

FLUCTUATING REDOX CONDITIONS AND PHOSPHORUS COMPETITION: CONTRIBUTORS TO ARSENIC RELEASE FROM WETLAND TAILINGS IN COBALT, ONTARIO¹

Suzanne Beauchemin² and Y.T. John Kwong²

Abstract: In the summers of 2002 and 2003, two successive sampling campaigns were carried out in the wetland area at the confluence of Mill and Farr Creeks in Cobalt (Ontario, Canada). The goal of these studies was to (i) characterize the geochemistry and mineralogy of the tailings, (ii) assess the spatial variability of those properties and (iii) relate them to water quality. A laboratory study supplemented the investigation by taking a detailed look at the impact of changes in redox conditions on the mobilization and speciation of As in these tailings. The objective of this presentation is to review part of the results showing two factors that might contribute to arsenic release from these tailings: the change in oxidizing/reducing conditions and phosphorus competition. The laboratory experiment showed that arsenic in mine tailings readily responded to changes in redox conditions and was remobilized during reduction. In the absence of added soluble C, reducing conditions in the mid-layer sample resulted in the transformation of As into more soluble As(III) species and an increase in dissolved P. When an external source of soluble C was added, solid-phase As(-1) species formed and dissolved P was apparently consumed and remained low. On the field scale, dissolved P in stream water is high and often exceeds the water quality criteria for surface waters. Indirect evidences from the chemical characterization of the tailings suggest that P sorbs more strongly on the substrate than As. Overall, these results suggest that prolonged flooding periods and the presence of sufficient soluble C could stimulate the microbial reduction of As and favour the stabilization of As into As(-1) species. Increased microbial activity might in turn help maintain lower dissolved P concentrations.

Key Words: XANES spectroscopy, arsenic stability, arsenic leaching, saturation degree

Introduction

Historic silver mining in the Cobalt area (Ontario, Canada) has led to widespread contamination of surface and ground waters with As due to indiscriminate discharges of mine wastes along water courses close to the mining and milling facilities (Percival et al., 2004). The Farr Creek wetland, located approximately 2 km northeast of the town of Cobalt, is a typical example. The wetland occupies the northern extension of Crosswise Lake partially filled with up to 2 m of mine tailings. The tailings were largely generated from five nearby mines which operated intermittently from 1908 to the late 1940s (Andersen, 1993). Whereas over 80% of the wetland is water-logged during the greater part of the year, only the northern half of the wetland remains flooded in the summer and early fall. The southern half is drained by Farr Creek and Mill Creek with channels generally less than 4.5 m wide and 1.5 m deep. Dumaresq (1993) estimated that Farr Creek discharged as much as 18,000 kg As annually into Lake Timiskaming, the main receiving water body downstream.

¹ Paper was presented at Mining and the Environment IV Conference, Sudbury, Ontario, Canada, October 19-27, 2007. CANMET-MMSL contribution no. 07-077-2 (OPJ).

² Suzanne Beauchemin* and Y.T. John Kwong, Research Scientists, Natural Resources Canada, CANMET-MMSL, 555 Booth, Ottawa, ON, K1A 0G1; *sbeauche@nrcan.gc.ca

In the summers of 2002 and 2003, field reconnaissance and sampling were conducted in this wetland at the confluence of Mill and Farr Creeks to facilitate (i) detailed characterization of the chemical and mineralogical properties of the tailings in relation to the stream water quality (Kwong et al. 2007), and (ii) investigation of the stability of As in wetlands tailings affected by alternating redox conditions (Beauchemin and Kwong, 2006). These studies showed that dissolved As concentrations in the streams were at least an order of magnitude higher than the Canadian drinking water criterion of 0.025 mg L^{-1} and that the submerged tailings were more likely a source than a sink of As to the stream water (Kwong et al., 2007). Indirect evidence also suggested that P might compete with As for available sorbing sites. Related laboratory experiments demonstrated that As speciation in the tailings was sensitive to changes in redox conditions and reduction led to an increase in the release of dissolved As (Beauchemin and Kwong, 2006).

The objective of this paper is to present additional data and discuss two factors contributing to As release from these tailings: the change in oxidizing/reducing conditions and the competitive interaction of P with As.

I. As and P in the stream water and sediments: Some field observations

Methodology

Details on the sampling strategy and analytical methods used for the water and sediment characterization were described in Kwong et al. (2007). For the purpose of this paper, only a brief summary is given. The term 'sediments' employed in this study refers to the permanently submerged tailings underneath the Farr and Mill Creek streams.

In late May 2002, three sites within 10 m from the confluence of Mill Creek with Farr Creek were sampled. At each station, composite sediments from two locations separated 5 to 8 m apart (along the stream) were sampled using clear plexiglass coring tubes 5 cm in diameter, and a 125-mL filtered sample of the stream water was collected using an in-line $0.45 \text{ }\mu\text{m}$ filter and a peristaltic pump. Parameters measured *in situ* included redox potential (Eh), dissolved oxygen (DO), conductivity (EC) and pH of the water. The water samples were quickly placed at 4°C in the dark until later determination of dissolved As by ICP-AES and dissolved P by the colorimetric stannous chloride method.

Anionic exchange membranes (AEMs) were also inserted in the top layer (0 - 10 cm) of the stream sediments for a 42-hour contact period to assess the pool of exchangeable As and P in the sediment pore water. AEMs provide a measure of the element fluxes in terms of the net change in the amount of total exchangeable As or P over the resin surface for the contact time of deployment ($\mu\text{g cm}^{-2} \text{ day}^{-1}$).

Ammonium-oxalate extractable Al, Fe, As, and P concentrations (Al_{ox} , Fe_{ox} , As_{ox} , P_{ox}) of the sediments were obtained as described by Ross and Wang (1993) and determined by ICP-AES. The ammonium-oxalate extraction is commonly used for estimating the pool of poorly-crystalline Fe and Al minerals as well as the organic-complexed Fe and Al in soils (Ross and Wang, 1993). Given that poorly crystalline Fe and Al phases are the main sorbents for P in soils, the ratio of oxalate-extractable P to that of Al+Fe has been proposed as an indication of the saturation degree of the sorbent phases for agricultural soils (Van der Zee et al., 1988). The degree of P saturation (DPS) for the tailings was calculated, with all concentrations expressed in mmol kg^{-1} , as $\text{DPS (\%)} = \text{P}_{\text{ox}} / (\text{Fe}_{\text{ox}} + \text{Al}_{\text{ox}}) \times 100$. The same approach was used to calculate a saturation index for As (DAsS).

Results and Discussion

In addition to high As concentrations, the stream water of both Farr Creek and Mill Creek had P concentrations at least 4 times higher than the norm for surface water quality of 0.03 mg/L (Table 1). Considering the known competitive interaction of As and P for the same sorbing sites (Manning and Goldberg, 1996; Jackson and Miller, 2000; Liu et al., 2001), we investigated the behaviour of As and P in the solid phase.

Table 1: Concentrations of dissolved P and As (0.45 μ m) in the stream water at the confluence of Farr and Mill Creek, May 2002.

Location	pH	Dissolved O mg L ⁻¹	Conductivity μ S cm ⁻¹	P mg L ⁻¹	As mg L ⁻¹
Farr- upstream	7.48	10.00	162	0.14	0.29
Mill	8.23	9.45	365	0.25	0.54
Farr - downstream	7.55	8.37	212	0.18	0.36

Various solubility pools of As and P in the surface layer of the sediments were determined and the results are reported in Table 2. For P, AEMs have been shown to be an effective *in situ* tool to detect changes in labile soil P as affected by such parameters as microbial demand, temperature and ion diffusion (Cooperhand and Logan, 1994). Similarly, the degree of soil P saturation is a widely used index for agricultural soils to identify potential fields that could contaminate waters with P (Beauchemin and Simard, 1999). In agricultural soils, the DPS has been shown to be well correlated with soluble P. Considering that As and P behave similarly in soils and, in general, poorly crystalline Al-, Fe- and Mn-oxides also represent the main sorbing phases for As (Violante and Pigna, 2002), we also determined the degree of As saturation for the sediments (DAsS) using the same approach as for P.

Table 2: Solubility pools[†] of As and P in the surface layer (0 – 10 cm) of stream sediments at the confluence of Farr and Mill Creeks, May 2002.

Location	As _{resin} _ μ g cm ⁻² day ⁻¹ _	P _{resin}	As _{ox}	P _{ox}	(Al+Fe) _{ox}	DAsS	DPS	As _{total}	P _{total}
				mmol kg ⁻¹		%		mmol kg ⁻¹	
<i>Farr- upstream</i>									
#1	0.38	0.07	1.23	4.90	83	1.5	5.9	4.6	19.0
#2	0.80	0.08	1.41	5.15	85	1.7	6.1	5.3	17.2
<i>Mill</i>									
#1	0.54	0.37	1.96	5.79	84	2.3	6.9	9.5	18.0
#2	1.13	0.23	1.88	6.80	84	2.3	8.1	5.6	20.3
<i>Farr- downstream</i>									
#1	0.92	0.09	1.17	4.52	63	1.9	7.2	10.9	19.8
#2	1.39	0.24	1.36	4.85	68	2.0	7.2	10.6	19.5

[†] As_{resin} and P_{resin}: As and P extracted by anionic exchange membranes; P_{ox}, (Al+Fe)_{ox}: oxalate-extractable P and (Al+Fe); DAsS, DPS: degree of As or P saturation for the tailings; As_{total}, P_{total}: total content of As and P.

The total and oxalate-extractable P contents were two to four times greater than those of As (Table 2). Accordingly, the DPS was two to four times greater than DAsS. In contrast, the sediment pore water carried more resin-extractable As than resin-extractable P. These observations suggest that P sorbs more strongly and occupies more sorption sites on amorphous Al- and Fe-oxides and oxyhydroxides than As. Violante and Pigna (2002) reported that phosphate sorbs more strongly on non-crystalline Al phases while arsenate preferentially sorbs on Fe and Mn oxides as well as ferruginous clays. The observations would thus indicate that the prevalent sorbing phases occurring in the wetland are dominantly aluminous instead of ferruginous in nature. This is in agreement with the mineralogical characterization of the tailings, which showed that Al-rich phases (e.g. feldspars) and carbonates were the major components while Fe- and Mn-oxyhydroxides occurred only in minor to trace amounts (Kwong et al, 2007).

II. As and P in tailings as affected by redox conditions: The laboratory experiment

Methodology

Details on the redox experiment were described in Beauchemin et al. (2005) and Beauchemin and Kwong (2006). Only the key points are summarized here.

In May 2003, tailings from fifteen locations along Mill Creek and Farr Creek were sampled using a coring tube down to 50 cm in depth (Kwong et al., 2007). One profile along Mill Creek with a mean total As content of 1300 mg kg⁻¹ (pH 7.4), and another along Farr Creek with 1177 mg As kg⁻¹ (pH 7.3) were selected to study the impact of change in redox conditions on As stability. The redox experiment was carried out in duplicate on each of the three layers of the two profiles (~0-12, 12-30 and > 30 cm).

Suspensions of tailings in 10 mM KCl at a solid to solution ratio of 1:10 were incubated under anaerobic conditions at 23°C for 30 days, during which dissolved metal concentrations were monitored. After 30 days of reduction, reoxidation of the samples was accomplished by air-drying. For tailings from the intermediate layer, an additional C-enriched treatment was included by adding 0.5% (w/w) glucose in the suspension at the beginning of the experiment. The glucose treatment was added to verify whether a soluble C input would enhance the reduction threshold achieved in our systems with a low organic C content ($\leq 1\%$). Oxalate-extractable As, P, Al and Fe were determined on the original, reduced and reoxidized tailings for the calculation of DAsS and DPS as described above. The As oxidation state in the same samples was determined using X-ray absorption structure (XAS) spectroscopy. XAS analyses were conducted at Beamline X-18B of the National Synchrotron Light Source, Brookhaven National Laboratory (NY).

Results and Discussion

For both of the Farr and Mill Creek mid-layer samples, the imposed reduction on tailings resulted in an increased release of dissolved As (Figure 1). The addition of glucose sped up the As dissolution in the first two weeks, which then decreased or stabilized. Without glucose input, dissolved P increased with reduction time whereas low dissolved P was observed in the glucose treatment (Figure 1). These results suggest that P was consumed by increased microbial activity resulting from the glucose input. As aerobic and anaerobic respiration leading to the degradation of glucose into pyruvic acid is an acid-generating process (Ponnamperuma, 1972), an increase in microbial activity would explain the drop in pH of ~1.2 units over the 30-day reduction in the glucose-amended treatment. The marked pH drop in this reduced treatment was also associated with a significant increase in dissolved Mn and Fe, which in turn could partially explain the increase in dissolved As noted in both the Farr and Mill Creek samples.

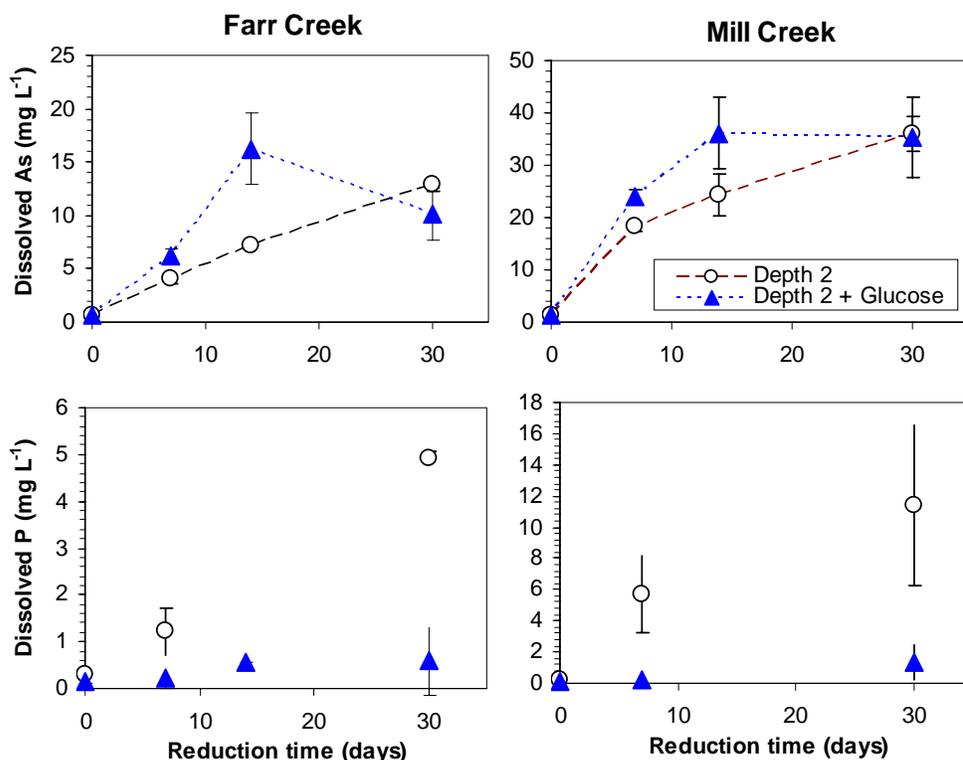


Figure 1: Changes in dissolved As and P concentrations over the time of reduction for both the Farr and Mill Creek samples from the mid-layer, with and without glucose addition.

For both of the Farr and Mill Creek tailings, the 30-day reduction also significantly impacted the As oxidation state and speciation in the tailings (Figure 2). At the beginning of the experiment (Day 0), the main As peak at around 7 eV in the K-XANES spectrum is consistent with As(V) species, indicating the dominance of the oxidized species in the sample. After 30 days of reduction, a clear peak at ~4 eV indicates the formation of As(III) species, coincident with the increase in dissolved As. The short reoxidation achieved by air-drying the samples was sufficient to transform most of the newly formed As(III) back into As(V) for the tailings from Farr Creek but As(III) persisted in the reoxidized Mill Creek sample. The addition of glucose resulted in a lower As oxidation state than that observed in the non-amended system and this effect was more pronounced in the Mill Creek than the Farr Creek samples (Figure 2). For the Mill Creek tailings, the overall As oxidation state in the glucose-amended, 30-d reduced sample was consistent with the formation of As(-1) species similar to safflorite (Beauchemin and Kwong, 2006). Given that this safflorite-like phase was detected only in the glucose-amended treatment, its formation may be microbially mediated.

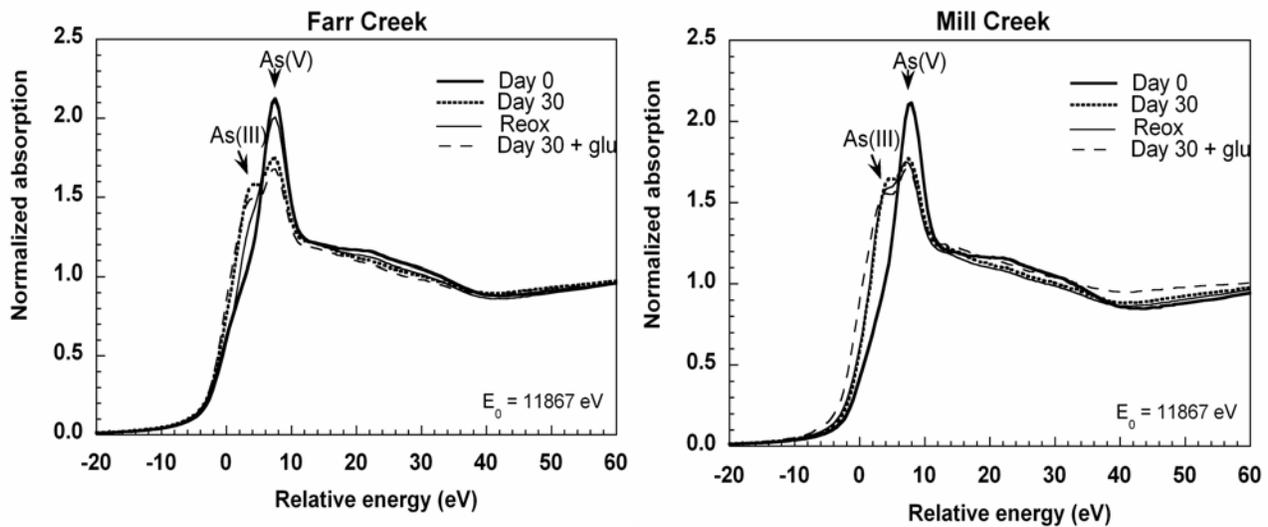


Figure 2: As K-XANES spectra for the Farr and Mill Creek mid-layer samples at the beginning of the experiment (Day 0), after 30 days of reduction with (Day 30 + glu) or without glucose (Day 30) and after reoxidation by air-drying (Reox).

Ammonium-oxalate extractions were carried out to assess the impact of reduction and reoxidation on the redox-sensitive, poorly crystalline sorbents (i.e. Mn and Fe oxides). The As and P sorption capacity of these tailings is low (~ 2000 mg As or P kg^{-1}). The 30-day reduction further decreased the pools of oxalate-extractable Fe and Mn but reoxidation reverted them back to their original values (Beauchemin et al., 2005). The amount of oxalate-extractable As was also significantly lower in the 30-day reduced sediments. However, the dissolution of poorly crystalline Fe and Mn phases with sorbed As would not be sufficient to explain the amount of dissolved As; the dissolution of As-bearing minerals is likely a main contributor (Beauchemin and Kwong, 2006). Of interest to note is the distinct impact of reduction on the degrees of As and P saturation of the tailings. Figure 3 shows that after 30 days of reduction, DPS increases for both the Farr and Mill Creek tailings, with or without glucose amendment. In contrast, DAS is significantly reduced after 30 days of reduction. Thus, apparently, P remained more strongly bound to the sorbing sites than As during the reduction.

These saturation indices should, however, be used with caution because the ammonium-oxalate extraction was developed for soils and its reliability for tailings has not been demonstrated. In addition, the usefulness of saturation index has been established for P in agricultural soils but its relevance for As remains to be further investigated. Nevertheless, the results on the competitive As and P interaction in these tailings are supported by other analyses. For instance, over the 15 field locations sampled, the proportion of water-extractable As correlates directly with the water-extractable P content of the tailings, suggesting that higher desorbable P concentrations were associated with higher proportions of the total As that could be desorbed (Kwong et al., 2007). In addition, a complementary laboratory experiment on the Mill Creek tailings (mid-layer: 12-28 cm) was carried out to determine the impact of P inputs on the desorption of As. P was added to a 10 mM KCl suspension of 6.67 g tailings kg^{-1} to obtain final concentrations of 0, 75, 150, 300, 600 and 1200 mmol P per kg of tailings (pH 8). After 42 hours of contact, the suspensions were centrifuged and As and P concentrations were determined in the 0.45 μm filtered decantates. The results confirm that P addition to the tailings led to an increase in dissolved As (Figure 4).

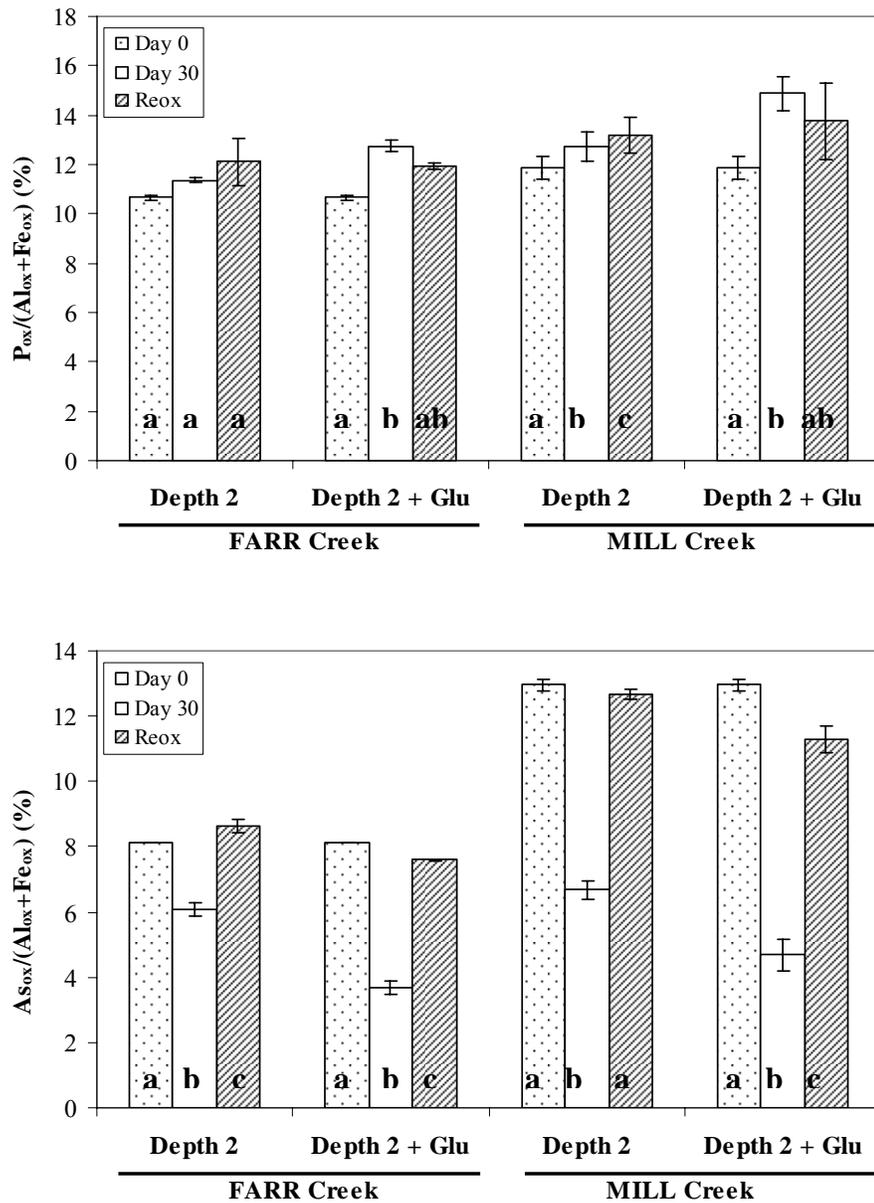


Figure 3: Degrees of P and As saturation in the sediment of Farr and Mill Creek mid-layer samples at the beginning of the experiment (Day 0), after 30 days of reduction with (Day 30 + Glu) or without glucose (Day 30) and after reoxidation by air-drying (Reox). For each set of analyses, the means marked with the same letter are not statistically different from each other at $\alpha = 0.05\%$.

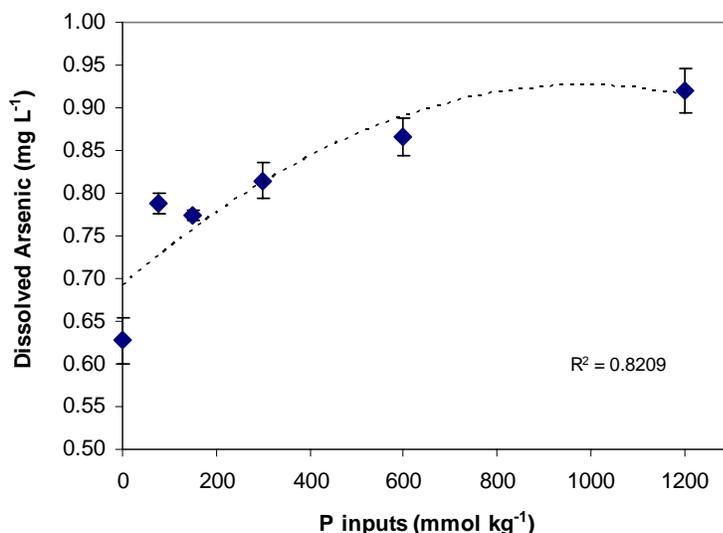


Figure 4: Variation of dissolved As with P input to the Mill Creek tailings (pH 8, 42 hours of contact, 22°C).

Conclusions

The redox experiment showed that As in the Cobalt tailings readily responded to changes in redox conditions and was remobilized during reduction. In the absence of added soluble C, reducing conditions in the mid-layer sample resulted in the transformation of As into more soluble As(III) species and an increase in dissolved As and P. When an external source of soluble C was added, solid-phase As(-1) species formed and dissolved P was apparently consumed. Soluble C rather than P would be the limiting factor for microbial reduction and stabilization of As in the wetland tailings. In the study wetland, dissolved P in stream water is high and often exceeds the water quality criteria for surface waters. Indirect evidences from the chemical characterization of the tailings suggest that P sorbs more strongly on the substrate than As. These results, coupled with the initial low As sorption capacity of these tailings, indicate that adsorption will not be an efficient process to attenuate As transport in this system. Other mechanisms like precipitation might be more effective if proper conditions are present. Prolonged flooding periods and the presence of sufficient soluble C could stimulate the microbial reduction of As and favour the stabilization of As in the form of As(-1) species. Increased microbial activity might in turn help to maintain a lower level of dissolved P.

Literature Cited

- Anderson, P., 1993. Cobalt mining camp tailings inventory, Cobalt, Ontario. Unpublished report, Ontario Ministry of Northern Development and Mines, 196pp.
- Beauchemin, S. and R.R. Simard. 1999. Soil phosphorus saturation degree: Review of some indices and their suitability for P management in Québec, Canada. *Can. J. Soil Sci.* 79: 615-625.
- Beauchemin, S., T. MacKinnon, and J. Kwong. 2005. Effect of alternating reducing / oxidizing conditions on As mobilization from sediments collected in a wetland impacted by mine tailings (Cobalt, ON). Natural Resources Canada. CANMET-MMSL # 05-022. Ottawa, ON. 37 p.
- Beauchemin, S. and Y.T.J. Kwong. 2006. Impact of redox conditions on arsenic mobilization from tailings in a wetland with neutral drainage. *Environ. Sci. Technol.* 40: 6297-6303.
- Cooperhand, L.R. and T.J. Logan. 1994. Measuring *in situ* changes in labile soil phosphorus with anion-exchange membranes. *Soil Sci. Soc. Am. J.* 58: 105-114.

- Dumaresq, C.G., 1993. The occurrence of arsenic and heavy metal contamination from natural and anthropogenic sources in the Cobalt area of Ontario. M.Sc. thesis, Carleton University, Ottawa, Canada.
- Jackson, B.P and W.P. Miller. 2000. Effectiveness of phosphate and hydroxide for desorption of arsenic and selenium species from iron oxides. *Soil Sci. Soc. Am. J.* 64: 1616-1622.
- Kwong, Y.T.J., S. Beauchemin, M.F. Hossain, and W.D. Gould. 2007. Transformation and mobilization of arsenic in the historic Cobalt mining camp, Ontario, Canada. *Journal of Geochemical Exploration* 92: 133-150.
- Liu, F., A. De Cristofaro and A. Violante. 2001. Effect of pH, phosphate and oxalate on the adsorption/desorption of arsenate on/from goethite. *Soil Sci.* 166: 197-208.
- Manning, B.A. and S. Goldberg. 1996. Modeling arsenate competitive adsorption on kaolinite, montmorillonite and illite. *Clays and Clay Minerals* 44: 609-623.
- Percival, J.B., Y.T.J. Kwong, C.G. Dumaresq, F.A. Michel. 2004. Transport and attenuation of arsenic, cobalt and nickel in an alkaline environment (Cobalt, Ontario). Geological Survey of Canada Open file 1680, 30 p.
- Ponnamperuma, F.N. 1972. The chemistry of submerged soils. In: *Advances in Agronomy* (N.C. Brady, ed.), Volume 24, Academic Press, New York, pp. 29-90.
- Ross, G. J. and C. Wang. 1993. Extractable Al, Fe, Mn, and Si. p. 239-246 in M. R. Carter (ed.). *Soil sampling and methods of analysis*. Lewis publishers, Boca Raton, FL.
- Van der Zee, S.E., Nederlof, M.M., Van Riemsdijk, W.H., de Haan, F.A.M., 1988. Spatial variability of phosphate adsorption parameters. *J. Environ. Qual.* 17: 682-688.
- Violante, A. and M. Pigna. 2002. Competitive sorption of arsenate and phosphate on different clay minerals and soils. *Soil Sci. Soc. Am. J.* 66: 1788-1796.

Acknowledgements

Part of this research was carried out at NSLS, Brookhaven National Laboratory, which is supported by the U.S. Dept. of Energy, Division of Materials Sciences and Division of Chemical Sciences. This research was supported by Natural Resources Canada. The technical support of Ted MacKinnon was greatly appreciated. Thanks are also extended to the Analytical Services Group of CANMET-MMSL for the ICP analysis. The authors thank Jean-François Fiset (CANMET-MMSL) for internal review.