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TRANSPORT AND ATTENUATION OF ARSENIC, COBALT AND NICKEL IN AN ALKALINE ENVIRONMENT (COBALT, ONTARIO)

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ABSTRACT

Understanding the behaviour of arsenic in natural waters is important because arsenic and its compounds are toxic to humans and aquatic organisms. The Cobalt area, once renowned for its bonanza silver deposits, is now characterized by numerous deposits of arsenic-rich tailings, waste rock piles and remnant historic mine workings. Very limited mitigation has been undertaken since the cessation of mining. Thus, despite its slightly alkaline character, the surface drainage system continues to be contaminated from leaching of the widespread mine wastes. This Open File documents the transport and attenuation of arsenic and associated elements in the surficial environment from mine wastes (tailings and waste rock) through surface waters to wetlands of the Farr Creek drainage basin in Cobalt, Ontario.

INTRODUCTION

Cobalt, located in northeastern Ontario in the District of Timiskaming (Fig. 1), is historically renowned for its silver production. Between 1904 and the mid 1930s silver was mined continuously, and then intermittently until 1989. By 1971 more than 450 million troy ounces ($\sim 14.0 \times 10^6$ kg) of silver were mined from the Cobalt area deposits (Petruck *et al.*, 1971). Other metal production figures include: 11.2×10^6 kg cobalt, 1.45×10^6 kg copper, 1.41×10^6 kg nickel, and 0.5×10^6 kg lead (D.J. Consulting, 2001). Today, the McAlpine mill still processes materials containing precious metals (e.g., waste electronic and microelectronic gear, jewellery, photographic and X-ray film, slag, crucibles, refractory brick). This 200-ton per day gravity-flotation mill is run by SMC (Canada) Ltd., a subsidiary of Sabin Metal Corporation of East Hampton, New York (Meyer *et al.*, 2003).

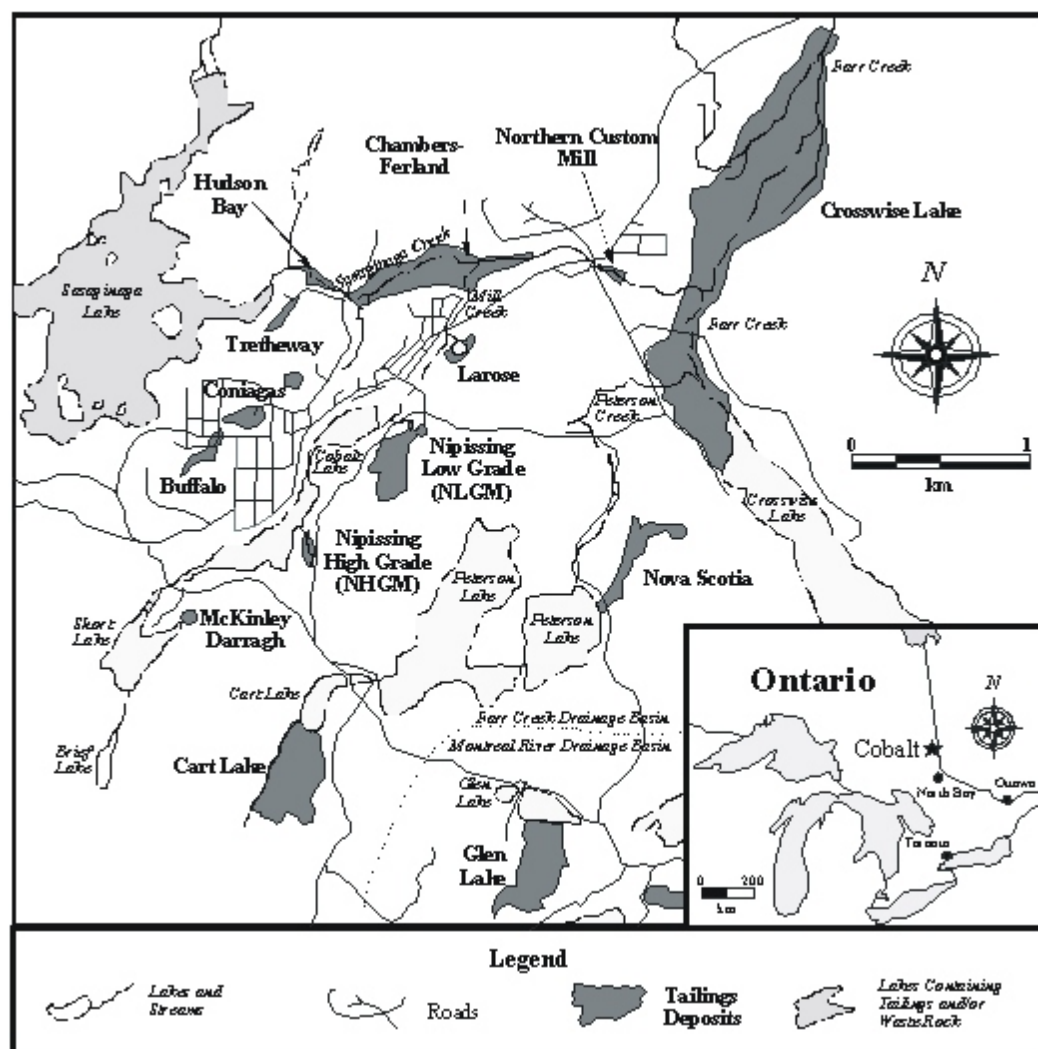


Fig. 1: Location map of Cobalt, Ontario showing details of the Farr Creek drainage basin and location of tailings deposits and waste rock dumps (after Anderson, 1993 and Dumaresq, 1993).

In 1997, Branchwater Resources Ltd. of Calgary acquired some properties in the Cobalt area and began exploration activities that included underground restoration, surface sampling and drilling. In 1998, Cabo Mining Corporation acquired 100% interest from Branchwater in the Cobalt area. Cabo Mining Corporation carried out an EM survey in 1999 followed by active surface exploration and drilling. The exploration targets included traditional Ag-Co arsenide veins, VMS-type deposits from the Archean basement and diamond potential in kimberlite and lamprophyre intrusions associated with regional structures (Pryslak, 2002). Meyer *et al.* (2003) reported that Cabo Mining Corp. recovered 95 diamonds, including 4 macrodiamonds, from a 9.3 kg sample from drill core on its Cobalt property. Results and reports are posted on their website at: www.cabo.ca.

Over the years, 18 mills operated within the area using methods such as flotation separation, cyanide dissolution and Hg pan amalgamation to extract silver. Tailings disposal was unplanned and generally proximal to the mills, either on surface or sub-aqueously. After a major outbreak of typhoid in 1909, Sasaginaga Lake was established as the town reservoir to provide clean drinking water in 1910 (Angus and Griffin, 1996). Today, numerous tailings deposits, waste rock dumps and mine workings are testimony to the extent of the early mining activity in the region (Fig. 1). Mitigation efforts have been limited to fencing obvious mine hazards (shafts, pits and some mill foundations), reprocessing tailings from some of the tailings deposits, and revegetation efforts on at least two major tailings deposits (the Nipissing Low Grade Mill Tailings (NLGM) and Crosswise Lake). In 1986, the Cobalt Resident Geologist Office (Ontario Ministry of Northern Development and Mines) designed a self-guided tour of the silver camp (McKinley-Darragh Mill site, Little Silver Vein, Nipissing Lookout and Right of Way Mine) to preserve some of the historical attributes of the Cobalt area. In 1998, Blackstone Developments Inc. (Cobalt) rehabilitated these sites and others with the assistance of a Northern Ontario Heritage Fund Grant (Ireland and Grabowski, 1999). The Heritage Silver Trail is maintained and managed by the Northern Ontario Mining Museum with support from Agnico-Eagle Mines Ltd. (Fig. 2).



Fig. 2: Heritage Silver Trail in the Cobalt area features old headframes and mine workings that capture the history of the region. This headframe was used by the Nipissing Mining Company from 1908-1923, and extended to 1972 by Agnico-Eagle Mines Ltd.

The Cobalt region has been the site of the Carleton University geology and environmental science field camp since the early 1970s. Since then, many students have completed B.Sc. and M.Sc. theses on a variety of research topics, especially related to economic aspects of the mineralization, and more recently, environmental contamination and remediation. The mineralogy of the Nipissing Low Grade Mill tailings (NLGM) and the formation of secondary alteration minerals were documented by Stoddart (1996). Stoddart (1996) found that the primary minerals cobaltite and nickeline (niccolite) were altered to secondary erythrite and annabergite at the tailing's surface. This was confirmed by Andrews (1996) in his detailed examination of a core taken from the former Hebert Pond at the same locale. Pore water analyses of this core, based on data by Andrews (1996), are reported in this Open File. A more detailed examination of niccolite weathering was conducted by Nadorozny (1995).

Dumaresq (1993) examined the distribution and concentration of metals in the surface and ground waters of the Farr Creek drainage basin. Grossmann (1995) used a Geographic Information System (GIS) to map As, Co, Hg and Ni concentrations in surface waters of the Farr Creek drainage system, based on data compiled by Dumaresq (1993). Gombar (1997) looked at As contamination in surface waters south of the town of Cobalt. He found that the As contamination was related to the location of mine tailings and waste rock materials, including waste used in road construction. Arsenic contamination of the surface waters in the Cobalt region has been documented over the past 30 years (OWRC, 1967; Boyle *et al.*, 1969; Hawley, 1980; Dumaresq, 1993; Percival *et al.*, 1996a, b; Gombar, 1997). Based on stream flow data and As concentrations as reported in OWRC (1967), Rychlo (1977) estimated that about 32,000 kg of As was being discharged into Lake Timiskaming annually. Stream flow for 1988-89 ranged from 0.15 to 2.65 m³/s with a mean of 0.68 m³/s (Environment Canada, 1992). Applying similar calculations, Dumaresq (1993) reported that the mean annual discharge of As from Farr Creek to Lake Timiskaming for 1988-89 was about 18000 kg.

The objective of this study, conducted in the mid-nineties, was to examine the transport and fixation of As in the surficial environment from tailings and waste rock sites through surface waters to wetlands in the Farr Creek drainage basin which drains into Lake Timiskaming (Figs. 1, 3 and 4). This Open File report documents major and trace element analyses for all surface and ground waters, tailings and lake cores collected between 1994 and 1997. Mineralogy of the tailings and lake cores is also summarized.



Fig.3: Farr Creek wetlands, looking NE.



Fig. 4: Core sampling near the confluence of the Mill and Farr creeks.

GENERAL GEOLOGY

In the Cobalt area, Archean volcanic and sedimentary rocks are overlain unconformably by Proterozoic sediments of the Cobalt Group. The oldest unit of this group, the Coleman Member of the Gowganda Formation, is composed of conglomerate, greywacke, quartzite and arkose. The Coleman Member is overlain by argillite of the Firstbrook Member and both are overlain by arkose and quartzite of the Lorrain Formation. All units are cut by early Proterozoic Nipissing diabase (Boyle, 1968; Jambor, 1971), with which the Ag-Co-Ni-As deposits are spatially associated.

Native Ag occurs in veins associated with native Au, As and Bi, as well as arsenides, sulfarsenides and sulfides such as nickeline (niccolite), cobaltite, safflorite, löllingite, rammelsbergite, gersdorffite, skutterudite, arsenopyrite, tetrahedrite, chalcopyrite, bornite, galena, sphalerite, pyrite and marcasite (Petruk, 1971). Gangue minerals include calcite, dolomite, quartz and chlorite. Oxidation of the primary ore minerals produces secondary minerals, in particular, erythrite, annabergite and scorodite. Sulphates (e.g., gypsum and thenardite), Fe and Mn oxides and oxyhydroxides as well as clay minerals are also present (Boyle and Dass, 1971).

ENVIRONMENTAL GEOCHEMISTRY

Arsenic Cycle

Arsenic exhibits four oxidation states: (-III), (0), (III) and (V), however, As(-III) only occurs as gaseous arsine (AsH_3). Arsenic may be present as a native metal/element in some mineral deposits, but usually occurs in compounds containing S and a variety of other metals (Boyle and Jonasson, 1973). In natural waters, dissolved As is present as inorganic As(III) and As(V) species, or as methylated As(V) compounds (Cullen and Reimer, 1989). Arsenic is mobile in both acid and alkaline waters due to its amphoteric nature (Boyle *et al.*, 1969).

Arsenate ($\text{As}^{\text{V}}\text{O}_4^{3-}$) species predominate in aerobic waters whereas arsenite ($\text{As}^{\text{III}}\text{O}_3^{3-}$) occurs under anaerobic conditions (Ferguson and Gavis, 1972; Cullen and Reimer, 1989). Ferguson and Gavis (1972) noted that arsenite can be found in surface waters if the Eh is less than 0.1 V or if oxidation to As(V) is incomplete. Removal of As from solution can result by co-precipitation with hydrous Fe- and Al-oxides, adsorption onto clays or through chelation with organic matter. Increases in pH, Eh, salinity, temperature or biological activity help to increase the rate of oxidation of arsenite to arsenate. This is important because arsenite is more toxic than arsenate.

Organisms bioaccumulate As from water, but As is not biomagnified through the food chain (CCREM, 1987). The decreasing order of toxicity is: arsine(-III) > organo-arsine derivatives > inorganic arsenite(III) > organic As(III) compounds > arsenoxides(III) > inorganic arsenates(V) > organic As(V) compounds > metallic As(0) (Penrose, 1974; NRCC, 1978; Eisler, 1988). In general, inorganic arsenical compounds are higher in toxicity than organic compounds and the trivalent arsenical compounds are more toxic than pentavalent compounds (NRCC, 1978). Methylated As compounds such as monomethylarsonic acid (MMA) and dimethylarsonic acid (DMA) are less acutely toxic than inorganic As compounds (Yamauchi

and Fowler, 1994; Le *et al.*, 2000). Derivatives of MMA and DMA are commonly used in agrochemicals and herbicides. Yamauchi and Fowler (1994) noted that methylation of inorganic As acts as a detoxification mechanism in mammals.

Groundwaters may contain high concentrations of inorganic As and poisoning due to ingestion has occurred in Taiwan (Chen *et al.*, 1986), Chile (Zaldivar and Guilier, 1977) and Mexico (Garcia-Vargas *et al.*, 1991; Armienta *et al.*, 2000). More recently, millions of people living in West Bengal, India and Bangladesh have been ingesting inorganic As from their tube wells, in concentrations up to 2 mg/L (Tondel *et al.*, 1999). This chronic exposure has led to the development of As-induced skin lesions that may develop into cancers (Bagla and Kaiser, 1996; Tondel *et al.*, 1999).

Cobalt and Nickel

Cobalt and nickel are Group VIIIB elements that exhibit both chalcophile and siderophile affinity. The two elements are often cited as a geochemical pair with near-ideal substitution for each other (Brookins, 1988). Although this is mostly true in igneous and metamorphic rocks and magmatic sulphides, the two elements show some differences in behaviour in the near-surface environment. Their geochemical characteristics under ambient conditions are briefly summarized as follows.

Cobalt: The common oxidation state of cobalt is (II), but (III) and (IV) are also possible. In aqueous solutions, cobalt primarily occurs as the Co^{2+} ion and is highly mobile under acid conditions ($\text{pH} < 7$). At progressively higher pH conditions, its mobility is limited by the precipitation of cobalt carbonate and cobalt hydroxide as stable solid phases. Under oxidizing and weakly acid to basic pH conditions, Co_3O_4 can form as a stable solid and under reducing conditions CoS becomes stable (Brookins, 1988). The aqueous transport of Co can also be attenuated through adsorption with Mn-oxides and less strongly with Fe-oxides (e.g., limonite) and clay (Levinson, 1980). Being a central atom in vitamin B12, cobalt is considered as an essential trace element. However, it is toxic to humans at doses of 25 mg/day or more (Reimann and de Caritat, 1998); excessive Co can cause Fe and Cu deficiencies.

Nickel: The common oxidation states of nickel are (0) and (II), with (–I), (I), (III) and (IV) being less common. In solution, nickel occurs primarily as the Ni^{2+} ion under acidic to slightly basic pH conditions and as the HNiO_2^- complex under highly basic pH conditions (Brookins, 1988). In the intermediate to basic pH ranges ($\text{pH} \sim 8\text{--}12$), the aqueous transport of nickel is limited by the occurrence of $\text{Ni}(\text{OH})_2$ as a stable solid phase. The mobility of aqueous Ni^{2+} can also be attenuated by sorption with Fe- and Mn-oxides as well as organic matter under ambient conditions and precipitation as NiS under reducing conditions (Levinson, 1980). As compiled by Reimann and de Caritat (1998), nickel is considered as an essential element for some organisms. Compounds of Ni^{2+} are relatively non-toxic, with recommended maximum acceptable concentration (MAC) levels of 0.1 mg/L by the United States Environmental Protection Agency (US EPA 1997) and 0.02 mg/L by the World Health Organization (WHO, 1996). The US EPA (1997) suggested that drinking water which exceeds MAC levels generally does not lead to health problems in the short term but may cause reduced body weight, heart and liver damage as well as skin irritation in the long term (Reimann and de Caritat, 1998).

METHODS

Water Sampling and Analysis

Surface water samples were collected in July and September 1994, May 1995 and September, 1997. Sample sites are shown in Figure 5 and numbered consecutively from the SW to the NE in the direction of drainage. Site descriptions and their location are detailed in Appendix A (Tables A2-A3). Groundwater samples were collected from a pipe draining a mineshaft near Sasaginaga Creek (GW1), overflow from a shaft near Cobalt Lake (GW2), and from a pumphouse and taps at the Bucke Park campground (GW3-GW7). Temperature, pH,

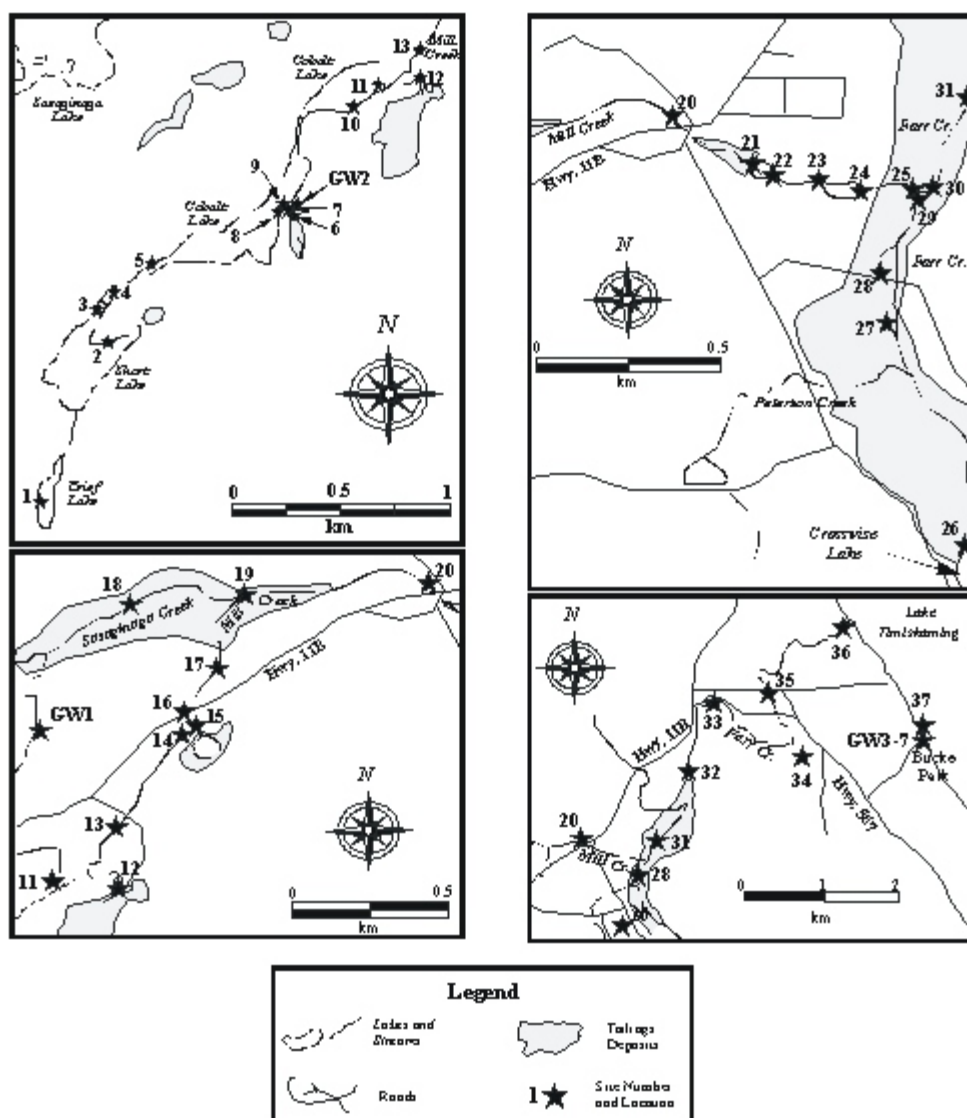


Fig. 5: Site locations of all sampling stations used in 1991-92, 1994 and 1995 surveys: A) Cobalt Lake area; B) Sasaginaga Creek and Mill Creek confluence; C) Mill Creek and Farr Creek confluence; and D) Bucke Park campground. Drainage of the Farr Creek basin is to the northeast to Lake Timiskaming.

Orp (oxidation-reduction potential) and electrical conductivity were determined in the field with a Cole-Parmer Water Test meter. The Eh values were calculated from Orp measurements using the correction factor furnished by Bates (1973). Dissolved oxygen (DO) measurements were made with a YSI-DO probe (Model 55). Multiple water samples from each site were filtered in the field through a 0.45 μm Millipore filter paper (type HAWP). One sample was acidified to 0.4% in HNO_3 (using Seastar double sub-boiling distilled) for cation determinations, one to 0.4% in HCl (using Merck Suprapur) for As speciation, and one untreated for anion determinations. Major and trace elements were determined on the HNO_3 -treated sample by inductively-coupled atomic emission spectrometry (ICP-AES) and inductively-coupled mass spectrometry (ICP-MS) (note that "total" in this paper implies total "dissolved"; i.e., through 0.45 μm filter). Total As and As(III) were determined by hydride generation quartz tube atomic absorption spectrometry (AAS) using NaBH_4 as a reducing agent. With a sample adjusted to a pH of 5 with citric acid, arsine (AsH_3) is generated only from As(III), As(V) being non-reactive. A separate aliquot is then pre-reduced with 5% KI and ascorbic acid to determine total As. Arsenic(V) is then determined as the difference between total As and As(III). Anions were determined using a Dionex ion chromatograph.

Tailings and Lake Sediment Sampling and Analysis

Tailings samples were collected as grab samples and by hand-coring. For sampling in the wetlands, a 2.5 cm plastic core tube was pushed into submerged or wet tailings (Fig. 4) whereas a stainless steel corer with a plastic liner (~5 cm diameter) was used to sample the Nipissing high- and low-grade tailings. In addition, a few pits were dug in the Nipissing low-grade tailings area to examine the stratigraphy and sample visibly different units at various depths (Fig. 6). Tailings from Cobalt Lake were sampled by dropping a gravity corer lined with a plastic core tube (2.5 cm diameter) into the sediment. Samples collected were homogenized and ball milled to about -200 mesh for analysis. Major and trace elements were determined by a combination of methods including X-ray fluorescence (XRF), inductively-coupled atomic emission spectroscopy (ICP-AES) and inductively-coupled mass spectrometry (ICP-MS). Subsamples were further processed for X-ray diffraction analysis.



Fig. 6: Hand-dug pit in the Nipissing low- grade tailings.

The clay-size fraction was separated from bulk samples in the Sedimentology Laboratory of the Terrain Sciences Division using centrifugation followed by freeze-drying. The mineralogy of bulk materials and clay-size separates was determined by X-ray powder diffraction analysis (XRD). Suspensions (in water) of the samples were pipetted onto glass slides and air-dried overnight to produce oriented mounts. X-ray patterns of the air-dried samples were recorded on a Philips PW1710 automated powder diffractometer equipped with a graphite monochromator and Co K α radiation set at 40 kV and 30 mA. The samples were also X-rayed following saturation with ethylene glycol and heat treatment (2 hours at 550 °C). Semi-quantitative analysis was determined with JADE™ (v. 3.1) software. For more information see Percival *et al.* (2001).

Grain mounts and polished thin sections were made for examination under petrographic and scanning electron microscopes (SEM). Polished thin sections were prepared by Vancouver Petrographics Ltd. For grain mounts, a very dilute (< 10-20 ppm) suspension was pipetted onto a carbon planchette and then carbon-coated before examination. A Leica Cambridge Stereoscan S360 SEM equipped with an Oxford/Link eXL-II energy-dispersion X-ray analyzer, Oxford/Link Pentafet Be window/light element detector, and an Oxford/Link Tetra backscattered electron detector was used. The SEM is operated at an accelerating voltage of 20kV. Images were digitally captured at 768 x 576 pixels at 256 levels of greyscale and stored for further processing.

RESULTS AND DISCUSSION

Water Quality

Parameters measured in surface water during the 1994, 1995 and 1997 surveys included temperature, pH and conductivity for all samples, and dissolved oxygen and Orp for some of the samples. Results are tabulated in Appendix A (Tables A4-A11). Surface water temperatures (mean 18.6 °C) vary depending upon the season of sample collection, although lower temperatures (mean ~ 11 °C) are representative of groundwater conditions. All surface waters are alkaline with an average pH of 7.7, are oxygenated (Eh from +200 to +444 mV), and have dissolved oxygen levels at or near saturation (average 8.7). Overall, the measured conductivity is relatively high (average 308 μ S/cm) with peak values corresponding to drainage from exposed tailings. Groundwaters are cooler (6.4 to 14.8°C), are alkaline (mean pH 7.4), with higher conductivities (mean 457 μ S/cm) and lower Eh (+138 to +154 mV) than the surface waters. One exception was Sample GW1 (Eh = +470 mV) which was taken from a mine shaft discharging from a pipe into Sasaginaga Creek. Further details can be found in Percival *et al.* (1996b), where Eh corrections were not made. The field measurements are generally comparable to those reported by Boyle and Dass (1971).

Although a comprehensive data set is available for major and trace elements, only details are given for observed As, Ni and Co trends. Arsenic concentrations in sampled surface waters in the Cobalt region exceed the MAC guidelines for Canadian drinking water of 25 μ g/L (Health Canada, 2003) and the interim MAC of 5 μ g/L for freshwater aquatic life (CCME, 1999; Summary Table updated 2002 available from www.ccme.ca), although none is used for drinking water (Appendix A, Table A5). Only 5 samples contain <100 μ g/L total As and the highest concentrations (15000 - 20000 μ g/L) are associated with drainage from a small area that

contains residual Nippising High Grade Mill (NHGM) tailings (Percival *et al.*, 1996b). The trend in As concentration within the Farr Creek drainage system is plotted in Fig. 7 as the mean concentration for data collected in this study and incorporating those collected by Dumaresq in 1991-1992 (Dumaresq and Michel, 1992; Dumaresq, 1993). Low concentrations (e.g., <300 µg/L) are observed in Brief Lake, Short Lake, Sasaginaga Creek, Crosswise Lake and Farr Creek. Brief Lake is located at the head of the Mill Creek system and does not contain any tailings, whereas at least two waste rock piles lie along the shores of Short Lake. The As concentration increases downstream from Short Lake. The drainage from the NHGM tailings, although extremely high in As, is low in volume and becomes insignificant when it mixes with the large volume of water in Cobalt Lake. However, the contributions from the NLGM and LaRose tailings give rise to an increase in As concentration further downstream as they mix with a smaller volume of water in Mill Creek. The concentrations then decrease and reach a low level at Site 19. The concentration in Sasaginaga Creek upstream of Mill Creek is less than 300 µg/L, despite the creek being underlain by tailings. At Site 20 the concentration has increased to about 1000 µg/L but the source of contamination is unclear. Higher As concentrations at Site 20 may indicate an unidentified groundwater discharge in this area. The concentrations generally decrease across a wetland area (between Sites 16 and 32), with some minor fluctuations, but increase again slightly before entering Lake Timiskaming. Some of

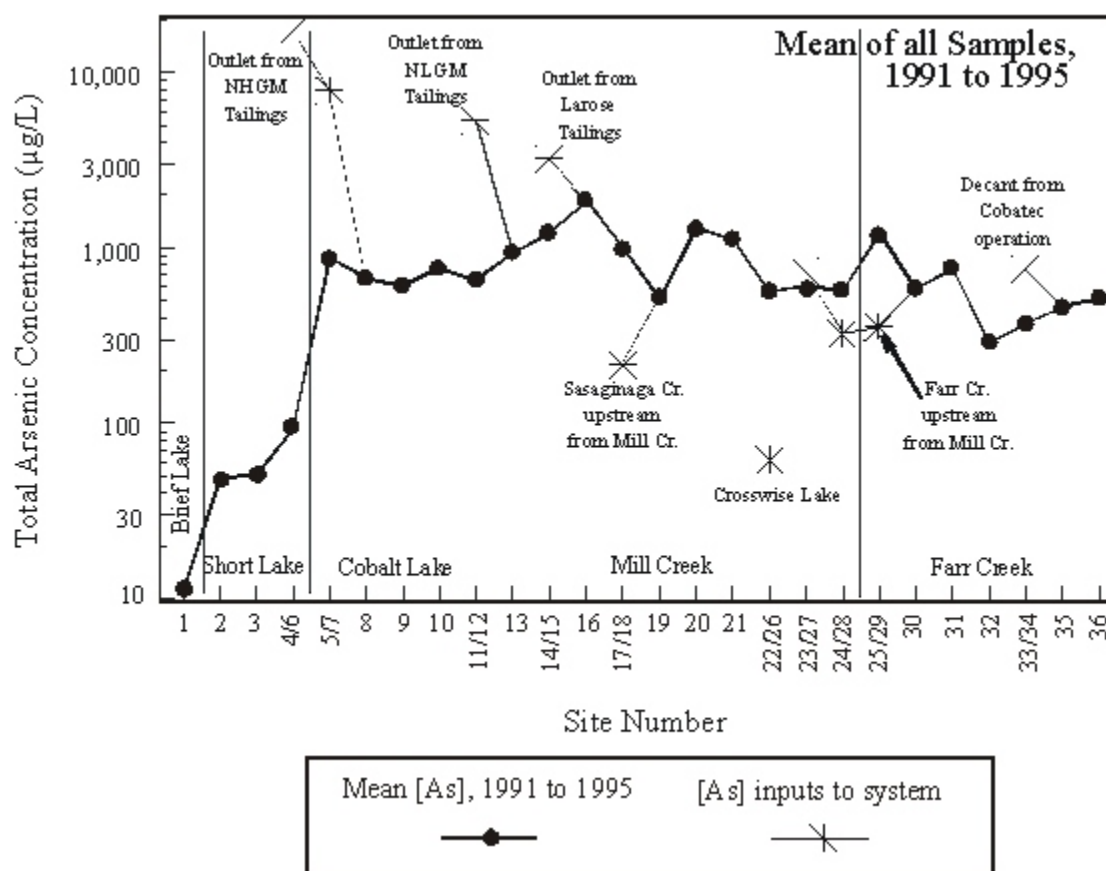


Fig. 7: Mean total dissolved As for all samples (1991-1995) plotted against relative distance downstream for each sampling site.

these minor fluctuations are easily explained. For example, an increase in concentration just before the Mill Creek-Farr Creek confluence (Site 25; Fig. 7) reflects a contribution from an unknown volume of tailings that were discovered in Mill Creek in 1994. These were likely discharged from the nearby Northern Customs Mill. Arsenic concentrations are higher in Farr Creek at Site 35 than at Site 32. In September 1994 Farr Creek was receiving decant water (Site 34; Fig. 7) from the settling pond at the Cobatec Inc. Refinery (now owned by Canmine Resources Corporation) during dewatering of the Pan Silver Mine. Although the decant may be a contributing factor to the increase in As concentration at Site 35, it is not the major factor, as a similar trend was reported by Dumaresq (1993). The Farr Creek basin contains no mine wastes downstream of Site 32. Thus, the probable source of contamination leading to increased As concentrations between Sites 32 and 36 is groundwater discharge along fault zones. The water course of Farr Creek near Site 33 is controlled by two faults which intersect just north of the creek, and another fault crosses the creek at Site 36. Previous studies (MOE, 1977) have shown that groundwaters, particularly those originating in the Coleman Formation, contain elevated concentrations of As and other associated metals.

The observed As trend suggests that metal fixation processes such as adsorption or chelation may be occurring in the wetlands along Mill Creek. Moreover, biogeochemical cycling and storage processes in wetland vegetation may remove heavy metals and other trace elements. Where additional As inputs downstream cannot be related to the presence of submerged or buried tailings, groundwater sources may be a contributor, an example of which is the increase in As concentration in Farr Creek before entering Lake Timiskaming.

Arsenic speciation studies are important to understand the source of inorganic As. Arsenic(III) is plotted against total As in Fig. 8. Arsenic(III) in surface waters generally accounts for less than 15% of the total As, except for samples with very low total As content (e.g., <30 µg/L). In contrast, the groundwater samples contain up to 77% of the total as As(III). The increases and decreases observed in As(III) content between sampling periods are likely indicative of a groundwater contribution to the total As budget in these surface waters.

Cobalt and Ni concentrations are also plotted by site number in Figure 9. The trends are similar to total As. Concentrations are very low (<20 µg/L) in the Brief-Lake-Short Lake area. Concentrations are high at Site 6, taken below the high grade mill tailings dam. Concentrations gradually decrease due to dilution in Cobalt Lake and increase again due to contributions from the Larose tailings outlet. Concentrations then stabilize or decrease towards Lake Timiskaming with a slight increase at Site 35 possibly due to the de-watering of the Pan Silver Mine (Canmine Resources Corporation/Cobatec Inc. facility).

Major and trace cation and anion concentrations, determined in surface and groundwater samples collected in 1994, 1995 and 1997, are provided in Appendix A (Tables A6 to A11). For trace metals, only Sb shows elevated concentrations suggesting that its leaching behaviour is similar to As. For major cations, the overall water chemistry reflects a major influence by carbonate dissolution. Calcium ranges from 21 to 82 mg/L and Mg from less than detection to 50 mg/L. The higher concentrations of Mg (e.g., 35 to 50 mg/L) are only observed in the groundwater samples from Bucke Park. There appears to be no relationship between Ca and Mg and other metals. Based on the hardness calculation (total hardness = $2.5(\text{Ca}^{2+}) + 4.1(\text{Mg}^{2+})$) of Freeze and Cherry (1979), these waters are considered hard, with values >100 mg/L (Meq CaCO₃; data not shown). The data reflect the extent of carbonate weathering in the

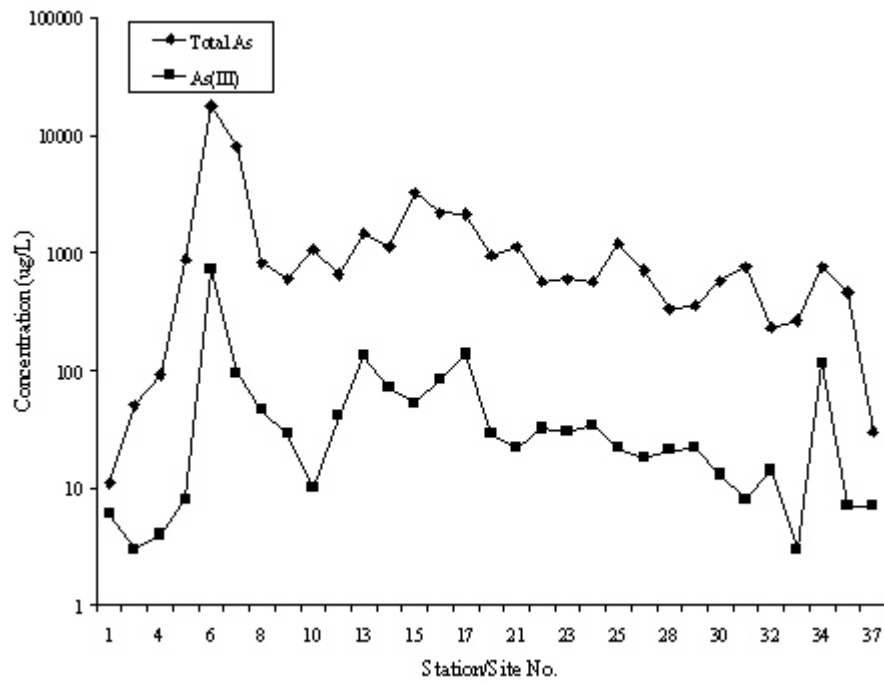


Fig. 8: Total As plotted against As(III) downstream by site number. Average values were used where more than one sample per site was available.

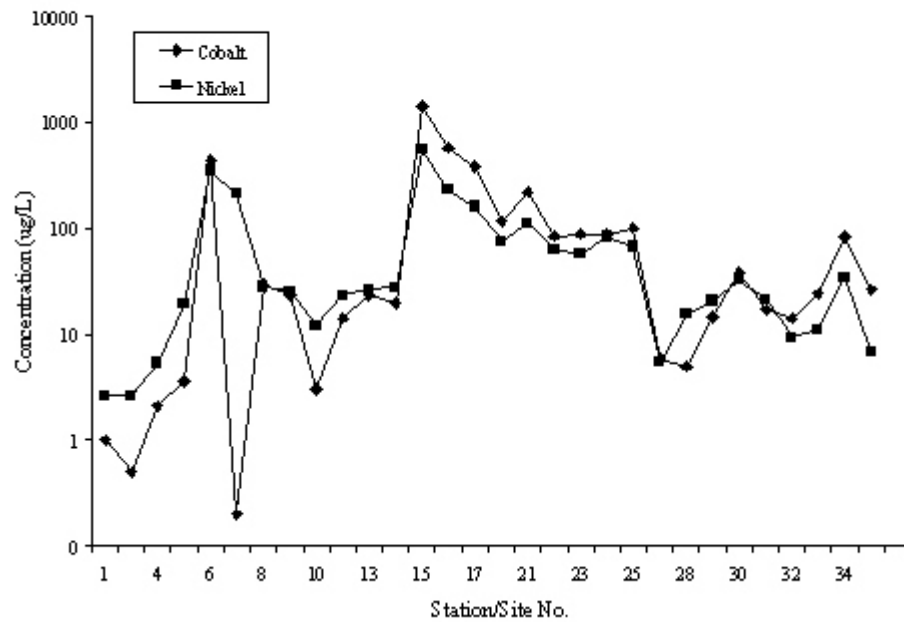


Fig. 9: Distribution of Co and Ni downstream by site number.

study area. Boyle and Dass (1971) reported that waters leaching the ore veins are mainly bicarbonate-sulphate-rich waters. Sulphate contents range from about 3 to 130 mg/L (Appendix A, Tables A7, A9 and A11). Sulphate may be derived from primary sulphide minerals or sulphosalts or from secondary efflorescent salts. Higher alkali and alkaline earth metal levels appear to correspond to elevated levels of SO_4^{2-} (e.g., sites 6, 14, 15 and 17). These concomitant increases probably reflect dissolution of the secondary alteration products.

Tailings

Tailings samples were collected from a variety of sites in the Cobalt area, including the Nipissing low and high grade mill sites, Cart Lake, Crosswise Lake, Peterson Lake, Mill Creek, Farr Creek and the Bucke Park campground. Most of the samples examined come from the Nipissing sites. At some stations, pits were dug and a series of depth samples were taken (Fig. 6). In addition, surface crusts and interesting samples from waste rock piles were collected. Results are given in Appendix B (Solids) where Table B2 summarizes information regarding sample location, Tables B4 and B5 give the bulk and clay-size mineralogy, and major and trace element chemistry are provided in Tables B6 and B7, respectively.

Physical Characteristics: The Nipissing low grade mill (NLGM) site (Fig. 10a) was sampled prior to revegetation efforts (Fig. 10b). The NLGM tailings cover about 60,000 m² and fully enclose the marshy area known as Hebert Pond (Fig 11; Dumaresq, 1993). Samples were collected above and below the main cribwork (centre area of Fig. 10a; dam #1 in Fig 11) and include samples from two small pits (see Fig. 6). Surface crusts were collected above the cribwork. In a related study, 4.5 m-long cores were taken from Hebert Pond for detailed mineralogical and chemical characterisation (Andrews, 1996; Stoddart, 1996).



Fig. 10: a) Nipissing Low Grade Mill (NLGM) tailings site as viewed from the lookout on the Heritage Silver Trail in July 1994. Cobalt town in distance (looking NNW); b) Same view of tailings after re-vegetation efforts (Sept. 1999).

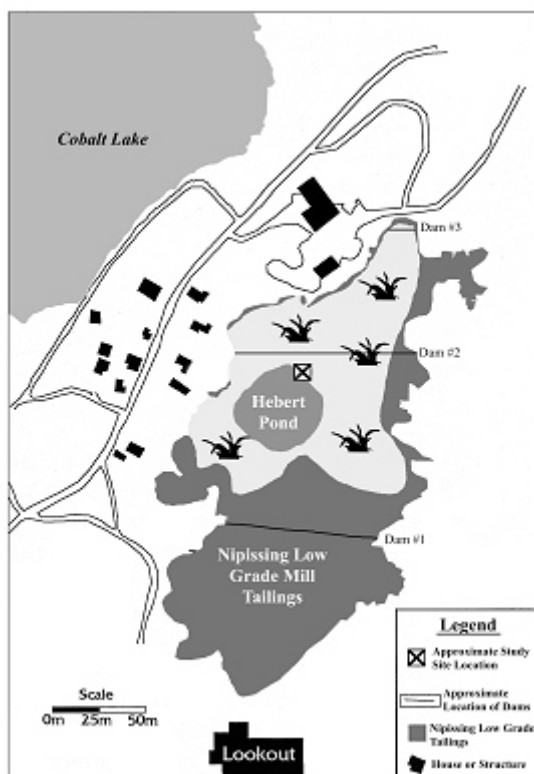


Fig. 11: Detailed map of Nipissing low-grade tailings site showing location of Hebert Pond and old cribwork dams (after Andrews, 1996).

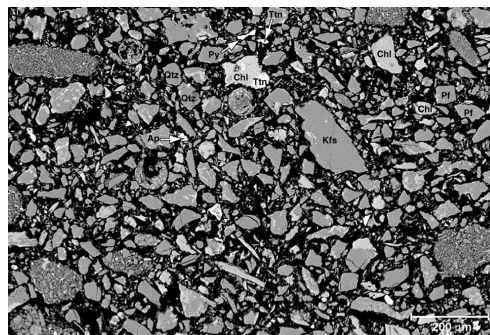


Fig. 12: SEM photomicrograph showing texture of the tailings typical of the Cobalt area (Sample PNA94-14; backscattered image).

The mineralogy of the NLGM tailings samples is similar to tailings from the other sites. The bulk samples contain abundant plagioclase with subordinate quartz, chlorite, calcite and dolomite. Less common are K-feldspar, amphibole and illite/mica (Fig. 12). Some samples contain secondary arsenates such as erythrite ($\text{Co}_3(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}$). Trace amounts of mixed-layer clay minerals can also occur. In the clay-size fraction, chlorite is abundant and quartz, plagioclase and illite/mica generally occur in minor amounts. Within the pits, the mineralogy only shows slight variations with depth. In Sample PNA94-13, erythrite occurs at a depth of about 40 cm (Appendix B, Tables B4 and B5), whereas in the Hebert Pond cores, erythrite and other secondary arsenates occur in the top 30 cm (Stoddart, 1996).

The crusts that were collected from the NLGM tailings surface ranged in colour from white to yellow, although Andrews (1996) reported the presence of grey to brown crusts as well. These crusts tend to contain gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) or thenardite (Na_2SO_4) and are formed by efflorescence during dry seasons. Dumaresq (1993) reported that these salt crusts tended to be elevated in Ni, Co and As contents relative to the tailings surface. These crusts readily dissolve during rainy periods and contribute to surface runoff or are windblown towards the town. Revegetation efforts will certainly help to mitigate this chronic problem.

At the Nipissing high grade mill (NHGM) site there were some interesting materials found. For example, near the adit, old newspapers from the fifties were still readable, no doubt well preserved due to the presence of As. In an area slightly east to the present-day lookout tower (Silverlands Heritage Trail), a small waste rock dump was found (Samples PNA94-01 to PNA94-04) containing primary sulphide minerals. The dump was noticeable as leachate

draining the dump contained amorphous Fe-oxides typical of acid rock drainage (ARD). The samples that were collected showed the presence of abundant pyrite and gypsum (PNA94-02) as well as jarosite. Kwong *et al.* (2000) reported the occurrence of minor amounts of chalcopyrite (CuFeS_2), bornite (Cu_5FeS_4), galena (PbS), sphalerite (ZnS) and pyrite (FeS_2) in the tailings. They also noted that erythrite with minor annabergite ($\text{Ni}_3(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}$) tended to occur only in unsaturated tailings and scorodite ($\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$) was observed in both saturated and unsaturated tailings.

A residual pile of material, possibly concentrate or ore, was found adjacent to the lookout tower on Nipissing Hill (Figs. 13a, b and c). This pile was well weathered and as the origin of the material is unknown, it is referred here as “furnace residue”. The material contains several pink and white blooms, similar to the efflorescent crusts formed on the tailings surface. These materials proved to be unique. The pink bloom contains erythrite, a secondary arsenate formed by the alteration of cobaltite (CoAsS). The minerals present in the white crust include gypsum (Fig. 14a), pharmacolite ($\text{CaHAsO}_4 \cdot 2\text{H}_2\text{O}$) and weilite (CaHAsO_4) (Fig. 14b) based on Debye-Sherrer powder diffraction and SEM analyses, as well as brassite ($\text{MgHASO}_4 \cdot 4\text{H}_2\text{O}$) based on XRD and SEM analyses (Figs. 14c and d).



Fig. 13: a) Concentrate or “furnace residue” discovered near the lookout at the Nipissing High Grade Mill site along the Heritage Silver Trail (since removed); b) pink (erythrite) and white (brassite) secondary minerals forming in situ due to active weathering; c) close-up view of brassite on surface.

Brassite was initially synthesized in 1970 by Réjane Brasse (Fontan *et al.*, 1973). It was reported to occur as a precipitate on museum specimens as a spontaneous dehydration of rösslerite ($\text{MgHASO}_4 \cdot 7\text{H}_2\text{O}$). It also occurs on specimens of pharmacolite, haidingerite ($\text{CaHAsO}_4 \cdot \text{H}_2\text{O}$) and wappelerite (mixture of rösslerite and pharmacolite) and is associated with weilite, rauenthalite ($\text{Ca}_3(\text{AsO}_4)_2 \cdot 10\text{H}_2\text{O}$), and picropharmacolite ($\text{H}_2\text{Ca}_4\text{Mg}(\text{AsO}_4)_4 \cdot 11\text{H}_2\text{O}$)

(Fontan *et al.*, 1973; Fleischer and Mandarino, 1975). This rare mineral forms through the reaction of As-rich solutions with Ca-Mg carbonates (Anthony *et al.*, 2000). This is the first known occurrence of brassite in Canada.

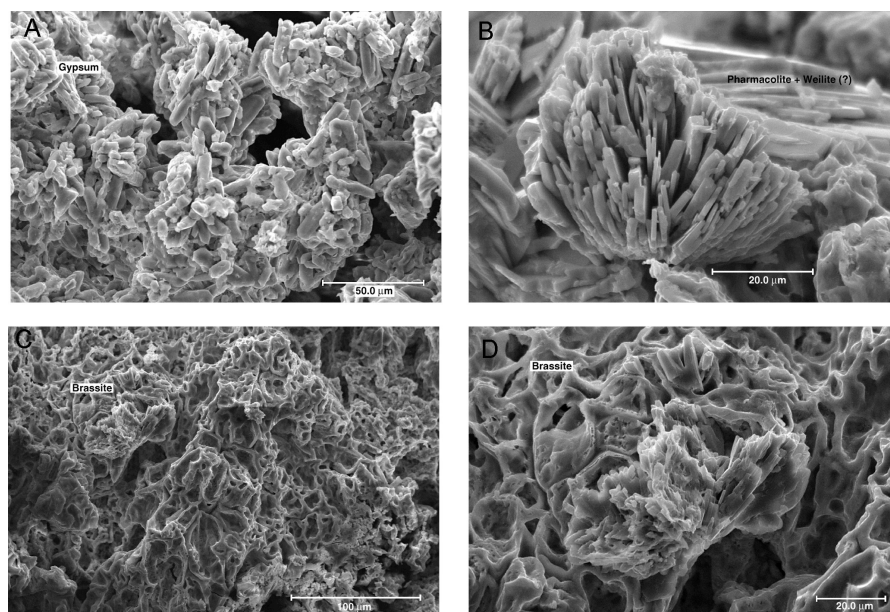


Fig. 14: SEM photomicrographs of minerals taken from the “furnace residue” from Sample PNA94-06. Examples of: a) gypsum; b) pharmacolite and weillite; c) brassite; and d) brassite (backscattered images).

Chemical Characteristics: Major and trace element chemistry of many of the solid samples taken are presented in Tables B6 and B7 of Appendix B. Duplicate analyses are provided at the bottom of each page and show very good agreement. Basic statistics (minimum, maximum and mean) of 25 surface and sub-surface tailings samples are given in Tables 1 and 2. Their chemical composition reflects their bulk mineralogy. Samples contain on average 57 wt% silica, 15 wt% alumina and 8 wt% total iron. The concentrations of Ca, Mg, Na and K reflect the presence of calcite, dolomite, plagioclase feldspar and mica. The mean total sulphur content is 0.15 wt%. The trace elements Co, Ni and Cu are the dominant trace elements in the tailings (note that As analyses were not done) with mean concentrations of 1228, 620 and 445 ppb, respectively. Silver can be found in concentrations up to 220 ppb with a mean value of 74 ppb.

Table 1. Summary data for major elements (wt % oxide) from tailings samples (n = 25) taken from several sites in the Cobalt area.

	SiO ₂	Al ₂ O ₃	Fe ₂ O _{3T}	MgO	CaO	Na ₂ O	K ₂ O	S _T
Min	44.9	13.1	5.4	3.43	1.18	2.7	0.49	0.05
Max	63	17.6	13.3	8.68	6.59	5.1	2.19	0.52
Mean	57.3	14.6	7.74	4.74	3.64	4.45	1.16	0.15

Table 2. Summary data for trace elements (ppb) from tailings samples (n = 25) taken from several sites in the Cobalt area.

	Ag	Co	Ni	Cu
Min	7.6	68	53	91
Max	220	5400	2400	1900
Mean	74	1228	620	445

There is little doubt that the elevated concentrations of trace elements, especially Co, made the tailings attractive to re-processing over the years. In the early to mid-nineties, Cobatec Inc. established a small refinery to process tailings to extract Co and other elements. In 1999, Cobatec Inc. was purchased by Canmine Resources Corporation (www.canmine.com). The refinery was retrofitted and production began in 2002 (Meyer *et al.*, 2003). Table 3 summarizes the many uses of Co in relation to health, industry and home use. Cobalt is considered a strategic metal and is used in many of today's technology-based industries. One prime function is in the production of ^{60}Co , used in the treatment of a variety of cancers.

Table 3. Common uses for cobalt (after www.canmine.com).

Health	Industry	Home
Vitamin B12	Cemented carbides	ABS brakes
^{60}Co for cancer treatment	Crude oil processing	Audio tapes
Animal feeds	Cutting tools	Car instruments and parts
Prosthetics	Electricity meters	Cellular phone batteries
	Hard-facing alloys	Compact disks
	High-speed steels	Laptop computer batteries
	Jet engine and turbine parts	Loud speakers
	Magnetic alloys	Paints and inks
	Pigments	Radial tires
	Porcelain enamels	Rechargeable batteries
	Superalloys	Security systems
		Video tapes

Lichens

Lichen samples were mainly collected from tombstones in Cobalt and New Liskeard towns for a study by Jörg Matschullat at the University of Freiberg. The lichens can be used as a proxy for measuring atmospheric deposition (Matschullat *et al.*, 1999). The intent was to

collect *Xanthoria elegans*, although in some cases this was not possible. The list of samples and their location are given in Table B3 in Appendix B. Samples were digested in nitric acid and then analyzed by ICP-MS. Concentrations of total As ranged from 1.7 to 140 mg/kg with the highest concentrations found in samples from the Ste. Thèrese Cemetery in Cobalt (J. Matschullat, Personal Communication, 1999). This cemetery is the most proximal to exposed tailings sites and is likely affected by wind blown dust on a regular basis. Matschullat *et al.* (1999) also noted that lichens in the Cobalt area were enriched in Ag, As, Bi, Cd, Co, Cu, Sb and Zn relative to other localities in Ontario (transect from Toronto to Moose Factory).

Sediment Cores and Pore Waters

To elucidate the geochemical behaviour of submerged tailings along the water course in the study area, eleven sediment cores were sampled from Cobalt Lake (eight from the south side and three from the north side in rough accordance to their relative surface area) and four from the Farr Creek/Mill Creek wetland (Figs. 4 and 5). Each of these cores was subdivided into several sections based on their visual differences in physical characteristics (i.e., colour, grain size, organic contents, etc.). Where possible, porewater was extracted from each section using high speed ultracentrifugation. The aqueous chemistry of the porewaters and the geochemistry and mineralogy of the tailings sediments were determined using analytical methods described above. The full data set is given in Appendix C. Some salient features are described and discussed below.

The profiles of dissolved As, Co and Ni across the water-sediment interface at the coring locations in the South and North Cobalt Lake are depicted in Figures 15 and 16, respectively. Invariably, the porewater As, Co and Ni contents are higher than those in the overlying water, suggesting a potential efflux of the trace elements from the submerged tailings to the overlying water by diffusion under a chemical gradient. With few exceptions, the dissolved As concentration is higher than those of dissolved Co and Ni by an order of magnitude, especially in the overlying water column. There also appears to be a concentration maximum for all of these elements in porewaters close to the water-tailings interface. However, the sampling method is too coarse to reveal the details in every case. High-resolution sampling technique like deployment of peepers or devices using diffusion gradient in thin films technology will better clarify the concentration profiles at the interface.

The porewater chemistry also differs significantly among the sampling locations, reflecting the heterogeneity in the deposited tailings. Not plotted in the figures are dissolved sulphate concentrations, which are invariably reduced by orders of magnitude across the water-sediment interface. This suggests that sulfide oxidation is insignificant in the submerged tailings but a natural process does occur under water leading to the release of As, Co and Ni to porewater in the tailings sediments.

Figure 17 shows the profiles of dissolved As, Co and Ni across the water-sediment interface at four coring locations in the Farr Creek-Mill Creek wetland. At all locations, porewater As, Co and Ni are higher in concentration than those in the surface drainage. This indicates that the

tailings disposed in the wetland act as a source of these elements to the surface water. As observed in the sediments of Cobalt Lake, the porewater As concentration is generally an order of magnitude higher than those of Co and Ni, reflecting that the porewater concentration of these elements is not controlled by the dissolution of simple,

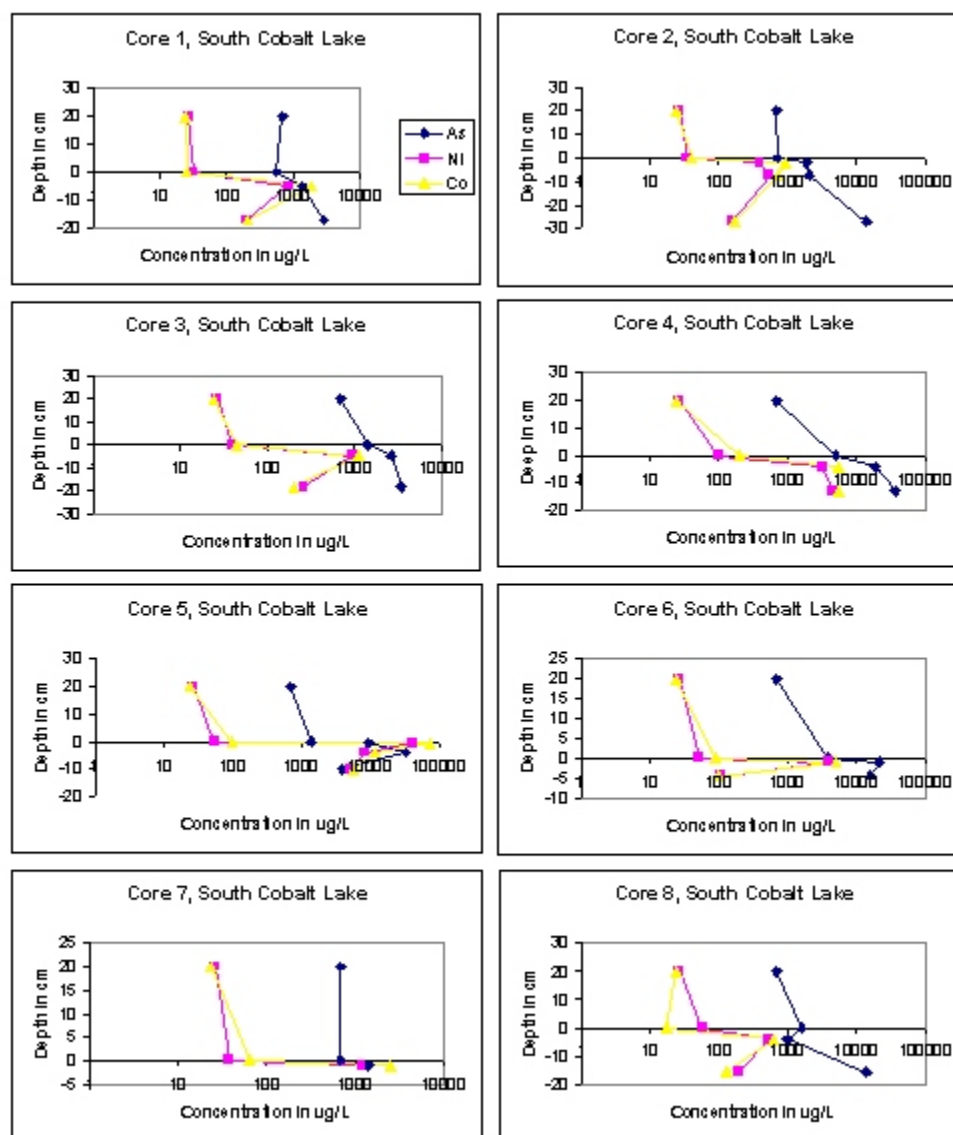


Fig. 15: Dissolved As, Co and Ni profiles in cores taken from South Cobalt Lake.

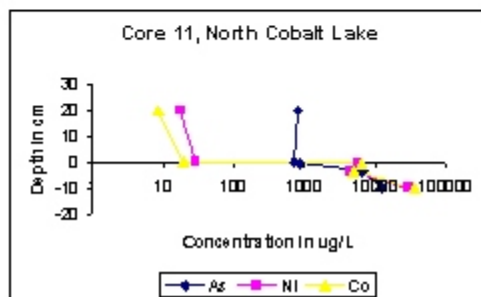
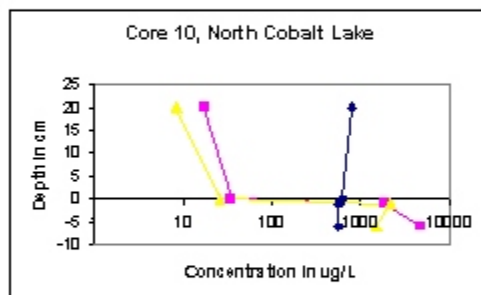
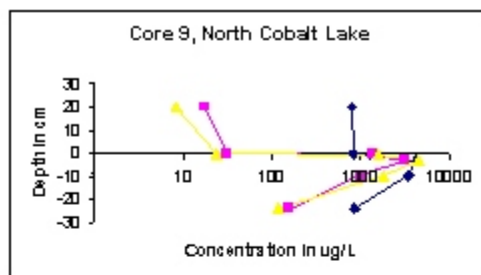


Fig. 16: Dissolved As, Co and Ni in cores taken from North Cobalt Lake.

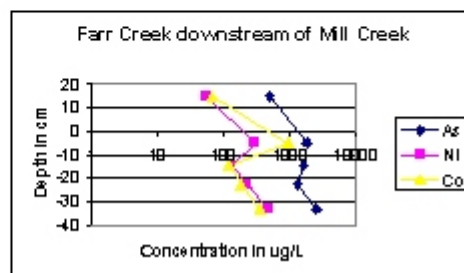
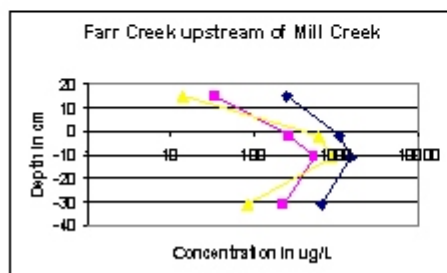
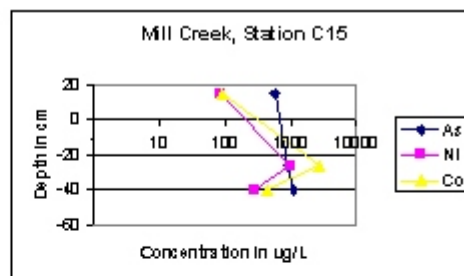
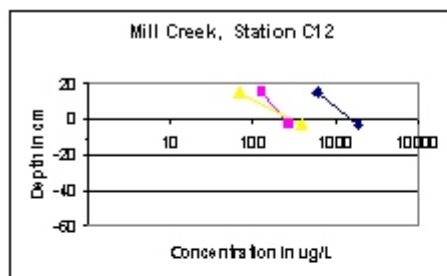


Fig. 17: Dissolved As, Co and Ni in cores from the Farr Creek-Mill Creek wetland.

secondary arsenate minerals. In the sediments of both Mill Creek and Farr Creek, dissolved Co and Ni appear to peak near the water-sediment interface. The behaviour of As is less consistent, suggesting that As is more mobile than Co and Ni. At shallow depth, the Mill Creek drainage contains more dissolved As, Co and Ni than the Farr Creek drainage. This leads to the higher concentrations of the elements observed in the Farr Creek sampling station downstream of the confluence with Mill Creek than those of the upstream station.

The porewater chemistry in the Nipissing low-grade tailings sampled close to and upstream of the lower dam is shown in Figure 18. At the time of sampling, the first 30 cm of tailings cored was moist but did not bleed water. In the saturated zone, dissolved As, Co and Ni generally increase with depth and the reverse is true for dissolved sulfate. Similar to that observed in the sediments of Cobalt Lake and the Farr-Mill Creek wetland, porewater As in the low-grade tailings is much more abundant (by at least two orders of magnitude in this case) than dissolved Co and Ni. The tailings porewater is also significantly more enriched in dissolved sulfate.

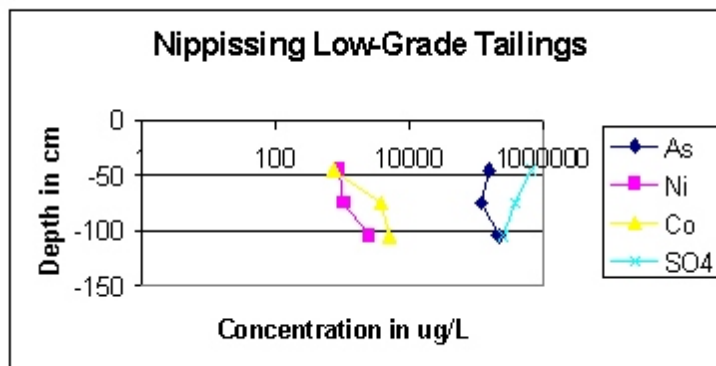


Fig. 18: Porewater chemistry of the Nipissing Low Grade Mill tailings.

The porewater chemistry of the Nipissing low-grade tailings at the former Hebert Pond has been reported by Andrews (1996)(see also Appendix C, Table C10). With dissolved As ranging from 63 to 1570 mg/L, Co ranging from 1 to 44 mg/L and Ni ranging from 0.13 to 85 mg/L, the porewater chemistry of these tailings generally lies between those of the low-grade tailings upstream of the lower dam and the submerged tailings in Cobalt Lake and the Farr-Mill Creek wetland. In contrast to the profiles observed in the submerged tailings, however, porewater As, Co and Ni invariably increases with depth in the Nipissing low-grade tailings (Andrews, 1996) instead of showing a local maximum near the water-sediment interface.

CONCLUSIONS

Based on extensive water and tailings sampling and subsequent analyses, the following conclusions can be drawn with regard to the source and aqueous transport of As and the associated metals in the weakly alkaline environment at the Farr Creek drainage basin, Cobalt, Ontario:

- With total dissolved As concentrations in surface waters ranging from 11 to 20 000 µg/L, the water quality criteria for drinking (25 µg/L) and sustaining aquatic life (5 µg/L) are often exceeded by 2 to 3 orders of magnitude. Although there is some attenuation downstream through the wetlands, drainage with elevated As concentrations (300-500 µg/L) continues to enter Lake Timiskaming, the receiving water body of the Farr Creek system.
- Widespread mine waste is the primary source of As in surface waters, but natural background levels in groundwater may constitute a significant contribution and need to be assessed more rigorously.
- Cobalt and Ni appear to correlate well with total As in the surface waters, suggesting that the source of the metals is likely weathering products of primary Co and Ni arsenides and sulpharsenides and secondary (efflorescent) minerals such as erythrite and annabergite.
- The efflorescent, weathering products are readily dissolved during wet periods and the elements are then flushed into the drainage system. Submerged tailings probably also release deleterious elements to the overlying surface waters but at a slower rate. Thus, mitigation of exposed surfaces such as revegetation of tailings surfaces will certainly help to abate the As contamination but will not eliminate it.

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