

Extremely arsenic-rich, pH-neutral waters from the Giant mine, Canada

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Abstract

Roasting arsenopyrite-bearing gold ore for more than fifty years has resulted in nearly 300,000 tons of arsenic trioxide waste at the Giant mine near Yellowknife, NWT, Canada. Most of this has been stored in underground chambers sealed with concrete bulkheads. Seepages from underground drillholes and fractures contain up to 4000 mg As L⁻¹. Approximately 70% of the total is As(III). The dominant dissolved constituents are As, Ca, Mg, Na and SO₄ with low Fe. Water samples are pH-neutral but an unfiltered sample exhibited a decrease in pH over several weeks, likely due to microbially-driven As(III) oxidation, which lowers pH through the following reaction: $2\text{H}_3\text{AsO}_3 + \text{O}_2 \rightarrow \text{HAsO}_4^{2-} + \text{H}_2\text{AsO}_4^- + 3\text{H}^+$. The low pH values are not observed at the underground seepage points because of rapid neutralization by the dissolution of carbonate-bearing wallrock and concrete. This natural oxidation of As(III) to As(V) is advantageous for water treatment, since As(V) is more easily removed than As(III).

Approximately 20,000 tons of arsenic trioxide was released through the roaster stack, mostly during the first few years of operation. Significant amounts of arsenic trioxide persist in near-surface soils. Total As in surface soil is as high as 5500 mg kg⁻¹, similar to concentrations in tailings. The most arsenic-rich soils are small pockets located on the large outcrops downwind from the roaster. Suction lysimeters were used to sample pore water in these areas immediately following summer rainfalls. Soil pore water concentrations are as high as 2 mg L⁻¹ of As, considerably less than the underground waters, but still two orders of magnitude higher than the World Health Organization drinking water guideline of 0.01 mg L⁻¹. The pore waters are pH-neutral and the major ions are Ca, Na and SO₄.

The solubility of arsenic trioxide-bearing dust from Giant has been reported as 11,000 to 15,000 mg L⁻¹ (Riveros et al. 2000). Although the underground seepage waters and the soil pore waters do not achieve those As concentrations, they are extremely enriched compared to most mine drainage as a result of their interaction with arsenic trioxide roaster waste. Remediation plans, currently under consideration, need to ensure that these are treated and the sources contained.

Introduction

The purpose of this paper is to describe waters in two settings that have interacted with arsenic trioxide (As₂O₃) at a former gold roasting operation: mine water that has encountered baghouse dust stored in underground chambers and pore water from soils on mine property that have received fallout from stack emissions. Plans to treat the extremely As-rich waters are also reported.

Arsenic trioxide is the most soluble, bioaccessible and toxic arsenic compound that might be encountered in mine waste. It is usually the product of roasting sulfide-hosted Au, Cu or Sn ore. Roasting is a pretreatment metallurgical process designed to decompose As-bearing sulfide minerals. Arsenic trioxide may also be formed from weathering (Nordstrom and Archer, 2003; Drahota and Filippi, 2009).

At Giant mine, located near Yellowknife, Canada, roasting was used from 1949 to 1999 to oxidize Au-bearing arsenopyrite (FeAsS) prior to cyanidation. Solid-phase As-bearing roaster products include As-bearing iron oxides (maghemite and hematite), arsenic trioxide and residual, As-bearing sulfide minerals including arsenopyrite and pyrite (Walker et al., 2005). During most of the years that Giant Mine operated, there were few emission controls employed (Bromstad and Jamieson, 2012).

Most (93%) of the arsenic trioxide produced by the Giant mine roaster was captured in a baghouse and placed in underground storage chambers. There are 10 purpose-built chambers and five mined-out stopes, mostly between 20m and 75m below the surface. On average, the baghouse dust contains 60% wt. As, and approximately 80% of the total As is As_2O_3 (INAC, 2007). The original design from the 1950s was based on the expectation that permafrost would prevent the arsenic trioxide from dissolving and entering groundwater but by the 1980s it was recognized that extensive underground mining had destroyed the permafrost. Current conditions include a temperature fluctuation from $-4^{\circ}C$ to $+5^{\circ}C$, and the presence of water in some chambers. Water in the underground mine workings originates either from relatively clean sources, such as direct infiltration from precipitation and streams, or from tailings pond waters. Contact with mine walls, backfill (including tailings backfill) and baghouse dust storage chambers increases the total dissolved arsenic locally (Bromstad and Jamieson 2012, SRK 2005a). We sampled seepage points where water is expected to have interacted with arsenic trioxide in the underground chambers.

In addition to the underground storage chambers, As_2O_3 is present in soils and other surficial materials on the mine property as a legacy of stack emissions prior to any stack emission capture technology. In the first two years of operation (1949-1950), when roaster vapours were freely vented, arsenic trioxide stack emission rates were 7.2 tonnes per day (tpd) (CPHA, 1977; Wrye, 2008). Approximately 7% of the total amount of arsenic trioxide produced was released through stack emissions. In 1951, the first of many generations of gas and dust capture technology was implemented in the form of an electrostatic precipitator. Although arsenic trioxide was released through stack emissions throughout the lifetime of the mine, the stack emission rates decreased substantially and were 0.01 tpd at closure in 1999. We have sampled soil pore water associated with pockets on soil developed on large outcrops downwind from the roaster to test the influence of legacy stack emissions on modern soil pore water (Wrye 2008; Bromstad 2011).

Water that has interacted with arsenic trioxide is expected to have high concentrations of dissolved As but other attributes, including pH and As(III)/As(V) are not readily predictable. Unlike many mine waters where the dominant influence on water composition is the oxidation of pyrite, the dissolution of arsenic trioxide in a carbonate-buffered groundwater produces circumneutral pH conditions. Carbonate neutralization appears to offset acidity produced during the oxidation of dissolved As(III).

Methodology

Underground seepage water sampling and analysis

Mine waters were sampled at four seepage points underground chosen for their proximity to the chambers storing arsenic trioxide (chambers B2-08 and C2-12). In most cases, the seepage was accompanied by the development of thick gelatinous biofilms (Figure 1) which previous research has shown to include psychrotolerant As(III)-oxidizing bacteria (Osborne et al. 2010). Water samples were filtered to <0.45 micron on site. Aliquots destined for cation analysis were preserved with high-purity HNO_3 and aliquots for redox determinations were preserved with high-purity HCl. Unfiltered acidified samples were also collected. Temperature, pH, specific conductance and Eh were all measured on site. The water samples

were analysed at the US Geological Survey laboratory in Boulder, CO, using inductively-coupled plasma atomic emission spectroscopy for metal determinations, ion chromatography for anion determinations, hydride-generation atomic absorbance spectroscopy for As redox species determinations, and FerroZine colorimetry for iron redox determinations (Table 1).



Figure 1: Biofilms formed from arsenite-bearing groundwater seeps in underground workings at Giant Mine (Photo courtesy of S. Simpson, Lorax Consulting)

Soil pore water sampling and analysis

Previous work (Bromstad, 2011) showed that pockets of soil cover 30% of the mine property and contain high concentrations of As, as much as $5,500 \text{ mg kg}^{-1}$ from grab samples. Several core samples were also collected and in one case, the upper organic-rich material contained $7,680 \text{ mg kg}^{-1}$ As (Figure 2). Mineralogical analysis demonstrated that most of the soil As is in the form of arsenic trioxide (Wrye 2008; Bromstad 2011). Soil pore water was sampled using suction lysimeters that were inserted in nine outcrop soil pockets at locations distant from any mine waste or activity. Water was extracted 5 to 8 days after installation. Field parameters (pH, Eh and specific conductance) were measured immediately, and 50 mL were preserved with nitric acid for cation analysis (and As and Sb) by inductively-coupled plasma mass spectrometry (ICP-MS) at Taiga Laboratory in Yellowknife. Where there was sufficient water, a second aliquot was analysed for anions by IC.

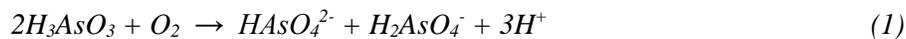


Figure 2: Map of the Giant Mine property indicating location of soil and pore water samples. (modified after INAC 2007)

Results

Table 1 shows the results of filtered mine waters collected for this study from underground locations where interaction between ground water and baghouse dust was suspected. The arsenic concentrations are similar to the samples of As-rich underground seeps reported by SRK (2005a) and are amongst the most As-rich waters underground mine waters at Giant. Most underground water, including seepage from tailings and waste rock backfill, is much lower in total arsenic concentration (Bromstad and Jamieson, 2012; SRK 2005a).

Although the filtered water samples exhibit neutral pH, an unfiltered sampled stored in a dark cold room decreased in pH to 3.9 after several weeks. The oxidation of As(III) to As(V), likely microbially-driven, lowers pH through the following reaction:



The low pH values are not observed at the underground seepage points because of rapid neutralization by the dissolution of ankeritie-bearing wallrock and, near the chamber bulkheads, concrete.

Table 1: Mine waters sampled from seepage points near baghouse dust storage chambers

Underground locations	Seep in tunnel	Near Chamber B2-8	Seep in tunnel	Near Chamber C2-12
pH (field/lab)	7.37/7.70	6.05/7.57	7.05/7.79	6.7/6.75
Eh (mV)	34.0	-231	–	-188
Temp (°C)	7.36	5.51	5.06	3.37
SC (µS/cm) (field/lab)	1185/2190	1011/1920	750/1363	1041/2110
Constituent, mg/L				
Al	<0.08	<0.08	<0.08	<0.08
Alkalinity	156	280	298	96.0
B	0.482	0.525	0.182	0.307
Ba	0.031	0.031	0.024	0.005
Be	<0.001	<0.001	<0.001	<0.001
Ca	220	234	169	313
Cd	<0.001	<0.001	<0.001	<0.001
Co	<0.007	<0.007	<0.007	<0.007
Cr	<0.002	<0.002	<0.002	<0.002

Cu	0.003	<0.003	0.010	<0.003
Fe(T)	0.164	0.150	1.57	0.134
Fe(II)	0.131	0.122	0.667	0.058
K	10.7	7.93	7.36	8.67
Li	0.155	0.107	0.048	0.230
Mg	161	110	65.5	140
Mn	1.17	1.09	0.458	0.446
Mo	0.09	0.068	0.054	0.07
Na	75.3	82.1	47.1	62.8
Ni	0.022	0.026	0.005	0.029
Pb	0.052	<0.008	<0.008	<0.008
SiO₂	13.6	16.9	9.68	24.1
Se	<0.03	<0.03	<0.03	<0.03
Sr	1.36	1.39	1.42	0.698
V	<0.005	<0.005	<0.005	<0.005
Zn	0.009	<0.004	0.024	0.027
As	659	923	9.36	4060
As(III)	454	574	6.6	2735
Sb	34.4	17.2	0.036	11.9
Sb(III)	2.73	1.64	<0.001	0.935
SO₄	924	716	442	500
F	0.49	0.36	0.16	0.26
Cl	59.4	59.5	50.3	96.6
Br	0.64	0.65	0.49	0.45
NO₃	0.032	<0.1	7.9	6.7

The composition of soil pore waters is reported in Table 2. In some cases, there was insufficient sample for a complete analysis. Sample 6 and the first sample taken from lysimeter 8 were filtered to

<0.45µm after extraction. For the rest of the samples, filtration was accomplished by the ceramic cup at the base of the lysimeter which acts as a filter to <0.45µm.

Table 2: Soil pore waters sampled from outcrop soil pockets using suction lysimeters

Sample locations (Figure 2)	6 (0.45µm filter)	8 (0.45µm filter)	8 re-install	9	14	15	17 ¹	18	19 ²	24.5
pH (field)	6.79	5.65	5.25	7.26	6.09	6.41	6.94	6.9	7.18	5.25
Temp (°C)	31.5	24	20.4	22.32	23.43	25.26	24.5	19.3	22.32	15.56
SC (µS/cm) (field)	150	50	40	200	70	170	160	185	410	60
Constituent, mg/L										
Ca			2.2	13.1	6	11.8		25.55		6.2
K			1.7	5.3	1.4	3.6		2.2		2.1
Mg			0.7	8.1	1.7	3.5		0.25		0.2
Na			2.9	13.5	3.3	8.9		6.9		2.7
Sb	0.080	0.045	0.055	0.011	0.0058	0.0219	0.0125	0.0232	0.004	0.013
As	0.163	1.44	2.085	0.251	0.0246	0.0065	0.0095	0.0513	0.180	0.850
SO ₄			4	33	16	24		11		6
F			0.3	0.5	0.1	0.1		0.25		0.2
Cl			2.5	2.2	1.4	1.6		5.6		1.5
NO ₃			0.09	0.16	0.1	8.59		0.44		0.1
NO ₂			0.04	0.04	0.04	0.06		0.5		0.04

¹Site 17 only 13ml sample recovered, no cation/anion analysis; ²Site 19 only 4ml sample recovered, no cation/anion analysis.

Figure 3 shows that the concentration of As in soil pore water increases exponentially with the increase in soil As. The five soil samples with the highest As content were chosen for mineralogical analysis. Scanning electron microscopy and synchrotron-based microanalysis demonstrated that the three samples shaded in light grey contained multiple grains of arsenic trioxide, whereas the two samples shaded as dark grey contain both roaster-generated, arsenic-bearing iron oxides and arsenic trioxide (Bromstad, 2011).

Iron and Mn content in outcrop soils is usually quite low in comparison to carbon (majority of Fe <2%, Mn <200ppm), so that the organic matter may govern the pattern of As adsorption. Soil water results support this, with higher aqueous:solid As ratios corresponding to higher soil carbon content (Figure 3b).

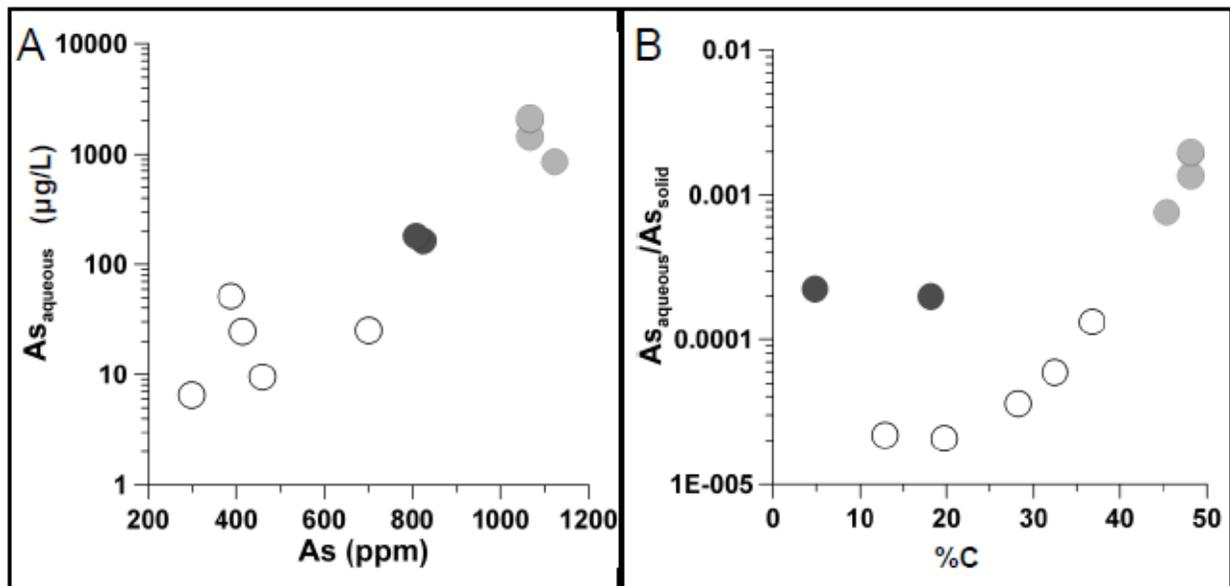


Figure 3: The relationship between soil and coexisting-pore water sampled near Giant mine. Samples shaded with dark and light grey are those characterized mineralogically, open circles indicated samples just analysed for total As. Most of the As hosting grains in the light grey samples are arsenic trioxide. The dark grey samples contain As-bearing roaster-generated iron oxides in addition to arsenic trioxide. **A.** The relationship between As in soils and coexisting waters. **B.** The relationship between carbon content and the ratio of solid and coexisting dissolved As.

Discussion

Throughout its lifetime, Giant mine was operated according to the best practices of the day. At the time that operation began, roaster stack emissions were not regulated. Roasting, which was used to precondition gold-bearing sulfide for cyanide leaching, was (and still is) an effective method of extracting gold but generates large quantities of fine-grained arsenic trioxide. Roasters are still used in some modern mines, albeit with stricter controls and better waste containment than those at the time of Giant mine operation.

The presence of arsenic trioxide appears to have a strong influence on underground and soil pore water compositions as shown by the variable but generally high dissolved As concentrations and the relatively high concentrations of Sb in these waters, an element known to be present in stack emissions and bagged dust from the Giant mine stack emissions (Fawcett and Jamieson 2011). However, even the highest As concentrations in the water samples in this study, all of which have interacted with arsenic trioxide, are much less than the reported solubility of Giant mine baghouse dust (11,000 to 15,000 mgL⁻¹, higher values corresponding to lower Sb content, Riveros et al. 2000). This suggests that there are kinetic barriers to reaching equilibrium. Based on As-Sb-Au correlations, it seems that most of the arsenic trioxide in the soils is more 50 years old, persisting from early stack emissions despite its high solubility and the expectation that arsenic trioxide would have dissolved after years of soil exposure (Bromstad 2011). We have also observed that reagent-grade arsenic trioxide is difficult to solubilize in the laboratory, usually requiring near-boiling temperatures, indicative of kinetic factors controlling dissolution under various conditions. Haffert and Craw (2008) also measured As in surface water that had dissolved arsenic trioxide-bearing

roaster waste and reported concentrations as high as 53 mgL^{-1} which is higher than our values from the Giant mine property but much lower than our highest concentrations from underground.

The concentration of As in these underground water samples and many of the soil pore waters is higher than Canadian Metal Mine Effluent Regulations (0.5 mgL^{-1}), Canadian drinking water guidelines (0.01 mgL^{-1}), and the Canadian Council of Ministers of the Environment guideline for the preservation of freshwater aquatic life (0.005 mgL^{-1}).

Remediation plans include the in-situ freezing of the chambers which is anticipated to decrease this source of As-rich seepage water. The mine will be flooded to a level below the storage chambers and the mine water isolated from surface water by sealing access points such as pits. Mine water, as well as some surface water, will be treated to decrease As concentration (INAC 2007). Typically, the removal of As from water involves oxidizing As(III) to As(V), as the latter precipitates more effectively with the addition of Fe. Our previous work (Osborne et al. 2010) has shown that microbial oxidation of As(III) to As(V) is active at Giant, and is likely to be optimized at low temperatures similar to those underground. However, the in-situ freezing process is expected to decrease the source of As(III) to the mine waters and the role of bioremediation in terms of facilitating water treatment may be relatively minor.

A previous survey of surface water seeps on Giant mine property that were unassociated with obvious mining activity had determined that total As concentrations were as high as 2 mgL^{-1} , suggesting the influence of historic stack emissions (SRK 2005b). Our measurements confirm historical trends. The soil pore water represents the interaction of precipitation with extremely contaminated soils. Although these waters are present in very low volume, human exposure could result from future public access to the outcrop areas. Remediation of surface soils at Giant is based on the Northwest Territories site-specific guideline for industrial soil of 340 mg kg^{-1} As. If the outcrop soil pockets are included with the soil to be removed and stored with various contaminated surface materials, possibly in a frozen pit, the high-As soil pore waters and associated risk should be minimized.

Conclusions

Some underground mine waters and surface soil pore waters at the Giant mine contain extremely high concentrations of As which have interacted with roaster-generated arsenic trioxide. These concentrations, several orders of magnitude higher than guidelines, occur in the absence of acid rock drainage.

Overall, a large, long-lived mine, especially one operated before the 1970s, leaves a complex environmental legacy. Giant mine contains an extremely large concentration of arsenic trioxide in addition to other forms of As contamination (Bromstad and Jamieson 2012). The planned remediation at Giant will reduce but not eliminate As release from the site. Specifically, the total As released (mostly in the form of dissolved As) will decrease from the current level of approximately 500 kilograms per year to less than 200 kilograms per year (INAC 2007). Without this remediation, assuming that Giant mine were allowed to flood as is the case for most underground mines after closure, As release could increase to many thousands of kilograms per year. Interestingly, the very high cost of the proposed remediation plan is still outweighed by the monetary value of the gold extracted over the lifetime of Giant mine (Bullen and Robb, 2006).

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References

- Bromstad, M.J. (2011) The characterization, persistence, and bioaccessibility of roaster-derived arsenic in surface soils at giant mine, Yellowknife, NWT. MSc thesis, Queen's University. 184 p.
- Bromstad, M.J. and Jamieson, H.E. (2012) Giant Mine, Yellowknife, Canada: Arsenite waste as the legacy of gold mining and processing. Chapter 2 (page 25-42) in *The Metabolism of Arsenite* (eds.) J.A. Santini and S.A. Ward. Volume 5 of the series *Arsenic in the Environment*. CRC Press ISSN. pp 1876-6218.
- Bullen, W. and Robb, M. (2006) Economic contribution of gold mining in the Yellowknife mining district. In: C.D. Anglin, H. Falck, D.F. Wright & E.J. Ambrose (eds): *Gold in the Yellowknife Greenstone Belt, Northwest Territories: Results of the EXTECH III Multidisciplinary Research Project*. Geological Association of Canada, Mineral Deposits Division, 2006, pp. 38–49.
- Canadian Public Health Association (CPHA) (1977). Final Report- Canadian Public Health Association Task Force of Arsenic, Yellowknife, Northwest Territories. Canadian Public Health Association, Ottawa, December 1977.
- Drahota P. and Filippi M. (2009) Secondary arsenic minerals in the environment: A review. *Environment Int.* 35, pp. 1243-1255.
- Fawcett, S.E. and Jamieson, H.E. (2011) The distinction between ore processing and post-depositional transformation on the speciation of arsenic and antimony in mine waste and sediment. *Chemical Geology* 283 (3–4), pp. 109–118.
- Haffert L. and Craw D. (2009) Field quantification and characterization of extreme arsenic concentrations at a historic mine processing site, Waiuta, New Zealand, *New Zealand Journal of Geology and Geophysics* 52(3), pp. 261-272.
- Indian and Northern Affairs Canada (INAC) (2007): Giant Mine remediation plan. Report of the Giant Mine remediation team- Department of Indian Affairs and Northern Development as submitted to the Mackenzie Valley Land and Water Board, Yellowknife, Canada, 2007, 260 pp. Available at: <http://www.mvlwb.ca/mv/Registry/Forms/FolderView.aspx?RootFolder=%2fmv%2fRegistry%2f2007%2fMV2007L8-0031%2fremediationplan&FolderCTID=&View={9F47DAB1-E4D7-4B6D-A050-461E63EB7AFE}>. Accessed 12 May 2011.
- Nordstrom D. K. and Archer D. G., (2003). Arsenic thermodynamic data and environmental geochemistry. In *Arsenic in Ground Water Geochemistry and Occurrence* (eds.) A. H. Welch and K. G. Stollenwerk). Kluwer Academic Publishers, U.S.A. pp. 1-25.
- Osborne, T.H., Jamieson, H.E., Hudson-Edwards, K.A., Nordstrom, D.K., Walker, S.R., Ward, S.A. and Santini, J.M. (2010) Microbial oxidation of arsenite in a subarctic environment: diversity of arsenite oxidase genes and identification of a psychotolerant arsenite oxidizer. *BMC Microbiology* 10, 205.
- Riveros P.A., Dutrizac J.E., and Chen T.T. (2000) Recovery of marketable arsenic trioxide from arsenic rich roaster dust. *Environmental Improvements in Mineral Processing and Extractive Metallurgy: Proceedings of the V International Conference on Clean Technologies for the Mining Industry*. Volume II, pp. 135-149.
- SRK Consulting Engineers and Scientists (SRK) (2005a) Giant Mine underground mine water chemistry. In: INAC (2007): Giant Mine Remediation Plan, supporting document B4. 124 pp.
- SRK Consulting Engineers and Scientists (SRK) (2005b) Giant Mine surface water chemistry. In: INAC (2007): Giant Mine Remediation Plan, supporting document B6. 40pp.
- Walker, S.R., Jamieson, H.E., Lanzirrotti, A., Andrade, C.F. and Hall, G.E.M. (2005). The speciation of arsenic in iron oxides in mine wastes from the Giant Gold Mine, N.W.T.: Application of synchrotron micro-XRD and micro-XANES at the grain scale. *The Canadian Mineralogist* 43 (4), pp. 1205–1224.
- Wrye L. (2008) Distinguishing between natural and anthropogenic sources of arsenic in soils from the Giant Mine, Northwest Territories, and the North Brookfield Mine, Nova Scotia. M.Sc. Thesis, Queen's University, Kingston, Ontario, Canada