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Article abstract

The Magnet Cove Mine, located near Walton in Hants County, Nova Scotia, produced a total of 4 Mt barite and 0.36 Mt of Cu-Pb-Zn-Ag sulphide ore between 1941 and 1978. Currently, primary dispersion of heavy metals from the mine site is by small-scale physical transport of tailings and flocculants into Rainy Cove Brook. Evidence from aerial photographs (1945-1992) indicates that much larger scale dispersion occurred during the life of the mine. Sediment samples collected from the tailings impoundments and local streams, and analysed by AAS and by and combination of ICP and INAA methods, show that downstream sediments are geochemically almost indistinguishable from tailings. Both are moderately to highly anomalous in Ba, Mn, Cu, Pb, and Zn, and in the associated trace metals Ag, As, Sb, Co, and Ni. Mean metal enrichments of downstream over upstream sediments are about 5x for Cu, Pb, and Zn, 10x for Mn, and up to 40x for Ba. Water samples from upstream, downstream, and on-site locations were analysed by ICP-MS and show that Rainy Cove Brook is contaminated by open-pit and on-site water. The open-pit water shows strong enrichment in TDS (total dissolved solids), and also in Se, As, Co, Ni, Cr, V, and U. In contrast, downstream water is moderately enriched in TDS, and slightly enriched only in As, Th, and U. Mixing of pit water with slightly more acidic waters from on-site and upstream tributaries apparently triggers precipitation of Fe-Mn hydroxides which reduce (probably by adsorption) concentrations of heavy metals in solution. Other factors which have contributed to natural amelioration include the stabilisation of the flood plain of Rainy Cove Brook and its reversion to a wetland since closure of the mine.

Dispersion of tailings from the Walton Ba-Cu-Pb-Zn mine site, Nova Scotia

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The Magnet Cove Mine, located near Walton in Hants County, Nova Scotia, produced a total of 4 Mt barite and 0.36 Mt of Cu-Pb-Zn-Ag sulphide ore between 1941 and 1978. Currently, primary dispersion of heavy metals from the mine site is by small-scale physical transport of tailings and flocculants into Rainy Cove Brook. Evidence from aerial photographs (1945-1992) indicates that much larger scale dispersion occurred during the life of the mine. Sediment samples collected from the tailings impoundments and local streams, and analysed by AAS and by combination of ICP and INAA methods, show that downstream sediments are geochemically almost indistinguishable from tailings. Both are moderately to highly anomalous in Ba, Mn, Cu, Pb, and Zn, and in the associated trace metals Ag, As, Sb, Co, and Ni. Mean metal enrichments of downstream over upstream sediments are about 5x for Cu, Pb, and Zn, 10x for Mn, and up to 40x for Ba. Water samples from upstream, downstream, and on-site locations were analysed by ICP-MS and show that Rainy Cove Brook is contaminated by open-pit and on-site water. The open-pit water shows strong enrichment in TDS (total dissolved solids), and also in Se, As, Co, Ni, Cr, V, and U. In contrast, downstream water is moderately enriched in TDS, and slightly enriched only in As, Th, and U. Mixing of pit water with slightly more acidic waters from on-site and upstream tributaries apparently triggers precipitation of Fe-Mn hydroxides which reduce (probably by adsorption) concentrations of heavy metals in solution. Other factors which have contributed to natural amelioration include the stabilisation of the flood plain of Rainy Cove Brook and its reversion to a wetland since closure of the mine.

La mine Magnet Cove, située près de Walton, comté de Hants, Nouvelle-Écosse, a produit au total 4 mt de barytine et 0,36 mt de minerai sulfuré de Cu-Pb-Zn-Ag entre 1941 et 1978. La dispersion des métaux communs depuis l'emplacement de la mine s'effectue aujourd'hui essentiellement par transport physique des résidus et des flocculants dans le ruisseau Rainy Cove. Les indications que procurent les photographies aériennes (1945-1992) démontrent qu'une dispersion à une échelle beaucoup plus vaste s'est produite au cours de la durée de vie de la mine. Des échantillons de sédiments prélevés des bassins d'accumulation de résidus et des cours d'eau locaux qu'on a analysés par spectrométrie d'absorption atomique, en combinaison avec des méthodes d'émission de plasma induit / d'analyse instrumentale par émission neutronique, révèlent qu'on ne peut pas distinguer les sédiments d'aval des résidus sur le plan géochimique. Les deux types d'éléments possèdent des teneurs anormales, de moyennes à élevées, en Ba, Mn, Cu, Pb et Zn, de même qu'en métaux-traces connexes, notamment en Ag, As, Sb, Co et Ni. Les enrichissements moyens en métaux en aval correspondent, par rapport à l'apport en amont, au quintuple dans le cas du Cu, du Pb et du Zn, au décuple dans le cas du Mn, et ils sont jusqu'à 40 fois supérieurs dans le cas du Ba. On a analysé des échantillons d'eau d'amont, d'aval et de divers points locaux par spectrométrie de masse par émission de plasma induit par haute fréquence, et ceux-ci ont révélé que le ruisseau Rainy Cove est contaminé par les eaux de surface et les eaux locales. L'eau de surface affiche un enrichissement prononcé en matières totales dissoutes (TSD) ainsi qu'en Se, As, Co, Ni, Cr, V et U. Par contraste, l'eau d'aval est modérément enrichie en TSD et légèrement enrichie en As, Th et U seulement. Le mélange de l'eau de surface avec les eaux légèrement plus acides des affluents locaux et de ceux d'amont semble provoquer une précipitation d'hydroxydes de Fe-Mn qui réduisent (probablement par adsorption) les concentrations de métaux lourds dans la solution. Les autres facteurs qui ont contribué à l'amélioration naturelle comprennent la stabilisation du périmètre d'inondation du ruisseau Rainy Cove et sa réversion à l'état de terre humide depuis la fermeture de la mine.

Traduit par la rédaction

INTRODUCTION

Although mining itself directly affects relatively small areas, the tailings can have a wider impact on the surrounding environment, e.g., where heavy metals from the tailings are dispersed via acid mine drainage into the aquatic environment, or where the tailings themselves are eroded and physi-

cally dispersed (Salomons, 1995; Miller, 1997). Of particular concern are mine sites abandoned prior to the introduction in 1977 of federal environmental regulations to control effluents from metal mining operations (Canadian Ministry of the Environment, 1994). Such sites are beyond the reach of these legislative control efforts, and suffer from a lack of monitoring and maintenance. The scale of this concern is indicated in a preliminary study into the potential for groundwater contamination from past and present mining activities in the Atlantic Region (Eaton *et al.*, 1994) which identified 207 abandoned mine sites

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in Nova Scotia alone as potential sources for such contamination. However, where those mined deposits are hosted by carbonate rocks and/or associated with carbonate gangue minerals, natural buffering may have eliminated or significantly reduced acid mine drainage and potential contamination problems.

The focus of this study is the abandoned Walton barite deposit (also known as the Magnet Cove Mine) which is hosted by carbonate rocks. The mine site is located 4 km southwest of Walton, Hants County, Nova Scotia, and is situated adjacent to Rainy Cove Brook approximately 2.5 km inland from the Minas Basin (Fig. 1). A gravel access road connects the mine site to Highway # 215 which links Walton to Windsor, 29 km to the southwest.

The mine operated from November 1941 until October 1978, during which time it produced over 4 Mt of barite, plus an estimated 0.36 Mt of sulphide ore grading 4.07% Pb, 1.96% Zn, 0.67% Cu and 418 g t⁻¹ Ag (Nova Scotia Department of Mines and Energy, 1984; Jacques, Whitford and Associates, 1985). Canadian Industrial Minerals Limited, a subsidiary of Springer Sturgeon Gold Mines Limited, opened the mine in 1941 after an extensive drilling program outlined what was to become Canada's largest barite quarry and mine (Boyle, 1972). Production of high-grade barite by quarrying and block caving was carried out until 1955 when the mine was sold to Magnet Cove Barium Corporation, a subsidiary of Dresser Industries Inc. The sulphide ore was discovered in 1956, and by 1959 all of the ore was obtained from underground development. In 1971, flooding in the mine caused a loss of production from the lower levels, and all further production was obtained by scavenging from stopes (above the 314 m level), the open pit, surface stockpiles and tailings. Production finally ended in October, 1978 (Nova Scotia Department of Mines and Energy, 1984). There has been a minimal amount of site remediation, but much less than would be required for present-day mine site closures under the Nova Scotia Environment Act (Nova Scotia Department of the Environment, 1995).

The purpose of this study was to determine to what extent dispersion of tailings and of derived heavy metal contaminants from the mine site was occurring, and to assess their possible impact on the downstream environment. At the present time small-scale dispersion occurs by (i) overflow of water from the flooded open pit, and (ii) erosion and leaching of the waste rock dump, the barite tailings from the sink-float plant, and the sulphide tailings from the mill-concentrator.

METHODS

Most of the sampling for this study was done in the fall of 1996 when water levels were stable and unaffected by recent precipitation. Budget constraints did not permit analysis of water samples collected at other times of the year in order to monitor seasonal variations in water chemistry, so the results presented here represent only a base-line study.

Streams, ponds, and seepages were measured directly for pH, conductivity, dissolved oxygen, and temperature at each sampling location, using YSI Model 3560 and Model 55 water quality monitoring systems.

Water samples (filtered to <0.5 µm and acidified to pH 2)

were analysed by inductively coupled plasma-mass spectrometry (ICP-MS) for 64 elements by Activation Laboratories Limited in Ancaster, Ontario. Equivalent samples (filtered but not acidified) were also analysed for their major cation-anion content using standard water quality methods by the Nova Scotia Department of Agriculture and Marketing laboratory in Truro, Nova Scotia.

All stream sediment and tailings samples were analysed for Ba, Fe, Mn, Cu, Pb, and Zn by AAS at Acadia University, and selected samples were analysed for a package of 48 elements by a combination of inductively coupled plasma-emission spectroscopy (ICP) and induced neutron activation analysis (INAA) by Activation Laboratories Limited in Ancaster, Ontario. For AAS analysis, samples were treated with 1:3 HNO₃ hot acid leach which was effective in getting most of the Mn, Cu, Pb, and Zn into solution (based on AAS results from USGS standards GXR-2, 5, 6, and from combined ICP and INAA results on duplicate samples (Whitehead, 1997)). However, Fe and Ba results by AAS are very low and can be considered only as partial analyses, possibly reflecting concentrations of more easily leached species of these metals.

DESCRIPTION OF SITE

Bedrock geology

Sedimentary rocks of the Lower Carboniferous Horton and Windsor groups underlie most of the area (Fig. 1). The contact between the continental Horton Group (comprising red and grey sandstone, shale, siltstone, arkose and conglomerate), and the marine Windsor Group (comprising limestone, minor sandstone, evaporite and red shale) is of economic interest because it acted as the locus for deposition of a series of manganese oxide and barite occurrences, including the Walton deposit (Boyle, 1972; Moore, 1995). The deposit is a large raking pipe-like mass localised within a folded and brecciated zone between two faults, and formed by replacement and fracture-filling of limestone of the lowermost Windsor Group (i.e., Macumber Formation). The limestone is overlain by a thick section of cavernous gypsum, anhydrite, and carbonaceous shale which is succeeded by soft, red shale and siltstone of the Tennycape Formation (Boyle, 1972).

The mined-out part of the deposit consisted of the main barite orebody with an average grade of 90% BaSO₄, together with several smaller sulphide lenses and irregular masses (Nova Scotia Department of Mines and Energy, 1984; Jacques, Whitford and Associates, 1985). Up to 0.9 Mt of barite ore as well as a deeper more tabular sulphide zone containing 0.03 Mt of Ag-rich ore remain in the ground because of premature closure of the mine (Patterson, 1989).

The mineralogy of the deposit is complex (Boyle, 1972), and consists of both primary and secondary assemblages which can be summarised as follows:

- (a) Primary Mineralogy (formed at depth under essentially reducing conditions)
 - Barite ore: barite, siderite, minor calcite and pyrite
 - Sulphide ore: pyrite/marcasite/bravoite, galena, sphalerite, chalcopyrite, silver sulfosalts

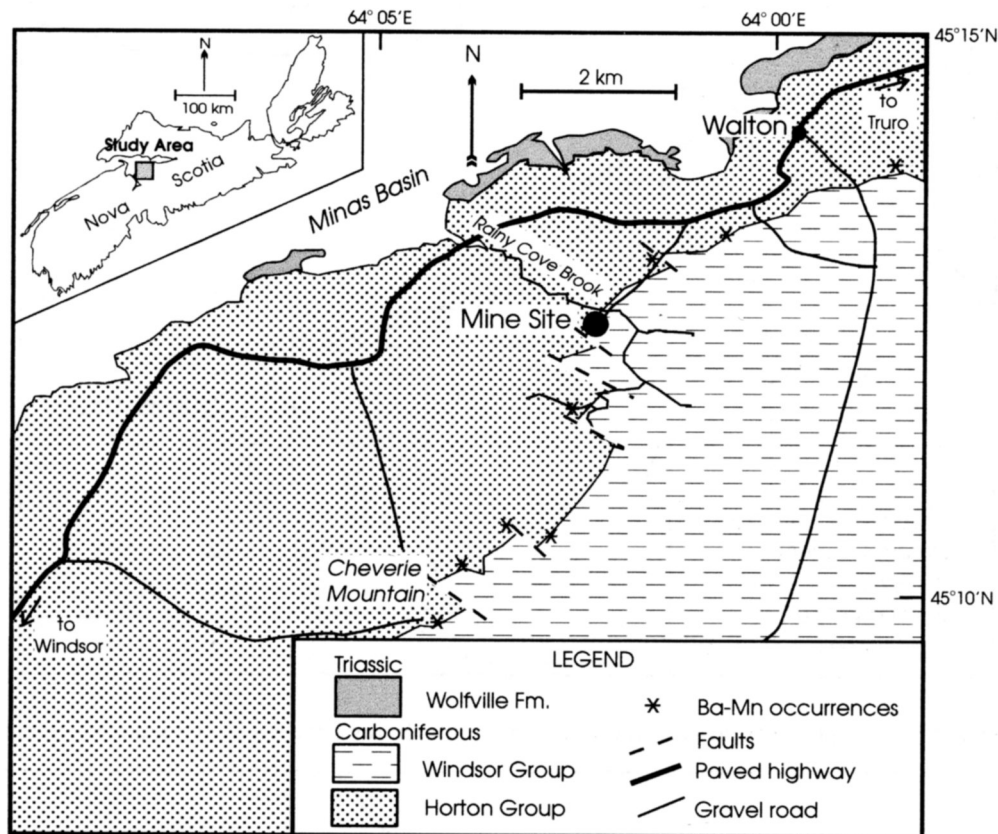


Fig. 1. Location and simplified geological map of the study area, Walton, Hants County, Nova Scotia (geology after Boyle, 1972).

(b) **Secondary Mineralogy** (formed at/near the surface by oxidation of the primary minerals)

Fe and Mn oxides and hydroxides, Fe sulfates, Cu and Co arsenates, sulfates, and carbonates.

Mine site

Topography in the mine area is undulating with a maximum relief of less than 50 m (Fig. 2). It is underlain by till and only a few bedrock outcrops are exposed in stream channels and along the southern face of the open pit. Rainy Cove Brook forms the main drainage system in the immediate area, and includes several tributaries, as well as still waters and swampy areas rich in decomposing organic materials. Wooded areas surround the site, and are composed predominately of mixed stands of second- and third-growth conifers and hardwoods. The total area disturbed by mining activity is about 1 km² which includes a flooded open pit, tailings ponds, waste rock dump, a breached dam site, and various other small ponds and pits.

After production was terminated in 1978, the crusher, concentrator, sink-float plant and the headframe were dismantled and sold (Nova Scotia Department of Mines and Energy, 1984), but several buildings remain. The most conspicuous feature of this mine site is the large (300 m by 200 m by 110 m deep), flooded open pit (Fig. 3). This was the original open pit from which the barite ore was quarried until 1956, when the first shaft for underground production was developed. There is an essentially continuous overflow into Rainy Cove Brook

from the pit along the original haulage road which is partially obstructed by an old beaver dam and carpeted with orange-brown flocculated Fe-Mn hydroxides/oxyhydroxides. There is also much scrap metal located on site, including what appears to be unsalvaged metal derived from mining activity and from dismantling of the site, in addition to more recently dumped motor vehicles, tires, household appliances, and garbage. This type of waste may have contributed metals, hydrocarbons, and other pollutants into the brook, but these aspects have not been considered in this study. Although signs are posted on a fenced-off storage building, and on other mine buildings, which state: "Danger, PCB Storage", it appears that transformers have been removed from the site.

Tailings

Two distinct accumulations of tailings occur on the site, one on the northwest corner of the mine property, which was derived from processing of barite ore, and one south of the open pit which was derived from processing of sulphide ore (Fig. 3). These tailings impoundments are located on shallow slopes adjacent to the drainage system and are contained by well constructed berms up to 15 m high. They are filled with mainly red-brown, interstratified fine sandy and muddy sediments.

The barite tailings accumulation is composed of three linked impoundments with differing elevations, covering about 0.05 km² on the south side of Rainy Cove Brook. More than 1 Mt of tailings may have been stored here, but it is difficult to determine the exact amount because most of the material in

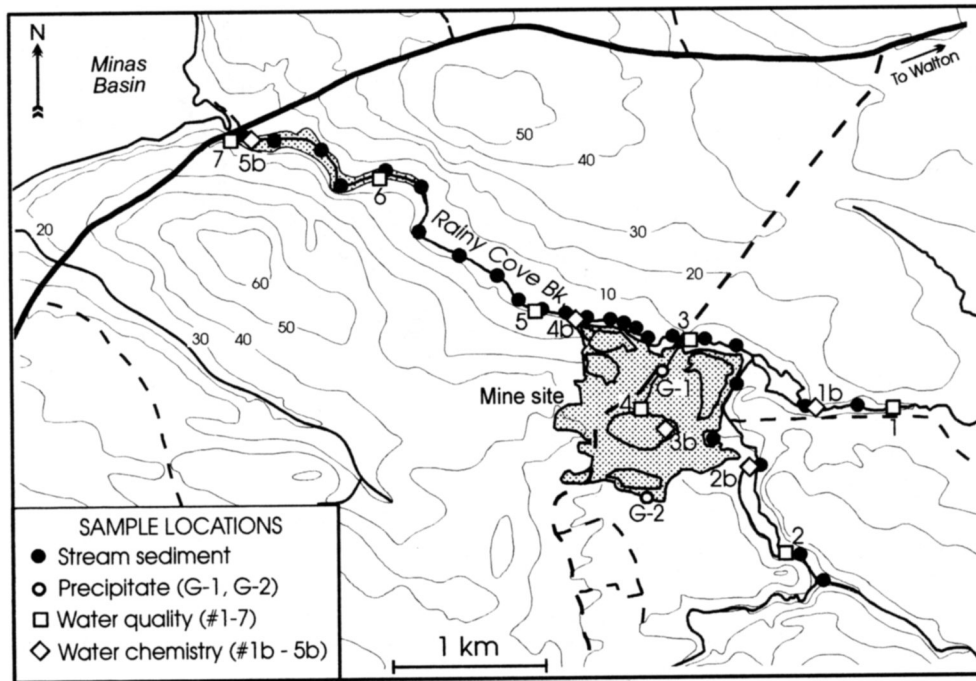


Fig. 2. Physiographic map showing the Walton mine site, Rainy Cove Brook and sample locations.

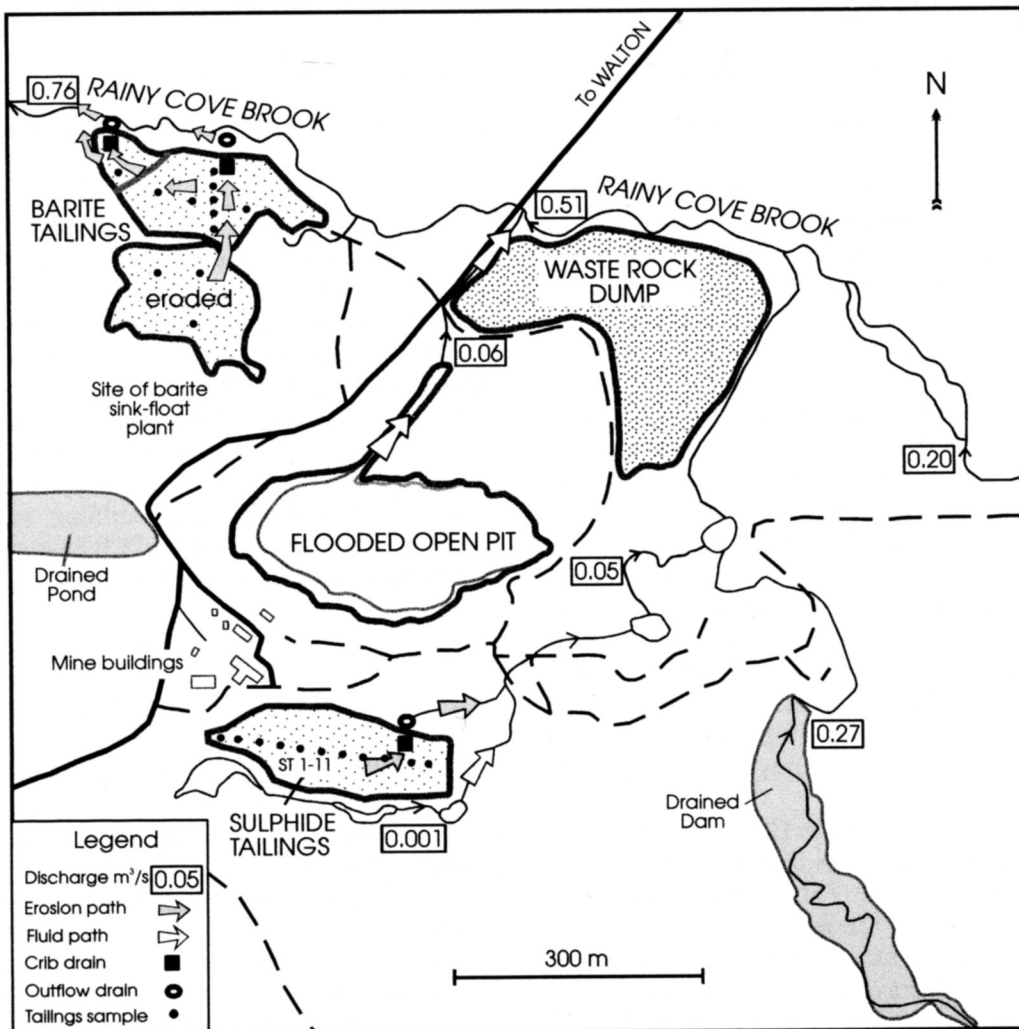


Fig. 3. Map of Walton mine site (based on a 1992 aerial photograph) showing mine features, and the main dispersion pathways and water discharge rates determined in October, 1996.

the upper impoundment (except for an eroded veneer), was removed during reworking of the tailings between 1971 and 1978. The waste material produced during this reworking is reported to have been dumped into the open pit (Nova Scotia Department of Mines and Energy, 1984), but aerial photographs from 1973 show evidence of extensive direct dumping into Rainy Cove Brook. The two adjacent, more northerly tailings impoundments have built-in crib drains which drain directly into Rainy Cove Brook. Very little vegetation has taken root on the surface of these impoundments, and a system of erosion gullies can be traced back to the destabilised upper impoundment; the retaining berms between them have been breached locally by erosion so that run-off can reach the brook either directly or via the crib drains (Fig. 2).

The sulphide tailings impoundment is about 260 m long by 100 m wide, and is up to 15 m deep, and could contain more than 0.5 Mt of tailings. The surface slopes slightly from west to east, and with moderate rainfall some standing water accumulates at the eastern end where an incorporated crib drain permits outflow on the north side; some erosional gullying is occurring around this drain. The outflow water migrates toward the on-site drainage which joins Rainy Cove Brook at the northeastern corner of the site. Frogs, insects, and plant life were observed in and around this discharge water, but virtually no vegetation was found to be growing on the tailings pond itself. An iridescent seepage was observed along the southeastern base of the impoundment, and where this seepage mixed with the adjacent slow-moving stream, a white to orange, layered, gelatinous mat of possible bacterial origin was formed.

Rainy Cove Brook

A network of small streams, ponds, and swampy areas occur throughout the mine site itself. These waters drain slowly northward into Rainy Cove Brook. The pH values for the surface waters found on the mine site are generally neutral to slightly alkaline, although some isolated shallow pools floored with sulphidic-oxidic rubble have pH down to 3.6.

Rainy Cove Brook, the nearest drainage system to the mine site, lies less than 300 m from the flooded open pit, and flows west-northwest about 3 km from the mine site to the Minas Basin (Fig. 2). The brook has a low gradient for most of its length, and has developed a narrow flood plain extending about 1.5 km back upstream from the highway crossing near its mouth. The average stream velocity is slow ($<1 \text{ m s}^{-1}$), but varies with the changes in the width and depth along its length. Although such variations influence the turbulence, there is no obvious correlation between these variations and the amount of dissolved oxygen in the waters ($11.04\text{--}14.34 \text{ mg l}^{-1}$). Higher levels of dissolved oxygen in the swampy areas ($14.04\text{--}14.34 \text{ mg l}^{-1}$) are likely due in part to the abundance of algae and rooted aquatic plants which release oxygen into the water through photosynthesis. Dissolved oxygen content may also have been enhanced by sampling during the afternoon when photosynthesis peaks, and by low water temperatures ($3.7\text{--}8.7^\circ\text{C}$). The upstream water of Rainy Cove Brook has pH levels in the acidic range ($5.7\text{--}6.7$), but downstream from the mine

site the pH varies from slightly alkaline to slightly acidic ($7.6\text{--}6.8$). The mouth of Rainy Cove Brook is tidal only for a short distance below the highway where it enters the Minas Basin.

Stream sediments

Stream sediments upstream from the mine site are grey-brown to grey-black sandy silts with high organic content. In contrast, downstream sediments are generally red-brown silty muds closely resembling the tailings in appearance. In the downstream reach of the brook between the mine site and the flood plain, the stream bed is generally cobbled and the only fine sediments occur either as a red-brown veneers deposited along high water marks during flooding, or as localised pockets of inactive bank sediment similar to the upstream sediments. Within the flood plain itself, which extends for 1.5 km and is 50 to 75 m wide, the fine red-brown sediments have accumulated to depths in excess of 1 m.

Colloidal precipitates

Precipitates of Fe-Mn hydroxide were collected from two specific locations on the mine site (Fig. 2). Sample G-1 was collected from flocculant carpeting the overflow channel from the open pit, and sample G-2 was collected from a gelatinous, possibly bacterial mat on the southeastern side of the sulphide tailings impoundment (Fig. 3).

GEOCHEMISTRY

Tailings

Forty-two samples collected from the sulphide and barite tailings impoundments were analysed by AAS for iron, manganese, barium, copper, lead, and zinc. For comparison with downstream sediments, the combined data from the sulphide and barite tailings sediments are used in this study (Table 1a), as it is not possible to distinguish between these materials after they have entered the brook. However, mean metal concentrations in the sulphide tailings are 1.2x to 4x higher than those in the barite tailings, and their variance generally is also higher. Total mean concentration of 550 ppm for Cu, Pb, and Zn in the sulphide tailings is relatively low, suggesting that recoveries achieved during milling and concentration of the sulphide ore were high.

Six samples of sulphide and barite tailings, two mine site sediments, and one iron hydroxide flocculant/precipitate were also analysed by combined ICP and INAA for 48 elements (Table 1b). In general, these show reasonably good agreement with the AAS results for Mn, Zn, Cu, and Pb, but much higher values for Fe and Ba (because of the more effective sample digestion procedures used in the ICP method). The tailings are characterised by very high Ba ($\sim 5\text{--}14\%$), high Fe ($\sim 2\text{--}4\%$), moderate Mn ($\sim 0.3\text{--}0.4\%$), and relatively low combined Cu, Pb, and Zn ($\sim 400\text{--}500 \text{ ppm}$). Pearson cluster analysis of ore-related elements in the tailings shows strong correlation of the trace elements Ag, As, Sb, Co, and Ni with the

Table 1a. Summary of geochemical data for all samples of stream sediments, tailings, and precipitates (AAS results).

| Element | Upstream Sediments n = 6 | | Downstream Sediments n = 20 | | Tailings n = 46 | | Precipitates n = 2 | |
|-----------|-----------------------------|--------|--------------------------------|--------|--------------------|--------|-----------------------|------|
| | Mean | S.D. | Mean | S.D. | Mean | S.D. | G-1 | G-2 |
| Fe* wt. % | 1.69 | ± 0.72 | 1.74 | ± 2.46 | 0.68 | ± 0.23 | 3.25 | 1.64 |
| Ba | 0.08 | 0.15 | 0.24 | 0.14 | 0.33 | 0.12 | 0.03 | 0 |
| Mn | 0.03 | 0.01 | 0.31 | 0.43 | 0.20 | 0.11 | 1.97 | 1.53 |
| Cu ppm | 13 | 4 | 77 | 83 | 96 | 37 | 283 | 100 |
| Pb | 49 | 17 | 259 | 568 | 165 | 141 | 214 | 182 |
| Zn | 64 | 15 | 243 | 467 | 83 | 47 | 103 | 227 |

*Values significantly lower than total values due to partial extraction method used in sample preparation.

Table 1b. Multi-element* geochemistry of selected samples of sediments, tailings, and precipitates (ICP and INAA results).

| Element | Waste Sediment n = 2 | | Downstream Sediments n = 3 | | Tailings n = 6 | | Precipitates n = 1 |
|----------|-------------------------|-------|-------------------------------|--------|-------------------|--------|-----------------------|
| | WS-1A | WS-1B | Mean | S.D. | Mean | S.D. | G-1 |
| Al wt. % | 2.57 | 2.09 | 2.84 | ± 1.22 | 2.53 | ± 0.92 | 2.49 |
| Fe | 1.52 | 1.29 | 3.99 | 0.97 | 3.21 | 1.12 | 4.74 |
| Mg | 0.51 | 0.45 | 0.55 | 0.20 | 0.65 | 0.20 | 0.39 |
| Ca | 1.71 | 2.24 | 0.94 | 0.33 | 1.79 | 0.55 | 10.92 |
| Na | 0.05 | 0.04 | 0.16 | 0.06 | 0.09 | 0.03 | 0.64 |
| K | 1.15 | 0.92 | 1.13 | 0.32 | 0.98 | 0.26 | 0.78 |
| Ti | 0.22 | 0.15 | 0.17 | 0.04 | 0.15 | 0.04 | 0.12 |
| P | 0.03 | 0.02 | 0.03 | 0.01 | 0.02 | 0.01 | 0.02 |
| Ba | 0.38 | 0.24 | 14.63 | 3.45 | 8.83 | 4.88 | 9.90 |
| Mn | 0.10 | 0.12 | 0.31 | 0.02 | 0.32 | 0.11 | 2.74 |
| Cu ppm | 29 | 28 | 112 | 25 | 105 | 30 | 322 |
| Pb | 20 | 19 | 258 | 49 | 232 | 132 | 267 |
| Zn | 64 | 50 | 171 | 32 | 106 | 25 | 129 |
| Ag | 0.6 | 0.4 | 6.5 | 1.3 | 2.6 | 1.3 | 8.9 |
| Cd | <0.5 | <0.5 | 1.0 | - | <0.5 | - | 0.8 |
| As | 17 | 13 | 130 | 24 | 60 | 15 | 300 |
| Sb | 0.7 | 0.7 | 2.3 | 0.3 | 2.1 | 0.6 | 0.4 |
| Mo | 5 | 3 | 6 | 2 | 9 | 4 | <2 |
| Co | 6 | 5 | 23 | 5 | 12 | 3 | 120 |
| Ni | 14 | 13 | 40 | 12 | 29 | 6 | 360 |
| V | 31 | 24 | 32 | 13 | 30 | 11 | 29 |
| Cr | 38 | 29 | 41 | 14 | 34 | 11 | 33 |
| Se | <3 | <3 | <3 | - | <3 | - | <2 |
| Bi | <5 | <5 | <5 | - | <5 | - | <5 |
| Hg | <1 | <1 | <1 | - | <1 | - | <1 |
| Au ppb | <2 | <2 | 4 | 4 | <2 | - | <2 |

*Not included are results for 22 other trace elements, including Rb, Sr, Zr, REE, etc.
< indicates values below detection limits, - indicates not detected.

more abundant Pb, Cu, Zn, Fe, and Mn, whereas Cr, V, U, and Th show separate, more moderate clustering, and collectively they show only weak correlation with barite (Fig. 4). Such clustering closely reflects the mineralogy and chemistry of the sulphide ore as described in detail by Boyle (1972), and represents a useful fingerprint for tracking dispersed tailings.

Stream sediments

Twenty-six samples of stream sediments were analysed by AAS for iron, manganese, barium, copper, lead, and zinc (Table 1a), and three selected samples of downstream sediment were also analysed by combined ICP and INAA for 48 elements (Table 1b).

Compared to upstream sediment, the downstream sediment is clearly enriched in Ba, Mn, and Cu, and to a less consistent extent Zn and Pb (Fig. 5). Also, compared to regional threshold (90th percentile) values for stream sediments in the Walton area (calculated from data in Boyle, 1972), the mean downstream sediment is anomalously enriched in these elements up to 9x, whereas the mean upstream sediment has very close to background (50th percentile) values.

The downstream sediments resemble the tailings not only physically, but also chemically. Mean metal concentrations between them are so similar (Table 1a, 1b) that they are almost indistinguishable, except for slightly higher Ba and Cu populations in the tailings (Fig. 5).

Water

Five water samples were analysed for 64 elements using ICP-MS (Table 2). Of these samples, two are from upstream, one is from the open pit, one is of on-site surface drainage, and one is from downstream.

The plot for major and minor elements (Fig. 6a) shows, in comparison to upstream water, that (i) the open-pit water is enriched approximately 10x in Ca, Mg, Na, K, Fe, and Mn (presumably reflecting the carbonate and evaporite bedrock surrounding the pit and outcropping along the southern wall), (ii) on-site surface drainage is enriched in Ca, Mg, and Na, and (iii) the downstream water is enriched only in Na.

The trace element plot (Fig. 6b) shows that (i) open-pit water is enriched approximately 10x in Se, As, Co, Ni, Cr, V, and U (presumably reflecting a contribution from sulphides present either in reworked tailings dumped into the pit between 1971 and 1978, or in ore at levels below the floor of the pit), (ii) on-site water is slightly enriched in As, Cr, V, and U, and (iii) downstream water is slightly enriched only in As, U, and Th. The plot also shows that one of the upstream waters is enriched in Zn, and to a lesser extent Cu and Pb compared to all the other waters. This difference could be caused by the more acidic upstream conditions (pH 5.7 at this site), predominantly shale bedrock, and/or point-source contamination.

Seven water samples (6 from Rainy Cove Brook and 1 from the open pit) were also analysed by standard methods for their major cation-anion concentrations and for other water quality parameters by the NSDAM laboratory. The results

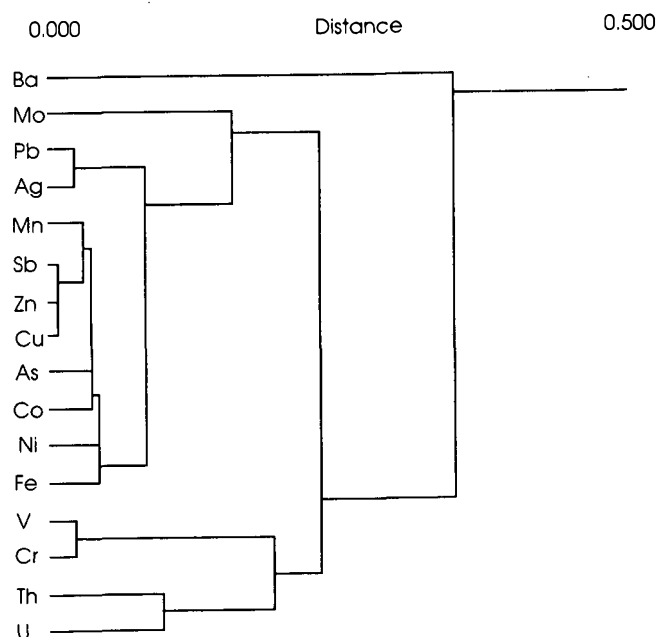


Fig. 4. Pearson correlation cluster analysis of metal concentrations in tailings (based on combined ICP and INAA results).

show a consistent pattern with sudden chemical enrichment, compared to upstream water, occurring at the mine site which then decreases progressively downstream (Fig. 7). This pattern is attributed mainly to influx of contaminated water from the open pit followed by progressive downstream dilution.

PHYSICAL DISPERSION AND SEDIMENT CONTAMINATION

Mining by its very nature involves the removal, processing, and disposal of vast volumes of rock and waste that have above normal chemical abundances. Unless properly controlled and contained, this material will be subject to erosional processes and dispersed off site and into a broader environment (Salomons, 1995; Miller, 1997). It is evident from the accumulation of tailings-derived sediment in the swampy flood plain of Rainy Cove Brook that this sort of dispersion has occurred from the Walton mine site (Fig. 8). Aerial photographs for the last five decades indicate that this downstream dispersal of tailings has been a long-term process, presumably mainly as a result of routine overflow through the crib drains installed in the tailings impoundments. According to the aerial photograph evidence from 1945, the original brook was meandering, with a narrow flood plain extending upstream about 0.8 km above its mouth (Fig. 8). The aerial photographs from 1954 suggest that significant amounts of mine tailings had been transported downstream by that time, as the stream width had increased and point bars had developed inside meanders along the flood plain. Large-scale release of tailings appears to have continued between 1954 and 1966, as shown by a significant increase in the size of the flood plain, and the absence of plant growth along its length. During this time Highway #215 was constructed, effectively damming the brook and elevating its base level 2 to 3 m above the high-tide

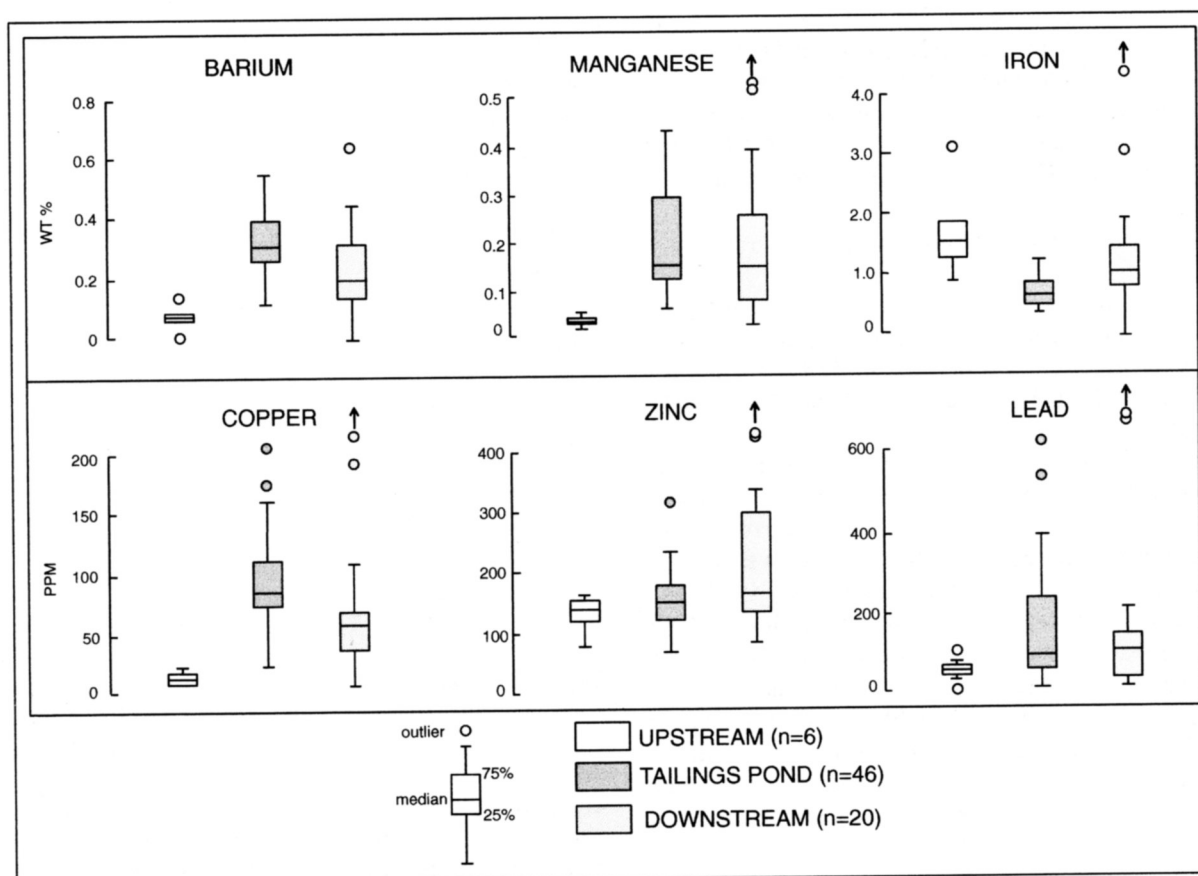


Fig. 5. Statistical comparison (box-and-whiskers plots) of metal concentrations (based on AAS results) in samples of upstream sediments, downstream sediments, and tailings.

mark which appears to have led to flooding and increased impoundment of tailings on the upstream side of the highway. There is additional 1973 aerial photograph evidence that the brook carried a very large sediment load while reworking of the barite tailings was occurring. At this time the brook increased in width, lessened its sinuosity, and showed an increase in the deposition of tailings near its mouth and along its length (up to 1.4 km from the highway) and also the complete absence of plant growth along its flood plain. The transport of tailings obviously declined after closure of the mine in 1978: in the 1981 aerial photograph, the brook shows a decrease in width and an increase in its sinuosity, and in the 1992 aerial photograph the morphology of the brook appears essentially as it does today, i.e., with an additional increase in sinuosity and braiding of the brook, but, at that time, with only incipient marshland plant growth along the length of its flood plain (Fig. 8).

Limited erosion of the tailings from the mine site continues at the present time during high precipitation and run-off. Only a small amount of material from the sulphide tailings is involved but a larger quantity is derived from the barite tailings, especially from the destabilised upper impoundment (Fig. 3). Obviously the quantity of the tailings that presently is being eroded, transported, and deposited in the brook is considerably less than has occurred in the past. This difference is evident downstream where marshland growth (cattails, rushes, pond weeds, etc.) has expanded since 1992 to virtually cover

the widened flood plain. More recently (1996-1997) several beaver dams have been built across the flood plain area, causing extensive localised flooding.

According to the guidelines established for the protection and management of aquatic sediment quality in Ontario (Persaud *et al.*, 1994) (used in this study in the absence of equivalent Nova Scotia guidelines), the tailings and downstream sediments would be considered to be grossly polluted in Mn and As, and marginally to significantly polluted in Fe, Pb, Cu, Ni, and Cr (Fig. 9a). Such levels of contamination are believed to have the potential to affect use of the sediment by some benthic organisms, and hence to impact negatively on the aquatic environment.

AQUEOUS DISPERSION AND CONTAMINATION

The ability of chemical elements to stay in solution is controlled by many factors, but primarily by (i) the redox conditions, (ii) the pH level of the water, and (iii) the ability of anions and organic matter to form soluble complexes with the metals (Gibbs, 1973).

Although mineralogical evidence is abundant for supergene oxidation of ore sulphides to hydroxides, sulphates, carbonates, and arsenates (Boyle, 1972), there is little direct evidence that acid mine drainage has developed as a consequence of current oxidation within the tailings piles. Sulphide concentrations within the tailings are low and presumably

Table 2. Selected geochemical data* for five water samples analysed by ICP-MS (values in ppb).

| Element | Upstream | | Mine Site | | Downstream |
|---------|----------|-------|-------------------|-------------------|------------|
| | WS-1b | WS-2b | WS-3b Open Pit | WS-4b Drainage | WS-5b |
| Ca | 9208 | 52830 | 421700 | 93520 | 35990 |
| Mg | 1044 | 2371 | 46140 | 21020 | 4402 |
| Na | 5604 | 7480 | 58390 | 39490 | 107400 |
| K | 594 | 957 | 16480 | 2323 | 1524 |
| Si | 1733 | 1447 | 3118 | 1390 | 1679 |
| Al | 368 | 153 | 48 | 15 | 230 |
| Fe | 773 | 1128 | 4235 | 1040 | 814 |
| Mn | 570 | 160 | 8019 | 109 | 79 |
| Ti | 0.65 | 0.49 | 0.76 | 0.41 | 0.91 |
| V | 3.8 | 4.6 | 30.5 | 7.3 | 2.2 |
| Cr | 10.6 | 13.0 | 93.8 | 21.3 | 6.3 |
| Co | 1.46 | 0.39 | 17.11 | 0.59 | 0.41 |
| Ni | 6.2 | 3.4 | 48.8 | 6.6 | 4.4 |
| Cu | 61 | 34 | 47 | 20 | 30 |
| Zn | 234 | 28 | 47 | 29 | 33 |
| Pb | 8 | 5 | 4 | 4 | 5 |
| As | 1.26 | 0.79 | 13.98 | 2.22 | 1.90 |
| Se | 2.00 | 0.53 | 6.12 | 0.65 | 1.21 |
| Mo | 0.1 | 0.29 | 0.57 | 0.37 | 0.52 |
| Cd | 0.58 | 0.48 | 0.68 | 0.29 | 0.50 |
| Sb | 0.11 | 0.06 | 0.08 | 0.07 | 0.08 |
| Ba | 118 | 93 | 53 | 48 | 100 |
| Tl | 0.02 | 0.02 | 0.20 | 0.05 | 0.06 |
| Bi | 0.02 | 0.04 | 0.01 | 0.04 | 0.02 |
| Th | 0.12 | 0.15 | 0.22 | 0.21 | 0.41 |
| U | 0.17 | 0.18 | 3.88 | 1.15 | 0.33 |

*Not included are results for 42 other trace elements, including Rb, Sr, Zr, REE, etc.

any acid generation is easily neutralised by dissolution of readily available carbonate minerals; the ore body itself was hosted by limestone, and also contained both calcite and siderite as gangue carbonates associated with the barite and sulphides. Where carbonates, such as calcite and dolomite, are present, dissolution rates can be of the same order of rate as the redox reactions responsible for acid generation in mine tailings (Sherlock *et al.*, 1995). The effectiveness of neutralisation is confirmed by the pH levels recorded in effluents/seepages derived from (i) sulphide tailings (pH 6.8), (ii) barite tailings (pH 8.2), and (iii) on-site drainage (pH 7.4). Most of the other on-site surface and seepage waters have essentially neutral pH values, with the exception of some pools of standing water in contact with abundant pyritic-oxidic rubble on the waste rock dump which have pH as low as 3.6, suggesting that acid generation is occurring on a localised scale.

The large body of open-pit water displays neutralised chemistry with pH values in the range 7.7 to 7.9, together with high Na^+ , Ca^{2+} , Cl^- , and SO_4^{2-} concentrations and alkalinity that are reflected in its very high conductivity value (11,000 μmhos) (Fig. 7). These results clearly show the effects of dissolution of limestone-evaporite bedrock and that the open pit water is essentially groundwater. This water is enriched in a suite of ore-related trace metals (Se, As, Co, Ni, Cr, V, U), perhaps because high concentrations of bicarbonate, sulphate, and chloride ions tend to form dissolved complexes with these metals which are stable under neutral to slightly basic conditions, e.g., as shown by Eh-pH diagrams for As, Cr, V, and U (Brookins, 1988). Flocculation of colloidal Fe-Mn hydroxides occurs where overflow from the open pit and effluent from the tailings mix with surface water, presumably as a result of oxidation and/or small changes in pH. The high trace-metal

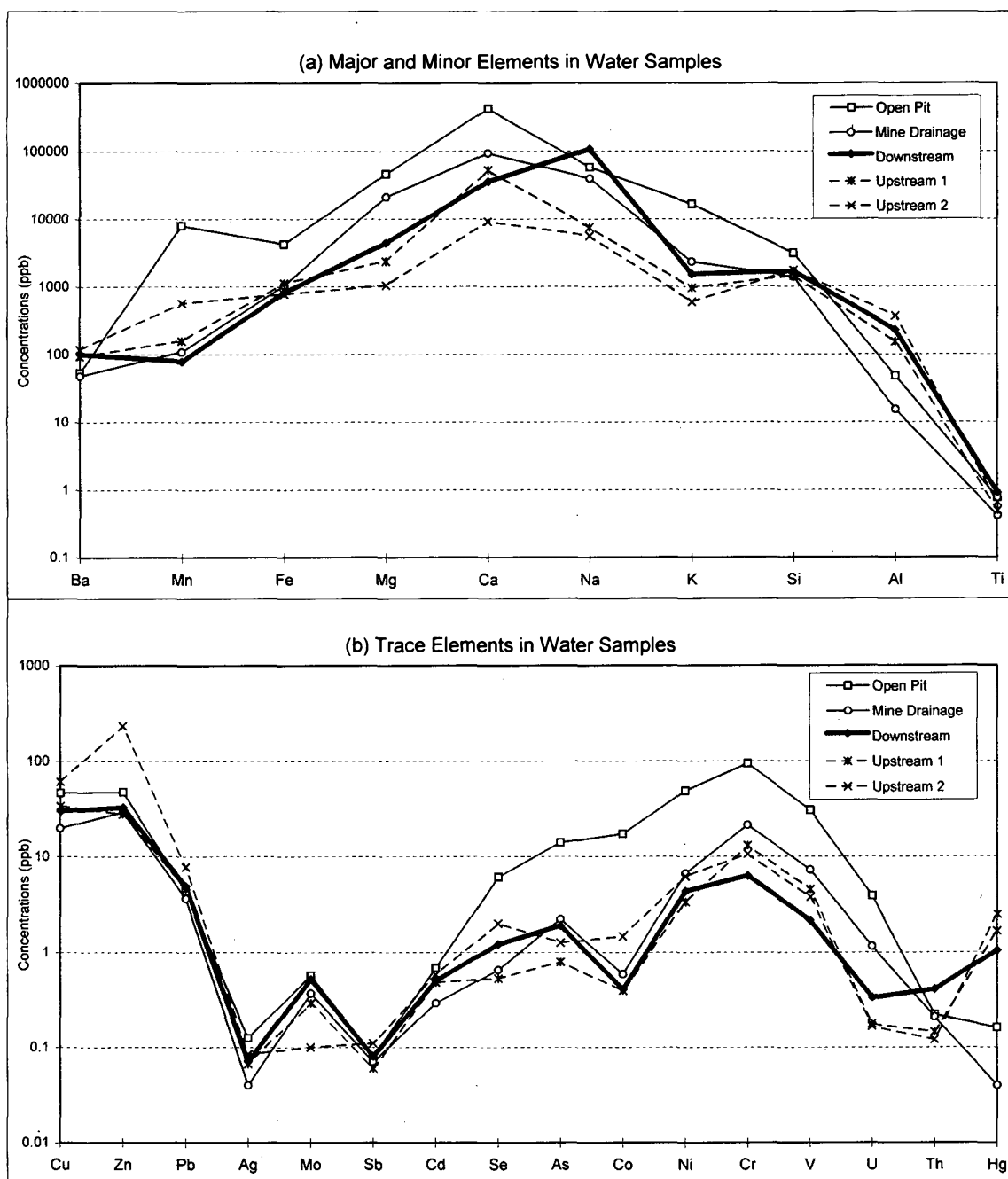


Fig. 6. Geochemical comparison of upstream, downstream, and mine site waters. (a) Major and minor elements; (b) trace elements. Data as in Table 2.

content of the flocculant (Table 1b) indicates that coprecipitation or adsorption is reducing the metal content of the overflow from the pit. This precipitated material is presumed to be physically transported downstream as fine sediment during periods of high discharge and mixed with tailings-derived sediment.

The upstream waters, which have minimal contact with the limestone-evaporite formations, are acidic (pH 5.7-6.7) and have values of Fe, Mn, Cu, Zn, and Pb that are equal to or higher than on-site and downstream waters. This presumably reflects the enhanced mobility of these metals under these pH values and perhaps also the influence of the shale-dominated upstream bedrock.

The downstream water, which is neutral to slightly acidic, shows the effects of the above solution and precipitation processes progressively modified by dilution (Fig. 7). Approximately $0.5 \text{ m}^3 \text{ s}^{-1}$ of upstream water flows along the eastern and northern portion of the waste rock dump. This water is mixed with approximately 0.1 to $0.2 \text{ m}^3 \text{ s}^{-1}$ of water from the open pit and from on-site drainage (including effluent from the sulphide tailings impoundment). Effluent from the barite tailings impoundment and northward surface run-off along the remaining length of the brook adds an additional $0.1 \text{ m}^3 \text{ s}^{-1}$, for a total discharge exiting the mine site of 0.7 to $0.8 \text{ m}^3 \text{ s}^{-1}$ (Fig. 2). The contaminated mine waters are therefore di-

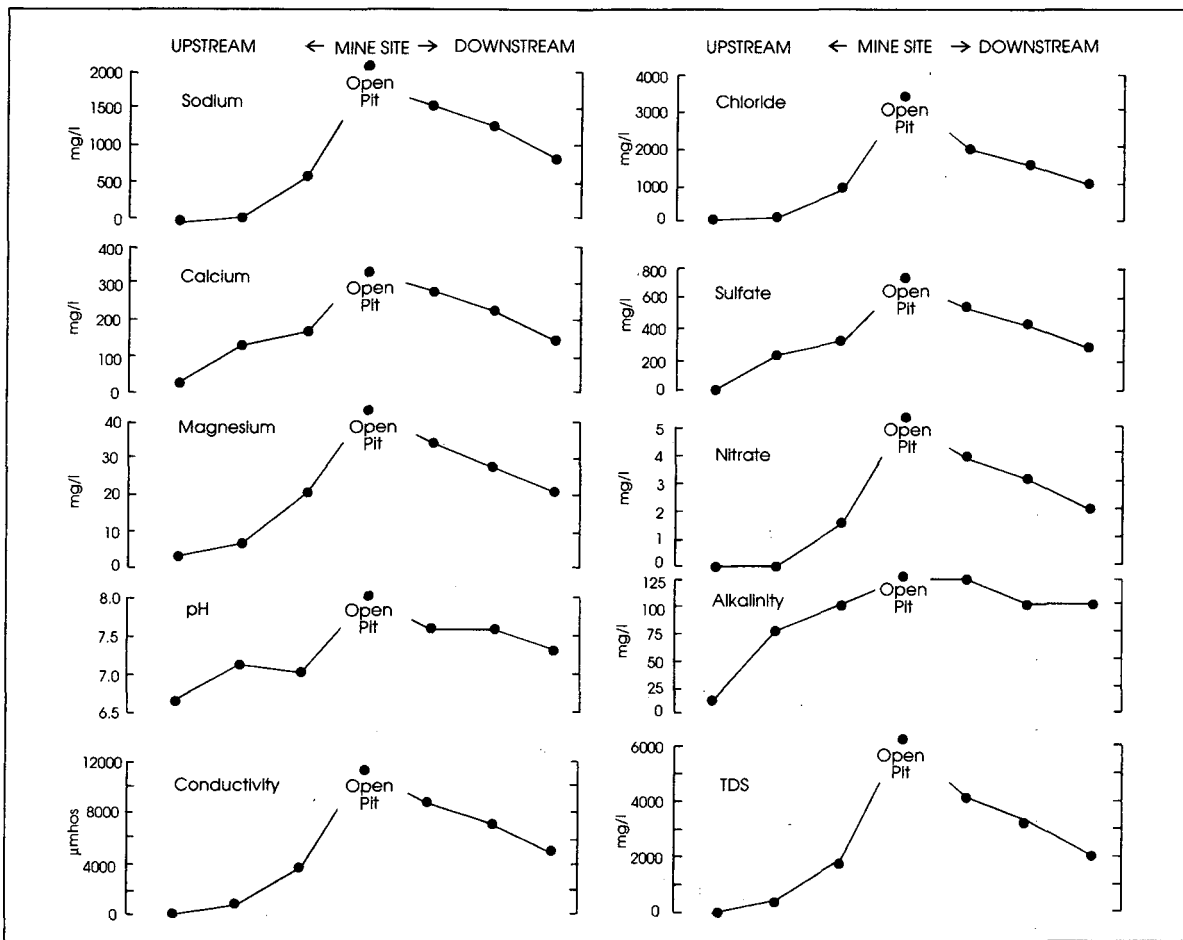


Fig. 7. Comparison of water quality parameters for samples of upstream, downstream, and mine site waters. Sample locations are shown on Figure 2, and data are from Whitehead (1997).

luted/mixed with upstream waters in the ratio of about 1:2. The diluted downstream water has a pH in the 6.8 to 7.6 range, and has trace metal concentrations lower than upstream waters for most elements, with the exception of As, U, and Th (Fig. 6b). These low values are attributed to dilution, and to the loss of metals by flocculation and precipitation with slightly increasing pH values. Major cation and anion concentrations (total dissolved solids) and conductivity also decrease progressively downstream, as would be expected with dilution (Fig. 7).

According to general water quality guidelines suggested by the Department of Fisheries, Nova Scotia (Jason LeBlanc, personal communication, 1997), the sampled downstream waters exceed the acceptable levels for (i) alkalinity values which are 4 to 5x above the suggested limit of 25 mg l⁻¹, and (ii) total dissolved solids which are 1.4 to 2.8x above the suggested limit of 1500 mg l⁻¹ (Fig. 9). The downstream water also has levels of Fe, Cu, and Cd that exceed water quality guidelines as defined by the Ontario Ministry of the Environment (Phypher and Ibbotson, 1990), but upstream water also exceeds these guideline levels, suggesting that the downstream water is not significantly contaminated in these elements (Fig. 9b). Ba, Co, Mn, Mo, and V have undefined tolerance limits and therefore cannot be evaluated under these guidelines.

AMELIORATION

Natural processes contributing to reduction of the heavy metal and chloride-sulphate content of Rainy Cove Brook include on-site buffering, dilution by upstream and meteoric waters, resultant pH changes, and flocculation of Fe-Mn hydroxides.

Reduction of tailings input into the brook following mine closure has allowed natural stabilisation of the flood plain and the re-establishment of a wetland environment over a 20 to 25 year period. Reduced sediment deposition and erosion in this environment, and progressive rapid accumulation of organic materials should promote uptake of metals, as well as bioreduction of sulphate (which is high in the brook water), leading to formation of iron monosulphides and co-precipitation of other metals.

Physical intervention at the mine site could further minimise downstream dispersion and prevent any future destabilisation due to erosion. Clay capping and re-vegetation of the tailings impoundments is an expensive option. A cheaper alternative would be to repair breached berms, and to recontour and stabilise the eroded upper barite tailings impoundment. Also, and perhaps most importantly, a dam of sufficient height to contain water-table fluctuations could be

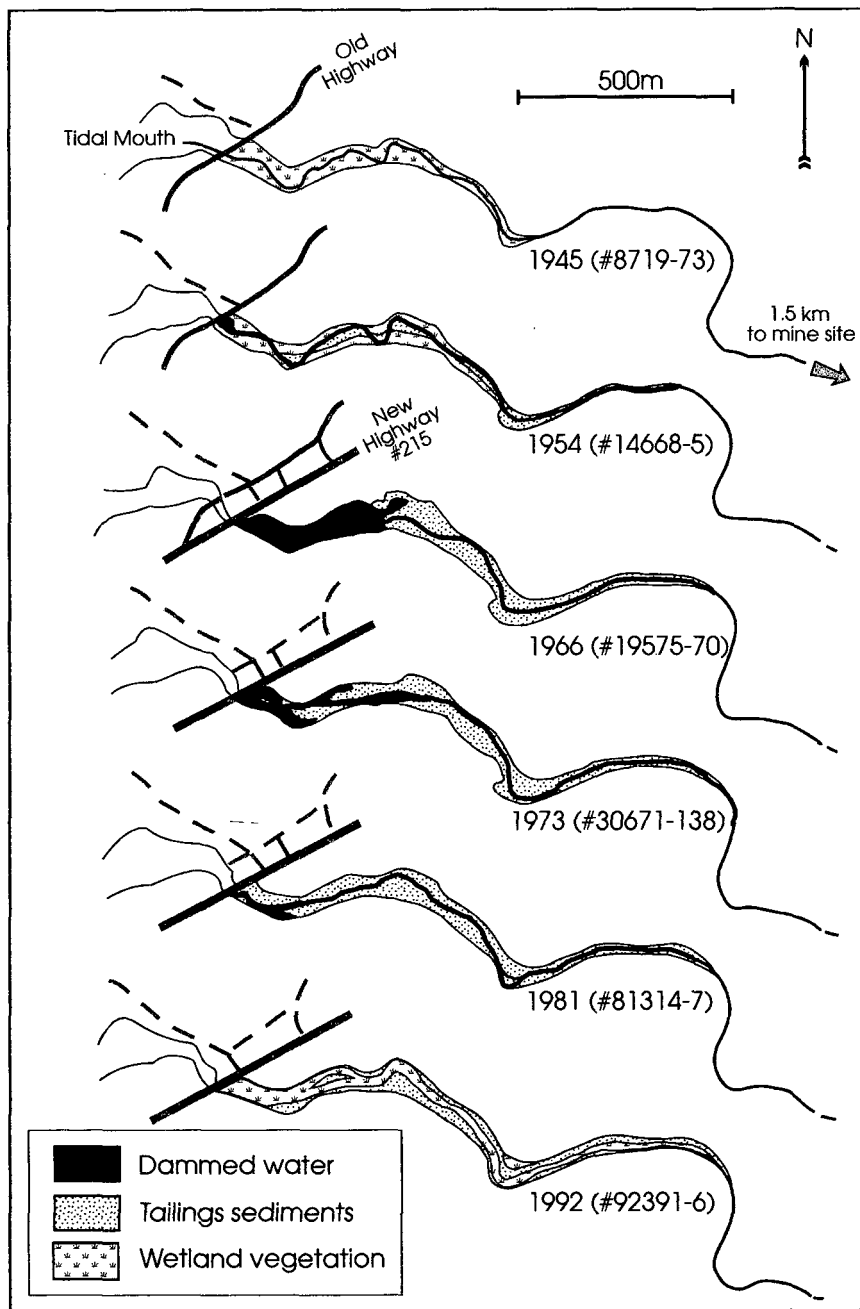


Fig. 8. Schematic diagram, based on aerial photographs (identified by number and scale), showing interpretations of the physical changes to the flood plain of Rainy Cove Brook from 1945 until 1992.

constructed across the haulage road from the open pit to contain the contaminated pit water and promote *in situ* flocculation and settling of contaminants.

SUMMARY AND CONCLUSIONS

The primary dispersion mechanism of heavy metals from Walton mine site into the downstream environment is by physical erosion and transport of tailings into Rainy Cove Brook. Aerial photograph evidence shows that large scale tailings releases have occurred throughout the life of the mine operation, and site investigation shows that it is continuing, on a much reduced scale, at the present time.

Downstream sediments are physically and chemically similar to the tailings and show mean metal enrichments in Ba (<40x), Mn (<11x), Cu, Pb, and Zn (<5x) compared to upstream sediments. Although they could be considered to be marginally to grossly polluted, their accidental impoundment above the highway and subsequent burial beneath naturally regenerated marshland probably help to significantly reduce any environmental impact.

The secondary process for the release of contaminants into the downstream environment is through solution, the main source being contaminated groundwater accumulated in the flooded open pit. This water contains elevated values of Fe, Mn, As, Se, Co, Ni, Cr, V, and U. Factors contributing to

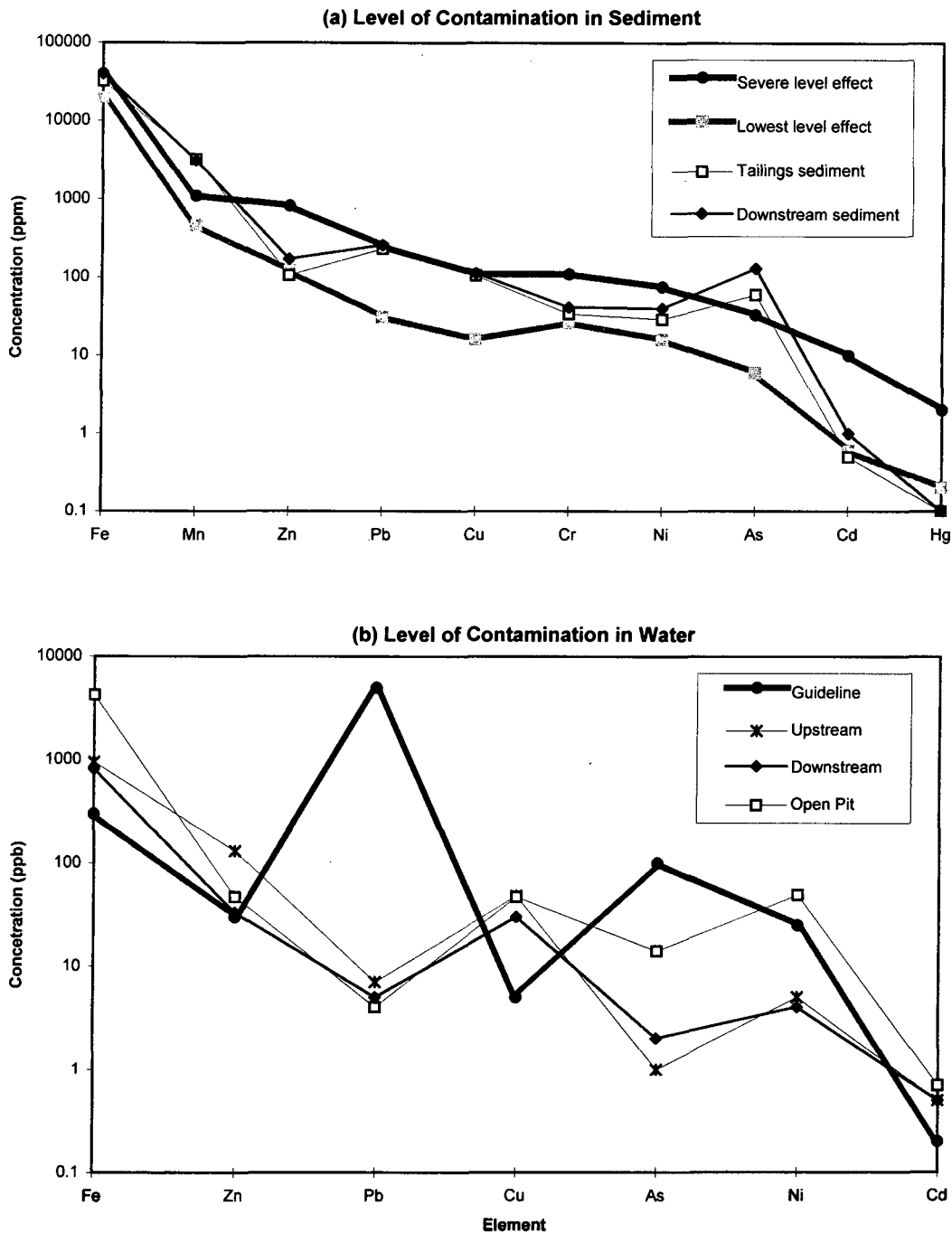


Fig. 9. Levels of contamination in Rainy Cove Brook (a) in sediment based on mean metal concentrations from Table 1b and (b) in individual water samples (Table 2), compared to Ontario guideline levels of Persaud *et al.* (1994) and Phyper and Ibbotson (1990), respectively.

the solubility of these metals include the high pH of 7.8, and the high concentration of bicarbonate, sulphate, and chloride ions which tend to form soluble complexes with the metals.

Mixing of the open pit water with slightly more acidic waters from on-site and from upstream tributaries of Rainy Cove Brook (i) reduces the pH, (ii) dilutes/changes heavy metal concentrations, and (iii) triggers flocculation/precipitation of Fe-Mn hydroxides which probably further reduce the concentrations of heavy metals in the water by adsorption and/or co-precipitation. By these processes, metal concentrations in Rainy Cove Brook, downstream from the mine site,

are reduced to levels at or below upstream levels, except for As, U, and Th which probably persist as stable complexes but at very low concentrations (no greater than average sea water). However, downstream water quality is not good for fish due to high alkalinity and total dissolved solids, and relatively high background Fe and Cu concentrations.

Remedial actions which might further minimise ongoing physical and chemical contributions from the mine site include (i) tailings stabilisation and (ii) damming of the flooded open pit to encourage *in situ* precipitation and containment of heavy metals.

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