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HYDROGEOCHEMICAL EVOLUTION OF AN INACTIVE PYRITIC URANIUM  
TAILINGS BASIN AND RETARDATION OF CONTAMINANT MIGRATION  
IN A SURROUNDING AQUIFER

ABSTRACT

At the inactive Nordic tailings impoundment in the Elliot Lake uranium mining district, Ontario, hydrogeochemical investigations are being conducted to determine the effects of pyrite oxidation on the chemistry of pore water in the tailings and on the subsurface leaching of metals and radionuclides from the tailings. The tailings have been inactive for more than a decade and in recent years the tailings surface has supported a cover of grass. Originally the pH of the tailings pore water was about 7, but since the tailings became inactive, near-surface pyrite oxidation resulting from exposure to oxygen and water has caused the pH of pore water above the water table in the tailings to decline to the range of 1.5-3, with an associated rise in dissolved iron, sulphate, metals and radionuclides to high concentration levels. The direction of net subsurface water movement in the tailings is downward, and therefore, the acidic pore water gradually moves downward through the tailings into the permeable sandy groundwater zone beneath the tailings. The rate of this downward migration is controlled by the rate of downward pore water flow and by geochemical processes, primarily those that consume acid, such as reactions involving residual lime-derived carbonate minerals and reactions involving iron and aluminum.

In most of the tailings area, the zone of low-pH pore water has not yet reached the bottom of the tailings. In one of the areas where it has passed all the way through the tailings, a plume of tailings-derived water with high iron and sulphate concentrations has moved in the sand aquifer a horizontal distance of 400 m beyond the tailings dam. Although the iron-sulphate plume has moved this far, the front of the low pH water is still close to the toe of the tailings dam. Three years of monitoring has established that the low-pH front is advancing in the sand aquifer at a rate that is less than 1 percent of the groundwater velocity. The rate of acid-front advance is severely retarded because of pH neutralization caused by the dissolution of trace amounts of carbonate minerals in the sand. Although the plume segment beyond the low-pH front has high concentrations of iron and sulphate derived from the tailings, it does not contain hazardous levels of radionuclides or heavy metals, because these constituents are either insoluble or strongly adsorbed at neutral pH.

A narrow zone, near the bottom of the tailings, was observed to have high solid-phase concentrations of various chemical and radioisotope constituents. This is attributed to the settling of fines in the bottom layer containing precipitates of gypsum

and metal hydroxides, and co-precipitation and adsorption of trace metals and radionuclides from the residual process water.

Investigations of the conditions on the surface of the tailings indicate that there is a slight accumulation of Ra-226 isotope in the vegetation with a vegetation to tailings concentration ratio (CR) of 0.03 on dry matter basis and a transfer coefficient of  $6 \times 10^{-6}$ . No significant variation between plant species or significant accumulation in the seeds were observed.

## INTRODUCTION

The uranium mining industry produces a large volume of low level radioactive waste material which, following milling, extraction and neutralization processes, is deposited in extensive tailings impoundments. In many cases the orebodies are associated with metal sulphides such as pyrite, marcasite and pyrrhotite which are not desired products and are released to the tailings as part of the mill wastes. Upon weathering, these metal sulphides are readily oxidized, producing acid mine drainage conditions from these tailings piles which is of considerable environmental concern.

The oxidation of pyrite and other iron sulphides produces highly acidic conditions within the tailings with the subsequent leaching of the tailings material resulting in highly acidic pore water containing significant concentrations of iron, sulphate, heavy metals and trace radionuclides. The migration of such a poor quality tailings water either by surface run-off or sub-surface groundwater can lead to serious deterioration in the quality of adjacent natural water systems.

During the operating phase of the mine the water quality of the surface and groundwater seepage can be controlled by on-site neutralization and treatment facilities. The potential for pyrite oxidation and acid generation should, however, persist for decades in abandoned tailings. The mining industry is thus faced with the difficult task of devising long term abandonment schemes that minimize pyrite oxidation and prevent the release of contaminants to the environment. These schemes should be cost effective and should require very little future maintenance or monitoring.

Hydrogeochemical investigations of an inactive pyritic uranium tailings basin at the Nordic Mine in Elliot Lake, Ontario, have been on-going for the past four years, to identify: 1) the zone of active pyrite oxidation; 2) geochemical characteristics of the pore water; 3) soil gas and solid phase composition of the tailings material; 4) migration of contaminants as a sub-surface seepage in the surrounding aquifer; and 5) interaction of the vegetative cover with the tailings material in relation to uptake of radioisotopes and other contaminants. Results obtained to date are briefly reported here, the details of some of the results can be found elsewhere [1-5].

## GEOLOGY AND HYDROLOGICAL SETTING

The Nordic Mine site is located about 5 km east of the town of Elliot Lake. The mine operated from 1957 to its closure in 1968. The uranium mined at the site was a metamorphosed quartz pebble conglomerate containing 5-10% pyrite, 0.11%  $U_3O_8$ , 0.02%  $ThO_2$  and 0.056% rare earths: yttrium, cerium and neodymium oxides.

The Nordic tailings impoundments are shown in Fig. 1. The largest impoundment, known as the Nordic main tailings, covers an area of 70 hectares and contains approximately 10 million tonnes of tailings with an average thickness of 12 m. The smaller impoundment situated immediately west of the Nordic main tailings, known as the Nordic West-Arm, covers an area of 15 hectares and contains approximately 2 million tonnes of tailings with an average thickness of 7 m. A peripheral dam of mine waste and overburden, and cross-valley dams complete the impoundment. The tailings impoundments are situated in a glaciated valley that runs east to west between bedrock uplands formed from Lower Proterozoic arenaceous sedimentary rocks that strike east-west and dip to the north. The valley floor is underlain by Pleistocene sediments that comprise, from the original surface downwards, sand and gravel of glacio-fluvial origin over a layer of sandy, bouldery glacial till. A layer of black peat, 0.5 to 1 m thick, covers the sand and gravel in much of the valley area in which the tailings were deposited. The peat formed in a spruce bog that formerly existed in the area. A dense vegetation cover over most of the tailings surface has been established for the past 3-5 years.

The tailings area receives approximately 0.8 m of precipitation annually, primarily as spring and fall rain and winter snow. The water table in the tailings ranges in depth from about 1 m to 10 m below ground surface and it fluctuates by a metre or so with the seasons.

The Nordic main tailings area also receives surface run-off from the rocky hill slope on the northern edge and drainage from a higher tailings area on the other side of the drainage divide. Water that does not seep into the tailings flows eastward across the tailings into a large channel that drains from the tailings through a decant structure to a seepage collection ditch beyond the north-eastern corner of the tailings. The effluent from the drainage ditch is treated with lime and barium chloride to control pH, dissolved metals and radionuclide concentrations. Other than the single decant passageway, the only other outlet for water flow from the tailings is by way of downward seepage through the tailings into the underlying sand and gravel. Groundwater in the tailings flows vertically downward in the upper zone turning gradually to a north-south horizontal flow near the bottom of the tailings because of the reduced permeability of the peat layer, and coarse and fine fraction interbedding planes.

## ORIGIN AND MIGRATION PATHWAY OF CONTAMINANTS

Contaminants that originate in the tailings are transported in the flowing pore water towards the bottom of the tailings where they enter the laterally-moving groundwater in the sand and gravel aquifer. In the zone above the water table in the tailings, referred to as the Vadose Zone, metals and radionuclides are released from solids to the pore water as a result of pyrite oxidation and subsequent leaching. With recharge events and infiltration, the reaction products are gradually transported downward into the zone below the water table known as the Phreatic Zone. In this zone, the residual neutralized pore water is thus gradually being replaced by the highly acidic, high total dissolved solids recharge pore water. The acidic pore water joins the horizontal flow in the sandy aquifer near the tailings impoundment dams and appears as a contaminant plume in the surrounding formation.

For the detailed investigation of the hydrogeochemical evolution of the pyritic uranium tailings pile, solid and solution samples were taken from various locations (Fig. 1) and analyzed for chemical and radioisotope constituents. The results obtained are discussed below.

## VADOSE ZONE

Samples for chemical analyses of the solid, liquid and gas phases were collected in detailed profiles above the water table at sites T-1, T-3 and T-5 (Fig. 1). T-1 was representative of areas with shallow water tables and fine grained tailings, T-3 represented medium to fine tailings with a deep water table while T-5 was situated in an area of coarse tailings with deep water table. Solid phase analyses included soluble-sulphate, pyrite, carbonate, Th-228, Th-230, Th-232, Ra-226 and Pb-210; solution phase analyses included pH, electrical conductance,  $\text{SO}_4$ , Fe(total), Ca, Na, K, Mg, Pb, Zn, Ni, Co, Mn, Cu, Al, Cl, Br and Si; and gas phase analyses included  $\text{O}_2$ ,  $\text{N}_2$  and  $\text{CO}_2$ . Selected parameters were determined on two occasions, in May and in August, in order to provide some indication of the seasonal variability in the profiles. The results for several parameters obtained at T-3 for the August sampling period are included in Fig. 2 and 3. The pH varied from about 3 near the ground surface to a minimum of about 2 at a depth of 1 m, then increased with depth to values near 6 as the water table is approached. Electrical conductance was reasonably uniform throughout the profile, but was at its minimum value (about 2,000  $\mu\text{S}$ ) near the ground surface, and its maximum value (20,000  $\mu\text{S}$ ) at a depth of about 1 m.  $\text{SO}_4$  and Fe in the solution phase behaved in a similar manner, varying from maximum values near 1 m depth (9,000 and 3,5000 mg/L, respectively) to relatively low values at a depth of 2 m below ground surface, then both show a gradual increase with depth. The  $\text{O}_2$  profile shows a decrease from about 20% at a depth of 0.1 m below ground surface to about 2% at a depth of 1.0 m, and then relatively constant values at greater depth. The solid-phase analyses show

the pyrite concentration to increase from near zero close to ground surface to a value of about 4% by weight at a depth of 1.5 m and then to remain relatively constant with greater depth.

The low pH, and high sulphate and iron, combined with the decline in  $O_2$  suggests that pyrite oxidation is predominately occurring in a relatively narrow zone at a depth of about 0.75 to 1.0 m below ground surface. This is also consistent with the low pyrite content near the surface and the relatively constant values below 1.0 m depth, and the high soluble sulphate observed in the solid phase profile at 0.75 m depth.

Consequently, the major zone of acid generation appears to be at a relatively shallow depth in the unsaturated tailings. Presumably, as the pyrite continues to be consumed, this zone will move to greater depths with time. Data collected in May, in the following year, indicated that the high sulphate and iron peaks had been displaced downwards as a result of the fall and spring recharge events. Although this does not alter the major conclusion given above, it presents a complicating factor in that it shows that the chemical characteristics observed at a particular point and at a particular time can be the result of not only the local geochemical processes, but also of translocation processes. Interpreting trends in chemical profiles on a purely equilibrium geochemical basis could, therefore, lead to inappropriate hypotheses.

Trends observed at T-1 and T-5 were consistent with those presented for T-3. Because of the finer texture and shallower water table, the zone of pyrite oxidation at T-1 appeared to be narrower and at a shallower depth than at T-3. In contrast, T-5, which was situated in coarse tailings, showed the zone of pyrite oxidation to extend over a zone from near ground surface to a depth of about 2-5 m.

#### PHREATIC ZONE

In the saturated zone below the water table, the chemical profiles of the tailings groundwater show a two layer system in which recharging precipitation, with high  $SO_4$ , Fe and heavy metal concentrations and low pH, has moved downward into the tailings, gradually displacing the original high pH, low Fe residual process water as indicated in Fig. 4. Depth of contaminant penetration is controlled by the physical properties and hydrologic setting of the tailings, the greatest penetration occurring in the areas with coarse grained tailings and high downward hydraulic gradients. The limit of the depth of displacement is marked by decreasing concentrations of Fe and  $SO_4$ , coincident with increasing concentrations of Cl derived from reagents added during ore processing.

The results also show that a decrease in groundwater pH occurs closer to the surface than the peak concentration of Fe and  $SO_4$  (Fig. 4). This retardation of the low pH front indicates the presence of  $H^+$ -consuming processes in the tailings. These

processes include the dissolution of primary aluminosilicate minerals and small amounts of carbonate mineral (0.025 weight %) added during neutralization of the mill effluent. Precipitation of siderite and hydroxides of Fe and Al resulting from the neutralization of low pH water during downward migration is suggested by calculated saturation indices.

It is also seen from the results that typical heavy metals like cobalt in the solution are mobilized in the high Fe recharge water and precipitate in the neutralizing zone. Data from observed sites indicate that uranium and Pb-210 behave similarly, while the highest Ra-226 concentrations are not associated with the peak Fe concentration. Precipitation, co-precipitation and sorption of trace heavy metals and radionuclides occur in the neutralizing zone.

#### ACIDIC SEEPAGE FROM THE TAILINGS

Acidic seepage from the Nordic Main impoundment occurs in three areas as shown in Fig. 1. Area C contains relatively little contaminants compared to areas A and B. Seepage in area B is at a pH of about 3 and contains high concentrations of contaminants, but is of minor extent. The well-developed contaminant plume in area A has been described by Blair et al. [2] and examined in detail by Morin et al. [3] and Cherry, Shepherd and Morin [5].

The plume originates within the tailings near the impoundment dam and moves parallel to the water table into the sand aquifer. The plume consists of three sections (Fig. 5). The inner core, which is at a pH less than 5, contains several thousand (6,000-10,000) mg/L of Fe and SO<sub>4</sub>, over 3,700 mBq/L (100 pCi/L) Ra-226 and relatively high concentrations of other contaminants. The outer zone, which surrounds the inner core and extends several hundred metres down-gradient, is at a pH greater than 5.7 and contains a few thousand (2,000) mg/L of Fe and SO<sub>4</sub>, approximately 370 mBq/L (10 pCi/L) of Ra-226, and relatively low concentrations of other contaminants. The neutralization zone is the transition region between the other two zones.

Groundwater near the dam has a velocity of about 700 m/y, however, the inner core is moving only a few metres per year (Fig. 5). The zone of low pH is strongly retarded, its velocity being only 0.1 to 0.3 percent of the groundwater flow rate. This retardation of contaminant movement is caused by pH neutralisation and chemical precipitation of siderite and gypsum as calcite dissolves in the neutralization zone.

#### DISTRIBUTION OF TAILINGS SOLID PHASE CONSTITUENTS

The solid phase distribution profiles of chemical and radioisotope constituents of the tailings were measured at various locations in the Nordic Main tailings and the Nordic West-Arm. Solid core samples were collected with split spoon and modified Shelby tube samplers at various depths and analyzed for moisture

content, soil pH, loss on ignition, pyrite, total and soluble sulphur,  $\text{SO}_4$ , Fe, Ca, Al, U, Th and radioisotopes Ra-226, Pb-210, Th-228, Th-230 and Th-232. Some of the results obtained are indicated in Fig. 6. The results show that within the tailings, two distinct zones of stratification exist; an upper zone of slightly increasing or uniform concentration of constituents with depth except in the top 1 m or so where the concentrations were low, and a lower zone, approximately 1 m in thickness, near the tailings-peat interface, where the constituents were concentrated. In the peat layer underneath the tailings, the concentrations of various constituents decrease rapidly with depth. No significant levels of contaminant penetration below the peat layer were observed. The top 2 to 5 m tailings layer has been acidified with an average pH in the range of 3.8 compared to 5.8-6.5 underneath it. Ra-226 concentrations measured in the solution phase were in the range of 3,700-5,550 mBq/L (100-150 pCi/L) for the tailings pore water and 50-80 mBq/L (1.5-2.2 pCi/L) for groundwater beneath the peat layer and near the bedrock contact.

Various possible mechanisms are believed to contribute to the observed trends of solid phase stratification. They are: a) accumulation of fines (particle size smaller than 74  $\mu\text{m}$ ) containing precipitates of gypsum and metal hydroxides, in the lower zone produced by the settling process during the initial deposition of the tailings; b) co-precipitation and adsorption of major heavy metals and radionuclides from the residual neutralized process water in contact with the lower zone; and c) co-precipitation and adsorption of major heavy metals and radionuclides from the neutralization of the highly acidic, high TDS water.

With the vegetative cover on the tailings for the past 3-5 years, a definite soil-like profile is developing in the top upper layer, approximately 10-20 cm thick, consisting mainly of decomposed organic matter. The vegetation cover has reduced the effect of wind and water erosion and probably reduced, to some extent, the amount of water that annually infiltrates to the water table in the tailings.

Samples of various species of plants growing on the tailings were collected at different times in a growth cycle (i.e., growing, flowering and seeding) and were analyzed for Ra-226 and other contaminant uptake. Species sampled were the grasses Red Fescue (*Festuca rubra* L.) and Red Top (*Agrostis alba* L.), and a legume, Birds Foot Trefoil (*Lotus corniculatus* L.). No variation between species was observed, though various plant parts, except seeds, showed slight accumulation of Ra-226 ranging from 74-370 mBq/g (2-10 pCi/g) with an average plant concentration of 166 mBq/g (4.5 pCi/g) dry matter basis compared to that of 5,550 to 7,400 mBq/g (150-200 pCi/g) in the tailings surface layer. In the seeds, Ra-226 concentration was observed to be low, 18.5 mBq/g (0.5 pCi/g) dry matter basis. The results gave, on a dry weight basis, vegetation to tailings concentration ratio (CR) of 0.03 for Ra-226 with an estimated transfer coefficient of  $6 \times 10^{-6}$  from solid to vegetation based on an average dry matter

yield of 0.06 kg/m<sup>2</sup> and root penetration depth of 0.2 m. No correlation between Ra-226 and other contaminants like Fe, Al, Ca and SO<sub>4</sub> uptake can be established from the data.

#### SUMMARY

In view of the above investigations, it can be stated that in pyritic uranium tailings impoundments the oxidation of pyrite and other metal sulphides is of considerable environmental concern in evaluating suitable abandonment options under wet climatic conditions. Pyrite oxidation takes place in a shallow upper zone of the unsaturated tailings below which it is limited by the availability of oxygen. The oxidation produces highly acidic conditions within the tailings which causes leaching of metals and radionuclides. With infiltration and recharge events, the reaction products gradually migrate downwards replacing the residual neutralized process water by the acidic recharge water. With the residual alkaline buffer in the tailings, the acidic pore water is neutralized as it migrates downward, precipitating hydroxides of Fe, Al and gypsum. Co-precipitation and adsorption of heavy metals and trace radionuclides also takes place in the neutralization zone. Acidity is also consumed by dissolution of aluminosilicate minerals and possibly gibbsite (aluminum hydroxide) before the neutralization zone. For a particular hydrological situation of the impoundment, this acidic pore water enters the horizontally flowing groundwater near the impoundment dams where it appears as a major contaminant plume. In the aquifer beneath the dams, the migration of contaminants is appreciably retarded to less than 1 percent of the groundwater flow because of the neutralization processes involved with calcite dissolution.

In the tailings solid phase, depletion of pyrite, other metals and radionuclides takes place in the shallow oxidation zone with the acidic front progressively moving downwards. A narrow zone, near the bottom of the tailings and peat layer interface, was observed to have high concentrations of various chemical and radioisotope constituents which is attributed to the settling of fines in the bottom layer, containing precipitates of metal hydroxides, and co-precipitation and adsorption of radionuclides from the residual process water. Little evidence of contaminant penetration below the peat layer was observed because of the groundwater hydrology of the system and sorption capacity of the peat layer.

Stabilization of the tailings surface with a vegetative cover has reduced wind and water erosion and has developed a top 10 to 20 cm soil-like layer. Slight accumulation of Ra-226 isotope was observed in the vegetation with a vegetation to tailings concentration ratio (CR) of 0.03 on dry matter basis and transfer coefficient of  $6 \times 10^{-6}$ . No significant variation between plant species or significant accumulation in the seeds were observed.

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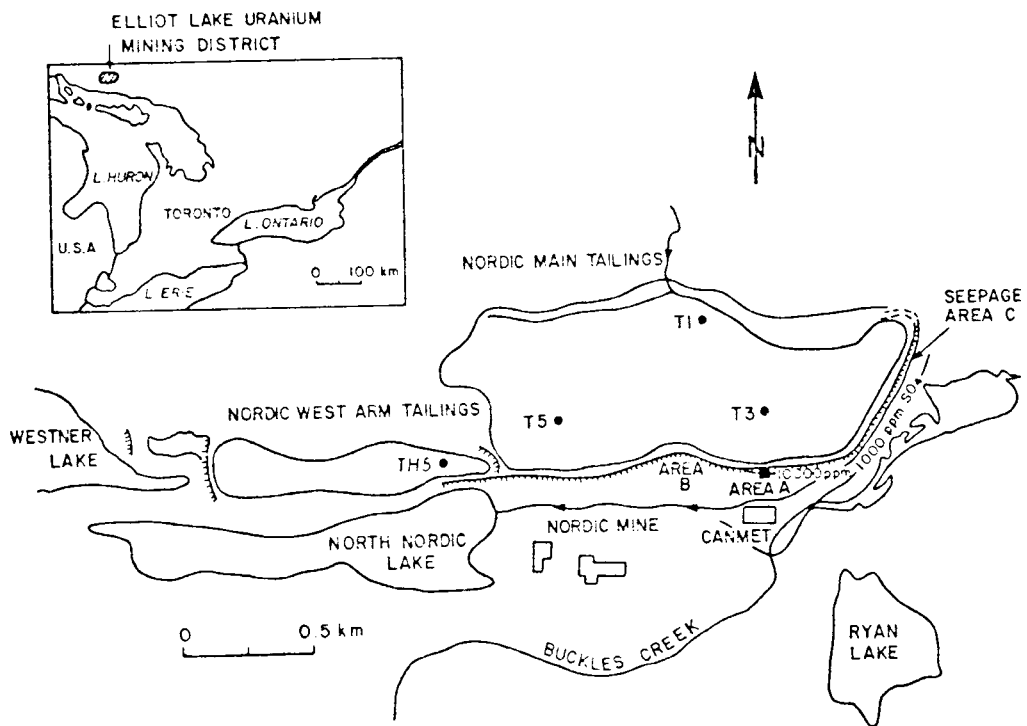
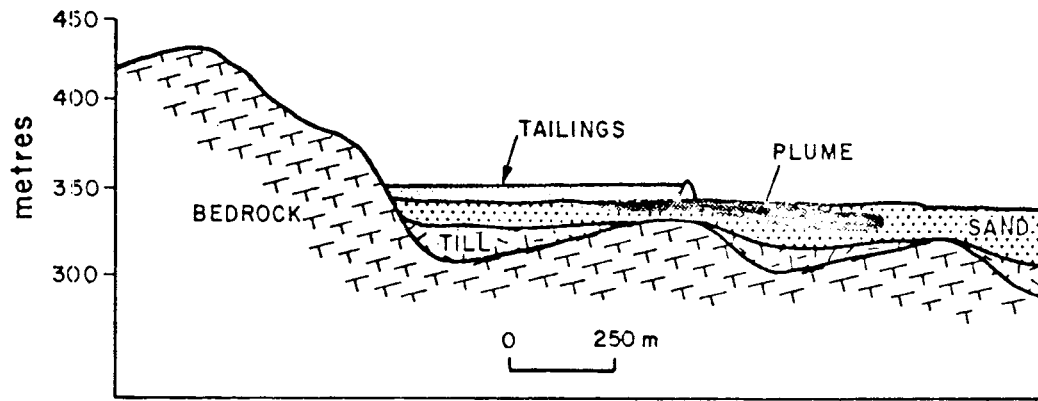


FIG. 1 - Generalized locations of the Nordic Mine tailings impoundments, monitoring sites and areas of acidic seepage, and geological cross-section through the Nordic Main tailings area.

T-3

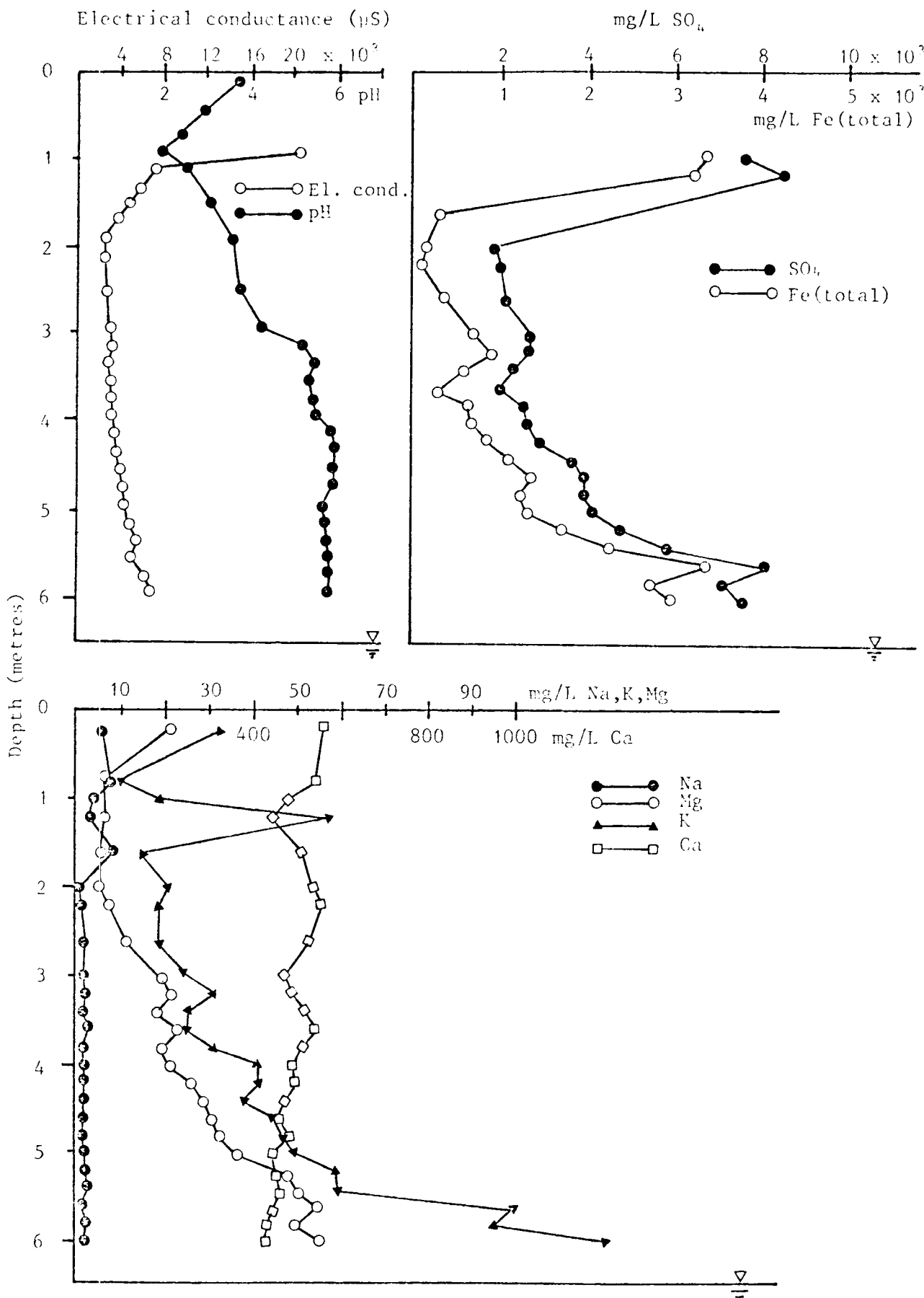


FIG. 2 - Hydrochemical profiles of pH, electrical conductance,  $SO_4$ , Fe(total), Na, K, Mg and Ca of unsaturated zone at T-3 site on the Nordic Main tailings in August 1980.

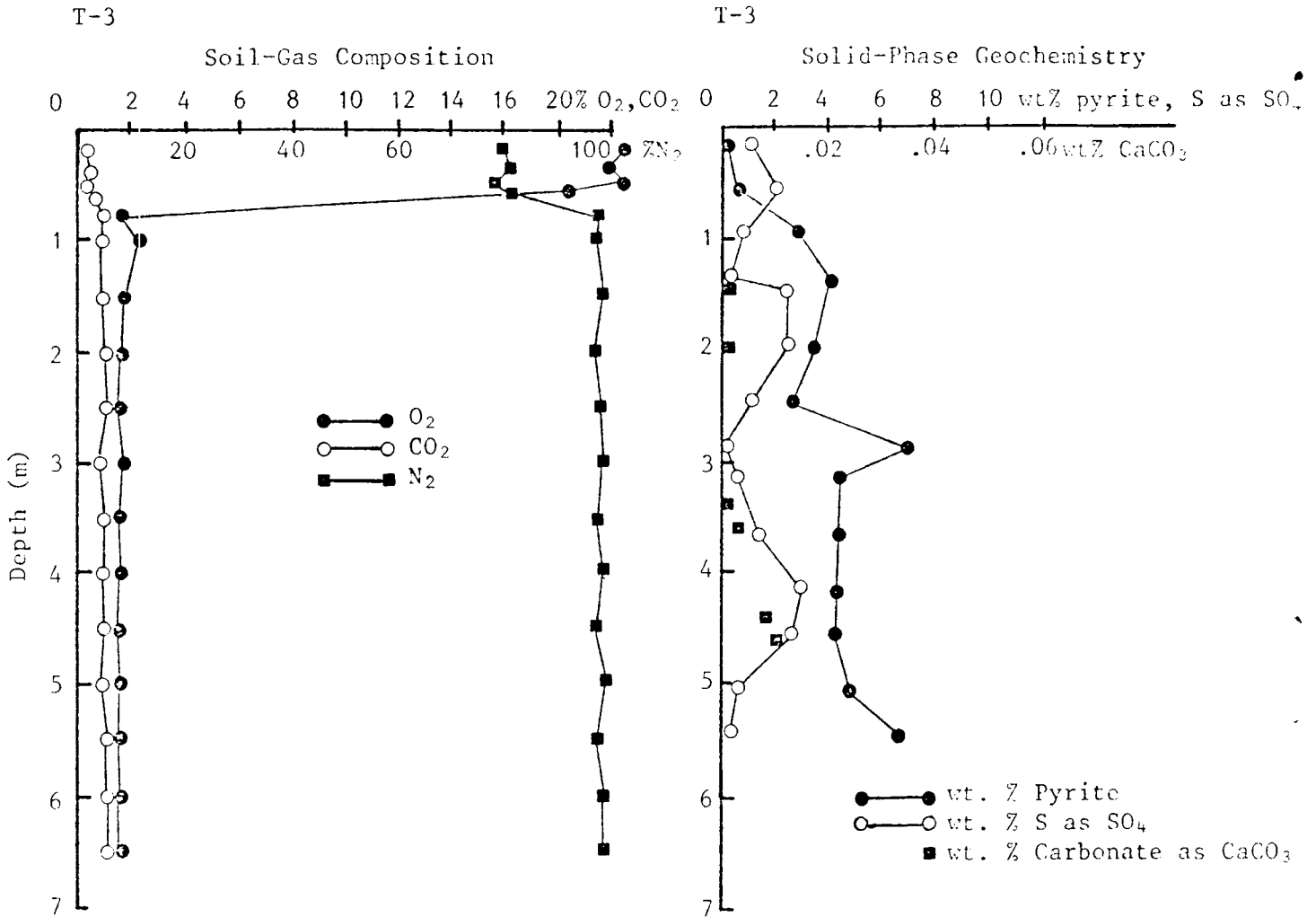


FIG. 3 - Soil-gas composition and solid-phase geochemistry profiles at T-3 sites on the Nordic Main tailings.

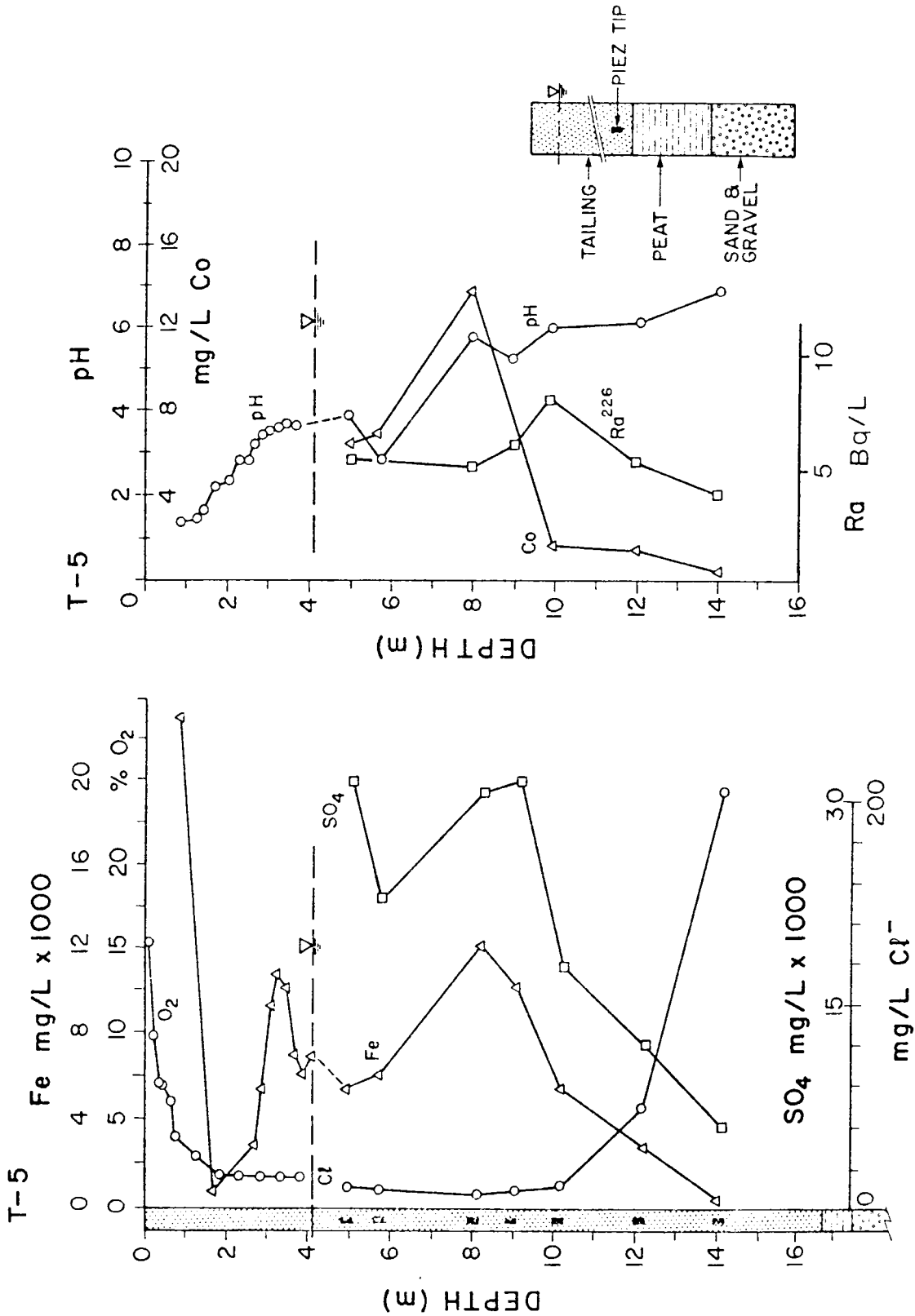


FIG. 4 - Hydrochemical profiles of pH, Cl, SO<sub>4</sub>, Fe(total), Co, and Ra-226 of saturated and unsaturated zones and O<sub>2</sub> gas content of unsaturated zone at T-5 site on Nordic Main tailings.

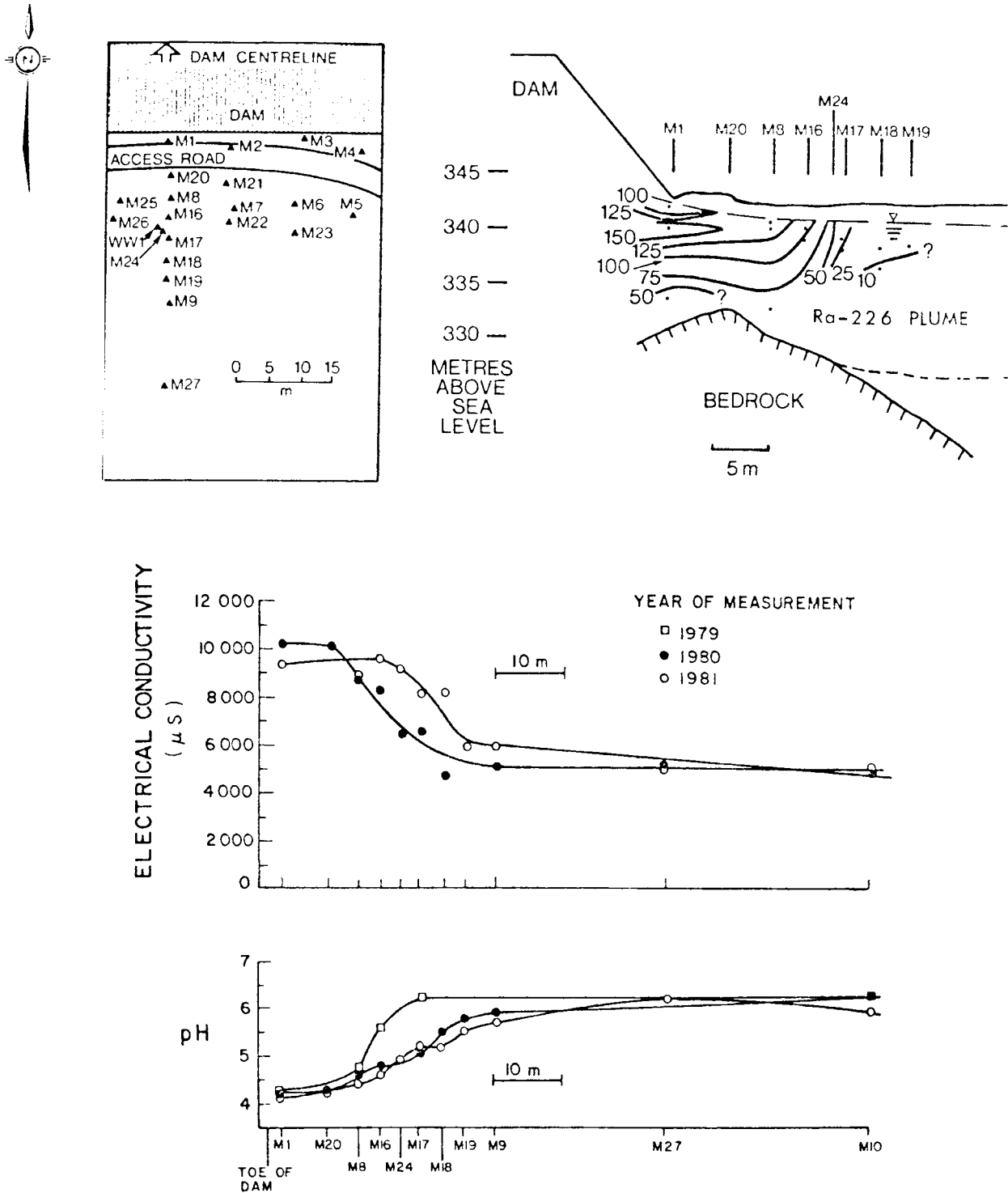


FIG. 5 - Cross-section of Ra-226 (pCi/L, 1 pCi = 37 mBq) in the plume area and variation of electrical conductance and pH with distance from the dam centre line at the Nordic Main site. Locations of monitoring bundle piezometers are shown in the inset.

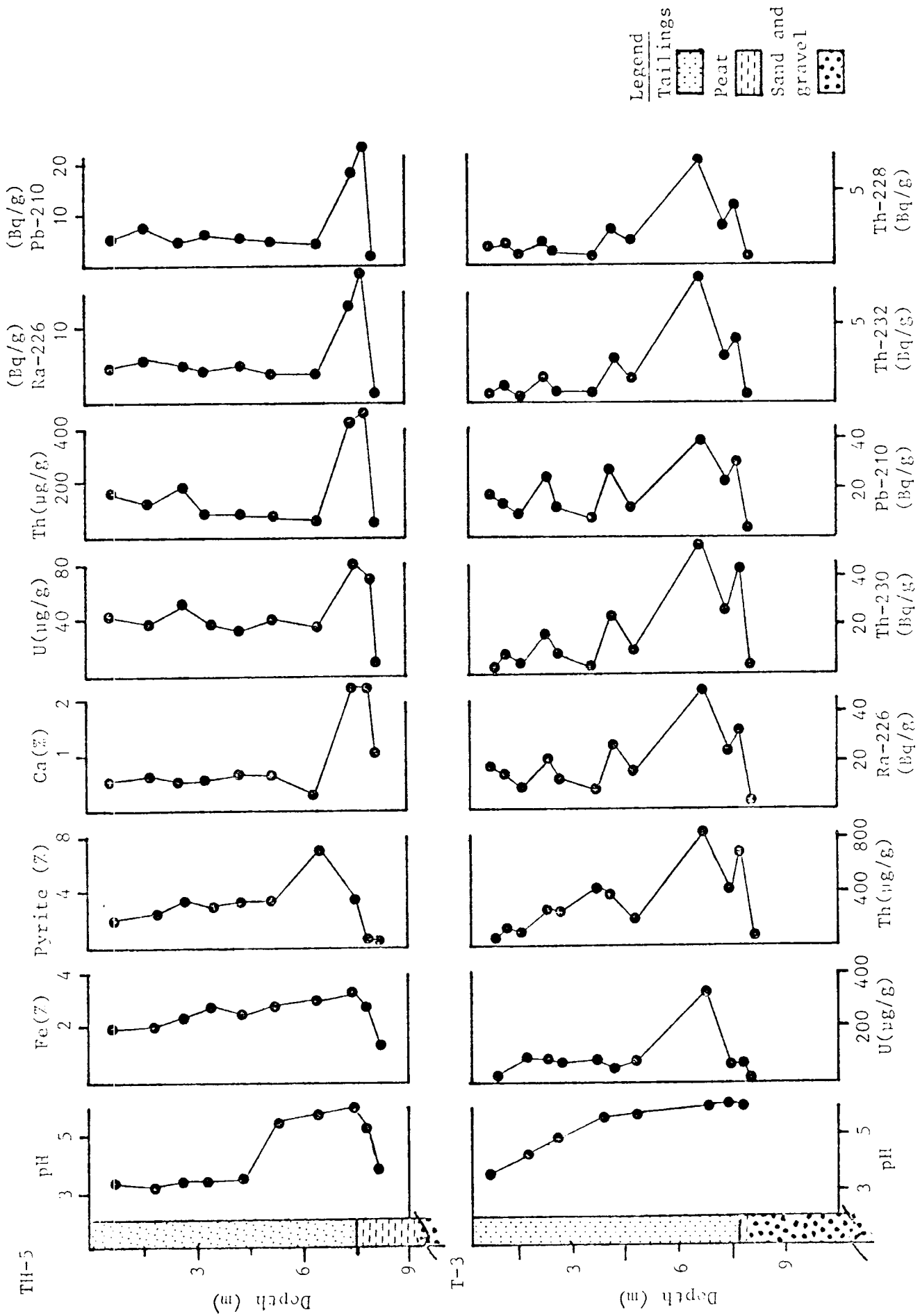


FIG. 6 - Chemical and radioisotope distribution profiles of the tailings solid phase at sites TH-5 on the Nordic West-Arm and T-3 on the Nordic Main tailings.

## FIGURE CAPTIONS

1. Generalized locations of the Nordic Mine tailings impoundments, monitoring sites and areas of acidic seepage, and geological cross-section through the Nordic Main tailings area.
2. Hydrochemical profiles of pH, electrical conductance,  $\text{SO}_4$ , Fe(total), Na, K, Mg and Ca of unsaturated zone at T-3 site on the Nordic Main tailings in August 1980.
3. Soil-gas composition and solid-phase geochemistry profiles at T-3 sites on the Nordic Main tailings.
4. Hydrochemical profiles of pH, Cl,  $\text{SO}_4$ , Fe(total), Co, and Ra-226 of saturated and unsaturated zones and  $\text{O}_2$  gas content of unsaturated zone at T-5 site on Nordic Main tailings.
5. Cross-section of Ra-226 (pCi/L, 1 pCi = 37 mBq) in the plume area and variation of electrical conductance and pH with distance from the dam centre line at the Nordic Main site. Locations of monitoring bundle piezometers are shown in the inset.
6. Chemical and radioisotope distribution profiles of the tailings solid phase at sites TH-5 on the Nordic West-Arm and T-3 on the Nordic Main tailings.