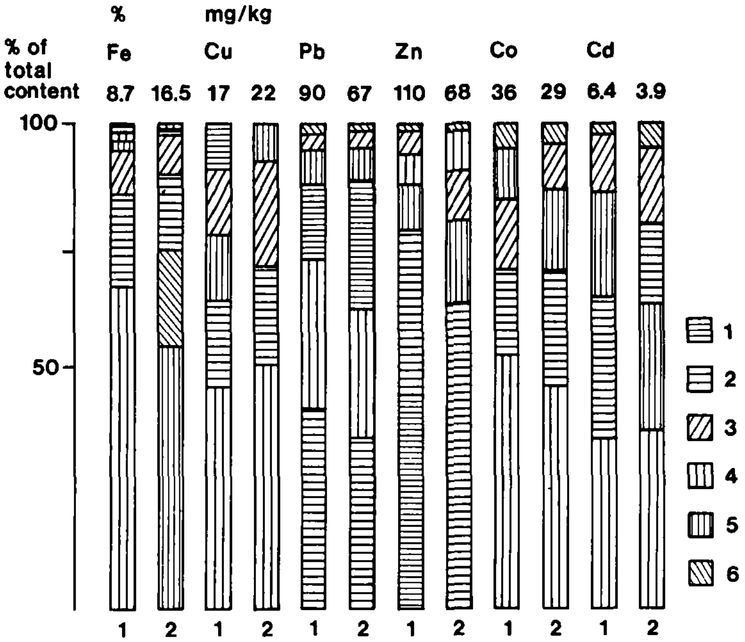


Figure 11 Heavy metal contents and speciation (% of total contents) in the greenish silicate (1) and magnetite-bearing (2) slag fragments from Nyberget.

1. NH_4Ac at pH 4.8 for sorbed and loosely bound metals.
2. HXl-HAc for oxidic and reducible loosely and moderately bound metals.
3. 5% NH_4Cl, followed by HXl-HAc for metallic and sulphidic metals.
4. 1 M NaClO, followed by HXl-HAc for metallic and sulphidic metals.
5. HF-digestion for silicate bound metals.
6. Acid ammonium oxalate (Tamm's reagent) for partial magnetite dissolution.

occur also in metallic or oxidic phase in the magnetite-bearing slag. Loosely bound Pb is also present.

The contents of Pb, Ag, Cd and Cu in slags from Nyberget, however, seem to be too low to produce by any mechanisms the observed high acute contents in the three horizons of Lake Lissjön sediments. The metals seem also to be present in a too tightly bound form in the slags to become dissolved under the prevailing conditions and to be transported into the lake.

DISCUSSION

Evidence of pollen analysis

Pollen analysis as a means of archaeometric investigation has since 1960's been increasingly used for searching ancient anthropogenic activities [24,30,36,37] (and literature cited). The evidence found in the sediments of Lissjön mainly represent the settlement of this area, water being the main way of transportation.[38] This is the case especially for most of increasing minerogenic matter and charcoal dust found in connection with pollen evidence of agriculture. The present investigation, however, seems to indicate that a considerable proportion of pollen may be transported by water in addition to field erosion by wind.[39]

FATE OF HEAVY METALS AT NYBERGET

The metals at the depths of the impacts were in loosely bound form in following order: Pb, Cd, Cu, Ag and over 50 % of Pb and Cd was soluble in the NH_4Ac and the rest and Ag and Cu in the HXl-HAc. Pb, however, was not soluble in the 0.25 M H_2SO_4. The high portion of loosely bound Pb resembles that of air-borne Pb around a highway in Southern Finland, where over 70 % of total Pb was in NH_4Ac soluble form in particulate matter accumulated in snow, in lichen and in humic soil matter,[32] whereas the air-borne traffic Pb was mainly in HXl-HAc soluble form in lake sediments nearby.[10] Smithsonite ($ZnCO_3$), willemite (Zn_2SiO_4), cerussite ($PbCO_3$), pyromorfite/$Pb_5(PO_4)_3Cl$/ and anglesite ($PbSO_4$) have been reported to be soluble in ammonium acetate at pH 4.5.[40] PbO is also soluble in NH_4Ac at pH 4.8.[10]

Despite the pollution of the lake sediments by heavy metals, the Pb and Ag contents in Lake Lissjön sediments show no correlation with the production of these metals in Lövå mine (Fig. 2) (the smeltery was located during the production period from about 1610 to 1878 ca. 2.5 km to the south from the mines,[5] and metal impacts especially at the depths of 35 and 27 cm seem to be too acute to be caused simply by the mining activity. The humic acids also differ at the depths of 35 and 27 cm from the other humic compounds in the column: they show high grade of polymerization and rather low content (Figs 7 and 12).

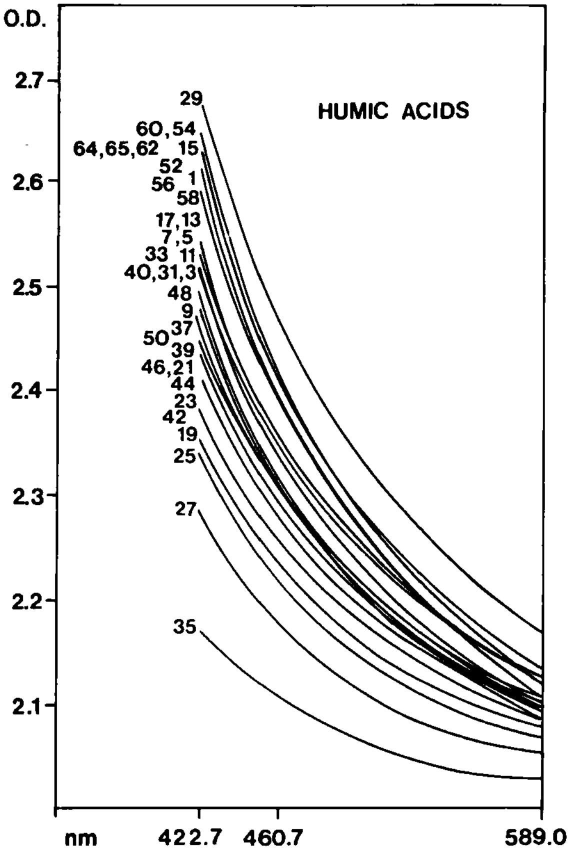


Figure 12. The optical density of humic acid extractants *vs.* wavelength of the samples from different depths (cm) of the sediment core.

Hence the heavy metals seem to be released most probably by the primitive sulphide-bearing iron ore smeltery which located adjacent to the stream draining into Lake Lissjön.[8]

In general, the anthropogenic Pb is observed to occur in lake sediments in loosely and reducible loosely bound fractions of successive extraction.[10] A surface enrichment of Pb on fly ash emitted from a conventional coal combusting power plant was observed by Keyser *et al.*[41], whereas Fe showed no surface enrichment. This was considered to support the hypothesis that the more volatile elements, or their compounds are vaporized during combustion and then condensed on the surface of particles at lower temperature. Following order of metal enrichment in aerosols emitted by metal smelteries has been observed[42]: Cd, Pb, Cu, Zn and Cu, Zn, Cd and Pb have been observed to occur mainly in metallic and oxide form in dry technogenic dust[4320] (Pb occurred also in sulphidic, sulphadic and in water-soluble form). On the other hand, elevated Pb contents in the vicinity of refineries were attributed mainly to increase in Pb associated with larger particles which settle relatively rapidly.[44,45] As a rule, the metals deposit rapidly from aerosols, and the increase in pH and the concentrations of emitted Pb and Cd in topsoils decrease rapidly with distance from the emitter.[45,46] Zn showed a steeper relative rate of declination in concentration with distance from a lead smelter than Pb or Cd.[45] Part of the loosely bound metals (soluble in the NH_4Ac at pH 4.8) may have been carbonate bound in sediments since Jorgensen and Willems[47] reported that metallic lead rapidly transformed into lead compounds in the soil environment. The main transformation products were hydrocerussite /$Pb_3(CO_3)_2(OH)_2$/, cerussite ($PbCO_3$), and (less commonly) anglesite ($PbSO_4$).

As high as 11 830 mg Pb/kg contents were observed in dust emitted from an emergency stacks of a staff furnace in a copper smelter,[48] and over 1000 mg Pb/kg was reported in soil B horizons near pre-existing Cu-Pb-Zn smelteries and charcoal furnaces at Östra Born and Löa in Sweden, respectively.[3] In the area, lakes Norrsjön and Sörsjön drain almost the whole mining area, but only small part of elements from mining area are present in lake sediments, whereas the sediments are contaminated over a wide area downstream. In addition, Pb was enriched in the top zone of the lake sediments. In contrast, the metals in present study show only subordinate content in the topmost sediments.

On the other hand, sulphidic tailings in the mining area comprise a source for pollution. Maximal contents of heavy metals (in mg per g, dry weight: 150 Zn, 0.4 Cd, 14 Cu and 50 Fe) were found at depths of 3–4 cm in Lake Gruvsjö sediments at Bersbo, Sweden, where there have been mining activity since 14th century, and poor copper ore ($< 1\%$ Cu) was dumped around the mainshafts in large waste tips containing sulphides of Cu, Zn, Cd, Pb and Fe.[49] The metals were considered to have released during 1920–1930 from the wastes when these were crushed to obtain

Cu. Pb and Zn has been produced also later in Lövås mine, e.g., during 1944–1954,[6] but no metal enrichment is observed in the topmost sediments of the Lake Lissjön.

The migration of contaminants, released by oxidation of sulphidic tailings would, however, be effectively hampered by neutralization reactions with carbonates present at Nyberget, because in an aquifer, the glacio-fluvial deposits of which contained 1% calcite proved sufficient in retarding the contaminant plume to less than one percent into groundwater.[50]

CONCLUSIONS

At the village of Nyberget, historical human activity is reflected by the chemical evidence and vegetational changes indicated by pollen data and charcoal dust content in the sediments of Lake Lissjön. The results are in agreement with mineral matter impacts into the lake, caused by soil and field erosion and with heavy metal impacts obviously caused by previous mining and smeltering activity. Natural acidity of the sediments was neutralized by the carbonate-bearing mineral matter impacts.

The heavy metal pollution caused by previous mining and smeltering activities was, in particular, reflected in three distinct horizons of loosely and moderately bound metals (especially Pb, Cd, Ag, Cu and Zn) in sediments of Lake Lissjön situated downstream from the pre-existing primitive iron smeltery.

High amounts of metals were scavenged by Mn oxides on small stones on a streambed nearby the smelter. In contrast, the metals had a relatively low content and were rather tightly bound in fragments of slag which were sampled from the streambed.

The distribution and mode of occurrence on the metals in materials investigated suggest that the most prominent and acute contamination in the area was caused by the metals released and distributed in the environment by the smelting processes. The mining activity and oxidation of sulphidic tailings, on the other hand, seem to have caused more likely a lesser, long-time pollution by a gradual flux of metals into the lake sediments.

REFERENCES

1. L. Håkansson, *Naturvardverket*, Rapp. SNV PM 839, 92, 155 pp. Uppsala, Sverige (1977).
2. L. Håkansson, *Naturvardverket*, Rapp. SNV PM 1398, 242 pp. Uppsala, Sverige (1981).
3. U. Qvarfort, *Striae* **7**, 1 (1977).
4. U. Qvarfort, *Bull. Geol. Inst. Univ.* Uppsala **10**, 111 (1984).
5. F. Tegengren, *Sver. Geol. Unders. Ca* **17**, 1 (1924).
6. N. Pilava-Podgurski, *Geol. Foer. Foerh.* **79**, 179 (1957).
7. E. Liljeroth, *Dalarnas hembygdsbok*, pp. 107 (1946).
8. Å. Hyenstrand, *Jernkontorets Forsk.*, Stockholm H 14, 1–78 (1972).
9. A. Vuorinen, R. Uusinoka and Pl Alhonen, *Bull. Geol. Soc. Finl.* **55**, 141 (1983).
10. A. Vuorinen, P. Alhonen and J. Suksi, *Environ. Pollut. Ser.* **A41**, 323 (1986).
11. A. Vuorinen, *Geologi* **6**, 95 (1985).
12. T. T. Chao and L. Zhou, *Soil Sci. Am. J.* **47**, 225 (1983).
13. K. Faegri and J. Iversen, *Textbook of Pollen Analysis* (Munksgaard, Copenhagen, 1975), 295 pp.
14. J. Stockmarr, *Pollen et Spores* **4**, 615 (1971).
15. C. Persson, *Geol. För. Stockholm Förh.* **88**, 361 (1966).
16. D. Moe, *Botaniska Notiser* **123**, 61 (1970).
17. P. A. Tallantire, *Journal of Biography* **4**, 219 (1977).
18. B. Huntley and H. J. B. Birks, *An atlas of past and present pollen maps for Europe: 0–13 000 years ago*, Cambridge University Press, 1-667 (1983).
19. K. Linkola, *Acta Soc. Fauna Flora Fennica* **45(1)**, 1 (1916).
20. V. Kujala, *Comm. Inst. Quaest. Forest. Finlandiae* **10**, 1 (1926).
21. E. Oinonen, *Acta Forest. Fennica* **83(1)**, 1 (1967a).
22. E. Oinonen, *Acta Forest. Fennica* **83(2)**, 1 (1967b).
23. E. Oinonen, *Acta Forest. Fennica* **87**, 1 (1968).
24. K.-E. Behre, *Pollen et Spores* **23**, 225 (1981).
25. P. D. Moore, A. T. Evans and M. Chater, in: K.-E. Behre (ed.), *Anthropogenic indicators in pollen diagrams*, 209, Rotterdam (1986).
26. I. Vuorela, *Memoranda Soc. Fauna Flora Fennica* **56**, 13 (1980a).
27. I. Vuorela, *Annales Botanici Fennici* **17**, 144 (1980b).
28. S. Welinder, *Acta Archaeologica Lundensia, Ser. im* 8°*Minore* **4**, 1 (1975).
29. H. Göransson, 99 in: T. Sjovold (ed.), *Introduksjonen av jordbruk i Norden*. Det Norske Videnskaps-Akademi (1982).
30. I. Vuorela, 53 in: K.-E. Behre (ed.), *Anthropogenic indicators in pollen diagrams*. Rotterdam (1986).
31. O. Heikinheimo, *Acta Forestalia Fennica* **4**, 1-264 (1915).
32. A. Vuorinen, *Int. Conf. Heavy Metals Environ.* 1983, Heidelberg, Proc., pp. 159–162.
33. A. Vuorinen and L. Carlson, *Int. J. Environ. Anal. Chem.* **20**, 179 (1985).
34. A. Vuorinen and P. Lahermo, 403–408 in: R. Perry, R. M. Harrison, J. N. B. Bell and J. N. Lester (eds.) *Acid rain: scientific and technical advances*, Selper Ltd, London (1987).

35. M. M. Shvartman, R. I. Shabelina and V. A. Kukoev, *Izv. Akad. Nauk SSSR, Metally* **2**, 12 (1986).
36. B. E. Berglund, *Oikos Suppl.* **12**, 9 (1969).
37. K.-D. Vorren, 1–18 in: K.-E. Behre (ed.) *Anthropogenic indicators in pollen diagrams*, Rotterdam (1986).
38. K. Tolonen, A. Siiriäinen and R. Thompson, *Ann. Bot. Fennici* **12**, 161 (1975).
39. I. Vuorela, *Bull. Geol. Soc.* Finland **55(1)**, 25 (1983).
40. E. C. Fonseca and H. Martin, *J. Geochem. Explor.* **26**, 231 (1986).
41. T. R. Keyser, D. F. S. Natusch, C. A. Evans, Jr. and R. W. Linton, *Environ. Sci. Technol.* **12**, 768 (1978).
42. V. V. Dobrovol'skij, Tyzhelye Metally v Okryzhayushshej Srede (Izd. Moskovskogo Universiteta, Moscow, 1980), p. 6.
43. M. A. Glazovskoj, Geokhimiya Tyzhelyh Metallov b Prirodnyh i Tehnogennyh Landshaftah (Izd. Moscovskogo Universiteta, Moscow, 1983), pp. 138–150.
44. J. J. Paciga, T. M. Roberts and R. E. Jarvis, *Environ. Sci. Technol.* **9**, 1141 (1975).
45. B. Cartwright, R. H. Merry and K. G. Tiller, *Aust. J. Soil Res.* **15**, 69 (1976).
46. G. Tyler, *Ambio* **13**, 18 (1984).
47. S. S. Jorgensen and M. Willems, *Ambio* **16**, 11 (1987).
48. B. Glowiak, A. Zwozdziak and J. Zwozdziak, *Environ. Protect. Eng.* **5**, 145 (1979).
49. C. E. Lundholm and L. Andersson, *Ambio* **14**, 167 (1985).
50. K. Morin, J. Cherry, T. Lim and A. Vivyrka, *Can. Geotech. J.* **19**, 1 (1982).