

Evaluation of Arsenic Leaching Potential in Gold Mine Tailings Amended with Peat and Mine Drainage Treatment Sludge

T. V. Rakotonimaro,* M. Guittonny, C. M. Neculita, F. Trépanier, and G. Pépin

Abstract

Peat and mine drainage treatment sludge can be valorized as amendments on mine sites to stabilize gold mine tailings and reduce the potential leaching of contaminants in pore water. However, the influence of organic amendments on the mobility of metalloids and/or metals in the tailings must be validated, as the leached contaminants may vary according to their type, nature, and origin. The objective of the present study was to evaluate over time the effect of peat- and/or Fe-rich sludge amendments on the mobility of As and metallic cations in the drainage water of tailings potentially producing contaminated neutral drainage. Ten duplicated weathering cell experiments containing tailings alone or amended with peat and/or Fe-rich sludge (5–10% dry weight) were performed and monitored for 112 d. The results showed that as low as 5% peat amendment would promote As mobility in tailings' pore water, with As concentrations exceeding Quebec discharge criteria ($>0.2 \text{ mg L}^{-1}$). In addition, As(III), the most mobile and toxic form, was predominant with 10% peat, whereas organic species were negligible in all cells. The use of peat alone as organic amendment for the stabilization of tailing contaminants could increase the risk of generating As-rich contaminated neutral drainage. Conversely, the mix of only 5% Fe-rich sludge with or without peat decreased As concentrations in leachates by 65 to 80%. Further studies on the use of "peat" or "peat + Fe-rich sludge" as cover or amendment should be conducted with a focus on Fe/As and Ca/As ratios.

Core Ideas

- Peat amendments enhanced the leaching of As from gold mine tailings.
- Amendments of 5% peat promoted As(V) leaching, whereas 10% peat increased As(III) leaching.
- As(III) was predominant at $\geq 20 \text{ mg L}^{-1}$ dissolved organic C from peat.
- Mine drainage treatment sludge could decrease As concentrations by 65 to 80% in tailings' pore water.

MINIMIZING potential environmental impacts is presently a pressing priority for the mining industry. In boreal regions, land, forest, water (surface and groundwater), and peatland may incur disturbances due to mining activities. Concerns are often associated with mine waste storage facilities (tailings and waste rock piles) from which contaminated mine drainage (acid mine drainage, contaminated neutral drainage, and saline mine drainage) could originate. The processing of gold-bearing sulfide ores associated with As-containing gangue minerals can result in high As concentrations in gold mine tailings (Morin and Calas, 2006; Wang and Mulligan, 2006; DeSisto et al., 2017). Typical encountered minerals in tailings are arsenopyrite (FeAsS), scorodite, ($\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$) and arsenian pyrite (As-rich FeS_2) (Wang and Mulligan, 2006; Corriveau et al., 2011). In gold tailings, metals (e.g., Fe, Al, Mn, Cu, Pb, and Zn) can also be associated with As, as well as with clay minerals and oxyanions (e.g., sulfates, phosphates, and carbonates) (Wang and Mulligan, 2006; Hare et al., 2018). Generally, As species from the oxidation of these minerals are predominantly As(V) and, in minor amounts, As(-I) (Campbell and Nordstrom, 2014; DeSisto et al., 2017). However, As(III), the most toxic form, is frequently present in moderately reducing conditions or in the presence of organic matter (OM) (Bauer and Blodau, 2006; Wang and Mulligan, 2006). As a note, the toxicity of As species toward humans would vary as follows: $\text{As(III)} > \text{As(V)} > \text{monomethylarsonic acid (MMA)} > \text{dimethylarsinic acid (DMA)}$ (Chu and Crawford-Brown, 2006; Hare et al., 2018). The As threshold toxicity in drinking water is $10 \mu\text{g L}^{-1}$, and greater concentrations can cause human diseases (e.g., skin disorders) and even death to animals such as mammals (Hong et al., 2014; Mandal, 2017; WHO, 2018). The speciation and mobility of As in soil or tailings' pore water are influenced by the physicochemical conditions (pH, redox potential [Eh], OM, anions, and Fe) and controlled by adsorption–desorption and dissolution–precipitation processes, microbiological mechanisms, and volatilization (Bolan et al., 2014; Rakotonimaro et al., 2018).

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Abbreviations: CEC, cation exchange capacity; DMA, dimethylarsinic acid; DOC, dissolved organic carbon; DOM, dissolved organic matter; Eh, redox potential; ICP–AES, inductively coupled plasma atomic emission spectroscopy; MMA, monomethylarsonic acid; OM, organic matter; SAX, strong anion exchange; SCX, strong cation exchange.

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J. Environ. Qual. 48:735–745 (2019)

doi:10.2134/jeq2018.11.0392

Supplemental material is available online for this article.

Received 5 Nov. 2018.

Accepted 14 Feb. 2019.

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Several promising approaches have been evaluated for the stabilization of As-rich tailings such as covers, amendments, or revegetation to limit the generation of contaminated mine drainage (Kim and Davis, 2003; King et al., 2008; DeSisto et al., 2017). Covers aim to create an oxygen barrier (e.g., covers with capillary barrier effect) or reduce water infiltration (Aubertin et al., 2016) and thus control, at the source, the oxidation of As-bearing minerals or its leaching. When As is present in pore waters, amendments can be used to modify its speciation and, potentially, reduce its mobility. Amendments consist of mixing tailings with organic or inorganic materials that are used to stabilize the contaminants and to improve the physicochemical (water retention capacity, porosity, and nutrients) and biological properties of tailings (development of the vegetation and microbial growth) (Bolan et al., 2014; Rakotonimaro et al., 2018). Water and soil remediation techniques for As removal from pore water include physicochemical processes (e.g., lime neutralization, fixation on oxides, and vitrification), biological processes (e.g., biomethylation and biomineralization), and plant-based remediation (Henke and Hutchison, 2009; Komárek et al., 2013; Hare et al., 2018). The use of mixtures with Fe-based materials is the most common remediation option for As-contaminated solids, including mine waste. Sometimes, covers and amendments may be used in a complementary way (Nason et al., 2014). Covers and/or organic amendments can also be combined with revegetation to increase physical stability (limitation of water and wind erosion) and decrease geochemical reactivity and, eventually, the generation of contaminated mine drainage (Rakotonimaro et al., 2018). Reuse of available organic materials on mine sites (e.g., forest residues, peat, compost, and sludge) for tailing reclamation is an innovative and economic concept (Nason et al., 2014; Palmer et al., 2015; Guittonny-Larchevêque and Pednault, 2016). Peat moss, which is an organic material often available in large quantities on northern mine sites, is excavated to allow mining activities to take place and is then stored awaiting valorization. Peat is of particular interest for reuse to stabilize the metallic contaminants in tailings. Peat is formed from the anaerobic accumulation of partially decomposed plant biomass in water-saturated environments (CSSC, 1998; APTHQ, 2019). In Quebec, peatlands cover nearly 8.27 million ha (APTHQ, 2019). The physicochemical characteristics are dependent on site and peatland vegetation (herbaceous, shrubby, or arborescent), but in general, peatlands contain >65% (w/w) OM, mainly composed of bitumen, cellulose, humus (humic acid and fulvic acid) and/or lignin, cutin, and suberin (Jinming and Xhuehui, 2002). Peat has high cation exchange capacity (CEC, 55–200 cmol[+] kg⁻¹), which facilitates the adsorption of contaminants in mine drainage, mostly metals (Rezanezhad et al., 2016). In addition, the high content of humic substances of peat, with functional groups such as carboxyl, phenol, and alcohol groups, was confirmed as efficient for the adsorption of heavy metals by surface complexation (Kumpiene et al., 2007). Peat is also effective in immobilizing very low concentrations of As (14–140 µg L⁻¹), Sb, and Ni in tailings, especially when they are combined or conditioned with Fe-based materials (Kumpiene et al., 2008; Anson et al., 2013; Palmer et al., 2015; Zhang et al., 2018). The use of peat can also be beneficial for the biotransformation of metallic elements into less toxic organometallic compounds, particularly in the case of As (organoarsenic) (Palmer et al., 2015;

Mikutta and Rothwell, 2016). Finally, peat mixed or modified with Fe-based materials was found to be efficient in removing metalloids. The better As removal was explained by the existence of As-O-Fe bonds in Fe-peat amendment (Anson et al., 2013; Kumpiene et al., 2013; Zhang et al., 2018). It is worth noting that Fe-based materials were reported to have a high metalloids scavenging capacity (Bolan et al., 2014). High-Ca-content materials also present an advantage for As immobilization through the formation of calcium arsenate and other stable Ca-As minerals (Bothe and Brown, 1999; Zhu et al., 2006). The valorization of Fe- and Ca-rich sludge from the treatment of acid mine drainage for As removal is well documented and represents an alternative amendment in mixture with peat (Rakotonimaro et al., 2017). However, the effect of peat on Fe-rich sludge is uncertain, due to the generally known instability of the latter. Moreover, organic amendments could enhance As mobility in gold mine tailings by changing its speciation with respect to pH, Eh, and OM (Bauer and Blodau, 2006; Bolan et al., 2014; Rakotonimaro et al., 2018). Site sorption competition between As and other oxyanions, as well as the potential mobilization in the presence of OM, may increase the complexity of predicting As mobility in amended mine tailings (Rakotonimaro et al., 2018). Precisely, chelating properties of leached dissolved organic matter (DOM) from peat can enhance the mobility of metallic elements such as Pb and As in pore waters (Bolan et al., 2014). Due to possible changes in physicochemical properties of peat over time, its beneficial use is still to be confirmed. Thus, peat's ability to immobilize contaminants from mine tailings may vary with its chemical composition and decomposability.

Assuming that peat and/or Fe-rich sludge could decrease metal leaching in tailings and could possibly transform toxic inorganic As into less toxic organoarsenic, their use as single or mixed amendments for tailing reclamation was tested in this study. More specifically, their effectiveness to stabilize gold mine tailings that contain potentially leachable As was evaluated. The effect of peat on the stability of As in sludges was also tested.

Materials and Methods

Site Description and Sampling

The materials used for the study were sampled at the Goldcorp Eleonore Mine, which is located in the James Bay region of Quebec, Canada (52°42'16.49" N, 76°4'15.82" W). The mine currently produces desulfurized (total S < 0.3%) and filtered (water content = 14%) tailings (Supplemental Fig. S1), mine drainage treatment sludge (dewatered in geotubes) from the water (all drainage collected on site) treatment plant (Supplemental Fig. S1), and waste rock, which must be managed in a responsible and sustainable way (Table 1). Paste pH of the solids was determined in deionized water using a solid liquid ratio of 1:2. Total metal concentrations were analyzed by inductively coupled plasma atomic emission spectroscopy (ICP-AES) on filtered (0.45 µm) and acidified (with 2% [v/v] nitric acid) digestate. Oxides were determined by X-ray fluorescence. The total C and total S contents were measured by combustion in an induction furnace (ELTRA CS-2000) coupled to an infrared analyzer (MA. 310-CS 1.0; CEAEQ, 2013). The CEC was determined using the sodium acetate method (Chapman, 1965). Water mass content was evaluated, in duplicate, by drying samples at 40°C during 2 d.

In the present study, the main As-bearing mineral in the tailings was arsenopyrite (FeAsS) (0.1–0.5% of the total mass of tailings), with löllingite (FeAs₂) as trace mineral. Briefly, arsenopyrite was associated with Ni and Sb. The two different forms of Fe oxides suggested an oxidizing environment of the tailings with a greater proportion of hematite (Fe₂O₃) than magnetite (Fe₃O₄), because the latter could be obtained by the reduction of hematite (Cornell and Schwertmann, 2003). Static testing of the tailings classified them as uncertain materials to generate As-contaminated neutral drainage, whereas leaching tests (toxicity characteristic leaching procedure and synthetic precipitation leaching procedure) showed potential mobility of As and Fe (data not shown). The first tailing's impoundment reached its maximum elevation in 2017. Hence, the mine presently evaluates several scenarios for the stabilization of As and other potential contaminants in its tailing facility. A technique that involves the use of available and stored materials onsite (e.g., peat, till, wood chips, overburden, sand, clay, and geotube sludge) is desired. Given the large amounts of available peat on the site, its use as an organic amendment would be an environmentally friendly and low-cost option. Water content, fiber content, and bulk density of peat were determined to evaluate its class and decomposition degree (Boelter, 1969). Water content was evaluated in duplicate by oven drying fresh samples at 60°C (ASTM, 2010). Samples were dried for 48 h and then cooled in a desiccator for 1 h and weighed every 4 h until the nearest values of weights differed by <1%. Water content was then calculated as the mass of water divided by the mass of dry material. Fiber content was determined using wet sieving on raw peat sample (100–200 g) soaked for 15 to 20 h in a dispersing agent solution (Calgon 5%). The samples were then washed through five sieve openings (0.1 [140 mesh], 0.25 [60 mesh], 0.5 [35 mesh], 1 [18 mesh], and 2 mm [10 mesh]). The fibers retained on each sieve were collected, dried, weighed, and compared with the initial dry weight of the sample (Boelter, 1969). The bulk density was measured using the dry weight of peat and the initial volume of the container ($\rho = \text{dry mass/volume}$; ASTM, 2018). In the present study, the fiber (>0.1 mm) content and bulk density of peat allowed us to determine its class among fibric (least decomposed

and contains more than two-thirds fibers), humic (intermediate decomposed, contains one-third to two-thirds fibers), or sapric (most decomposed, contains less than one-third fibers) classes (Boelter, 1969). Given the results, Eleonore peat was classified as fibric peat and was thus the least decomposed, with a fiber content of 78% and bulk density of 0.25 g cm⁻³. The release of dissolved organic C (DOC) from fibric peat is expected to be less than from humic or sapric peat. The water content reached as high as 244% as an indication of a high water-holding capacity.

Geotube sludge was also tested as an amendment due to its alkaline pH (8.06) and high concentrations of Fe (35.4 g kg⁻¹) and Ca (274.4 g kg⁻¹) (Table 1). The tailings, peat, and geotube sludge were characterized (physically and chemically, Table 1).

Weathering Cell Setup and Monitoring

Weathering cell experiments (in duplicate) were performed in Büchner funnels where 60 to 70 g (dry weight) of solids was placed on a geotextile and filter paper (Whatman, 0.45 μm). The tested scenarios consisted of tailings (abbreviated as T in treatment names), peat (abbreviated as P), geotube sludge (abbreviated as S), and mixtures of tailings + peat (abbreviated as TP), tailings + geotube sludge (abbreviated as TS), or tailings + peat + geotube sludge (abbreviated as TPS), at differing solid proportions (Table 2).

The mini-cells filled with samples were exposed to wet and dry cycles (one to two wettings per week with ~140 mL of deionized water according to precipitation in the James Bay region; Government of Canada, 2017), spaced with 2 d of air drying, during 112 d. Erlenmeyer flasks installed underneath each Büchner funnel allowed collecting the leachates (Supplemental Fig. S2).

Physicochemical Analysis

Leachates from the mini-cells experiments were collected at predetermined intervals (weekly to biweekly) for physicochemical analyses immediately after collection for a total duration of 112 d (December 2017–April 2018). Water pH was measured with a B30PCI electrode linked to a benchtop VWR Symphony meter, and the redox potential was determined with an Orbisint CPS12-OPA2GSA potentiometer coupled with an

Table 1. Initial physicochemical characteristics of the filtered tailings, peat, and geotube sludge.

Physicochemical properties	Tailings	Peat	Geotube sludge
pH	n.a†	3.71	8.06
Al, %	5.7	0.16	1.19
As, %	0.09	–	0.24
Fe, %	2.7	0.46	3.5
Mn, %	0.05	0.01	0.04
Ca, %	2.2	0.24	27.4
Total S, %	0.24	0.06	0.68
Sulfate S, %	0.12	–	1.25
CaMg (CO ₃) ₂ , %	1.20	–	–
Fe ₂ O ₃ , %	4.6	–	5.51
Fe ₃ O ₄ , %	0.20	–	–
Al ₂ O ₃ , %	13.60	–	2.70
Cation exchange capacity, cmol(+) kg ⁻¹	–	95	46
Water content, %	14	244	289
Ca/(Ca+Fe+As)	0.44	0.34	0.88

† n.a., not available.

Table 2. Composition of the mixtures used during the weathering cell testing.

Cell†	Solid proportions		
	Tailings	Peat	Geotube sludge
	% dry wt.		
T100	100	–	–
P100	–	100	–
S100	–	–	100
TP5	95	5	–
TP10	90	10	–
TS5	95	–	5
TS10	90	–	10
SP10	–	10	90
TP5S5	90	5	5
TP10S10	80	10	10

† T100, 100% tailings; P100, 100% peat; TP5, 95% tailings + 5% peat; TP10, 90% tailings + 10% peat; SP10, 90% sludge + 10% peat; TS5, 95% tailings + 5% sludge; TS10, 90% tailings + 10% sludge; TP5S5, 90% tailings + 5% peat + 5% sludge; TP10S10, 80% tailings + 10% peat + 10% sludge.

internal Pt/Ag/AgCl electrode (± 0.1 mV). The Eh was then calculated relative to standard hydrogen electrode potential (+204 mV). Electrical conductivity (EC) was measured with a HACH Sension 1 electrode. Alkalinity and acidity were determined with a Metrohm Binkmann 716 DMS Trinitro titrator (APHA, 2012). Phenolic compounds were analyzed only at the beginning and the end of the experiments by automated colorimetric method with 4-amino-antipyrine on acidified (with H_2SO_4) samples ($\text{pH} < 2$). The DOC was determined at 680°C using an infrared total organic C analyzer (SHIMAZU, Model TOCVcph). The $\text{NH}_4\text{-N}$ was determined by steam distillation in a basic medium (dilution with NaOH, $\text{pH} > 12$) of acidified samples (H_2SO_4 , $\text{pH} < 4$), and ammonium ions were measured with an ISE electrode (Orion 9512 HPBNWP). Total metal concentrations were analyzed by ICP-AES (PerkinElmer 3000 DV) on filtered ($0.45\ \mu\text{m}$) and acidified (with 2% v/v nitric acid) samples. Anion concentrations (F^- , Cl^- , NO_2^- , NO_3^- , PO_4^{3-} , SO_3^{2-} , SO_4^{2-} , Br^- , CNO^- , $\text{S}_2\text{O}_3^{2-}$, and SCN^-) were analyzed on filtered samples ($0.45\ \mu\text{m}$) using ion chromatography (Metrohm 881 Compact IC Pro). Speciation of dissolved As species (arsenite [As(III)], arsenate [As(V)], monomethylarsonic acid [MMA(V)], and dimethylarsinic acid [DMA(V)]) was analyzed (within the first hour after sampling) using the solid-phase extraction cartridge methodology (Watts et al., 2010). The strong anion exchange (SAX) and strong cation exchange (SCX) cartridges were preconditioned to wash the resin and promote the adsorption of As species. The SCX cartridge was preconditioned with 15 mL of 50% methanol followed by 15 mL of 1 M phosphoric acid and 5 mL of deionized water (18 M Ω cm). The SAX cartridge was preconditioned using 15 mL of 50% methanol and 5 mL of deionized water. Then, the separation was performed by passing a 30-mL water sample collected in a plastic syringe through a membrane filter of $0.45\ \mu\text{m}$ into an SCX cartridge connected in series to an SAX cartridge. The DMA(V) was retained onto the SCX cartridge, whereas both MMA(V) and As(V) were retained onto the SAX cartridge, and As(III) was not retained and was collected in the effluent. The SAX and SCX cartridges were detached and stored in individual sealed plastic bags. Prior to analysis with inductively coupled plasma mass spectrometry (ICP-MS Agilent 7700), different species from each cartridge were eluted; DMA(V) was eluted with 5 mL of 1 M nitric acid and 5 mL of 80 mM acetic acid for MMA(V), followed by 5 mL of 1 M nitric acid for As(V). The PHREEQC code, version 3.35.00, was used to evaluate the main precipitated minerals through calculation of saturation index (USGS, 2015). The simulation was run using the initial and final leachate quality, using the redox potential to determine the distribution of the element among its oxidation states.

Results

Pore Water Chemistry of Amended Tailings

The pH of collected leachates from all weathering cells remained stable (Fig. 1a) and complied with the Quebec discharge criteria (6–9.5), except for 100% peat ($\text{pH} 4.9 \pm 0.3$, Table 3; MDDELCC, 2012). The presence of residual neutralizing agents (lime and carbonate) in amended tailings may explain these findings (Table 1). In addition, the tailings amended with peat presented relatively higher Eh than those amended with

geotube sludge (Table 3). It is worth noting that the weathering cells that were operated in an open system could have influenced the Eh (Fig. 1b). The NO_3^- concentrations were high, especially in the geotube sludge, probably originating from the cyanide treatment. The $\text{NH}_4\text{-N}$ was only high at the beginning of the tests ($14\text{--}61\ \text{mg L}^{-1}$), except for peat, where it remained at $< 0.4\ \text{mg L}^{-1}$ across all the experiments (Supplemental Fig. S3). Water collected from the geotube sludge (alone [S100] or mixed with peat [SP10]) had greater electrical conductivity than the other weathering cells due to the presence of DOC, salts of Na, K, and Mg, anions, and metals or metalloids (Fig. 1c and 1d). Since the geotube sludge may still hold a residual neutralizing potential, the sludge-amended tailings had higher alkalinity ($9\text{--}162\ \text{mg CaCO}_3\ \text{L}^{-1}$) than those amended with peat ($0\text{--}89\ \text{mg CaCO}_3\ \text{L}^{-1}$) (Fig. 1e). The acidity was high in S100 and SP10 probably due to organic acids (from the sludge) and the hydrolysis of residual acidogenic metals (Fe and Al) in the sludge (Fig. 1f, Table 3). The fibric peat was reported to have a low leaching of organic compounds, particularly DOC (Moore and Dalva, 2001). Indeed, DOC concentration in P100 was $33 \pm 7\ \text{mg L}^{-1}$ and varied from 30 to $105\ \text{mg L}^{-1}$ in S100. These results confirm the probable low decomposability of the fibric peat used. The DOC concentration in SP10 could be as high as $255\ \text{mg L}^{-1}$, resulting from the cumulative soluble organic compounds from the geotube sludge and peat (Fig. 1d). Peat could then compromise the stability of sludge due to its acidity, which may enhance anion and metalloid dissolution.

Effects of Peat-based Amendments and Geotube Sludge on Arsenic and Other Metals Leaching in Tailings' Pore Water

First, important As release in pore water was found from the unamended tailings and the tailings amended with peat (TP5 and TP10), with concentrations exceeding the regulations ($10\ \mu\text{g L}^{-1}$, WHO, 2003; $0.2\ \text{mg L}^{-1}$, MDDELCC, 2012; $0.5\ \text{mg L}^{-1}$, Ministry of Justice of Canada, 2018) (Fig. 2a). The As concentrations in the pore water from these two weathering cells increased by 13 to 70% compared with tailings alone (T100). This was probably due to the maximal solubility of As at near-neutral pH (mean of 7.6 ± 0.3) in the presence of OM (Carbonell-Barrachina et al., 2000). Indeed, even at low concentrations ($1\text{--}20\ \text{mg L}^{-1}$), DOM may still influence As mobility and can even increase up to three times the As release in pore water through competition onto sorption sites, formation of soluble complexes, and electrostatic interaction (Redman et al., 2002; Bauer and Blodau, 2006; Wang and Mulligan, 2009; Hwang and Neculita, 2013). In the amended tailings, and at pH 7 to 9, As in the leachates would predominantly be under the form of As(V) as HAsO_4^{2-} or H_2AsO_4^- . For the control (T100), As(V) represented up to 81% of the total As (with a mean of 53%), whereas As(III) was $\sim 9\%$, at a weak alkaline pH (8.1 ± 0.6) and oxidizing condition ($\text{Eh} = 482 \pm 277\ \text{mV}$) (Fig. 2a'). With an amendment of 5% peat (TP5), As(III) and As(V) concentrations increased to 11 and 60%, respectively ($\text{pH} 7.8 \pm 0.4$; $\text{Eh} = 441 \pm 286\ \text{mV}$) (Fig. 2a'). Then, with an amendment of 10% peat (TP10), As(III) became predominant (44%) over As(V) (34%) ($\text{pH} 7.4 \pm 0.3$ and $\text{Eh} = 423 \pm 268\ \text{mV}$). The methylated species (monomethylarsonic [MMA(V)] and dimethylarsinic [DMA(V)]) were at very low

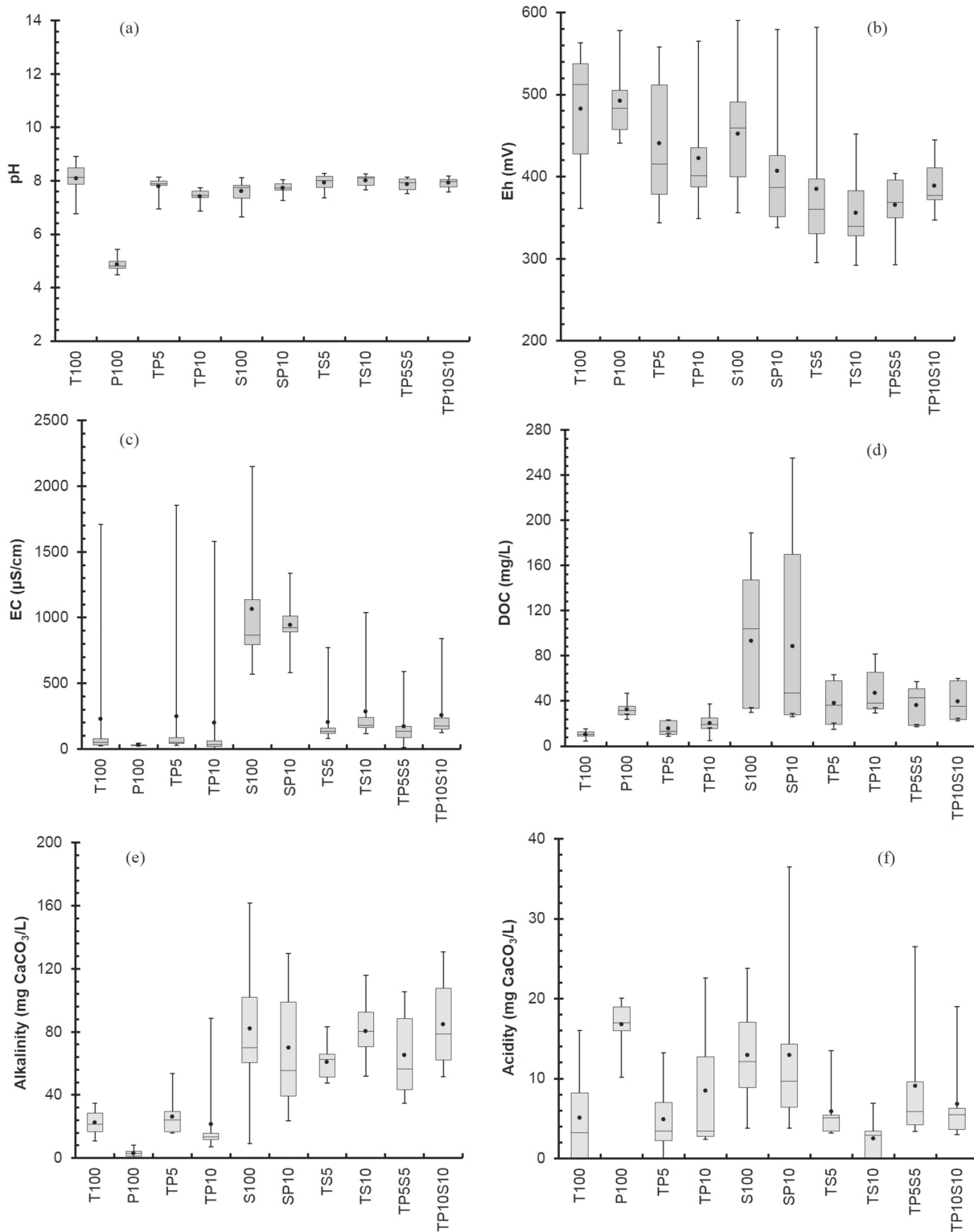


Fig. 1. Physicochemical characteristics [(a) pH, (b) redox potential (Eh), (c) electrical conductivity [EC], (d) dissolved organic C [DOC], (e) alkalinity, and (f) acidity] of leachates collected from either unamended tailings or amended with peat and/or Fe-rich sludge tested in mini-cells experiments for a total duration of 112 d (T100, 100% tailings; P100, 100% peat; TP5, 95% tailings + 5% peat; TP10, 90% tailings + 10% peat; SP10, 90% sludge + 10% peat; TS5, 95% tailings + 5% sludge; TS10, 90% tailings + 10% sludge; TP5S5, 90% tailings + 5% peat + 5% sludge; TP10S10, 80% tailings + 10% peat + 10% sludge).

concentrations in T100 (0–5.1 µg L⁻¹) and represented <2.4% (0.3–14.2 µg L⁻¹) of the total As in TP5 and TP10, with the highest proportion of DMA(V) in TP10. The increasing proportion of As(III) in TP10 compared with TP5 could be due to the low oxidation kinetics of As(III) into As(V) at the highest

content in DOM (DOC and phenolic compounds). As already mentioned, the As-bearing minerals in the tested tailings were arsenopyrite (FeAs) and löllingite (FeAs₂). Literature reported that As(III) was the predominant species in solution during the oxidation of these minerals (Filippi, 2004; Yunmei et al., 2004).

Table 3. Pore water quality of peat-amended and unamended tailings during a 112-d experiment in weathering cells.

Parameter†	Unit	Cell#									
		T100	P100	TP5	TP10	S100	SP10	TS5	TS10	TP555	TP10S10
pH	-	6.77-8.91	<u>4.47-5.44</u>	6.95-8.14	6.86-7.75	6.64-8.12	7.27-8.04	7.36-8.28	7.67-8.25	7.52-8.14	7.58-8.17
Eh	mV	361-563	441-578	344-558	349-565	356-590	338-579	295-582	292-452	293-404	347-445
EC	$\mu\text{S cm}^{-1}$	22.3-1711	23.5-43	26-1856	3.4-1578	474-2150	517-1337	82-770	118-1039	11.4-588	126-841
Acidity	$\text{mg CaCO}_3 \text{ L}^{-1}$	0-16	10.2-20.1	0-13.2	2.4-22.6	4-24	4-37	3.1-14	0-7	3.4-27	0-19
Alkalinity	$\text{mg CaCO}_3 \text{ L}^{-1}$	11-35	0-8	16-54	7.3-89	9-162	23-130	48-83.3	52.1-116	35-106	52-131
NH_4^+	mg L^{-1}	0.001-16	0.001-0.4	0.001-17	0.001-14	0.014-47.3	0.05-61	0.02-28.2	0.021-34	0.03-15.1	0.02-22.4
DOC	mg L^{-1}	9-15.1	24-36	10.4-37.3	15.4-25.5	30-105	26-255	26-84	15-63	17-45	22-60
NO_2^-	mg L^{-1}	<0.7	<0.7	<0.7	<0.7	0.7-238	0.7-33.3	0.7-5	0.7-4	0.7-4	0.7-14.1
NO_3^-	mg L^{-1}	0.7-65	0.7-54	0.7-59	0.7-7	0.7-378	3.3-257	0.7-56	0.7-15	0.7-65	0.7-38
Cl^-	mg L^{-1}	0.7-3.4	0.7-4.3	0.7-4	0.7-3	0.7-171	22-65	2-17	0.7-23	0.7-11.4	0.7-21
Al	mg L^{-1}	0.052-0.23	0.3-0.7	0.11-0.35	0.06-0.5	0.021-0.05	0.1-0.2	0.05-0.1	0.03-0.073	0.1-0.16	0.04-0.273
As	mg L^{-1}	<u>0.208-1.14</u>	<0.06	<u>0.58-1.11</u>	<u>0.65-1.44</u>	0.06-0.11	0.06-0.102	0.087-0.221	0.09-0.199	0.072-0.133	0.04-0.168
Ba	mg L^{-1}	0.001-0.037	0.005-0.009	0.001-0.018	0.001-0.052	0.001-0.047	0.002-0.036	0.004	0.004-0.01	0.003-0.005	0.004-0.013
Ca	mg L^{-1}	1.92-273	0.955-3.61	2.75-237	1.1-219	104-186	128-185	12.7-23.1	18.5-38.2	11-19	20-38.3
Co	mg L^{-1}	0.004-0.3	<0.004	0.005-0.3	0.004-0.3	0.025-0.2	0.1-0.2	0.01-0.03	0.011-0.053	0.012-0.03	0.014-0.04
Cu	mg L^{-1}	0.01-0.022	0.005-0.035	0.003-0.02	0.005-0.027	0.003-0.011	0.003-0.009	0.003-0.006	0.003-0.006	0.003-0.005	<0.012
Fe	mg L^{-1}	0.04-0.13	0.38-2.02	0.031-0.272	0.043-0.501	0.4-2.43	0.85-2.08	0.15-0.262	0.24-0.62	0.15-0.26	0.14-0.48
K	mg L^{-1}	3.2-70	1.7-3.7	4.4-66	2.1-61	21.3-39	22.1-32.4	6-11	8.3-14.2	6.5-12.1	10.1-15.4
Li	mg L^{-1}	0.008-0.083	0.017-0.038	0.007-0.073	0.004-0.091	0.04-0.088	0.04-0.05	0.01-0.02	0.02-0.03	0.01-0.02	0.02-0.03
Mg	mg L^{-1}	0.3-10	0.7-1.2	0.3-3.1	0.2-13.3	4.6-8.3	5.4-8	0.5-0.9	0.9-1.6	0.6-1.2	1.0-2.1
Mn	mg L^{-1}	0.002-0.097	0.033-0.061	0.002-0.022	0.002-0.262	0.015-0.03	0.012-0.025	0.002-0.003	0.003-0.004	0.002-0.005	0.003-0.008
Na	mg L^{-1}	0.734-146	0.6-1.16	1.1-132	0.8-121	25-100	33-61	1.1-6.3	1.2-9.1	1.2-5.2	1.5-8
Ni	mg L^{-1}	0.004-0.022	0.004	0.004-0.011	0.004-0.04	0.036-0.043	0.022-0.042	<0.009	<0.009	<0.006	<0.007
S	mg L^{-1}	0.734-346	1.31-7.3	0.861-320	0.4-299	75-114	72.2-128	1.4-8.4	2.13-15	1.8-7.3	3-12
Si	mg L^{-1}	5.63-16.4	7-20	3.3-19	8.5-19.2	5.6-11.4	3.6-133	41-55.2	23-72.4	7.4-79	4.4-104
Zn	mg L^{-1}	0.005-0.08	0.007-0.1	0.005-0.064	0.005-0.074	0.022-0.043	0.033-0.061	0.008-0.011	0.008-0.014	0.008-0.02	0.005-0.02

† Eh, redox potential; EC, electrical conductivity; DOC, dissolved organic C.

‡ T100, 100% tailings; P100, 100% peat; TP5, 95% tailings + 5% peat; TP10, 90% tailings + 10% peat; SP10, 90% sludge + 10% peat; TS5, 95% tailings + 5% sludge; TS10, 90% tailings + 10% sludge; TP555, 90% tailings + 5% peat + 5% sludge; TP10S10, 80% tailings + 10% peat + 10% sludge.

§ Underlined values do not respect the regulation criteria (As < 0.2 mg L^{-1} ; pH 6-9.5; (MDELCC, 2012).

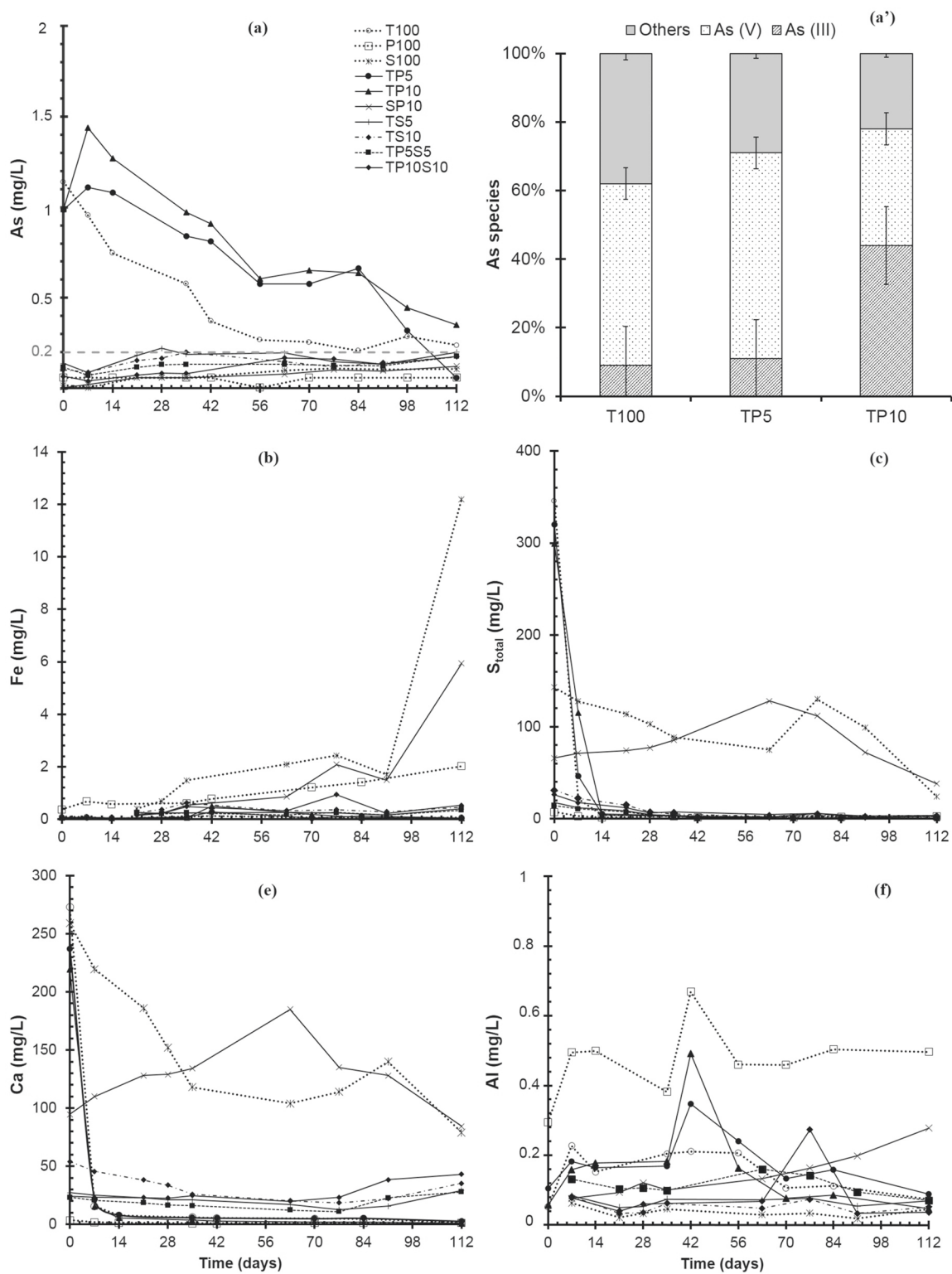


Fig. 2. Evolution of leached elements ([a, a'] As, [b] Fe, [c] total S [S_{total}], [d] Ca, and [e] Al) from the weathering cells during the 112-d period (T100, 100% tailings; P100, 100% peat; TP5, 95% tailings + 5% peat; TP10, 90% tailings + 10% peat; SP10, 90% sludge + 10% peat; TS5, 95% tailings + 5% sludge; TS10, 90% tailings + 10% sludge; TP5S5, 90% tailings + 5% peat + 5% sludge; TP10S10, 80% tailings + 10% peat + 10% sludge).

As such, the high proportion of As(V) in T100 could originate from the following:

1. Arsenopyrite or löllingite oxidation. Other studies reported that in the presence of aerated water, As present on the surface of arsenopyrite rapidly oxidizes (10 times greater than in air) from As(-I) and As(0) to As(II), As(III), and finally to As(V) (Nesbitt et al., 1995; Henke and Hutchison, 2009).

2. The oxidation of As(III) released into the solution during the oxidation of arsenopyrite (and löllingite) to As(V).

In TP5 and TP10, the redox active functional groups (e.g., carboxylic, ester, phenolic, quinone, amino, and sulfhydryl, hydroxyl) in DOM that are negatively charged at neutral pH (due to deprotonation) might have influenced As(V) reduction and As(III) oxidation (Macalady and Ranville, 1998; Redman et al., 2002). Hence,

the oxidation kinetics of As(III) could have been slowed down as the DOM content increased. The DOC in TP5 was $15.6 \pm 6.2 \text{ mg L}^{-1}$, then increased to $20.1 \pm 9.5 \text{ mg L}^{-1}$ in TP10. Since the separation of As species was performed right after sampling, the As(III) that was released from the oxidation of arsenopyrite might not have time to reach equilibrium. Hence, the ratio of As(III) to As(V) remained high (0.2–1.3). These findings are consistent with Weerasooriya et al. (2003), who reported As(III) and As(V) occurrence in oxic conditions because of the kinetic slow-process oxidation of As(III) to As(V). The high proportion of As(III) could also be partially explained by the reduction of As(V) by DOM. It is well known that DOM can modify As speciation through redox processes and the formation of DOM–As complexes (McArthur et al., 2001, 2004; Redman et al., 2002; Kumpiene et al., 2008). Moreover, the speciation change could have been catalyzed in the presence of metal (hydro)oxides where DOM could form aqueous complexes with As(III) and As(V) (Redman et al., 2002). Hematite was reported as a surface catalyst or electron-transfer intermediate between the DOM and As(V) (Redman et al., 2002). Indeed, in the present study, the tailings contained $\sim 5\%$ hematite.

Second, leached As concentrations from tailings decreased down to 65 to 80% with addition of “geotube sludge” or “peat + geotube sludge” amendments, allowing to respect the regulatory requirements ($<0.2 \text{ mg L}^{-1}$). Adsorption of As on Fe or Al oxides from the geotube sludge could have favored its removal. In addition, the geotube sludge had high CEC ($46 \text{ cmol[+]} \text{ kg}^{-1}$), and at pH between 7.4 to 8.25, its surface is positively charged (zero point charge pH 8.26), thus attracting oxyanions. Besides, the OM could have chelated the dissolved Fe or Fe oxides colloids in solution, thereby forming stable colloidal complexes of As-Fe-OM (Lin et al., 2004; Ritter et al., 2006). The formation of Ca-arsenate phases could also occur, considering the high Ca content of the geotube sludge (27%). However, at the end of the experiment, Fe concentrations increased seven times and four times in leachate water from S100 and SP10, respectively (Fig. 2b). Contrarily, smaller increases in Fe concentrations (two to three times) and total As concentrations (1.2 to 1.5 times) in leachates from tailings amended with “geotube sludge” and “peat + geotube sludge” were found (Fig. 2a). The coprecipitated and adsorbed As on the surface of Fe oxides and/or hydroxides could have been released due to the reductive dissolution of these oxides and/or hydroxides (Zhang et al., 2018). The reductive dissolution of Fe oxides and/or hydroxides could have been promoted by the DOC (Lindsay et al., 2009, 2011). The decrease in SO_4^{2-} concentrations to $<2 \text{ mg L}^{-1}$ corroborates the reducing condition in all cells, except for S100 and SP10, where total S and SO_4^{2-} concentrations in leachates remained high (Fig. 2c, Supplemental Fig. S4). Calcium concentration in S100 and SP10 leachates was also high, probably originating from the lime used during the mine drainage water treatment (Fig. 2d). Lime could have been dissolved during reaction with protons generated by the oxidation and hydrolysis of Fe. Other metallic element concentrations in all weathering cells were initially very low ($<0.3 \text{ mg L}^{-1}$) and stayed low until the end of the experiments, except for Al (Fig. 2e).

Discussion

Overall, the results of the current study showed that As leaching was enhanced in gold tailings amended with peat alone, but

the leaching was limited with the addition of Fe-bearing materials. In the absence of Fe, Al, or Mn oxides and/or hydroxides, peat-based amendments for tailing reclamation were previously reported to potentially mobilize metalloids (Kumpiene et al., 2008; Lindsay et al., 2009, 2011). In the same time, peat could be used for tailing stabilization, as organic acids (humic and fulvic acids) are able to form stable complexes with metal cations ($\text{Fe}^{3+} > \text{Al}^{3+} > \text{Pb}^{2+} > \text{Ca}^{2+} > \text{Mn}^{2+} > \text{Mg}^{2+}$) (Gu et al., 1994; Abad-Valle et al., 2017). Peat also has high CEC ($94 \text{ cmol[+]} \text{ kg}^{-1}$) and allows efficient immobilization of metal cations from pore water. Peat mixed or modified with Fe-based materials was effectively used for efficient removal of metalloids (Ansone et al., 2013; Kumpiene et al., 2013). In the present study, the amendment of peat mixed with Fe-rich sludge decreased up to 85% the total As concentrations in tailings. Other studies showed that Fe-peat amendments improved water-holding capacity of soil, sustained high redox potential, yielded a low bulk density, and offered better air diffusion to the deeper layers of soil (Kumpiene et al., 2013). As a result, the stability of Fe oxides and Fe-bound As favored the decrease of dissolved As in soil pore water throughout the first 2-m soil profile (Kumpiene et al., 2013). Moreover, aged amorphous Fe oxides were found to have a stronger attachment of potentially available As (Seidel et al., 2005). It was also reported that peat contained stable OM with a high degree of humification, and gradual decrease of DOC occurred after 2 yr of experiment with “Fe + peat” amendment (Kumpiene et al., 2013). Fibric peat mixed with Fe-rich sludge may represent a more suitable amendment option for tailing reclamation provided that sludge characteristics do not present major change over time (e.g., increased OM content). An amendment of 5% peat + 5% geotube sludge potentially would be enough given the similar As release behavior in TP5S5 and TP10S10 (tailings amended with 5% peat + 5% geotube sludge and tailings amended with 10% peat + 10% geotube sludge, respectively). Despite the advantages of Fe-based amendments in As immobilization, the long-term stability has yet to be confirmed. The apparent satisfactory pH and redox conditions yielded with a mixed amendment of Fe-rich sludge and peat do not exclude a potential release of As from the amended tailings’ pore water in the presence of OM. The geotube sludge showed greater potential decomposition rate of OM than fibric peat OM. Hence, the latter can be easily spread to deeper soil layers and catalyze other redox reactions (Kumpiene et al., 2013). The use of “Fe + sewage sludge” as amendment of As-rich soil was reported to promote a lower redox potential, a sulfidization accelerated by the presence of microorganisms and a high risk of As release (Kumpiene et al., 2013). The reducing conditions associated with OM decomposition could cause the dissolution of the Fe oxyhydroxides that immobilized As, resulting in the release of As in the aqueous phase (Paktunc, 2013). Considering that neo-formed soluble Ca-Fe arsenate and/or Ca-arsenate could be present, Fe enrichment could also be entailed by the dissolution of the formed mineral and the increase in As leaching, depending on the Ca/Fe ratio and As concentration (Pantuzzo and Ciminelli, 2010). Indeed, initial proportions of $\text{Ca}/(\text{Ca}+\text{Fe}+\text{As}) > 0.1$ tested in the materials (tailings, peat, and sludge) suggested a probable formation of Ca-Fe arsenate (Paktunc et al., 2015). However, PHREEQC modeling did not show a possible precipitation of Ca-Fe arsenate, probably due to the high solubility of the mineral,

but indicated that precipitation of Ca arsenate associated with Al could occur (arsenocandallite $[\text{CaAl}_3(\text{AsO}_4)_2(\text{OH})_5\text{H}_2\text{O}]$). Therefore, a change in the geotube sludge characteristics, especially the DOC content, could enhance the As release. The peat, via fulvic or humic acids, may also form stable complexes with mineral surfaces, inhibiting As adsorption onto Fe oxides and hydroxides (Kaiser et al., 1997; Grafe et al., 2001, 2002). A possible anoxic condition, stimulated by the high content in DOC, that could delay the stabilization process of As in the amended soils should also be considered. Adjusting Fe/As and Ca/As ratios of the mixture of amendment and tailings should be performed to ensure a longer stability of As in the tailings. A higher Fe/As molar ratio (≥ 4.5) and lower Ca/As molar ratio (< 6) would suggest long-term stability of As in the tailings (Seidel et al., 2005; Pantuzzo and Ciminelli, 2010).

In a long-term perspective of peat use, mixed or not mixed with geotube sludge, for tailing reclamation, two aspects should be carefully considered: (i) the potential leaching of DOC, and (ii) the stability of sludge. As the results of the present study show, the OM in peat not only increased the concentration of total As leached out from the amended tailings but also modified As speciation. As a result, the use of peat alone would not be recommended as organic amendment for tailings containing possibly problematic concentrations of metalloids, such as As.

Conclusion

The mobility of As from gold mine tailings amended with “peat alone” or “peat + geotube sludge” was evaluated over a 112-d period. The use of peat alone as amendment increased As leaching. Hence, 10% (dry weight) peat promoted the leaching of As(III) (most toxic form), whereas 5% (dry weight) promoted As(V) leaching. The increase in As(III) resulted either from the slow oxidation kinetics of As(III) from arsenopyrite or the reduction of As(V), which could have been favored by the presence of peat OM. The findings of the present study show that significant predominance of As(III) could occur when DOC is $\geq 20 \text{ mg L}^{-1}$ in the absence of Fe or Al oxides and/or hydroxides that could enhance As adsorption. The mobility of As is governed by many factors: pH, Eh, OM content including organic acids, and Fe and/or Al and Ca content. Fe-rich sludge amendment (alone or with peat) decreased the As concentration in leachates by 65 to 80%, but attention should be focused on the reductive dissolution of Fe oxides and/or hydroxides due to possible decomposition of OM from the sludge itself in the longer term. When defining the proportions of materials in mixtures, high Fe/As and low Ca/As molar ratios should be sought. Other studies should focus on the effectiveness of differing qualities of peat in terms of decomposition degree and pH with other types of tailings (e.g., with high metal cations, acid generating) in a long-term run.

Supplemental Material

Additional figures are presented in the supplemental material: a schematic preview of the tailings production from the gold ore processing (left) and the geotube sludge production from the water treatment plant (WTP) (Supplemental Fig. S1); mini-cells for wetting and drying cycles (Supplemental Fig. S2.); $\text{NH}_4\text{-N}$ concentrations from the weathering cells (Supplemental

Fig. S3); and sulfate concentrations from the weathering cells (Supplemental Fig. S4).

Conflict of Interest

The authors declare no conflict of interest.

Acknowledgments

This research has received financial support from the Natural Sciences and Engineering Research Council of Canada (NSERC) through the Canada Research Chairs Program, Mitacs as part of the Mitacs Accelerate Program, and the industrial partner Goldcorp Eleonore Mine. The authors want to sincerely thank Marc Paquin, Mélinda Gervais, Patrick Bernèche, and Joël Beauregard for technical assistance.

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