

Arsenic in surface waters, Cobalt, Ontario

J.B. Percival, C.G. Dumaresq¹, Y.T.J. Kwong², K.B. Hendry³,
and F.A. Michel⁴

Mineral Resources Division

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Abstract: Water samples from the Farr Creek drainage basin, Cobalt, Ontario, were collected to study the aqueous transport of As and other metals in a weakly alkaline environment. New data on downstream changes in total As, As(III), and As(V) concentrations are presented. Temporal (1991-1995) changes in aqueous As distribution in the study area are also examined. Total dissolved As concentrations in surface waters range from 11 to 20 000 µg/L. Arsenic concentration generally decreases downstream, especially through wetlands, and appears to decrease with time. Widespread mine waste is undoubtedly the primary source of As in surface waters, but natural background levels in groundwater may also contribute and need to be assessed. Without mitigation, however, exposed tailings and waste rock will continue to release significant amounts of As and associated trace elements to the drainage system.

Résumé : Des échantillons d'eau ont été prélevés dans le bassin de drainage du ruisseau Farr (Cobalt, Ontario), dans le but d'étudier le transport par l'eau de l'arsenic (As) et d'autres métaux dans un milieu faiblement alcalin. De nouvelles données sur les changements en aval des concentrations totales en As, As(III) et As(V) sont présentées. Les variations temporelles (1991-1995) pour ce qui est de la distribution dans l'eau de l'As dans la région à l'étude sont également analysées. Les concentrations totales en As dissous dans les eaux superficielles varient entre 11 000 et 20 000 µg/L. Elles sont généralement moindres vers l'aval, en particulier à travers les terres humides; elles semblent également diminuer avec le temps. L'abondance des résidus miniers est sans aucun doute la principale source d'As dans les eaux superficielles, mais les concentrations de fond naturelles dans les eaux souterraines pourraient également y contribuer et doivent être, de ce fait, évaluées. Sans mesure de réduction, cependant, les stériles et les terrils continueront de libérer des quantités importantes d'As et d'éléments traces associés dans le réseau de drainage.

¹ AQUAMIN Secretariat, Evaluation and Interpretation Branch, Environment Canada, Ottawa, Ontario K1A 0H3

² Environmental Sciences Division, National Hydrology Research Institute, 11 Innovation Boulevard, Saskatoon, Saskatchewan S7N 3H5

³ Department of Geology, University of New Brunswick, Fredericton, New Brunswick E3B 5A3

⁴ Department of Earth Sciences, Carleton University, Ottawa, Ontario K1S 5B6

INTRODUCTION

Cobalt, located in northeastern Ontario in the district of Timiskaming, is historically renowned for its silver production. By 1971 more than 600 million ounces (1.698×10^7 kg) of silver were mined from the Cobalt area deposits (Petruk et al., 1971). Numerous tailings deposits, waste rock dumps, and mine workings are testimony to the early prosperity of the region (Fig. 1). Mining continues on a smaller scale today, with Co as the main commodity. Mitigation efforts to date have been limited to fencing of obvious mine hazards (shafts, pits, and some mill foundations), reprocessing of tailings from some of the tailings deposits, and some revegetation efforts on at least two tailings deposits.

Arsenic contamination of the surface waters in the Cobalt region has been documented previously (OWRC, 1967; Boyle et al., 1969; Hawley, 1980; Dumaresq, 1993). On the

basis of surface water chemistry and stream flow data, Dumaresq (1993) estimated that the mean annual discharge of As from Farr Creek to Lake Timiskaming is about 18 000 kg. The present study is concerned with the transport and fixation of As in the surficial environment from the mine waste sites (tailings and waste rock) through surface waters to wetlands. This is part of a larger study which includes litho-geochemistry and mineralogy of tailings sample sites and chemistry of surface and groundwaters in the Farr Creek drainage basin which drains into Lake Timiskaming (Fig. 1). Understanding the behaviour of As in natural waters is important because As and its compounds are potentially toxic to humans and to aquatic organisms (Government of Canada et al., 1994).

In this progress report, we present new data on the general water chemistry of the study area. Special emphasis is placed on the downstream changes in total As, As(III), and As(V)

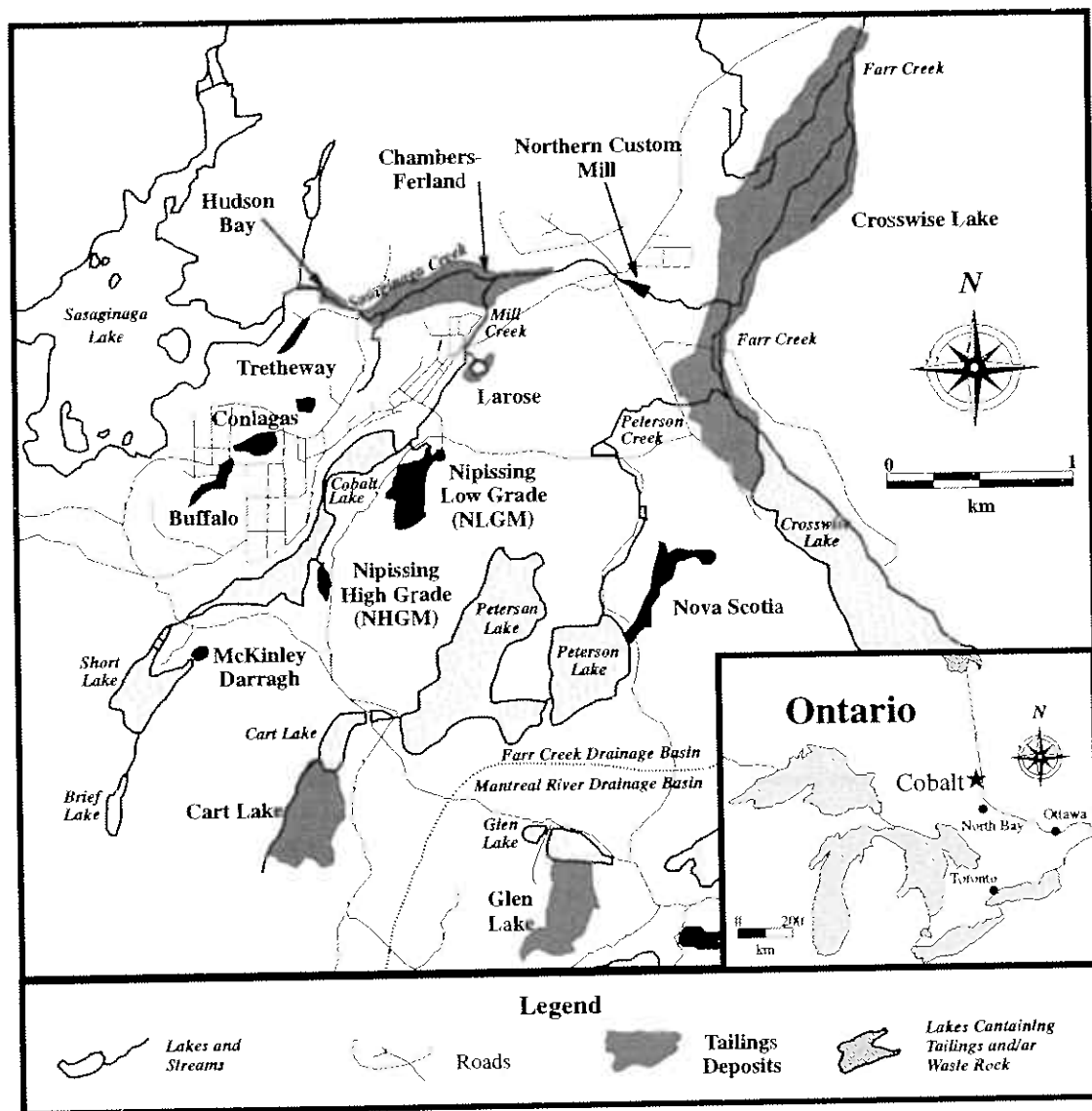


Figure 1. Location map of Cobalt, Ontario showing details of the Farr Creek drainage basin and location of tailings deposits and waste rock dumps (after Dumaresq, 1993).

concentrations in relation to other chemical and physical water parameters. Where appropriate, the current data set is also compared with that of Dumaresq (1993) to discern temporal changes in aqueous As distribution in the study area.

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, sulpharsenides, and sulphides such as nickeline, cobaltite, safflorite, loellingite, 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).

ARSENIC CYCLE

Arsenic is stable in four oxidation states: (-III), (0), (III), and (V). Arsenic (-III) is found only in gaseous AsH_3 (arsine). Arsenic can occur in the metallic state in some mineral deposits, but usually occurs in compounds with 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 by 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 foodchain (CCREM, 1987). The decreasing order of toxicity is: arsine(-III) > organo-arsine derivatives > inorganic arsenite(+III) > organic As(III)

compounds > arsenoxides(+III) > arsenates(+V) > organic As(V) compounds > metallic As(O) (Penrose, 1974; NRCC, 1978; Eisler, 1988). In general, inorganic arsenical compounds are higher in toxicity than organic compounds and the trivalent As-species is more toxic than the pentavalent As-species (NRCC, 1978).

METHODS

Surface water samples were collected in July and September 1994, and in May 1995. Sample sites are shown in Figure 2 and numbered consecutively from the southwest to the northeast in the direction of drainage. 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 well house and taps from the Bucke Park campground (GW3-GW7). Temperature, pH, Eh, and electrical conductivity were determined in the field using a Cole-Parmer Water Test meter. Water samples 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 remained unacidified for anion determinations. Major and trace elements were determined on the HNO_3 -treated sample by inductively-coupled plasma-atomic emission spectrometry (ICP-AES) and inductively-coupled plasma-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 AAS using NaBH_4 as a reducing agent. With sample adjusted to a pH of 5 with citric acid, arsine (AsH_3) was generated only from As(III), As(V) being nonreactive. A separate aliquot was then prereduced with 5% KI and ascorbic acid to determine total As. Arsenic(V) was then determined as the difference between total As and As(III). Anions (SO_4^{2-} reported here only) were determined using a Dionex ion chromatograph.

RESULTS AND DISCUSSION

Water quality

Selected physical and chemical parameters of surface and groundwaters are shown in Tables 1 and 2, respectively. Surface water conditions observed during the 1994 and 1995 surveys included temperatures of 21.7 to 27.8°C for July (1994), 9.8 to 21.5°C for September (1994), and 11.1 to 18.5°C for May (1995). The low temperature of 9.8°C was more representative of groundwater conditions as this sample was taken from the decant pond during dewatering of a mine (Cobatec operation). All surface waters were alkaline with an average pH of 7.9, well-oxygenated (Eh from +67 to +208mV), and had dissolved oxygen levels (data not shown) at or near saturation. Overall, conductivity was high but with peak values corresponding to drainage from exposed tailings (e.g., from Nipissing high-grade mill (NHGM), LaRose tailings etc.). Groundwaters were cooler (6.4 to 14.8°C), slightly

less alkaline (mean pH 7.4), with higher conductivities, but they were reducing (Eh from -57 to -72 mV). One exception was sample GW1 (Eh = +252 mV) that was taken from a mine shaft discharging from a pipe into Sasaginaga Creek.

Arsenic

Relative to the guidelines for Canadian drinking water quality (25 µg/L; Health and Welfare Canada, 1989), As concentrations in surface waters in the Cobalt region are excessive (note: with the exception of Sasaginaga Lake, surface waters in the study area are not used for drinking water). Only

6 samples contain less than 100 µg/L total As (Table 2). The highest concentrations, 15 000-20 000 µg/L, are associated with drainage from a small area that contains Nipissing high-grade mill tailings. This drainage discharges into Cobalt Lake at sites 6 and 7 (Fig. 2A). Water from the outlet of the LaRose tailings site (site 15, Fig. 2C) is also characterized by high total As (>3000 µg/L). Conversely, some samples that contain greater than 1000 µg/L total As are not associated with tailings (e.g., sites 14 and 20, Fig. 2B) whereas others that contain less than 500 µg/L are (e.g., sites 18 and 19, Fig. 2C). This suggests that tailings from different mines vary in composition and that the tailings may not be the only source of As in the study area.

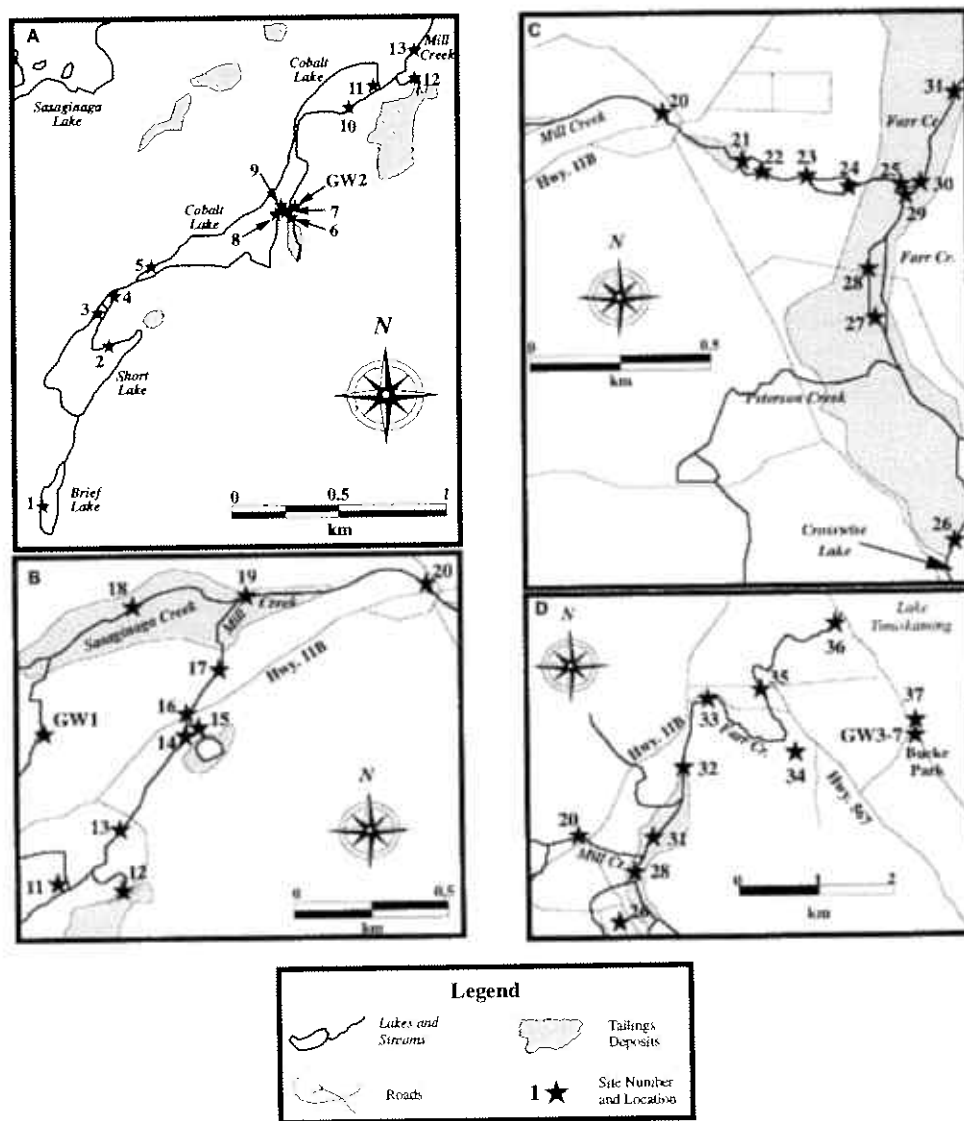


Figure 2. Site locations of all sampling stations used in 1991-1992, 1994, and 1995 surveys: A) Cobalt Lake area; B) Sasaginaga Creek and Mill Creek confluence; C) Mill Creek and Farr Creek confluence; and D) Buckle Park campground. Drainage of the Farr Creek basin is to the northeast to Lake Timiskaming.

The trend of As concentration within the Farr Creek drainage system is plotted as the mean concentration for all data (1991 to 1995) per sampling site in Figure 3. 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 Short Lake contains at least two waste rock piles along its shores. These waste rock piles appear to make only a small contribution (e.g., ~50 µg/L) to the As budget. Both Sasaginaga and Farr Creeks contain submerged tailings and meander through wetlands situated on tailings upstream from the Mill Creek

confluence. Metal fixation processes such as adsorption or chelation may occur in the wetlands to account for the lower total As than is observed in Mill Creek.

The As concentration rises downstream from Short Lake, in Cobalt Lake. Several mills deposited tailings in Cobalt Lake, and the lake was drained from 1914 to 1932 to recover some of the tailings for reprocessing. The south end of the lake was also drained in the early 1950s and in the mid 1960s. It is estimated that about 250 000 t of tailings remain submerged in Cobalt Lake (Dumaresq, 1993). The drainage from the Nipissing high-grade mill although extremely high in As, is low in volume and becomes insignificant when it mixes with the large volume of water in Cobalt Lake. To investigate

Table 1. Characteristics of surface water and some groundwaters from Cobalt, Ontario. Site locations shown on Figures 2A to 2D.

SITE	DATE	TEMP °C	pH	Eh mV	COND µS/cm
1	09/94	15.3	7.4	+185	181
2	91-92	na	7.7	na	170
3	09/94	15.9	8.1	+181	174
4	09/94	16.6	7.6	+171	176
5	09/94	17.3	8.1	+171	345
6	91-92	na	8.4	na	360
	07/94	27.8	8.8	+130	542
	09/94	17.7	8.5	+133	439
	05/95	18.5	8.1	+134	424
7	05/95	13.1	8.0	+159	332
8	91-92	na	8.3	na	175
	05/95	13.7	8.0	+140	354
9	05/95	12.8	8.0	+143	349
10	91-92	na	8.1	na	243
	07/94	23.5	8.5	+173	387
11	05/95	13.9	8.0	+125	372
12	91-92	na	7.4	na	228
13	91-92	na	8.0	na	242
	07/94	23.0	8.2	+189	384
14	91-92	na	7.5	na	265
	07/94	23.6	9.6	+121	494
	09/94	21.5	8.6	+94	341
15	91-92	na	7.3	na	480
	07/94	24.7	7.6	+182	584
	09/94	19.2	7.0	+207	573
16	91-92	na	7.9	na	410
	07/94	24.2	8.4	+167	469
	09/94	19.6	8.0	+148	454
17	91-92	na	8.0	na	285
	07/94	24.7	8.7	+154	584
18	91-92	na	7.6	na	185
19	91-92	na	7.6	na	270
20	91-92	na	7.4	na	260
	07/94	22.6	7.5	+191	440293
	05/95	16.3	8.3	+159	
21	09/94	16.5	7.4	+118	439

SITE	DATE	TEMP °C	pH	Eh mV	COND µS/cm
22	05/95	14.7	8.1	+117	288
23	05/95	15.2	8.2	+94	290
24	05/95	11.1	7.9	+208	297
25	07/94	21.7	7.5	+187	421
	05/95	12.2	8.1	+136	291
26	91-92	na	8.0	na	110
27	07/94	25.3	8.0	+151	188
28	91-92	na	7.6	na	153
	07/94	26.6	8.1	+142	172
	05/95	15.0	7.9	+173	169
29	07/94	26.2	7.9	+165	173
	05/95	13.6	7.8	+133	192
30	07/94	25.3	7.7	+200	254
	05/95	12.6	7.7	+104	218
31	07/94	24.0	7.9	+202	247
32	91-92	na	7.6	na	475
	07/94	22.9	6.9	+243	250
33	91-92	na	7.9	na	217
	09/94	18.2	8.3	+114	317
34	09/94	9.8	7.8	+110	416
35	09/94	17.5	7.9	+118	379
	05/95	13.9	7.7	+148	216
36	91-92	na	8.5	na	290
37	09/94	17.2	7.6	+67	181
GW1	91-92	na	7.2	na	420
	09/94	6.4	7.2	+252	290
GW2	91-92	na	7.7	na	280
GW3	91-92	na	7.5	na	537
	07/94	11.3	8.1	-72	513
	09/94	7.5	7.4	-71	463
GW4	09/94	9.4	7.5	-61	477
GW5	09/94	na	na	na	na
GW6	09/94	12.2	7.2	-70	491
GW7	09/94	14.8	7.1	-57	526

Note - na: not analyzed

possible localized effects near the Nipissing high-grade mill outlet in Cobalt Lake, determination of As in pore waters and sediments sampled from the vicinity are in progress. On the other hand, the contributions from the Nipissing low-grade mill (NLGM) and LaRose tailings give rise to an increase in downstream As concentration as they mix with a smaller volume of water in Mill Creek. The source of contamination leading to the higher As concentration at site 20 is unclear. Samples collected upstream in Sasaginaga Creek contain low As concentrations (<300 µg/L) despite the fact that this creek is underlain by tailings. Higher As concentration at site 20 may suggest that there is an unidentified groundwater discharge in this area. The concentration generally decreases across a wetlands area (between sites 16 and 32), with some minor fluctuations, but increases again slightly before entering Lake Timiskaming. Some of these minor fluctuations are

easily explained. For example, the increase just before the Mill Creek-Farr Creek confluence (site 25, Fig. 2C) reflects contribution from an unknown volume of tailings that were discovered in Mill Creek in September 1994. These tailings were not reported in Anderson (1993) and probably were 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 (site 34; Fig. 2D) from the settling pond at Cobatec 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

Table 2. Chemistry of surface waters and some ground waters from Cobalt, Ontario. Site locations shown on Figures 2A to 2D. Data for total As, As(III), As(V), Co, and Ni in µg/L; Ca, Mg, and SO₄ in mg/L.

SITE	DATE	As(T)	As(III)	As(V)	Co	Ni	Ca	Mg	SO ₄
1	09/94	11.1	5.7	5.4	1.0	2.6	38	6.3	3.3
2	91-92	48	na	na	nd	nd	32	9	14
3	09/94	51	2.7	48	0.5	2.6	35	6.0	9.6
4	09/94	93	3.6	89	2.1	5.3	36	6.1	9.5
5	09/94	877	7.8	869	3.6	19	50	9.9	17
6	91-92	17470	na	na	364	293	75	26	55
	07/94	20238	1470	18768	410	330	78	17	43
	09/94	17018	411	16607	450	340	80	18	42
	05/95	15799	266	15533	440	390	37	14	32
7	05/95	7981	95	7886	370	230	52	12	26
8	91-92	638	na	na	20	nd	47	14	18
	05/95	819	46	773	29	28	47	8.7	18
9	05/95	602	29	573	23	25	47	8.7	17
10	91-92	695	na	na	nd	nd	42	14	44
	07/94	1056	10	1046	3.0	12	45	9.9	19
11	05/95	653	41	612	14	23	49	9.2	18
12	91-92	534	na	na	217	152	39	8	24
13	91-92	834	na	na	25	nd	48	12	16
	07/94	1459	132	1327	23	26	46	9.5	17
14	91-92	1280	na	na	41	nd	53	16	20
	07/94	1106	130	976	19	29	43	7.3	106
	09/94	1147	11.8	1135	20	26	43	9.5	16
15	91-92	3210	na	na	2028	643	63	5.2	87
	07/94	3477	84	3393	1300	440	62	13	89
	09/94	3004	21	2983	1500	660	60	12	95
16	91-92	1180	na	na	296	107	56	4.4	27
	07/94	2303	136	2167	460	160	48	10	77
	09/94	2074	29	2045	680	300	51	11	50
17	91-92	792	na	na	nd	nd	45	12	40
	07/94	2137	137	2000	380	160	62	9.2	128
18	91-92	217	na	na	nd	nd	45	6	21
19	91-92	515	na	na	69	nd	33	2.6	14
20	91-92	1421	na	na	159	101	47	13	19
	07/94	1281	15	1266	140	73	51	10	32
	05/95	605	43	562	90	76	37	7.6	17
21	09/94	1119	22	1097	220	110	54	11	26

Total Arsenic Concentration ($\mu\text{g/L}$)

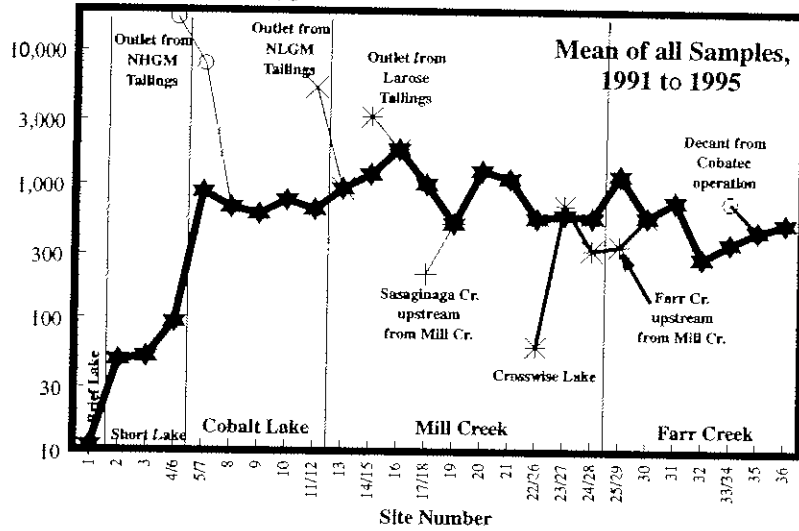


Figure 3.

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

Table 2. (cont.)

SITE	DATE	As(T)	As(III)	As(V)	Co	Ni	Ca	Mg	SO ₄
22	05/95	565	32	533	84	63	36	7.5	16
23	05/95	602	30	572	88	57	36	7.5	17
24	05/95	571	34	537	88	83	37	7.7	16
25	07/94	1815	14	1801	110	68	53	10	21
	05/95	573	30	543	90	64	37	7.7	16
26	91-92	62	na	na	nd	nd	21	8	7.9
27	07/94	710	18	692	5.9	5.4	29	7.1	9.1
28	91-92	324	na	na	nd	nd	47	21	18
	07/94	416	15	401	3.4	3.8	25	6.1	8.4
	05/95	252	27	225	6.4	27	25	6.3	9.9
29	07/94	393	29	364	4.0	5.2	26	6.1	8.5
	05/95	312	15	297	25	36	27	6.4	11
30	07/94	823	8.6	814	35	23	33	7.4	13
	05/95	334	16	318	40	41	29	6.6	12
31	07/94	761	8.2	753	17	21	34	7.4	12
32	91-92	313	na	na	nd	nd	43	11	18
	07/94	231	14	217	14	9.2	37	8.3	2.1
33	91-92	406	na	na	nd	nd	39	10	13
	09/94	265	3.2	262	24	11	44	9.4	10.6
34	09/94	755	115	640	83	34	67	25	64
35	09/94	522	3.7	518	19	10	51	13	23
	05/95	397	9.1	388	33	53	30	6.8	11
36	91-92	522	na	na	nd	nd	42	11	19
37	09/94	30	6.5	23	4.0	3.5	6.7	2.0	6
GW1	91-92	880	na	na	144	83	76	nd	32
	09/94	750	4.6	745	140	100	71	13	29
GW2	91-92	2090	na	na	235	100	47	11	25
GW3	91-92	6970	na	na	1673	458	77	50	32
	07/94	9707	6032	3675	1700	440	80	35	27
	09/94	9693	7531	2162	1800	450	82	36	25
GW4	09/94	9452	7268	2184	1700	440	81	35	25
GW5	09/94	8869	3874	4995	1700	440	82	36	25
GW6	09/94	9933	7117	2816	1800	450	82	36	25
GW7	09/94	9168	5629	3539	1700	440	81	35	25

NOTE: na: not analyzed; nd: not detectable

fault zones. The 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, do contain elevated concentrations of As and other metals.

The variation of total As with time is shown in Figure 4 for eight sites. These sites were selected as they had been sampled repeatedly during the 1991-1992 and 1994-1995 sampling programs. Only three sites, 6, 20, and 28, are relatively complete in terms of the number of data points. Sites 8, 10, and 13 show a general increase in total As with time. Sites 8 and 10 are located in Cobalt Lake site; 8 is south of the Nipissing high-grade mill drainage adjacent to a waste rock pile and site 10 is about 50 m north of the park that separates the lake into two basins. Site 13 is located near the Right of Way mine, just downstream from the Nipissing low-grade mill drainage. Site 8 is unlikely influenced by the Nipissing high-grade mill drainage but is influenced by the waste rock pile and the submerged tailings. The data for 1991-1992 show a slight, continual increase which levels off between 1992 and 1995. Sites 10 and 13 follow a similar trend with peak concentrations in 1994. Arsenic released from the submerged tailings in Cobalt Lake is probably gradual and

continual. Release from the Nipissing low-grade mill tailings may also be continual but would peak during periods of high surface runoff due to the dissolution of efflorescent salts which form on the surface of the tailings during the summer months. Analyses of these salts by Dumaresq (1993) showed that they contained very high concentrations of As and other metals. At these three sites, the increase in total As with time may be related to the type of source material rather than as a consequence of seasonal variations during the sampling events. The tailings will continue to release significant amounts of As to the drainage system for many years.

In general, As concentrations at sites 6, 14, 20, 28, and 33 show a decreasing trend with time. Samples from site 6 were taken from the Nipissing high-grade mill drainage, hence the very high total As concentrations. The other sites are located progressively downstream in either Mill or Farr Creek. At most of these sites there is an initial decrease within the first sampling period (1991-1992) that may be seasonally related. For example, efflorescent salts would first dissolve, flushing As and other metals into the drainage system. As the fall season progresses and the area becomes wetter, dilution would occur due to increased runoff and groundwater discharge.

During the 1994 sampling period, rainfall was, on average, about 70 mm per month from May to October. During this period a decrease in concentration was observed at site 6. The wetlands in 1994 were saturated and difficult to walk through. In May 1995, a total of 134 mm of rain fell, 104 mm of which occurred days before the sampling period. During this period, however, the wetlands downstream from the Farr Creek-Mill Creek confluence were dry and easily traversed on foot. The higher rainfall and lower total As concentrations in May 1995 relative to 1994 suggests dilution through increased runoff, yet water levels in the creeks were lower in 1995. It is possible that the antecedent heavy rain in May 1995 had thoroughly depleted the source area of accumulated, readily-soluble oxidation products prior to the sampling event. Rapid transport of the released As through the surface drainage system rendered low analyses in the samples subsequently collected.

Arsenic speciation data are also shown in Table 2. For surface waters sampled in July 1994, As(III) constitutes 0.8 to 11.8% of total As; for September 1994, 0.7 to 51.4%; and for May 1995, 1.2 to 10.7%. The two high values (51.4 and 21.7%) for September 1994 correspond to total As concentrations of only 11.1 (site 1; Brief Lake) and 30 µg/L (site 37; Lake Timiskaming), respectively. The high proportion of As(III) in the Lake Timiskaming sample appears to reflect the mixing of the well water from Bucke Park with surface waters. At Brief Lake, groundwater may be mixing with the surface waters. If these data are spurious and these samples are not considered, then As(III) content ranges from 0.7 to 15.2% of total As. These values indicate that strongly oxidizing conditions prevail in the surface waters. In contrast, in the more reducing groundwater samples As(III) constitutes 43.7 to 77.7% of total As. The high proportion of the more toxic species is of concern as these samples represent drinking water from the Bucke Park campground (note: as of early summer, 1995, the well was closed to the public by the

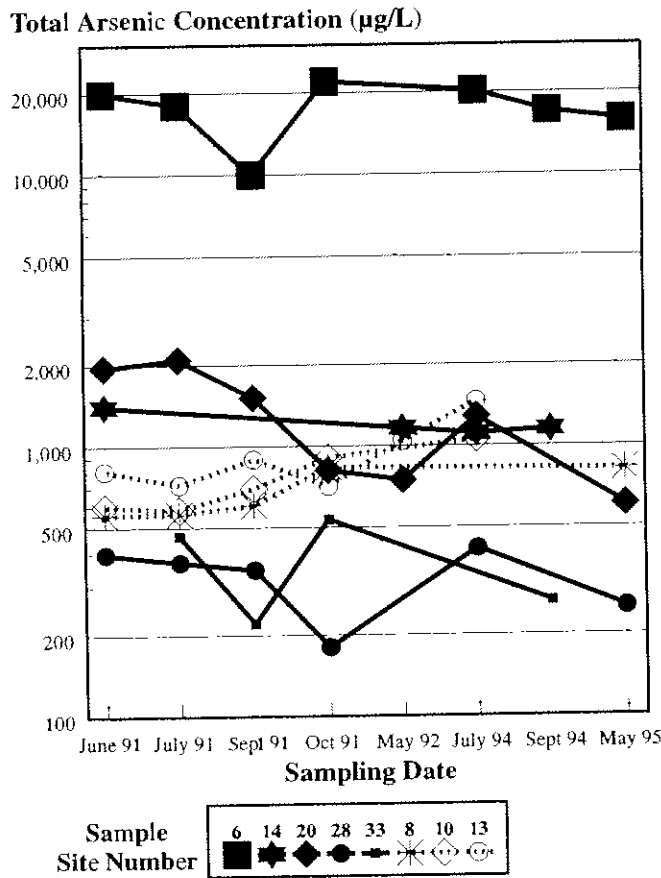


Figure 4. Temporal variation in total dissolved As for selected sample sites.

Timiskaming Health Unit, New Liskeard; S. Deegan, pers. comm., 1995). Dumaresq (1993) measured As in 39 samples from 23 private wells in the area and found that "total dissolved" As ranged from 1 to 13 $\mu\text{g/L}$ (mean of 3 $\mu\text{g/L}$). The Bucke Park well, therefore, is an anomaly.

At sites where two or more samples were taken during the 1994-1995 period the As(III) content decreased for half of the samples and increased in the rest. The increase in As(III) relative to As(V) may reflect a greater groundwater input at the time of sampling or may indicate that less secondary minerals are being dissolved. All these factors must be considered along with the seasonal variations to determine the mechanisms of As release from the tailings sites.

Cobalt and nickel

The concentrations of dissolved Co and Ni in the samples are highly variable (Table 2). Cobalt ranges from less than detection to more than 3000 $\mu\text{g/L}$ and Ni from less than detection to more than 600 $\mu\text{g/L}$. High concentrations are found in the Nipissing high-grade mill (sites 6 and 7) and LaRose (site 15) surface samples and in the Bucke Park groundwater samples (GW3-GW7) and correlate well with total As. The LaRose samples are more enriched in Co relative to the Nipissing high-grade mill samples confirming the heterogenous nature of the tailings. The high concentrations observed at Bucke Park suggests that the Coleman Formation (and related nearby Agaunico mineralization) is the source of the groundwater in this well. Previous studies have shown that groundwater from the Coleman Formation contain the highest average concentrations of As, Co, and Ni of any groundwaters in the area (MOE, 1977). For surface water samples, high Co and Ni contents can be related to the dissolution of secondary minerals such as erythrite and annabergite that are produced and stable during drier periods. Cobalt and nickel in the groundwater samples, however, may be derived directly from primary ore minerals such as cobaltite or nickeline.

The concentrations of Co and Ni observed in this study are comparable to those documented in Boyle et al. (1969), except that the Co content from LaRose and Bucke Park determined in this study are an order of magnitude greater. Boyle et al. (1969) observed that both Co and Ni were relatively mobile up to pH 8 and that Ni has a greater mobility in waters associated with the Palaeozoic (carbonate-rich) rocks. The dramatic decrease in concentrations for both Co and Ni observed in Mill Creek (e.g., from sites 15 to 20, Table 2) indicates that co-precipitation or sorption processes are occurring.

Surface water quality objectives for drinking water have not been established for Co but maximum values of 1000 $\mu\text{g/L}$ for livestock and 500 $\mu\text{g/L}$ for irrigation have been set elsewhere (e.g., Saskatchewan Environment and Public Safety, 1988). Most of the surface water samples are well below these limits. For Ni, a maximum of 50 $\mu\text{g/L}$ is set for drinking water and variable amounts for freshwater aquatic life based on the hardness of water (CCREM, 1985; Saskatchewan Environment and Public Safety, 1988). Some of the surface water samples are within the guidelines, others may be considered hazardous.

Calcium, magnesium, and sulphate

Calcium and magnesium concentrations are given in Table 2. 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 is no apparent relationship between Ca and Mg with the other metals reported. Based on the hardness calculation (total hardness = $2.5(\text{Ca}^{2+}) + 4.1(\text{Mg}^{2+})$) of Freeze and Cherry (1979), these waters would be considered hard with values greater than 100 mg/L (m-eq CaCO_3 ; data not shown). The data reflect the extent of carbonate weathering in the 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 (Table 2). Sulphate may be derived from primary sulphide minerals or sulphosalts or from secondary efflorescent salts such as gypsum and thenardite. Higher 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.

SUMMARY AND CONCLUSIONS

Water samples from the Farr Creek drainage basin, Cobalt, Ontario, were collected to study the aqueous transport of As and other metals in a weakly alkaline environment. The Cobalt area, once renowned for its bonanza silver deposits, is now characterized by numerous tailings deposits, waste rock piles, and remnant historical mine workings. Very limited mitigation has been undertaken since mining ceased and thus contamination of the surface drainage system from leaching of the widespread mine waste continues. Currently, concentrations of total dissolved As exceed water quality criteria for drinking (25 $\mu\text{g/L}$) and sustaining aquatic life (50 $\mu\text{g/L}$) by, in some cases, 2 to 3 orders of magnitude. There is some attenuation downstream through the wetlands but drainage with high As concentrations (300-500 $\mu\text{g/L}$) still enters Lake Timiskaming, the receiving water body of the Farr Creek system. Increases in As concentration downstream from the wetlands area suggest that a groundwater contribution to the drainage system must be considered.

With weakly alkaline pH (average 7.9) and Ca and Mg as the dominant cations, the overall water chemistry in the study area reflects a major influence by the carbonate-equilibria. Cobalt and nickel appear to correlate well with total As in the surface waters, suggesting that the source of the metals is likely ephemeral secondary minerals produced by weathering of Co and Ni arsenides and sulpharsenides. The weathering products are readily dissolved during wet periods and the metals flushed into the drainage system. Submerged tailings probably also release metals to the surface waters but at a slower rate. Thus, mitigation of exposed surfaces will certainly help abate this situation but will not eliminate it.

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