ASSESSMENT OF EXISTING NATURAL WETLANDS AFFECTED BY LOW pH, METAL CONTAMINATED SEEPAGES (ACID MINE DRAINAGE)

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ASSESSMENT OF EXISTING NATURAL WETLANDS
AFFECTED BY LOW pH, METAL CONTAMINATED SEEPAGES
(ACID MINE DRAINAGE)

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ENVIRONMENT CANADA
Conservation and Protection Branch
Hull, Quebec   K1A OH3

Prepared by

P. Lane and Associates Limited
5439 Cogswell Street
Halifax, Nova Scotia   B3J 1R1

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EXECUTIVE SUMMARY

Acid mine drainage (AMD) occurs when pyritic mine tailings are exposed to oxygen and water. Surface runoff and groundwater seepage through waste piles are typically very acidic and contain high concentration of dissolved metals including iron, aluminum, manganese, copper, lead, nickel and zinc. Conventional treatment of AMD usually involves liming the runoff to neutralize the water and chemically precipitate the metals. Liming is expensive and may be required long after the mine has ceased operating. Recently, attempts have been made to develop low—maintenance, low—cost AMD treatment systems that can restore water quality. One method of passive treatment utilizes the vegetation and sediment microbial communities found in natural wetlands to reduce acidity and precipitate the metals.

This study examined natural wetlands near six base metal mines in eastern Canada for evidence of biological AMD mitigation. Potentially suitable wetlands were identified by Environment Canada in consultation with mining companies and provincial resource departments. A field program was conducted to describe and compare these sites in terms of water and sediment chemistry, hydrology, and vegetation. Two sampling periods, summer and late fall, were originally planned to enable within—site comparisons between presumed "biologically—active" and "inactive" periods. The project was started too late to conduct a summer campaign. This report presents the results of the early fall sampling period.

There were large differences among wetlands in metal loadings, groundwater inputs, water retention times, metal concentrations in wetlands sediments, and vegetation communities. None of the sites, however, appeared to significantly reduce downstream loadings of metals or acidity levels during the fall. Prolonged drought at one site, Nickel Rim, severely reduced flows and prevented calculation of influent and effluent metal loadings. The apparent lack of biologically—related improvement of AMD was most likely a consequence of (1) low temperatures, ca. 4 °C, (2) channelized flow patterns within the wetlands, and (3) limited contact of AMD with anoxic sediments. Inputs of other seeps and groundwaters to the wetlands were significant complicating factors, especially at the Kam—Kotia site. High metal concentrations in wetlands sediments indicates that the wetlands had removed metals in the recent past.

SOMMAIRE

Les eaux de mine acides proviennent des résidus de mine de pyrite au contact de l'oxygène et de l'eau. Les eaux qui ruissellent en surface et celles qui s'infiltrent dans le sol après avoir traversé des amas de déchets sont en général très acides et présentent des concentrations élevées de métaux dissous (fer, aluminium, manganèse, cuivre, plomb, nickel et zinc, entre autres). On utilise habituellement de la chaux pour neutraliser les eaux de ruissellement et pour faire précipiter les métaux. Cependant, cette méthode est coûteuse et risque de devoir être appliquée longtemps après que l'on a cessé d'exploiter la mine. Récemment, on a donc tenté de mettre au point des systèmes peu coûteux et qui demandent peu d'entretien pour traiter les eaux de mine acides et pour les assainir. L'un des traitements passifs envisagés consiste à faire appel aux communautés microbiennes de la végétation et des sédiments pour réduire l'acidité et pour faire précipiter les métaux.

Dans le cadre de la présente étude, on a recherché des signes de neutralisation biologique des eaux de mine acides dans des milieux humides naturels situés à proximité de six mines de métaux de base de l'est du Canada. Environnement Canada a choisi, après avoir consulté des compagnies minières et les ministères provinciaux des ressources, les milieux humides qui pourraient convenir. Des travaux ont été effectués sur ces terrains pour décrire et comparer la chimie des eaux et des sédiments qui s'y trouvent, leur hydrologie et leur végétation. À l'origine, on avait prévu deux périodes d'échantillonnage, en été et à la fin de l'automne, pour comparer, à l'intérieur d'un même site, les périodes présumées "biologiquement actives" et "biologiquement inactives". Ces travaux ont été entrepris trop tard pour que l'on puisse étudier la période de l'été. Dans le présent rapport, on fait donc état des résultats correspondant à la période d'échantillonnage couvrant le début de l'automne.

On a constaté que les charges en métaux, les apports des eaux souterraines, les temps de rétention des eaux et les concentrations de métaux étaient très différents dans les sédiments et dans les communautés végétales des milieux humides. Pour aucun des sites étudiés, toutefois, on n'a noté de diminution des charges de métaux ou de l'acidité en aval, pendant l'automne. À cause d'une sécheresse prolongée dans un des sites (Nickel Rim), qui avait sérieusement fait diminuer les débits, il n'a pas été possible de calculer les charges de métaux dans les affluents et dans les effluents. L'absence d'amélioration, due à des processus biologiques, de la qualité des eaux de mine acides est probablement due aux raisons suivantes : 1) températures basses (environ 4 °C), 2) écoulement en canaux dans les milieux humides et 3) contact limité des eaux de mine acides avec des sédiments anoxiques. L'arrivée d'autres eaux d'infiltration et d'eaux souterraines a également compliqué la situation, particulièrement au site Kam-Kotia. Les milieux humides avaient récemment extrait des métaux car les sédiments qui s'y trouvaient présentaient de fortes concentrations de métaux.

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1. Introduction

This report is submitted to Environment Canada, Conservation and Protection Branch, in accordance with the amended terms and conditions of Contract Number KE144-9-6140. The water and sediment chemistry, hydrology, and vegetation communities were examined at six natural wetlands adjacent to base metal mines in Eastern Canada between September 28 and October 12, 1989.
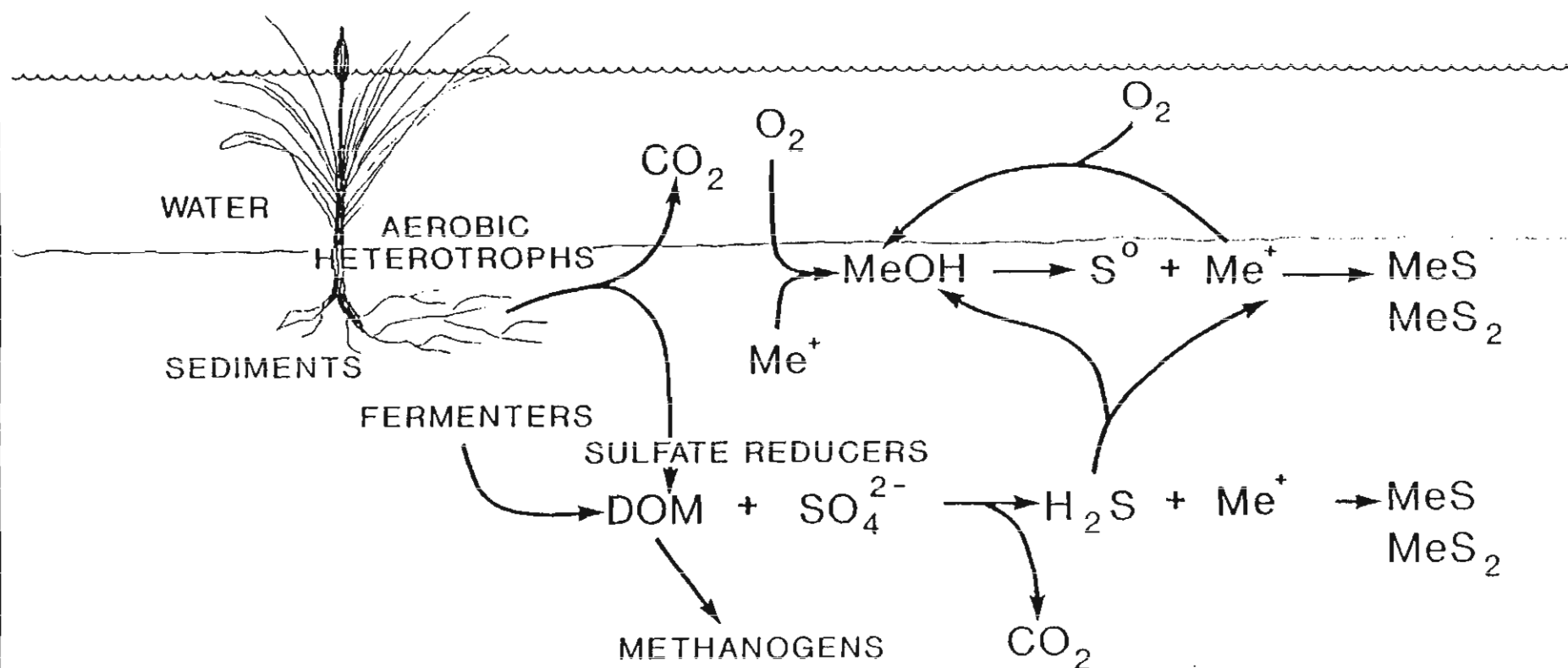
1.1 Background Information

Over the past 20 to 30 years, many investigators have documented the ability of natural wetlands to survive, and even flourish, in acidic, metal-rich seepages from mining sites. In some areas, water flow through wetlands actually improved water quality (Wieder and Lang, 1984; 1986; Eger and Lapakko, 1988). Peat bogs and cattail marshes in particular were able to remove up to 99% of some metals and to lower effluent acidity by 100 to 1000 fold (pH values rose from about 2 to values in the order of 4 to 6). These observations led to further experimentation with both natural and artificial "constructed" wetlands as low-cost, self-sustaining alternatives to conventional chemical treatment of mine seepages. However, results to date are still equivocal about the efficacy of wetlands for amelioration of acidic mine drainage, AMD (Kleinmann, 1987; Dollhopf et al., 1988; Emerick et al., 1988; Heil and Kerins, 1988). Poor performance of natural and constructed wetlands is usually attributed to (a) low retention times within the wetland, (b) skimming flow over the top of the marsh communities, and, /or (c) depressed microbial activity within the marsh sediments.

Wetland processing of AMD is generally believed to be a consequence of the sum of biological activities within the wetland systems. The vegetation communities only remove a small proportion (< 1%) of the metals (Sencindiver and Bhumbla, 1988). Efficient removal of metals and pH control requires microbial intervention, especially by sulfate reducing bacteria (SRB) and fermentative bacteria (see Figure 1-1). In anoxic environments, SRB oxidize dissolved organic matter (DOM) by coupled reduction of sulfate to obtain energy for growth and reproduction. This process consumes hydrogen ions, thereby reducing total acidity, and produces carbon dioxide and hydrogen sulfide (H_2S). Some of the H_2S will precipitate metals in the anoxic zone, reducing metal losses from the wetland. The balance diffuses upwards and is involved in a complex set of biological and chemical reactions. It can react directly with oxygen to form sulfate again, or more often with metal oxides and hydroxides that precipitated-out at or near the oxic-anoxic interface. Manganese oxides in particular may play a key role in sulfide oxidation (Burdige and Nealson, 1986; Myers and Nealson, 1988). The metal-sulfide reactions consume hydrogen ions, further reducing acidity (Aller and Rude, 1988), and regenerate the reduced metals (which in turn can react with either oxygen or H_2S). Hydrogen ions are also consumed during reactions with silicate minerals (Stumm and Morgan, 1981) and by fermentative bacteria (yielding energy, ATP, and a supply of molecular hydrogen, H_2; Brock, 1974; Ward and Winfrey, 1985). Elemental sulfur that accumulates near the oxic-anoxic interface also participates in a variety of biological and chemical reactions yielding sulfate, metal sulfides, and additional labile organic matter (microbial biomass; Howarth, 1984; Swider and Mackin, 1989).

THEORY OF AMD MITIGATION IN WETLANDS

WATER

AEROBIC HETEROTROPHS

CO_2

O_2

O_2

$MeOH \longrightarrow S^o + Me^+ \longrightarrow MeS$

MeS_2

Me^+

SEDIMENTS

FERMENTERS

SULFATE REDUCERS

$DOM + SO_4^{2-} \longrightarrow H_2S + Me^+ \longrightarrow MeS$

MeS_2

METHANOGENS

CO_2

CO_2 = carbon dioxide; O_2 = oxygen; Me^+ = metal ions;

MeOH, MeS, MeS_2 = metal hydroxide and metal sulfide precipitates;
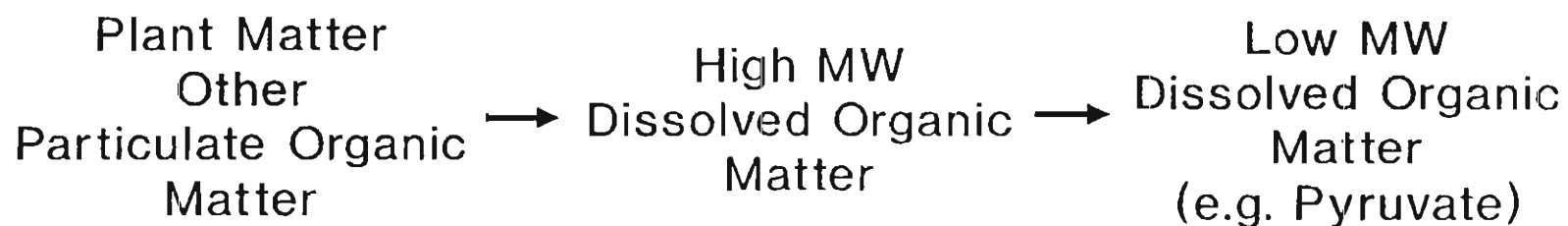
S^o = elemental sulfur; DOM = dissolved organic matter;

SO_4^{2-} = sulfate ion; H_2S = hydrogen sulfide

FIGURE 1-1

Nitrogen-cycling bacteria are also believed to be important in the control of pH in wetland sediments. Fermentative hydrolysis of proteins and amino acids by the so-called "ammonifiers" yields a supply of ammonia and H_2 (Klump and Martens, 1983). The ammonia produced subsequently reacts with hydrogen ions to produce ammonium ions, thereby reducing water acidity. If there is sufficient nitrate available in AMD, either from natural atmospheric inputs or from mine seepages carrying oxidized explosive residues, anaerobic denitrifying bacteria (nitrate reducers) will further decrease acidity by consuming both hydrogen ions and the H_2 produced by the fermenters (Hattori, 1983; Seitzinger, 1988).

Successful prediction of the suitability of a wetland for treating AMD requires an understanding of the factors that govern microbial activities in sediments. Current paradigms suggest that SRB are the key organisms to the entire process. However, SRB require a supply of highly labile, low molecular weight (MW) DOM in order to influence AMD chemistry. SRB cannot directly utilize particulate organic matter (POM) or high MW DOM from dead plants and bacteria. In nature, SRB rely on other organisms, especially fermentative bacteria, to provide this DOM. Indeed, fermentation reactions may be the rate-limiting step for both metal control and acid consumption (see Figure 1-2). As noted above, fermentative degradation of complex organic materials increases pH and yields H_2, via the "phosphoroclastic" reaction (Brock, 1974). The H_2 is rapidly consumed by SRB, methanogenic and denitrifying bacteria in anoxic sediments (Nedwell, 1984; Capone and Kiene, 1988), and by hydrogen-oxidizing chemosynthetic bacteria near the oxic-anoxic interface (Brock, 1974). Indeed, maintenance of low ambient concentrations of H_2 is essential to keep the fermenters working at maximal rates. This in turn results in even more labile organic matter (microbial biomass) for the sediment microbial community, and a greater potential for treating AMD.

Other factors controlling sediment microbial activity include temperature, physical mixing of DOM substrates and electron acceptors (e.g. sulfate, nitrate, and several metals) to the microbes, and the activities of grazers and viruses. Microbial reaction rates generally follow seasonal temperature patterns, with rates increasing by a factor of = 2 to 3 for every 10 $^{\circ}$C rise in temperature. However, the lability of available organic matter (a function of the type of vegetation present, molecular weight and surface charge of DOM, etc.) may control the degree of temperature dependence (Westrich and Berner, 1988). Sediments with a large pool of labile organic matter should be more effective at AMD mitigation during cold periods than sites with little, or poor quality, organic matter. At present, however, there is little published information concerning the effect of cold temperatures or substrate quality on wetland amelioration of AMD. Mass transport of electron acceptors and substrates to the bacteria is mainly dependent upon concentration gradients and sediment porosity. Because of the high sulfate concentrations in most AMD, reaction kinetics are probably limited by diffusion of DOM within sediment interstitial spaces. Fine-grained sediments in most natural wetlands inhibit physical mixing of DOM within interstitial spaces and mixing of AMD into the sediments. Finally, grazer and viral activity may also be an important factor govering AMD processing in some circumstances. The few data available suggest that protozoans isolated from mine seepages can sharply reduce dense populations of cultured acidophilic bacteria (Christison et al., 1986).

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IMPORTANT FERMENTATION REACTIONS
IN WETLAND SEDIMENTS

Plant Matter
Other
Particulate Organic $\longrightarrow$ High MW $\longrightarrow$ Low MW
Matter Dissolved Organic Dissolved Organic
Matter Matter
(e.g. Pyruvate)

$$Pyruvate + ADP + PO_4^{-3} + H^+ \longrightarrow Acetate + ATP + H_2 + CO_2$$

Coenzyme a
Ferredoxin

FIGURE 1-2

The degree of processing of AMD by a given wetland is also dependent upon a number of physical factors. Some of the more important factors include: discharge rates, the surface area to volume ratio of the wetland (influencing oxygen and sulfate penetration and supply of labile DOM), the amount of build-up of metal hydroxides at the oxic-anoxic interface, and the packing density of sediment particles in both oxic and anoxic layers (Hedin et al., 1988). These physical factors collectively alter retention times and flow rates within the wetlands, and consequently the degree of AMD processing by resident microbes.

1.2 Objectives of the Present Study

In order to investigate how AMD is treated in natural wetlands adjacent to base metal mines, preliminary studies of the water quality and hydrologic regime were carried out at six mine sites in eastern Canada (see Figure 1-3). Comparisons of pH and metal concentrations in water samples taken above and below the wetlands should indicate which of the wetlands were successfully treating AMD. Assuming the influent and effluent discharges are comparable, pH values should be higher and metal concentrations lower in effluent waters, if the AMD is being successfully treated by wetland communities. Because additional seepages to the wetlands, or groundwater inflow, can either dilute or augment the metal content and pH of effluent waters, all visible sources of AMD entering the wetlands, and effluent leaving the wetland were also estimated. Finally, additional sampling of the vegetation and sediments was also carried out to provide further comparative information about the wetlands.

2. Methods and Materials

2.1 Study Sites

The natural wetlands were selected by Environment Canada in consultation with other government agencies and the mining industry. The six sites chosen for initial study were associated with the following mines:

1 - Nickel Rim, near Sudbury, Ontario
2 - Kam-Kotia, near Timmins, Ontario
3 - Waite Amulet, near Rouyn-Noranda, Quebec
4 - Heath-Steele, near Newcastle, New Brunswick
5 - Nigadoo River, near Bathurst, New Brunswick
6 - Brunswick #12, near Bathurst, New Brunswick

The Nickel Rim mine is not presently operating and the tailings, which were dumped in and around a small lake, have been partly revegetated. The area studied is a small, sedge-dominated wetland receiving effluent from this lake. At the time of the field survey, the area had experienced two months of drought. Consequently, there were no surface water flows out of the lake or into or out of the wetland (Figure 2-1).

Mining operations at Kam-Kotia ceased in the 1960's, and most of the tailings were not contained. Two separate tailings areas have since spread out across the relatively flat landscape and flowed along small channels towards the

Mine Site Locations in Eastern Canada

QUEBEC

NFLD.

ONTARIO

Heath-Steele

Nigadoo River

Brunswick #12

P.E.I.

N.B.

N.S.

Kam-Kotia

Waite Amulet

Nickel Rim

Little Kamiscotia River. They have entered the river at two points, making any future attempts at containment extremely difficult. The wetland studied is located where one tailings flow enters a shallow, cattail-dominated widening of the river (Figure 2-2).

The Waite Amulet tailings deposit has been capped with clay and success-fully revegetated. A small stream collects runoff and seepage from these tailings and flows through a relatively small cattail-dominated wetland (Figure 2-3).

The Heath-Steele mine is active, and the tailings are occasionally treated with lime. The wetland is located below a large bermed tailings pond and receives seepage and spring discharge, both of which appear to originate from the tailings pond. Water flows through a channel containing a fairly diverse plant association (Figure 2-4).

The Nigadoo River Mine has been abandoned, and the tailings are partly covered with waste rock. Runoff and seepage from the tailings enter a settling pond which flows into a cattail-dominated wetland bermed on both sides and dyked at the outlet. A relatively small amount of tailings also enters this wetland directly at its upper end (Figure 2-5). The Nigadoo site is unique in that the host bedrock is high in calcium, causing the runoff to have a relatively high pH.

The Brunswick #12 mine is active, and the tailings effluent is limed and held in a sludge pond. An infill pond below the sludge pond receives under-berm seepage. This area contains a small cattail-dominated wetland (Figure 2-6).

Of the six wetlands visited, the Nickel Rim, Kam-Kotia, and Heath-Steele, wetlands were examined in greater detail because they appeared to have the greatest potential for amelioration of AMD. The selection was based primarily on water chemistry characteristics of inlet and outlet discharges. Sediments and vegetation from these sites were analyzed for metal content.

2.2 Water Quality Investigations

The sampling program began on 28 September 1989 and concluded on 12 October 1989. Field measurements of pH, conductivity, dissolved oxygen, and redox potential were made near the surface and bottom of the water column at the inlet, middle and outlet of each wetland, and at six other locations along the wetland. As a result of equipment failures, not all field water chemistry parameters were measured at each location. More detailed laboratory analysis of surface water samples from the inlet, middle and outlet stations provided information about major ions, nutrients, dissolved and particulate organic composition and trace metal content of these waters. The extensive list of parameters measured included: pH, acidity, conductivity, hardness, alkalinity, sodium, potassium, magnesium, calcium, sulfate, phosphate, nitrate plus nitrite, ammonia, silicate, colour, humic acids, total organic carbon, total dissolved solids, total suspended solids, aluminum, antimony, arsenic, boron, barium, beryllium, cadmium, chromium, cobalt, copper, iron, lead, manganese, mercury, nickel, selenium, tin, vanadium, and zinc.
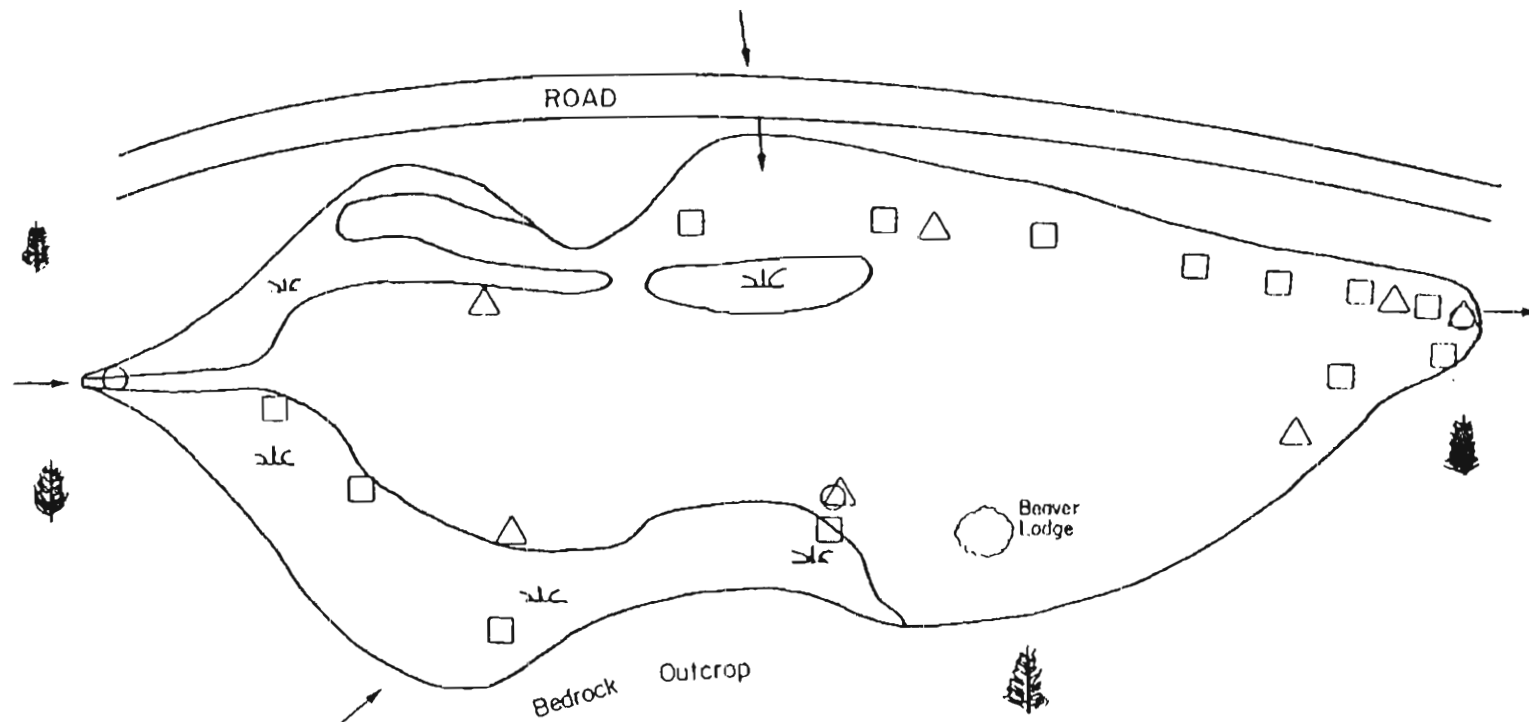
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Nickel Rim Wetland and Sampling Stations

ROAD

Beaver
Lodge

Bedrock   Outcrop

LEGEND

◯ WATER SAMPLE TAKEN FOR LAB ANALYSIS

△ FIELD WATER CHEMISTRY, SEDIMENT, AND DEPTH SAMPLED

▢ VEGETATION AND WATER DEPTH SAMPLED

0   15   30m

Approx Scale

FIGURE 2-1

South
Tailings
Zone

seeps

Little
Kamiscotia
River

Edge of Tailings Delta

LEGEND

◯ WATER SAMPLE TAKEN FOR LAB ANALYSIS

△ FIELD WATER CHEMISTRY, SEDIMENT, AND DEPTH SAMPLED

▢ VEGETATION AND WATER DEPTH SAMPLED

0   8   16   24   32   40m

Approx Scale

Kam-Kotia Wetland and Sampling Stations

FIGURE 2-2

Width Varies
from 6-10m

200m

LEGEND

○ WATER SAMPLE TAKEN FOR LAB ANALYSIS

△ FIELD WATER CHEMISTRY, SEDIMENT, AND DEPTH SAMPLED

□ VEGETATION AND WATER DEPTH SAMPLED

Waite Amulet Wetland and Sampling Stations

FIGURE 2-3

Heath-Steele Wetland and Sampling Stations

Tallings Dam

Access Road

Spring(s)

Spring

seeps

BERM

BERM

Spring

Weir

seeps   seeps

LEGEND

○ WATER SAMPLE TAKEN FOR LAB ANALYSIS

△ FIELD WATER CHEMISTRY, SEDIMENT, AND DEPTH SAMPLED

▢ VEGETATION AND WATER DEPTH SAMPLED

0   3   6   9   12   15m

Approx Scale

→ Flow of Water

PLANO AND ASSOCIATES LIMITED

50m

Tailings Delta

ROAD

Flow from
Tailings

260m

LEGEND

○ WATER SAMPLE TAKEN FOR LAB ANALYSIS

△ FIELD WATER CHEMISTRY, SEDIMENT, AND DEPTH SAMPLED

☐ VEGETATION AND WATER DEPTH SAMPLED

FIGURE 2.5

Nigadoo River Wetland and Sampling Stations

Brunswick No.12 Wetland and Sampling Stations

LEGEND

○ WATER SAMPLE TAKEN FOR LAB ANALYSIS

△ FIELD WATER CHEMISTRY, SEDIMENT, AND DEPTH SAMPLED

☐ VEGETATION AND WATER DEPTH SAMPLED

135m

41m

Sludge Pond

ROAD

Seeps

Dyke

Spillway

Surface water samples for laboratory analysis were collected in 500 mL Nalgene bottles (acid-washed; rinsed with sample), and stored in coolers until they could be analyzed. Samples for mercury analysis were preserved with nitric acid and potassiu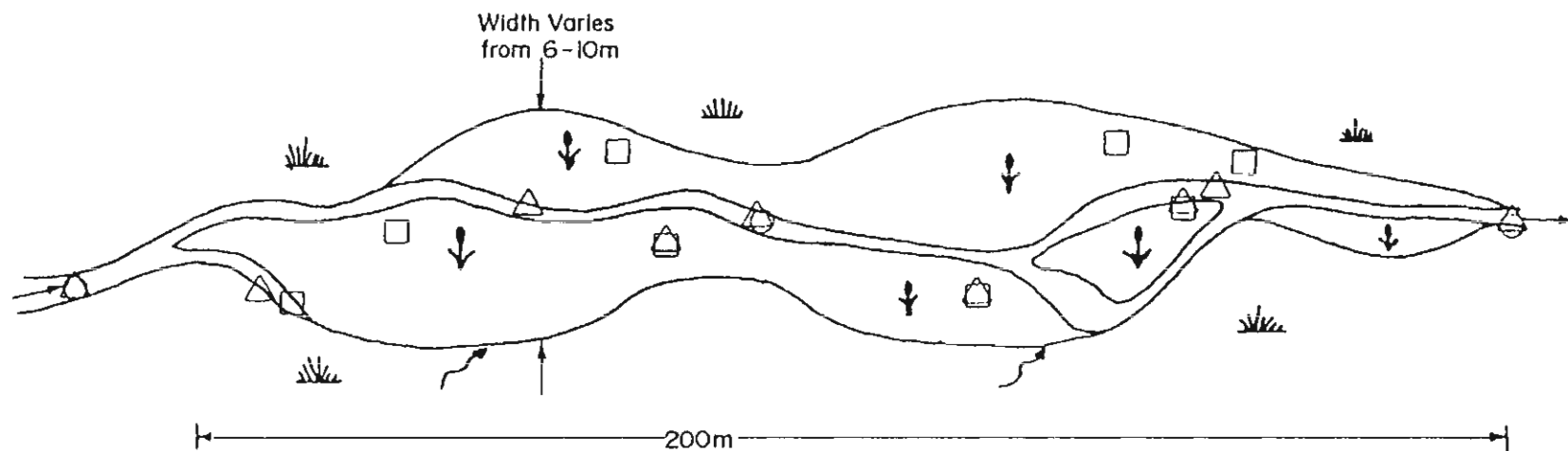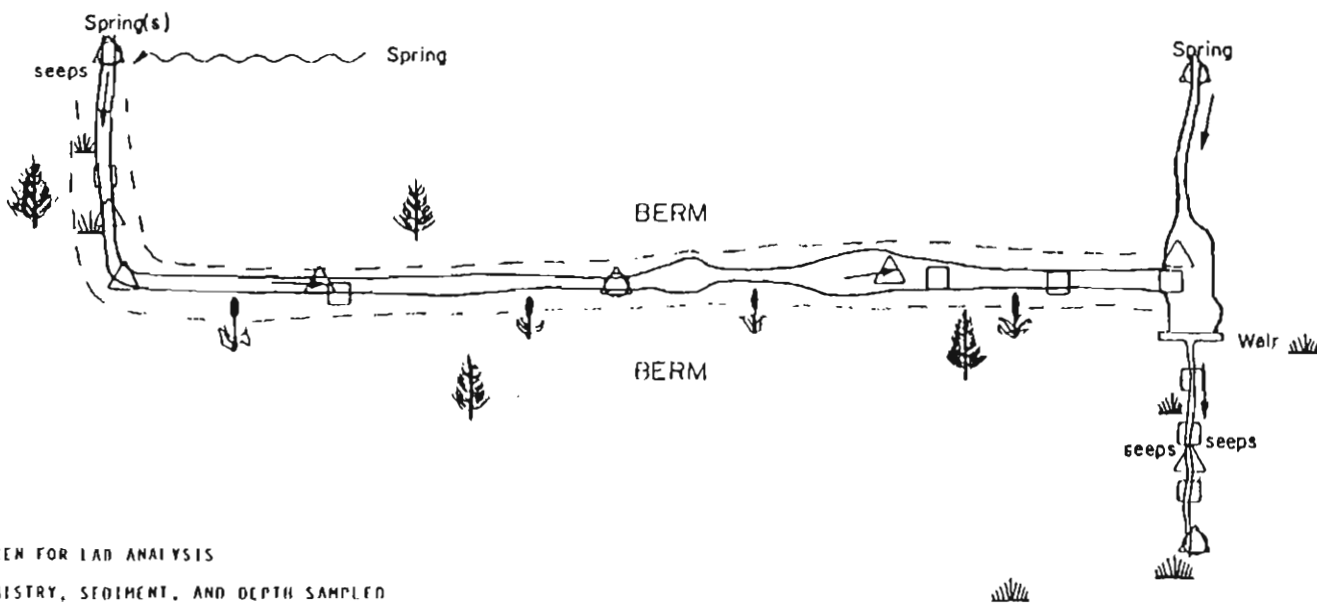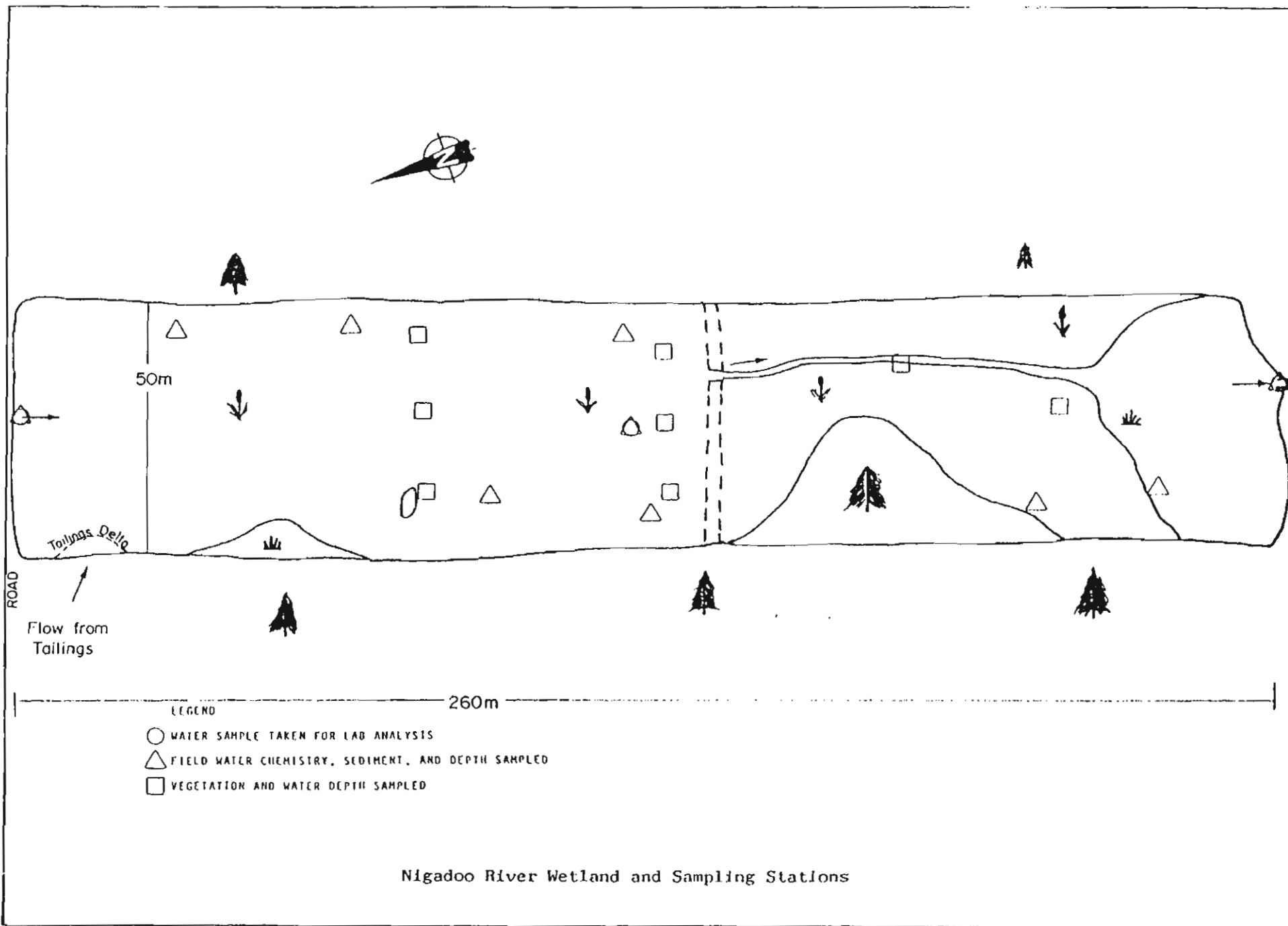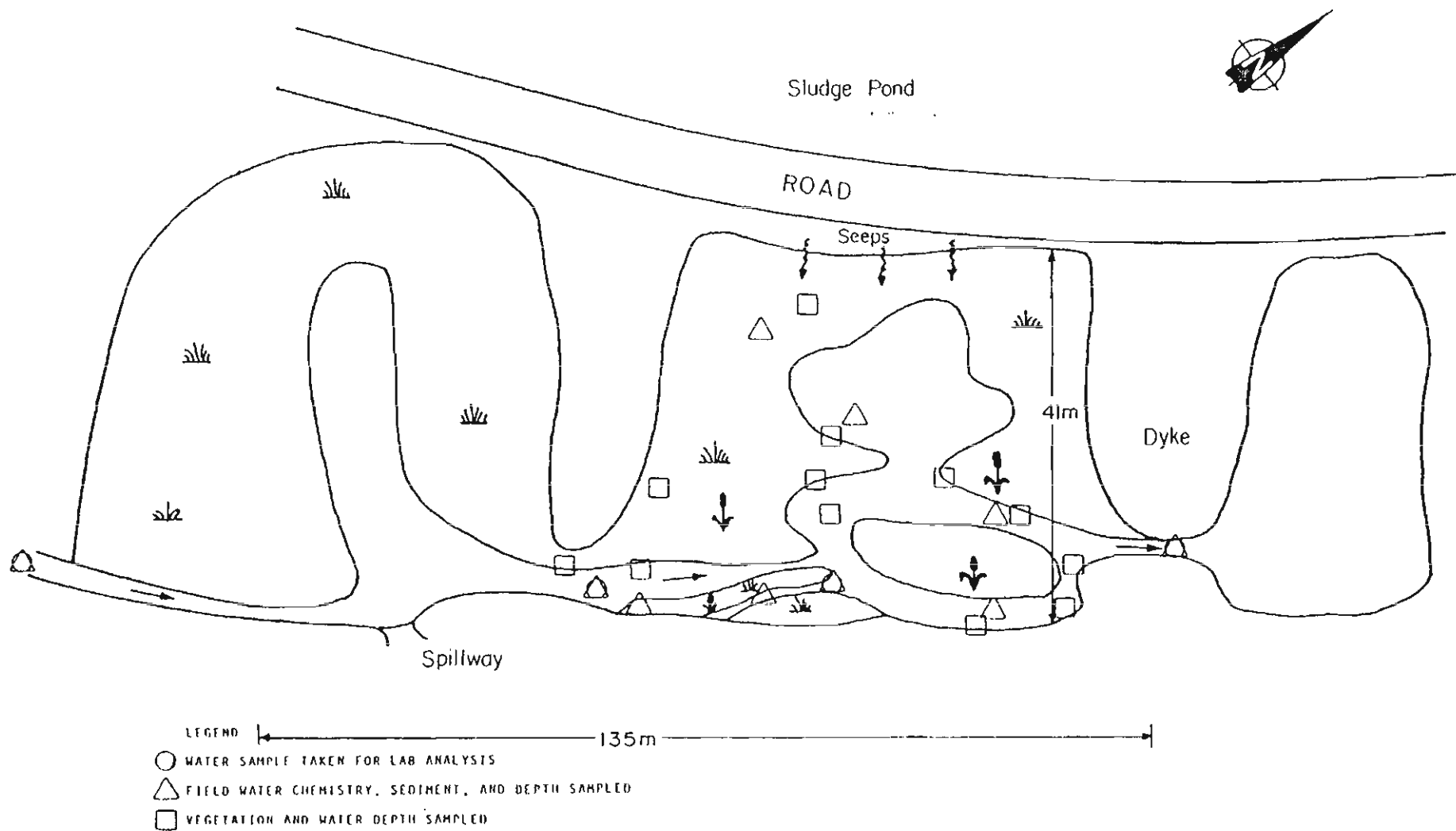m dichromate. All water samples were analyzed by standard limnological methods at the Environmental Chemistry Laboratory of the Victoria General Hospital in Halifax. Standard reference materials (U.S. Environmental Protection Agency and National Bureau of Standards) were analyzed as part of routine laboratory protocols (one to three samples out of ten were standards or control materials). The quality assurance/quality control (QA/QC) determinations for the metal analyses indicate consistent recovery and high precision measurement of all metal concentrations (see Appendix 1). As a further check on our methods, additional water samples from the Waite Amulet, Heath-Steele and Brunswick #12 sites were collected and analyzed by personnel from Noranda Technology (see Appendix Table 1b). Metal concentrations for the two data sets were generally identical, but our pH values were approximately one pH unit lower than those recorded by Noranda.

2.3 Hydrological Investigations

The fall program included a reconnaissance survey and determination of the major components of inflow and outflow from the study sites. A water balance was then developed and used to estimate contributions by other seeps and groundwater.

The discharges encountered varied in magnitude within and between sites, and a flexible approach was necessary. The measurement of seeps and springs was particularly exacting because of their characteristic low volume, thin sheet flows. Shallow collection ditches or other flow restrictions were built to channel the flows. Measurements of flows were by either direct collection or through the development of cross-sectional area-velocity profiles. Velocities were measured using a calibrated pygmy flow meter or approximated by measurement of suspended or floating matter in the water stream. The differing measurement techniques were employed wherever possible to act as independent checks on discharge estimates. Values were generally within 20 percent of each other for shallow flows.

In faster, deeper flows, the area-velocity profile was used, with multiple readings across the flow at a minimum of two depths. At weirs, culverts, or obstructions resulting in water free falls, direct measurements of discharge (collected volume over measured time) were made. The general agreement in larger flows between area-velocity profiles and direct measurement was about 10 percent.

Because the hydrologic regimes represents only a "snap shot" of conditions, only limited extrapolations can be made from the data. Surface hydrology, particularly in small watersheds characteristic of this study, can vary significantly with recent weather conditions. The Nickel Rim wetland is a good example. As a result of summer drought, water levels had dropped markedly, and there was no measurable flow into or out of the wetland. From the reconnaissance survey, we found evidence of flows in excess of 1000 L per minute (L/min) through the wetland.

2.4 Sediment Characterization

Samples of the upper 10 cm of wetland sediment were collected by hand at each of the field water sampling sites. One deep sample, from approximately 10 to 20 cm depth, was also taken at the Nickel Rim wetland. All samples were placed in individual plastic bags, stored in coolers while in the field, and frozen upon return to Halifax. Sediment samples from the Nickel Rim, Kam-Kotia, and Heath-Steele wetlands were thawed, dried, and homogenized prior to analysis. Measures of total aluminum, arsenic, cadmium, chromium, copper, iron, lead, manganese, mercury, nickel, and zinc were performed by standard geochemical techniques (strong acid digestions; colourimetric and atomic absorption methods) at the Mineral Engineering Centre of the Technical University of Nova Scotia in Halifax. Laboratory protocols included the analysis of standard reference ore and sediment materials that are available from CANMET-Energy Mines and Resources Canada, National Research Council of Canada, and the U.S. Geological Survey (one or two samples out of ten were standards or control materials). A summary of QA/QC determinations for sediment metal analyses is given in Appendix 1. Except for arsenic, all metals were accurately measured by methods used by staff of the Minerals Engineering Centre. Arsenic determinations appeared to be under-estimated by approximately 20 % (NB: CANMET has not yet established a true value for its low-arsenic sample, SY-2).

2.5 Vegetation Surveys

Percent cover of vegetation in each wetland was estimated using randomly-positioned 1 m^2 quadrats. From each quadrat, a 0.25 m^2 subsample of total above-ground biomass was collected, stored in bags, and dried. To obtain a represent-ative record of species composition and cover, 8 to 15 quadrats were sampled at each site. Water depth was also recorded at each sampling location.

Most plant species were of the families Cyperaceae, Juncaceae, and Gramineae, and were not identifiable in the field. Unidentified species were collected, pressed, and dried for laboratory identification. Species identif-ications were made using a dissecting microscope and standard floral keys for Eastern Canada (e.g. Britton and Brown 1913; Roland and Smith 1969; Hinds 1986).

Metal concentrations (Fe, Al, As, Cd, Cr, Cu, Hg, Mn, Ni, Pb and Zn) in dominant plant species at Nickel Rim, Kam-Kotia, and Heath-Steele were determined on dried tissue samples. Samples were digested in nitric acid and analysed using standard colourimetric and atomic absorption spectrophotometric methods by staff at the Mineral Engineering Centre of the Technical University of Nova Scotia in Halifax. As with sediment analyses, standard reference vegetation samples (U.S. National Bureau of Standards #1571 - Orchard Leaves) were also analyzed in order to quantify QA/QC for the lab methods. Except for Fe, Cd and Ni, all other metals were quantitatively recovered by methods used by staff of the Minerals Engineering Centre (Al values were not provided by NBS). Iron concentrations were low by about 50 %, while Cd and Ni were approximately two times higher than the certified values. The values reported herein have not been adjusted to reflect these differences.

3. Results and Discussion

3.1 Water Chemistry and Hydrology

The chemical characteristics of influent and effluent waters at the six wetlands suggest little amelioration of AMD was occurring in the fall (Figures 3-1 and 3-2, Tables 1 and 2; see also Appendix 2). Except for Kam-Kotia, only small changes in field and laboratory measures of pH, conductivity and sulfate were observed as water flowed through the wetlands (Figures 3-1 and 3-2). Many of these differences are probably within the range of variability for the instruments and analytical procedures (replicate samples were not collected). Presumably, the low water temperatures (= 4 °C) had already depressed sediment microbial activity at these sites.

At the Kam-Kotia site, the large increase in pH and reduced sulfate content (Figures 3-1 and 3-2) would suggest considerable biological activity in this wetland. However, influent waters to the wetland were diluted by a substantial input of water from the Little Kamiscotia River (see Figure 3-3). Effluent discharge was 40 times higher than the estimated inflow to the Kam-Kotia wetland. Considerable differences in discharge estimates were also noted at the Heath-Steele and Nigadoo River sites (5 and 3 fold differences, respectively). The extra inputs at Heath-Steele elevated the effluent pH by 1.6 units, whereas they decreased the pH 0.9 units at Nigadoo River (Figure 3-2). Sulfate concentrations were lowered by · 100 mg/L in each case.

Most of the surface water flow within wetlands was also observed to be largely channelized. Because of this "short-circuiting" of water flow, much of the surface water appeared to have limited contact with wetland sediment (even less with anaerobic sediments). Field pH and conductivity determinations in backwaters and semi-isolated ponds that were scattered throughout the wetlands were not different from those observed in principal channels.

Few consistent trends emerged from the trace metal data sets (see Table 1). As outlined above, this was probably a consequence of (a) depressed microbial activity, (b) variable dilution of influent waters by other seepages, (c) channelized flow patterns, and (d) our inability to distinguish natural variability from that associated with sampling and laboratory analysis. The data do indicate considerable export of metals to downstream environments (Table 2). On a daily basis in late September-early October, 1989, we estimate that up to 36 g of chromium (Cr), 0.1 kg of lead (Pb), 0.5 kg of nickel (Ni), 17 kg of copper (Cu), 72 kg of manganese (Mn), 130 kg of aluminum (Al), 240 kg of zinc (Zn), and 1100 kg of iron (Fe) leaves the wetlands in effluent waters. These exceptionally high loadings are mostly from the Kam-Kotia site (which had the highest effluent discharge). Large losses were also evident from the Waite Amulet site (with the highest trace metal concentrations) and from the Brunswick #12 site. Loadings for arsenic (As) and mercury (Hg) could not be calculated as the concentrations were always below the analytical limits of detection (listed in Appendix 2).

In the following discussions of individual site data, we will only highlight what we consider to be "significant" results at the six sites.

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Field Measurements of Surface pH and Conductivity at the Six Natural Wetlands

Heath-Steele

Nickel Rim

Kam-Kotia

Nigadoo River

Brunswick # 12

Waite Amulet
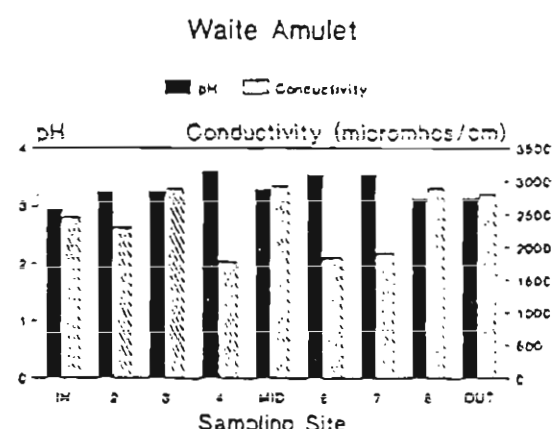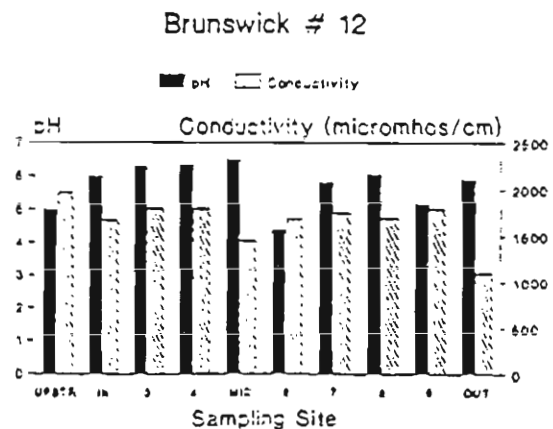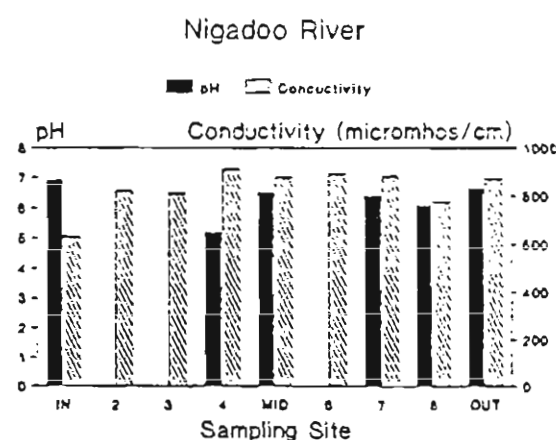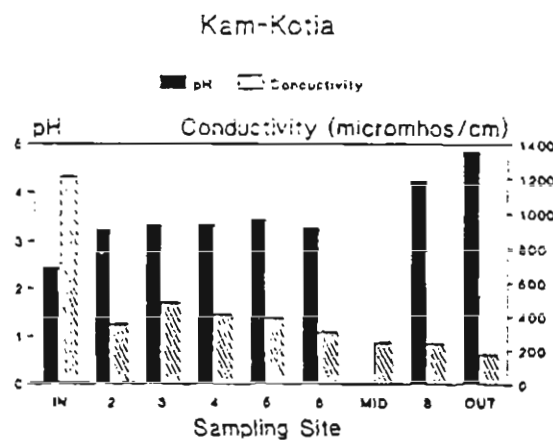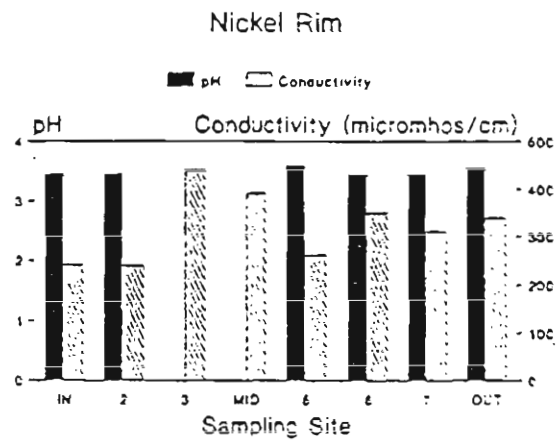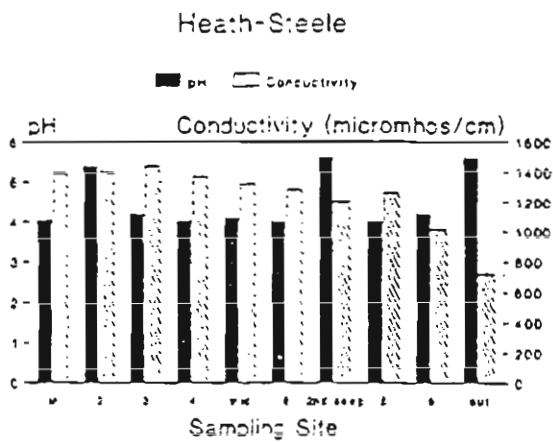
Laboratory Measurements of Sulfate and pH (except where noted) at the Six Natural Wetlands
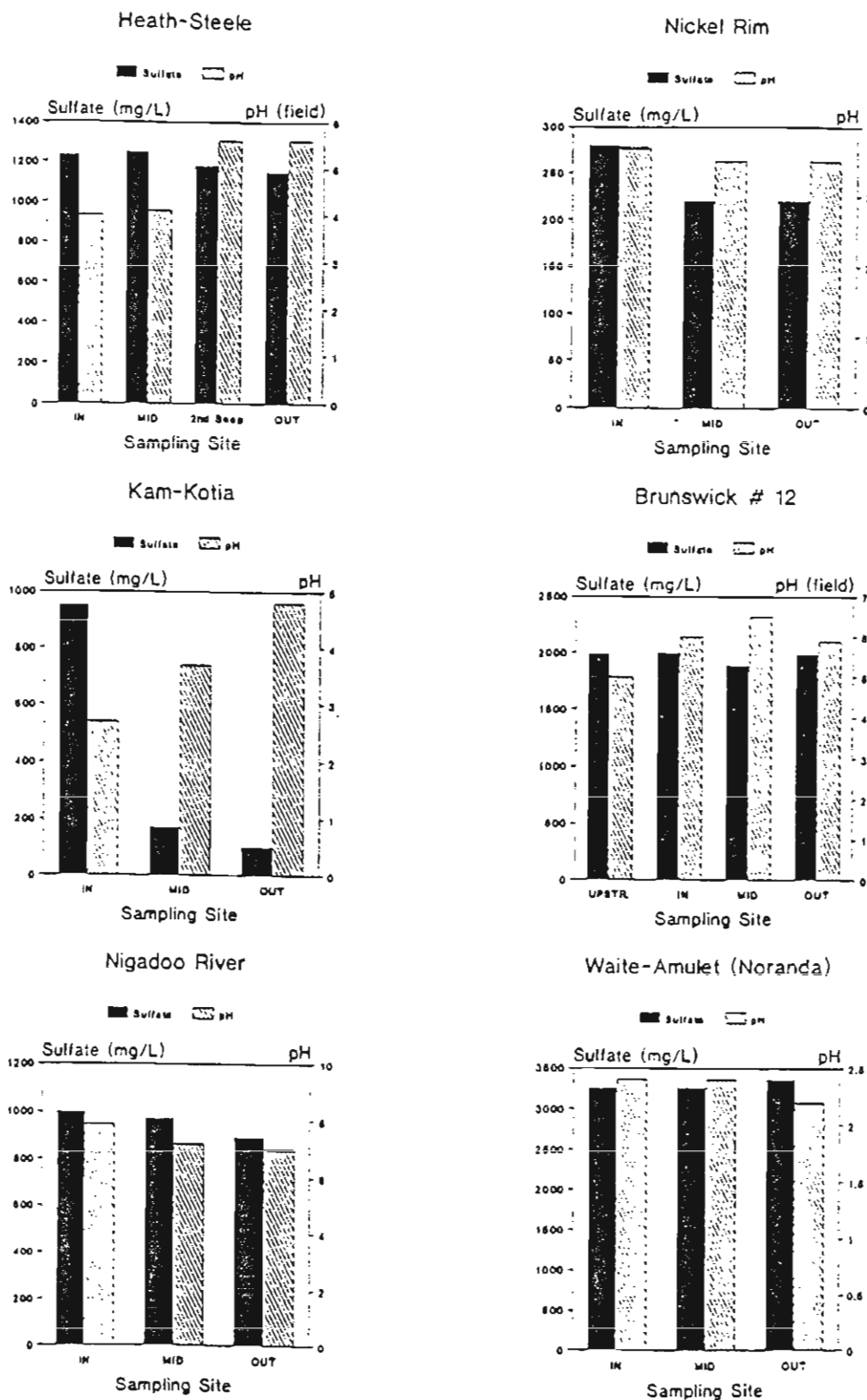
Stream Discharge Measured at the Inlet and Outlet
of the Six Natural Wetlands

Heath-Steele

Discharge (L/min)

Nickel Rim

Discharge (L/min)

Not Detectable   Not Detectable

Kam-Kotia

Discharge (L/min x 1000)

Nigadoo River

Discharge (L/min)

Brunswick # 12

Discharge (L/min)

Waite-Amulet

Discharge (L/min)
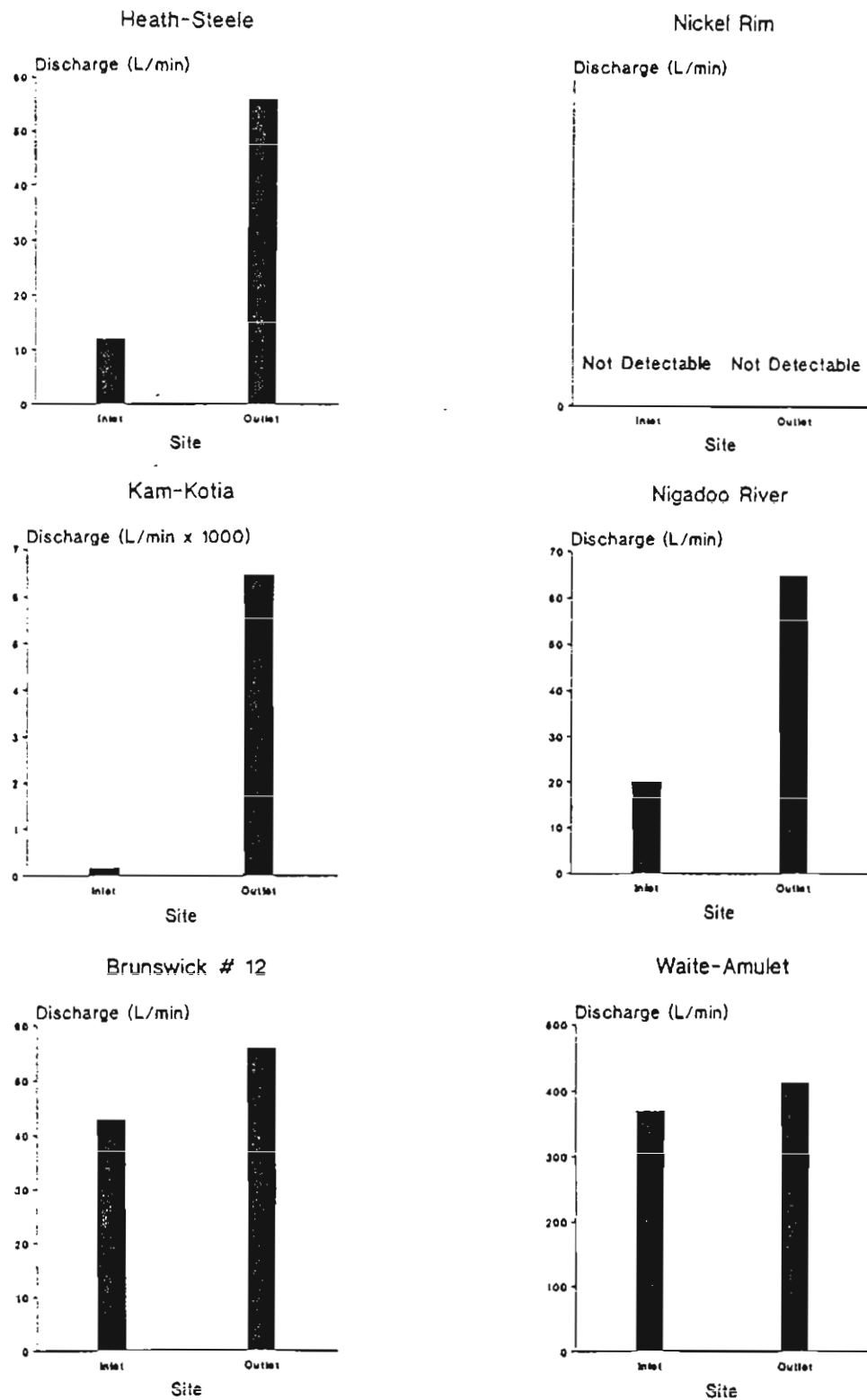
Table 1. Metal concentrations observed in water samples taken at the inlet, middle and outlet of six natural wetlands in eastern Canada. Concentrations of iron (Fe), manganese (Mn), aluminum (Al), chromium (Cr), copper (Cu), lead (Pb), nickel (Ni), and zinc (Zn) are given in mg/L. Zero values are below the analytical detection limits.

Study Site	Sampling Locations	Fe	Mn	Al	Cr	Cu	Pb	Ni	Zn
Nickel Rim	Inlet	1.2	1.3	10.0	0	0.2	0.01	2.4	0.1
	Middle	1.1	0.9	3.6	0	0.1	<0.01	1.1	0.1
	Outlet	1.0	1.0	3.6	0	0.1	0.01	1.1	0.1
Kam-Kotia	Inlet	120	7.9	14.0	0.02	1.8	0	0.04	27.0
	Middle	15	1.2	1.8	0	0.3	0	<0.01	3.5
	Outlet	120	7.7	14.0	0	1.8	0	0.05	26.0
Heath-Steele	Inlet	0.7	0.8	8.6	0	0.2	0.03	0	1.2
	Middle	0.8	8.9	4.8	0.03	0.1	<0.01	0	0.7
	Outlet	2.5	7.3	17.0	0	0.1	0.01	0	0.8
Nigadoo River	Inlet	0.1	20.0	0.2	0	0	0	0	2.1
	Middle	0.1	5.8	0.3	0.01	0	0	0	1.2
	Outlet	0.1	3.2	0.3	0	0	0	0	0.8
Brunswick #12	Inlet	6.4	28	2.8	0	<0.1	0.14	0.05	0.7
	Middle	3.5	26	2.2	0.01	<0.1	0.15	0.05	2.0
	Outlet	5.8	26	2.0	0.02	<0.1	0.13	0.05	0.8
Waite Amulet	Inlet	1080	5.8	44	0.03	2.9	0.17	0.04	19
	Middle	960	9.6	44	0.07	2.8	0.21	0.05	19
	Outlet	990	7.7	43	0.06	3.1	0.17	0.04	18

Table 2. Daily metal loadings to, and losses from six natural wetlands in eastern Canada. Units for iron (Fe), manganese (Mn), aluminum (Al), chromium (Cr) copper (Cu), lead (Pb), nickel (Ni) and zinc (Zn) are given in grams per day, except where noted.

Study Site	Location	Fe	Mn	Al	Cr	Cu	Pb	Ni	Zn
Kam-Kotia	Input	28 kg	2 kg	3 kg	5	0.4 kg		9	6 kg
	Output	1100 kg	72 kg	130 kg		17 kg		470	240 kg
Heath-Steele	Input	12	14	150		3	0.4		21
	Output	200	590	1400		8	1.0		65
Nigadoo River	Input	3	580	6					60
	Output	9	300	28					75
Brunswick #12	Input	400	2 kg	170		2	9	3	43
	Output	470	2 kg	160	2	2	10	4	65
Waite Amulet	Input	580 kg	3 kg	23 kg	16	2 kg	90	21	10 kg
	Output	590 kg	5 kg	26 kg	36	2 kg	100	24	11 kg

Concentrations of iron (Fe), manganese (Mn), aluminum (Al), copper (Cu) and nickel (Ni) were lower in waters leaving the Nickel Rim wetland than in influent waters (Table 1). Lacking quantitative estimates of discharges, we cannot ascertain if this wetland was indeed removing them. Chromium (Cr) and lead (Pb) were not detectable in either influent or effluent waters.

There was little apparent removal of trace metals by the Kam-Kotia wetland. Concentrations were essentially identical at both the inflow and outflow stations (Table 1). As noted earlier, additional inputs of seepage water, groundwater, and the Little Kamiskotia River must also deliver large quantities of metals to the wetland, and subsequently to downstream environments. Only Cr seemed to be trapped within the wetland. Because of the large effluent discharge, 6460 L/min, this site had the highest exports of Fe, Mn, Al, Cu, Ni, and Zn of the six wetlands examined (Table 2).

Additional input of waters to the Heath-Steele wetland, especially by the second seep identified in Figure 2-4, resulted in higher observed concentrations of Fe, Mn, and Al in effluent waters (Table 1; seep data in Appendix Table 2.3). Cu, Pb, and Zn concentration data suggests wetland uptake, but the loadings calculations, Table 2, reveal a net export of these metals.

The Nigadoo River site had the lowest trace metal concentrations of the six wetlands examined (Table 1). Only Mn and Zn appeared to be removed by the wetland. In fact, downstream losses of Mn were lower than input loadings (a unique observation in the total data set).

Comparisons of metal loadings into and out of wetlands at the Brunswick #12 and Waite Amulet sites indicate very little metal accumulation and large exports of Fe, Mn, Al, Cr, Cu, Pb, Ni and Zn (Table 2). The Waite Amulet site had the largest losses of Cr and Pb of all six sites examined, 36 g/day and 100 g/day, respectively.

3.2 Sediment Chemistry

Concentrations of metals in wetland sediments were two to eight orders of magnitude higher than those observed in overlying waters (see Table 3; data in Appendix 3). No visible evidence of mine tailings were evident in the sediment samples. Obviously, the wetlands had taken up metals at some time in the past. We are not aware of any literature that suggests a finite capacity for metal uptake. Consequently, we would expect continued uptake by the wetlands during more favourable, summer conditions.

Samples taken along the wetland axes did not show any strong spatial patterns (data in Appendix 3). This may have been a consequence of variability in sampling depth. The one deep sample from the middle of the Nickel Rim wetland generally had much higher metal concentrations than those observed in surface sediments (Table 3). Arsenic, lead, manganese, and zinc concentrations were 100 to 1000 times higher at depth. Only copper, mercury, and nickel contents of the deep sample were lower, or comparable, to surface values. The presence of high concentration gradients suggests that as the organic matter in the sediments is consumed by microbes, many metals become more concentrated in deeper sediments.

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Table 3. Comparison of metal concentrations in wetland sediments and overlying waters at the Nickel Rim, Kam-Kotia, and Heath-Steele sites. Except for one deep sediment sample, values are the means (± standard deviation) for 3 water samples and 6 to 7 sediment samples. Units are given as ppm (where 1 ppm ≈ 1 µg/g dry sediment ≈ 1 mg/L water).

| Metal | Nickel Rim | | | Kam-Kotia | | Heath-Steele | |
	Water	Surface Sediment	Deep Sediment	Water	Sediment	Water	Sediment
iron	1.1 (0.1)	1,300 (900)	11,000	90 (60)	21,000 (2000)	1.3 (1.0)	16,000 (3000)
aluminum	5.7 (3.7)	2,000 (800)	5,000	10 (7)	2,400 (500)	15 (10)	5,100 (1600)
arsenic	<.005	13 (5)	13,000	<.005	20 (11)	<.005	500 (100)
cadmium	<.01	1.2 (0.9)	110	<.005	1.4 (0.6)	<.005	7 (4)
chromium	<.01	45 (15)	680	0.01 (0.01)	57 (13)	0.02 (0.02)	48 (9)
copper	0.09 (0.06)	550 (370)	570	1.3 (0.9)	600 (140)	0.1 (0.9)	1,300 (400)
lead	0.005 (0.001)	64 (44)	3,100	<.002	20 (10)	0.014 (0.009)	1,700 (1000)
manganese	1.1 (0.2)	150 (100)	52,000	5.6 (3.8)	210 (50)	6.2 (3.7)	460 (390)
mercury	<.0001	0.14 (0.03)	0.07	<.0001	0.43 (0.06)	<.0001	0.22 (0.08)
nickel	1.5 (0.8)	780 (340)	50	0.03 (0.03)	21 (9)	<.02	32 (13)
zinc	0.1	70 (30)	8,100	20 (14)	780 (170)	1.2 (0.6)	5,600 (5000)

The gradients also suggest that the wetlands could occasionally be sources of metals to overlying waters, especially in the spring and after storm events. The concentration gradient would be even higher at these times, enhancing upward diffusion of some metals out of the sediment and into effluent waters.

3.3 Vegetation Analyses

No clear pattern emerged from the vegetation data that might help to explain inter-site variability in AMD mitigation potential (Table 4). This is due in part to the fact that none of the wetlands significantly mitigated AMD during the fall sampling period. Total vegetation cover (TVC) ranged from 11% at Kam-Kotia to 82% at Heath-Steele. All sites except Nickel Rim (77% TVC) had significant Typha associations. Typha was dominant at Nigadoo (25% TVC) and Brunswick #12 (42% TVC), and was second in abundance to Nymphaea odorata and Carex retrorsa at Kam-Kotia and Waite Amulet (54% TVC), respectively. The Nickel Rim association consisted primarily of various sedges and rushes, while that at Heath-Steele consisted of sedges, rushes, horsetails, unidentified filamentous green algae, and some Typha. All sites except Kam-Kotia appeared to have good circulation of water through the vegetation. At Kam-Kotia, very little vegetation grew in the water (approximately 5% TVC in water), although there were extensive Typha beds on both sides of the channel (see Figure 2-2). The rapidly-accumulating, flocculent precipitates at Kam-Kotia may have prevented plant colonization of submerged areas, thereby limiting the amount of labile organic matter available to assemblages of sediment microbes.

There was considerable variability in metal concentrations of plant tissues among the different species. In every species, concentrations in tissues were higher than those in surface waters, and in a few species, higher than in sediments (Table 5). For example, at Nickel Rim, Eleocharis ovata and Scirpus subterminalis had more Fe, As, and Mn than did surface sediments, and more Fe and Hg than noted in the deep sediments. At Kam-Kotia, Vallisneria americana (tentative identification) had more Fe, Al, and Mn than did sediments. At Heath-Steele, only Mn was more concentrated in tissues than in sediments, but several species, including Typha, Equisetum fluviatile, Carex crawfordii, Juncus brevicaudatus, J. effusus, and an unidentified filamentous green alga had high concentrations of some metals. Those species best able to concentrate metals (Eleocharis ovata, Scirpus subterminalis, and Vallisneria americana) grew completely submerged, the first two forming dense green mats on the bottom. The proportions in which metals are removed from surface waters and sediments is unknown. If these species absorb metals from surface water, they may mitigate AMD by bringing both metals and organic matter in contact with sediment microbial communities. If metals are taken up from sediments, then plants may function solely as a carbon source for microbes, aiding little in the transfer of metals from water to sediment.

Table 4.   Estimates of mean (standard deviation) vegetation cover at the six natural wetlands. N = the number of 1 m^2 quadrats.

SPECIES	Nickel Rim (N=13)	Kam-Kotia (N=15)	Heath-Steele (N=8)
filamentous green algae			10.6 (26.3)
mosses and bryophytes	10.4 (24.1)		0.3 (0.7)
Equisetum arvense			
Equisetum fluviatile			17.8 (25.2)
Equisetum pratense			
Abies balsamea			
Typha spp.		4.0 (8.2)	10.4 (19.8)
Sparangium americanum		0.1 (0.5)	
Sparangium spp.			
Vallisneria americana		0.1 (0.5)	
Agrostis canina			
Calamagrostis inexpansa			
Calamagrostis spp.			
Glyceria striata			7.0 (16.3)
Oryzopsis spp.			0.1 (0.2)
Carex aurea and C. recta	2.3 (5.8)		
Carex crawfordii			3.6 (3.8)
Carex crinita			1.0 (1.6)
Carex pairaei			
Carex retrorsa			
Carex spp.			
Dulichium arundinaceum	<0.1 (0.1)		
Eleocharis acicularis	0.1 (0.3)		
Eleocharis obtusa			
Eleocharis ovata	11.2 (21.7)		
Eleocharis smallii			18.8 (49.6)
Eleocharis spp.		2.0 (5.4)	
Scirpus atrocinctus			3.6 (5.3)
Scirpus microcarpus			
Scirpus rubrotinctus	0.8 (2.7)		
Scirpus subterminalis	16.2 (26.5)		
Juncus brevicaudatus			1.4 (3.3)
Juncus canadensis	2.7 (3.7)		
Juncus effusus	1.7 (5.3)		6.5 (12.8)
Juncus pelocarpus	28.8 (53.9)		
Juncus subtilis			0.3 (0.4)
Unknown monocot			
Alnus incana			
Betula papyrifera			
Myrica gale	<0.1 (0.1)		
Nymphaea odorata	2.7 (5.8)	4.7 (10.4)	
Ceratophyllum demersum		<0.1 (0.1)	
Cornus sericea			
Viola americana			0.1 (0.2)
Lycopus americanus			
Mentha arvensis			
Tussilago farfara			0.1 (0.3)
Solidago graminifolia			0.8 (1.6)
TOTAL	76.8 (59.0)	11.0 (15.3)	82.1 (41.0)

Table 4.   Continued.

SPECIES	Nigadoo River (N=8)	Brunswick #12 (N=12)	Wait-Amulet (N=8)
filamentous green algae			
mosses and bryophytes	2.5 (5.0)		
Equisetum arvense	0.9 (1.6)		
Equisetum fluviatile			
Equisetum pratense			0.1 (0.3)
Abies balsamea	0.1 (0.2)		
Typha spp.	16.3 (14.9)	33.8 (31.8)	13.3 (16.9)
Sparangium americanum			
Sparangium spp.		<0.1 (0.1)	
Vallisneria americana			
Agrostis canina		0.1 (0.3)	
Calamagrostis inexpansa			0.2 (0.3)
Calamagrostis spp.	0.1 (0.2)		
Glyceria striata			
Oryzopsis spp.			
Carex aurea and C. recta			
Carex crawfordii			
Carex crinita		5.5 (16.5)	
Carex pairaei		<0.1 (0.1)	
Carex retrorsa			37.3 (34.3)
Carex spp.	2.5 (6.6)		
Dulichium arundinaceum			
Eleocharis acicularis			
Eleocharis obtusa		1.8 (5.5)	
Eleocharis ovata			
Eleocharis smallii			
Eleocharis spp.			
Scirpus atrocinctus			
Scirpus microcarpus			2.7 (3.5)
Scirpus rubrotinctus			
Scirpus subterminalis			
Juncus brevicaudatus			
Juncus canadensis			
Juncus effusus		0.6 (1.4)	
Juncus pelocarpus			
Juncus subtilis			
Unknown monocot		0.1 (0.3)	
Alnus incana	0.2 (0.3)		
Betula papyrifera	1.3 (3.3)		
Myrica gale			
Nymphaea odorata			
Ceratophyllum demersum			
Cornus sericea	0.1 (0.2)		
Viola americana			
Lycopus americanus	1.3 (3.3)		
Mentha arvensis	0.1 (0.2)		
Tussilago farfara			
Solidago graminifolia			
TOTAL	25.1 (23.1)	42.0 (30.4)	53.5 (33.2)

Table 5. Comparison of metal concentrations in vegetation samples taken at the Nickel Rim, Kam-Kotia, and Heath-Steele sites. Tissue concentrations of iron (Fe), manganese (Mn), aluminum (Al), arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), lead (Pb), nickel (Ni), and zinc (Zn) are given as ppm-dry weight, while those for mercury (Hg) are given in ppb-dry weight.

Plant Species	Fe	Mn	Al	As	Cd	Cr	Cu	Hg	Pb	Ni	Zn
Nickel Rim:											
Carex spp.	450	330	50	7	0.2	5	11	94	6	28	24
Eleocharis ovata	22400	200	700	20	0.2	10	36	37	4	54	38
Juncus pelocarpus	910	250	280	6	0.4	4	23	100	4	38	38
Juncus canadensis	990	240	310	3	0.5	5	23	94	6	42	40
Nymphaea odorata	860	200	160	16	0.4	4	29	74	10	61	20
Scirpus subterminalis	25600	190	1900	18	0.2	12	67	170	12	83	42
Kam-Kotia:											
Vallisneria americana	36000	390	3000	5	0.8	9	150	260	5	7	430
Heath-Steele:											
filamentous green algae	15000	260	1400	220	1.2	42	560	170	860	15	580
Carex crawfordii	1600	500	290	10	0.3	4	14	94	19	3	77
Carex crinita	280	1000	100	7	0.3	4	12	54	6	4	64
Eleocharis smallii	860	80	540	6	<0.1	5	15	49	18	2	66
Equisetum fluviatile	1100	750	680	6	0.4	2	20	44	63	2	170
Glyceria striata	410	620	220	7	<0.1	5	15	170	10	2	100
Juncus effusus	380	1000	190	12	1.4	5	11	64	10	4	120
Juncus brevicaudatus	830	1800	590	9	2.5	4	14	54	22	2	210
Scirpus atrocinctus	560	910	190	6	0.6	4	10	94	10	2	81
Typha spp. leaves	8500	740	1700	14	<0.1	4	84	150	103	2	48
flowers	290	2800	60		<0.1	4	8		3	4	48

4. Conclusions and Recommendations

The chemical characteristics of water collected from the six wetland sites in late September-early October 1989 suggest little biologically-related improvement of mine effluent waters. Lacking any other seasonal data, we believe the poor efficiency of metal removal and pH control are a consequence of (1) low temperatures, ca. 4 °C, (2) channelized flow patterns within the wetlands, and (3) limited contact of AMD with anoxic sediments. Inputs of other seeps and groundwaters to the wetlands were significant complicating factors, especially at the Kam-Kotia site.

High metal concentrations in wetland sediments indicates that the wetlands had removed metals in the recent past. Metal accumulations in the sediments occurs as a consequence of (a) chemical precipitation reactions of metals with hydrogen sulfide, and (b) incorporation into plant and bacterial biomass. Future studies should carefully examine vertical profiles for more historical information.

Because of the high metal loadings observed on the fall survey, further seasonal sampling should be carried out at some or all of the sites. We would suggest at least three other periods be examined: (1) during warmer months when biological activity is higher, (2) following summer storm-events to see how the wetlands handle short pulses of AMD, and (3) in the spring when discharges are higher. Spring runoff and storm freshets may dilute AMD but the actual loadings (discharge X concentration) may still be quite large. Wetland sediments could also augment concentrations during high discharge periods. Obviously, the storm survey would have to be carried out by on-site mine employees or provincial lake/stream surveyors. Ideally, time series samples would be collected before and on several occasions after a large storm. This programme would only provide maximum and minimum values for metal uptake and losses from natural wetlands.

Variations in plant associations among sites may lead to differences in suitability for AMD mitigation, but this is difficult to assess from our fall data. We recommend that any subsequent sampling programme(s) concentrate on those sites with widely different plant associations. The Nickel Rim, Heath-Steele, and Nigadoo River sites provide examples of sedge-rush, sedge-rush-Typha, and Typha wetlands, respectively. Further study of the Kam-Kotia wetland as a practical means of controlling AMD is not warranted. Large discharges from the Little Kamiscotia River appear to pass quickly through the small wetland. Waite Amulet has a relatively high proportion of channelized flow, and its sediments appear to be primarily rapidly-accumulating, flocculent precipitates which may hinder exchange of water between surface and sediments. Brunswick #12 wetland had seepage along most of its length and some channelization of flow. This site could, however, represent an alternate Typha wetland for comparison with the Nigadoo River, Heath-Steele and Nickel Rim wetlands.

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6. Appendices

Appendix 1.   QA/QC determinations for metal analyses of water, sediment and vegetation samples as provided by the Environmental Chemistry Laboratory at the Victoria General Hospital, Halifax, and the Minerals Engineering Centre of the Technical University of Nova Scotia, Halifax.

Appendix 2.   Water chemistry data from the inflow, middle and outflow of natural wetlands near the Nickel Rim, Kam-Kotia, Heath-Steele, Nigadoo River, Brunswick #12, and Waite Amulet mine sites (September 28 to October 12, 1989).

Appendix 3.   Sediment chemistry data at Nickel Rim, Kam-Kotia and Heath-Steele wetlands.

Appendix 1.

A summary of QA/QC determinations for metal analyses of water, sediment and vegetation samples as provided by the Environmental Chemistry Laboratory at the Victoria General Hospital, Halifax, the Minerals Engineering Centre of the Technical University of Nova Scotia, Halifax, and the Centre de Technologie Noranda, Pointe-Claire, Quebec.

Appendix Table 1a. QA/QC determinations for metal analyses in standard reference water samples (from the U.S. Environmental Protection Agency and National Bureau of Standards) as performed by the Environmental Chemistry Laboratory of the Victoria General Hospital, Halifax.

Appendix Table 1b. Comparison of water quality measures in samples collected simultaneously by personnel from P. Lane and Associates Limited (PLA) and Noranda Technology (NT) at the Waite Amulet, Heath-Steele, and Brunswick #12 natural wetlands.

Appendix Table 1c. QA/QC determinations for metal analyses of standard reference sediment and ore materials (from CANMET, NRCC and the U.S. Geological Survey) as performed by the Minerals Engineering Centre, Technical University of Nova Scotia, Halifax.

Appendix Table 1d. QA/QC determinations for metal analyses on standard reference vegetation samples (U.S. National Bureau of Standards #1571 - Orchard Leaves; 5 samples analyzed) as performed by the Minerals Engineering Centre, Technical University of Nova Scotia, Halifax.

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Appendix Table 1a.

QA/QC determinations for metal analyses in standard reference water samples (from the U.S. Environmental Protection Agency and National Bureau of Standards) as performed by the Environmental Chemistry Laboratory of the Victoria General Hospital, Halifax. Units for all metals are in mg/L, except lead and mercury which are given in μg/L. Lead concentrations were measured by two methods, Inductively Coupled Plasma Spectroscopy (ICP) and Graphite Furnace Atomic Absorption (HGA). NV = value not provided

Metal	Sample Identification	Mean	Standard Deviation	Recommended Value
aluminum	WP-386	0.512	0.034	0.500
	WP-686	1.547	0.092	1.500
arsenic	EPA Conc.#2	0.052	0.002	0.053
	EPA Conc.#13	0.148	0.003	0.150
barium	WP-386	0.465	0.009	NV
	WP-686	4.664	0.094	NV
beryllium	WP-386	0.109	0.004	0.100
	WP-686	0.324	0.013	0.300
boron	WP-386	0.015	0.004	NV
	WP-686	0.046	0.004	NV
cadmium	WP-386	0.024	0.002	0.025
	WP-686	0.070	0.005	0.075
calcium	WP-386	0.491	0.016	0.500
	WP-686	4.944	0.143	5.000
chromium	WP-386	0.100	0.010	0.100
	WP-686	0.302	0.022	0.300
copper	WP-386	0.101	0.005	0.100
	WP-686	0.304	0.011	0.300
iron	WP-386	0.099	0.006	0.100
	WP-686	0.303	0.014	0.300
lead (HGA)	WP-287	2.303	0.316	2.500
	WP-578	21.22	1.68	22.00
	NBS-1643b	22.03	1.74	23.70
lead (ICP)	WP-386	100	12	100
	WP-686	264	13	300

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Appendix Table 1a. Continued.

Metal	Sample Identification	Mean	Standard Deviation	Recommended Value
magnesium	WP-386	0.048	0.004	0.050
	WP-686	0.492	0.031	0.500
manganese	WP-386	0.102	0.008	0.100
	WP-686	0.302	0.018	0.300
mercury	EPA 1172 C-1	69.80	2.35	70.00
	EPA 1172 C-2	140.90	3.28	140.00
	EPA 1172 C-3	209.70	4.82	210.00
nickel	WP-386	0.100	0.005	0.100
	WP-686	0.294	0.013	0.300
vanadium	WP-386	0.243	0.012	0.250
	WP-686	0.670	0.034	0.700
zinc	WP-386	0.104	0.009	0.100
	WP-686	0.309	0.023	0.300

Appendix Table 1b.

Comparison of water quality measures in samples collected simultaneously by personnel from P.Lane and Associates Limited (PLA) and Noranda Technology (NT) at the Waite Amulet, Heath-Steele, and Brunswick #12 natural wetlands.

Location	pH PLA	pH NT	zinc (mg/L) PLA	zinc (mg/L) NT	iron (mg/L) PLA	iron (mg/L) NT	sulfate (mg/L) PLA	sulfate (mg/L) NT
Waite Amulet								
IN	2.4	-	19	13	1075	912	3250	3800
OUT	2.2	-	18	13	987	941	3360	2900
Heath-Steele								
IN	4.0	6.4	1.2	1.4	0.7	1.5	1230	1450
MID	4.1	5.3	0.7	0.8	0.8	1.3	1250	1400
2ND SEEP	5.6	6.1	2.0	2.0	5.7	5.4	1180	1400
OUT	5.6	6.6	0.8	0.8	2.5	1.3	1150	1350
Brunswick #12								
UPSTREAM	5.0	-	2.2	-	1.5	-	1990	-
IN	6.1	-	1.0	0.9	6.4	5.9	2000	2300
MID	6.5	-	0.9	0.8	3.5	7.2	1890	<2
OUT	5.8	-	1.0	0.9	5.8	7.0	1990	2300

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Appendix Table 1c.

QA/QC determinations for metal analyses of standard reference sediment and ore materials (from CANMET, NRCC and the U.S. Geological Survey) as performed by the Minerals Engineering Centre, Technical University of Nova Scotia, Halifax. Units are given as ppm. NV = value not provided. ? = approximate value only.

Metal	Sample Identification	Mean	Standard Deviation	Recommended Value
aluminum	SY-3	11790	146	11800
	BCR-1	13740	90	13680
	G-2	15420	156	15350
arsenic	SY-3	15.5	0.6	20 ?
	MP-1	6425	806	7700
cadmium	MCSS-1	0.610	0.014	0.59
	BCSS-1	0.240	0.019	0.25
chromium	CG-1	57	7	NV
	CB-1	179	15	NV
	MRG-1	433	20	420
copper	SY-3	15.0	1.3	17
	MRG-1	132	6	135
	CB-1	416	8	NV
iron	G-2	2620	48	2670
	GSP-1	4280	42	4330
	SY-2	6340	101	6290
	BCR-1	13410	78	13520
lead	MRG-1	8.60	1.34	10
	SY-2	83	2	80
	SY-3	131	4	130
manganese	CG-1	67	3	NV
	SY-2	306	12	32
	SY-3	315	11	33
mercury	SO-1	0.022	0.005	0.022
	BCSS-1	0.137	0.017	0.129
	MESS-1	0.179	0.015	0.171
nickel	SY-2	10.0	0.9	10
	CB-1	62	2	NV
	MRG-1	191	5	200
zinc	CG-1	74	2	NV
	SY-3	246	5	250
	SY-3	251	5	250

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Appendix Table 1d.

QA/QC determinations for metal analyses on standard reference vegetation samples
(U.S. National Bureau of Standards #1571 - Orchard Leaves; 5 samples analyzed)
as performed by the Minerals Engineering Centre, Technical University of Nova
Scotia, Halifax. Units are given as ppm. NV = value not provided.

Metal	Mean	Standard Deviation	Recommended Value
aluminum	111	5	NV
arsenic	10.4	0.6	10 ± 2
cadmium	0.20	0.06	0.11 ± 0.01
chromium	2.20	0.45	2.6 ± 0.3
copper	12.88	0.18	12 ± 1
iron	160	6	300 ± 20
lead	47.8	1.1	45 ± 3
manganese	92.0	0.7	91 ± 4
mercury	0.150	<0.001	0.155 ± 0.015
nickel	2.16	0.22	1.3 ± 0.2
zinc	28.6	0.9	25 ± 3

Appendix 2.

Water chemistry data from the inflow, middle and outflow of natural wetlands near the Nickel Rim, Kam-Kotia, Heath-Steele, Nigadoo River, Brunswick #12, and Waite Amulet mine sites (September 28 to October 12, 1989). Zero values are below the analytical detection limits. Units for each parameter are in mg/L, except where noted. Abbreviations for the general water quality parameters and trace metals in the six Appendix Tables are summarized below (LD = limit of detection; given as mg/L, except where noted).

Abbreviation	Meaning	Trace Metals		LD
Cond.	specific conductivity	Al - ICP[1]	aluminum	.05
$CaCO_3$	calcium carbonate	As	arsenic	.005
Na	sodium ion	B	boron	.02
K	potassium ion	Ba	barium	.005
Mg	magnesium ion	Be	berylium	.005
Ca	calcium ion	Cd	cadmium	.01
Cl	chloride ion	Co	cobalt	.01
SO_4	sulfate ion	Cr	chromium	.01
PO_4	reactive phosphate	Cu	copper	.01
$NO_3 + NO_2$	nitrate plus nitrite	Fe	iron	.02
NH_3	ammonia	Hg	mercury	.05 µg/L
SiO_2	reactive silicate	Mn	manganese	.01
TOC	total organic carbon	Ni	nickel	.02
TDS	total dissolved solids	Pb - HGA[2]	lead	.002
TSS	total suspended sediments	Pb - ICP	lead	.05
		Sb	antimony	.05
		Se	selenium	.1
		Sn	tin	.03
		V	vanadium	.01
		Zn	zinc	.01

[1] ICP - Inductively Coupled Plasma Spectroscopy is the method used for all metals except arsenic and mercury (Hydride Generation/Cold Vapour Atomic Absorption method used for As and Hg determinations)

[2] HGA - Graphite Furnace Atomic Absorption is a more accurate method for measurement of low concentrations than is the ICP method

Appendix Table 2.1:   Nickel Rim wetland

Parameter	Inflow	Mid	Outflow
pH (no units)	3.7	3.5	3.5
Acidity	70.5	51.3	51.0
Cond. (µmhos/cm)	720	585	620
Hardness ($CaCO_3$)	279	195	195
Alkalinity ($CaCO_3$)	0	0	0
Na	2	3	2
K	0	1.7	1.7
Mg	38	28	28
Ca	49	32	32
Cl	0	0	0
SO_4	280	220	220
PO_4	0	0.01	0.01
$NO_2 + NO_3$	0	0	0
NH_3	0.1	4.3	4.4
SiO_2	0	12	11
Color (TCU)	8	0	0
Humic acid	5.3	1.0	1.0
TOC	6.4	1.6	1.8
TDS	411	337	328
TSS	4	4	2
Al - ICP	10	3.6	3.6
As	0	0	0
B	0	0	0
Ba	0.038	0.063	0.064
Be	0	0	0
Cd	0	0	0
Co	0.11	0.07	0.07
Cr	0	0	0
Cu	0.16	0.05	0.05
Fe	1.2	1.1	1
Hg (µg/L)	0	0	0
Mn	1.3	0.9	1.0
Ni	2.4	1.1	1.1
Pb - ICP	0	0	0
Pb - HGA	0.006	0.004	0.005
Sb	0	0	0
Se	0	0	0
Sn	0	0	0
V	0	0	0
Zn	0.1	0.1	0.1

Appendix Table 2.2: Kam-Kotia wetland

Parameter	Inflow	Mid	Outflow
pH (no units)	2.7	3.7	4.8
Acidity	493.0	44.8	22.5
Cond. (μmhos/cm)	3600	470	260
Hardness ($CaCO_3$)	591	151	109
Alkalinity ($CaCO_3$)	0	0	0
Na	3	2	2
K	0	0	0
Mg	66	15	8
Ca	128	36	30
Cl	1	3	3
SO_4	950	170	100
PO_4	0.02	0	0
$NO_2 + NO_3$	0	0	0
NH_3	5.3	1.0	0.6
SiO_2	29	5.3	3.1
Color (TCU)	86	12	110
Humic acid	12.3	21.9	42.3
TOC	9.6	11	17
TDS	1400	273	199
TSS	3	24	25
Al - ICP	14.0	1.8	14
As	0	0	0
B	0.06	0	0.06
Ba	0.014	0.007	0.014
Be	0	0	0
Cd	0	0	0
Co	1.50	0.28	1.50
Cr	0.02	0	0
Cu	1.80	0.26	1.80
Fe	117.0	15.0	116.0
Hg (μg/L)	0	0	0
Mn	7.9	1.2	7.7
Ni	0.04	0	0.05
Pb - ICP	0	0	0
Pb - HGA	0	0	0
Sb	0	0	0
Se	0	0	0
Sn	0	0	0
V	0.02	0	0.02
Zn	27.0	3.5	26.0

Appendix Table 2.3:   Heath-Steele wetland

Parameter	Inflow	Mid	2nd Seep	Outflow
Acidity	61.2	45.2	43.6	31.2
Hardness ($CaCO_3$)	1250	1249	1204	1168
Alkalinity ($CaCO_3$)	1	0	12	11
Na	23	3	20	24
K	4.4	4.4	5.2	5.6
Mg	23	28	29	35
Ca	462	455	435	410
Cl	14	14	12	13
SO_4	1230	1250	1180	1150
PO_4	0.01	0.03	0	0
$NO_2 + NO_3$	0.3	0	0.7	0.2
NH_3	0.2	0.3	0.3	0.2
SiO_2	6.4	5.3	6.1	5.7
Humic acid	3.5	2.7	6.9	4.7
TDS	1983	1962	1830	1838
TSS	1	0	178	84
Al - ICP	8.6	4.8	28.0	17.0
As	0	0	0	0
B	0	0	0	0
Ba	0.013	0.021	0.026	0.024
Be	0	0	0	0
Cd	0	0	0	0
Co	0.10	0.08	0.32	0.07
Cr	0	0.03	0.03	0
Cu	0.24	0.08	0.09	0.09
Fe	0.7	0.8	5.7	2.5
Hg (μg/L)	0	0	0	0
Mn	0.8	8.9	7.9	7.3
Ni	0	0	0.02	0
Pb - ICP	0	0.08	0	0
Pb - HGA	0.025	0.003	0.013	0.013
Sb	0	0	0	0
Se	0	0	0	0
Sn	0	0	0	0
V	0	0.01	0.01	0
Zn	1.2	0.7	2.0	0.8

Appendix Table 2.4:   Nigadoo River wetland

Parameter	Inflow	Mid	Outflow
pH (no units)	7.9	7.2	7.0
Cond. (μmhos/cm)	2440	2300	2210
Hardness (CaCO$_3$)	1038	1022	965
Alkalinity (CaCO$_3$)	65	19	16
Na	12	13	12
K	5	4.3	4.1
Mg	29	31	24
Ca	368	358	347
Cl	8	9	9
SO$_4$	1000	970	890
PO$_4$	0.01	0	0
NO$_2$ + NO$_3$	0	0	0
NH$_3$	0	0	0
SiO$_2$	4.2	6.7	6.7
Color (TCU)	5	0	0
Humic acid	1.8	1.8	1.8
TOC	3	2.3	2.3
TDS	1558	1468	1362
TSS	2	2	2
Al - ICP	0.2	0.3	0.3
As	0.01	0	0
B	0	0	0
Ba	0.033	0.011	0.016
Be	0	0	0
Cd	0.02	0	0
Co	0.03	0.04	0.01
Cr	0	0.01	0
Cu	0	0	0
Fe	0.06	0.07	0.08
Hg (μg/L)	0	0	0
Mn	19.8	5.8	3.2
Ni	0	0	0
Pb - ICP	0	0	0
Pb - HGA	0	0	0
Sb	0	0	0
Se	0	0	0
Sn	0	0	0
V	0	0	0
Zn	2.1	1.2	0.8

Appendix Table 2.5: Brunswick #12 wetland

Parameter	Upstream	Inflow	Mid	Outflow
Acidity	69.5	40.0	34.8	31.8
Hardness (CaCO$_3$)	1455	1413	1339	1408
Alkalinity (CaCO$_3$)	0	9	9	10
Mg	69	57	54	54
Na	350	360	320	360
K	5.6	7.4	6.1	6.4
Ca	469	472	447	475
Cl	63	62	60	63
SO$_4$	1990	2000	1890	1990
PO$_4$	0.01	0.03	0	0.02
NO$_2$ + NO$_3$	0	0	0	0
NH$_3$	0	1.5	1.5	1.6
SiO$_2$	12.0	8.7	8.2	8.0
Humic acid	4.4	6.2	6.0	6.5
TDS	3232	3209	3051	3228
TSS	0	18	12	14
Al - ICP	7.5	2.8	2.2	2.0
As	0	0	0	0
B	0	0	0	0
Ba	0.019	0.015	0.013	0.015
Be	0	0	0	0
Cd	0	0	0	0
Co	0.19	0.15	0.14	0.14
Cr	0	0	0.01	0.02
Cu	0.09	0.03	0.02	0.02
Fe	1.5	6.4	3.5	5.8
Hg (µg/L)	0	0	0	0
Mn	31.5	28.4	26.2	25.7
Ni	0.08	0.05	0.05	0.05
Pb - ICP	0.25	0.14	0.15	0.13
Sb	0	0	0	0
Se	0	0	0	0
Sn	0	0	0	0
Va	0	0	0	0
Zi	2.2	1.0	0.9	1.0

Appendix Table 2.6:   Waite Amulet wetland

Parameter	Inflow	Mid	Outflow
pH (no units)	2.4	2.4	2.2
Acidity	1990	1990	1990
Cond. (μmhos/cm)	10500	12950	11250
Hardness ($CaCO_3$)	1324	1418	1432
Alkalinity ($CaCO_3$)	0	0	0
Na	14	14	13
K	5.6	6.0	5.2
Mg	170	180	190
Ca	250	271	260
Cl	5	5	5
SO_4	3250	3260	3360
PO_4	0.12	0	0
$NO_2 + NO_3$	0	0	0
NH_3	0.1	0.1	0
SiO_2	5.6	0	12
Humic acid	16	30	47
TOC	5.8	6.0	6.4
TDS	5337	5236	5260
TSS	195	186	124
Al - ICP	44	44	43
As	0	0	0
B	0.33	0.35	0.38
Ba	0	0	0
Be	0	0	0
Cd	0	0	0
Co	3.0	6.1	4.3
Cr	0.03	0.07	0.06
Cu	2.9	2.8	3.1
Fe	1075	964	987
Hg (μg/L)	0	0	0
Mn	5.8	9.6	7.7
Ni	0.04	0.05	0.04
Pb - ICP	0.17	0.21	0.17
Sb	0	0	0
Se	0	0	0
Sn	0	0	0
V	0.18	0.18	0.20
Zn	19	19	18

Appendix 3.

Sediment chemistry data at the Nickel Rim, Kam-Kotia and Heath-Steele wetlands. Units for total sulfur, iron and aluminum are in mg/g dry weight. All other concentrations are given as µg/g, except mercury which is given in ng/g.

| | Sampling Location | | | | | | | |
Parameter	1	2	3	Mid[1]	Mid[2]	5	6	7
Nickel Rim wetland								
total sulphur	0.5	0.9	1.2	1.5	5.5	1.4	2.2	0.7
iron	1.3	0.9	0.6	0.6	11.3	2.9	1.8	1.9
aluminum	3.2	1.7	1.2	1.3	5.2	2.6	2.0	3.0
arsenic	2	16	13	14	13000	16	15	21
cadmium	0.4	0.7	1.7	2.7	105	0.6	1.2	0.3
chromium	56	40	21	37	680	57	59	64
copper	210	670	400	1200	570	300	490	260
lead	16	46	130	100	3100	35	50	30
manganese	150	73	68	330	52000	140	130	140
mercury	95	125	165	185	70	125	165	115
nickel	250	610	1100	1100	50	650	960	280
zinc	32	41	110	100	8100	64	67	29
Kam-Kotia wetland								
total sulfur	0.9	0.4	0.6	0.6		0.8	0.4	
iron	21	18	20	23		23	22	
aluminum	1.7	2.0	2.3	2.8		3.1	2.5	
arsenic	11	12	15	36		34	10	
cadmium	0.5	1.7	1.6	1.6		0.7	2.2	
chromium	50	43	49	80		70	51	
copper	440	550	590	650		520	870	
lead	22	27	15	36		13	9	
manganese	110	210	210	270		240	220	
mercury	375	425	425	375		450	530	
nickel	14	17	20	40		17	18	
zinc	500	840	910	700		700	1000	
Health-Steele wetland								
total sulfur	6.5	10.4	5.7	12.9		7.9	7.5	6.0
iron	22	19	15	14		18	11	13
aluminum	4.0	5.6	1.8	5.8		4.7	6.6	6.9
arsenic	490	530	420	650		560	560	300
cadmium	8.1	16.1	3.6	4.7		5.4	8.5	5.2
chromium	46	34	45	38		58	59	53
copper	1500	1200	900	2100		1000	1100	900
lead	1200	1800	800	4000		1300	1300	1500
manganese	300	230	240	190		400	450	1400
mercury	215	185	120	285		345	195	165
nickel	22	56	20	47		24	30	24
zinc	3400	12000	1400	15000		2500	3400	1800

[1] sample taken of the upper 10 cm of sediments
[2] sample taken from approximately 10 to 20 cm depth in sediments