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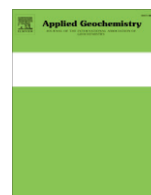
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Distribution, characterization, and geochemical controls of elements of concern in uranium mine tailings, Key Lake, Saskatchewan, Canada

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ABSTRACT

The distribution of As, Mo, Ni and Se in the aqueous and solid phases of U mine tailings in the Deilmann Tailings Management Facility (DTMF), located at the Key Lake mine in northern Saskatchewan, Canada, was defined using as-discharged tailings samples collected monthly starting in 1996 and core samples collected from the DTMF from 3 locations on 3 occasions between 2004 and 2009. These data indicated that the DTMF can be divided into two geochemical zones; tailings generated from the Deilmann ore body between 1996 and 2000 and tailings from the McArthur River ore body, mined after July 2000. The Deilmann tailings solids are generally characterized by greater elemental concentrations than those in the McArthur River tailings, particularly for As, Co and Ni. These elevated concentrations are attributed to the abundance of Ni–Co–As–S minerals in this ore. The mean aqueous concentrations of As, Mo, Ni, and Se are 3.7, 23.2, 0.14, and 0.02 mg L⁻¹, respectively, in the Deilmann porewaters and 0.20, 4.16, 0.06, and 0.03 mg L⁻¹, respectively, in the McArthur River porewaters. Similarly, the mean As, Mo, Ni, and Se solid phase concentrations are 5.89 × 10³, 69.9, 3.20 × 10³, and 17.4 μg g⁻¹, respectively, for the Deilmann tailings and 440, 13.6, 551, and 3.03 μg g⁻¹ in the McArthur River tailings. Statistically, pH remained unchanged from the time of discharge while Eh values have remained oxic with no significant change between the two tailings types over 15 a of residence time. Results from sequential extractions, thermodynamic modeling, and results of complimentary research indicated that ferrihydrite solubility is the dominant control on aqueous As concentrations and also plays a role in controlling dissolved Mo, Ni and Se.

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1. Introduction

Uranium tailings in northern Saskatchewan, Canada, have been deposited below the groundwater table in engineered in-pit tailings management facilities (TMF) that have been constructed from mined out ore bodies (in-pit). These TMFs have been designed to create low hydraulic gradients across the tailings body. This ensures that the migration of aqueous elements of concern (EOC) from the low hydraulic conductivity tailings to the surrounding groundwater will be dominated by diffusive transport (Gulf, 1981), thus minimizing the flux of EOCs from the tailings body to the surrounding groundwater.

Based on their potential adverse effects on human health, EOC in the TMFs include As, Mo, Ni and Se (e.g., Lener and Bibr, 1984; US EPA, 1998; Goldhaber, 2003). Arsenic has been the most studied EOC, with detailed geochemical investigations conducted at the

Rabbit Lake In-pit TMF (RLITMF; Donahue et al., 2000; Donahue and Hendry, 2003; Moldovan et al., 2003, 2008) and the McClean Lake TMF (JEB; Langmuir et al., 1999, 2006; Mahoney et al., 2005) (Fig. 1). These studies demonstrate a strong relationship between Fe, often added during the milling process, and As, naturally occurring in the mined ore, concentrations and the amount of As sequestered within the tailings solid phase. Through a series of sequential extractions, X-ray diffraction (XRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM) analyses on RLITMF samples, Pichler et al. (2001) concluded that As in the tailings is mainly adsorbed on 2-line ferrihydrite and approximately 20% remains bound within sulfide minerals present in the originally mined U-ore. XRD and synchrotron-based analyses were used by Moldovan et al. (2003) to demonstrate that As in the RLITMF occurs primarily as As(V) and is adsorbed onto the surface of a 2-line ferrihydrite. In a study focused on tailings generated for the JEB TMF, Langmuir et al. (1999) showed that As is precipitated as scorodite at low pH, and ferrihydrite formation increases as the pH is increased by the addition of slaked lime. In addition, these authors suggest that As is retained by the precipitated ferrihydrite

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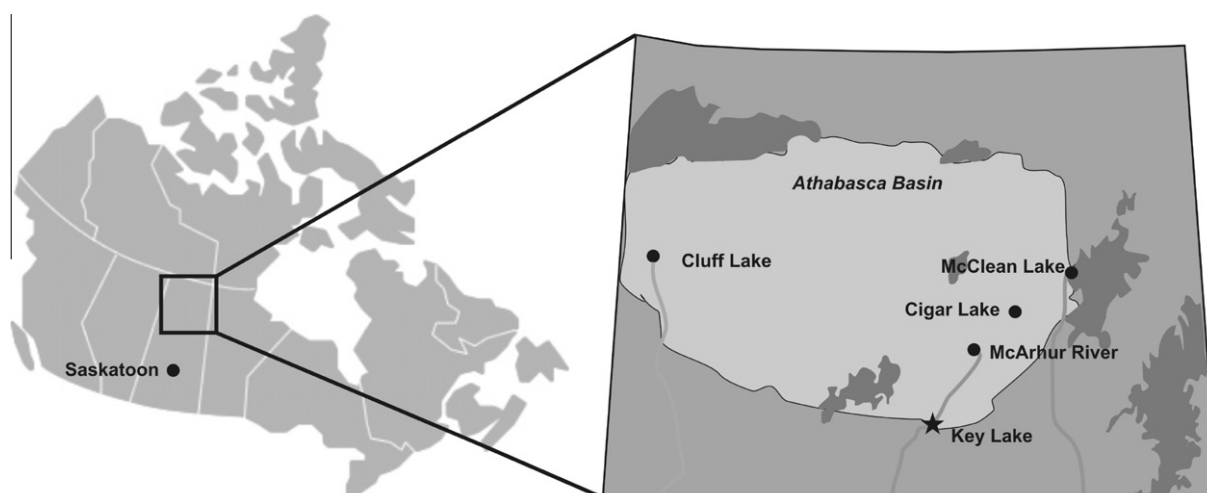


Fig. 1. Location map for Key Lake and McArthur River mine sites.

when the Fe:As molar ratio is sufficiently above 1:1 and at pH values <8.0.

More recently, the mineralogical controls on As, Se, Mo and the associated elements Ni and Fe have been studied at the Key Lake Deilmann TMF (DTMF; Essilfie-Dughan et al., submitted for publication-a) (Fig. 1). X-ray absorption spectroscopy (XAS) conducted on selected tailings solids samples from the DTMF show that these EOCs are mainly present as As(V), Fe(III), Mo(VI), Ni(II), and Se(IV), respectively. These reflect their oxidation states in the mill tailings neutralization circuits in as-discharged tailings slurries deposited in the DTMF. XAS spectra of the mine tailings indicate Mo exists mainly as NiMoO_4 and as molybdate adsorbed on ferrihydrite and CaMoO_4 (Essilfie-Dughan et al., 2011); As exists mainly as arsenate adsorbed on ferrihydrite (Essilfie-Dughan et al., submitted for publication-a).

To evaluate and predict the long-term fate and transport of EOCs in TMFs, a rigorous characterization of their present-day distribution and geochemical controls is warranted. Thus, the objectives of the current investigation were to determine the spatial and temporal distribution of EOC in the solid and aqueous phases and characterize the geochemical controls on EOC. In meeting these objectives, this study will provide baseline data for subsequent studies of the long-term (10 ka) mineralogical and geochemical controls within the DTMF and other TMFs for specific EOCs. The study objectives were met by collecting high-resolution vertical profiles of solid and aqueous parameters through the DTMF on 3 occasions between 2004 and 2009, measuring solid and aqueous parameters in the as-discharged tailings on a monthly basis since 1996, quantifying the mineralogy of solids, conducting sequential extraction testing of solid samples, determining speciation of dissolved As and Se, and geochemical modeling of aqueous phases.

2. Background

2.1. Setting

The Key Lake U mine is located at the southern rim of the Athabasca Basin in north-central Saskatchewan, approximately 650 km north of Saskatoon, Saskatchewan ($57^{\circ}13'N$, $105^{\circ}38'W$; Fig. 1). Mining operations commenced in 1983. The DTMF was constructed in the mined out Deilmann pit and consists of an east cell and a west cell (Fig. 2).

The deposition of mill tailings in the DTMF commenced in 1996. Tailings were initially deposited in the east cell until the Deilmann

ore body, located in the west cell, was mined out in 1999. Subsequently, tailings were deposited in both cells. The base of the DTMF was constructed with a pervious sand layer envelope (Fig. 2) to allow for de-watering and consolidation of the tailings. In 1998, tailings deposition in the DTMF was converted from subaerial deposition to subaqueous deposition by disabling the perimeter drains and allowing the facility to naturally flood. From 1998 to 2007, the depth of water overlying the tailings increased to 50 m. In the fall of 2001, sloughing of the sand surrounding the west cell resulted in the deposition of an extensive sand wedge over the west cell and the western portion of the east cell (Fig. 2).

2.2. Milling of ore

The milled ore feed has changed since the start of the DTMF operation. Between January 1996 and February 2000, the mill feed was derived entirely from the polymetallic U–Ni Deilmann ore body containing varying amounts of Ni–Co–As–S minerals (von Pechmann, 1981). Since March 2000, ore from the McArthur River mine, located 80 km north of Key Lake ($59^{\circ}27'N$, $104^{\circ}58'W$; Fig. 1), has been the primary source of mill feeds for the Key Lake mill. In general, the McArthur River ores are high-grade U ore bodies containing significantly fewer Ni–Co–As sulfide minerals than the Deilmann ore body (Jamieson and Frost, 1997).

The primary mineralogy of the Deilmann ore consists of chlorite, kaolinite, quartz and dolomite, with trace minerals associated with graphite, gersdorffite, vaesite, millerite, clausthalite, safflorite and jodisite (Carl et al., 1992). The McArthur ore consists of quartz, kaolinite, and chlorite, with trace metals associated with pyrite, chalcopyrite, covellite, and arsenopyrite (Delaney et al., 1998). A more detailed analysis of the McArthur ore by Heinrich et al. (2010), indicated Mo and Se associated with sulfides, uraninite, and phyllosilicates. During milling, the McArthur River ore is mixed with varying amounts of lower grade ores and waste materials from the Key Lake and McArthur River mines.

A conventional H_2SO_4 leach process is used to recover U from the ore. In general, the processed ore is acidified using H_2SO_4 after which the solubilized U is stripped from the acidic leachate using an organic solvent extraction process. Subsequently, the acidic raffinate reports to a series of 4 neutralization tanks (pachucas) where hydrated lime is added in stages to incrementally increase the pH (pH = 1.0, 3.5, 6.5, and 9.2). The slurry from the final pachuca (pH = 9.2) overflows to a tailings thickener where flocculent is added and the leach residues are recombined. Finally, lime

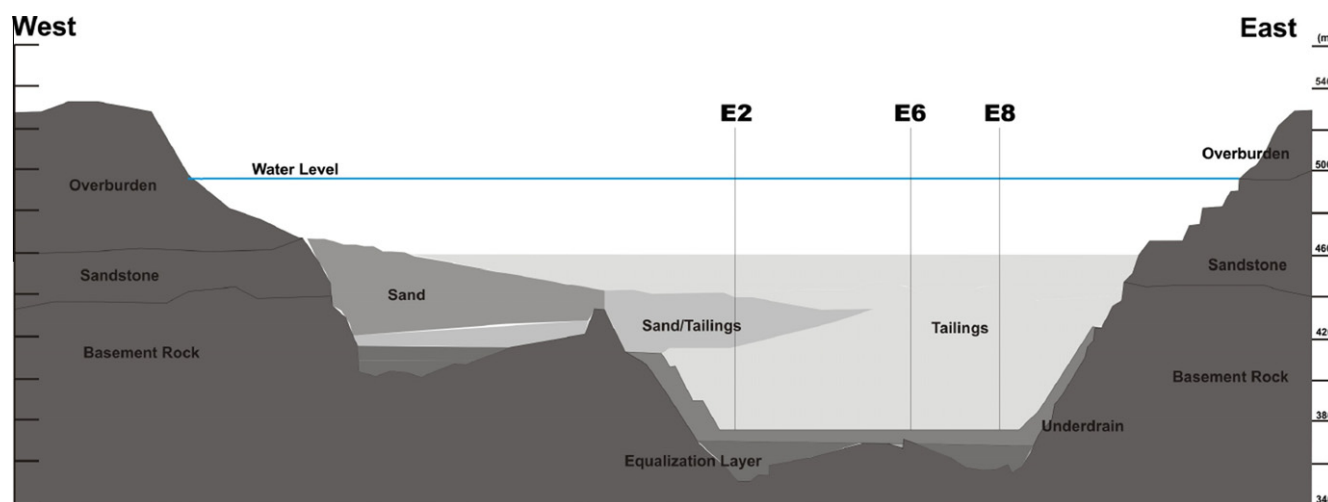


Fig. 2. Schematic cross section of the Deilmann tailings management facility as of 2009. The location of the tailings, sloughed sand, and local bedrock layers are presented as are the locations of the three coreholes (E2, E6, and E8).

is added to increase the final tailings discharge to approximately pH 10.5. In the milling process, most of the solubilized EOCs in the raffinate are precipitated as secondary minerals as lime neutralization proceeds. Discharged tailings contain approximately 35% solids which are largely comprised of original clay and silicate gangue minerals, minor sulfides and oxides and gypsum precipitates from neutralization.

3. Materials and methods

3.1. As-discharged tailings

Since 1996, the chemical composition of the as-discharged tailings was monitored on a monthly basis. Samples of as-discharged tailings slurries were collected in the mill on a daily basis. From these, sub-samples of pore water and tailings solids were combined in separate, sealed plastic containers throughout the month to make up monthly composite samples.

All aqueous samples were preserved with 0.2% HNO_3 (trace-grade). Monthly composite solid samples were homogenized and oven dried, then a 1 g sub-sample acid was digested with aqua regia ($\text{HNO}_3\text{-HCl}$), diluted, and analyzed for major and trace metals. Analyses were conducted on both aqueous and solid samples, using inductively-coupled plasma-optical emission spectroscopy (ICP-OES) for major and trace metals and ion chromatography for anions, with an RSD of $\pm 8\%$. Analysis of the monthly composite porewater and solids samples were completed within 30 days of sampling.

3.2. Core sampling

Coreholes were drilled at three locations along the central axis of the east cell (E2, E6, and E8) in 2004 (04-E6, 04-E8), 2005 (05-E2), 2008 (08-E2, 08-E6, 08-E8), and 2009 (09-E2) (Fig. 2) using a sonic, track mounted drill rig placed on a pontoon barge and positioned over each corehole with a series of cables and anchors. Successive corehole data collected at these sites were located within 5 m of the original corehole, hence providing an accurate spatially-equivalent representation of temporal changes in the tailings. All coreholes were drilled through 50 m of ponded water to depths between 30.9 m and 79.0 m below the tailings surface. Continuous core samples were collected from each corehole using a 3.1 m long \times 75 mm ID diameter core barrel. Samples were

retrieved on the barge by vibrating the core barrel into a plastic sleeve. Tailings samples were immediately logged for color, consistency, texture, and layering. After characterization, tailings were sampled at approximately 1 m intervals in 500 mL containers that were sealed and stored for moisture content and grain-size analyses. Tailings samples were also sampled at 1.5–3.0 m intervals in polyethylene containers that were tightly sealed and stored in the dark for geochemical analyses.

3.3. Solids analyses

Tailings solid samples from all seven coreholes ($n = 169$) were analyzed for major ions and trace metals. Prior to analysis, aliquots of the tailings solids were dried at 105°C and ground to <200 mesh with a ring grinder. Approximately 0.5 g of the dried tailings was digested on a hot plate with 20 mL of an aqua-regia acid mixture ($\text{HNO}_3\text{-HCl}$). Samples were digested until approximately 5 mL of acid remained and then diluted to 50 mL with de-ionized water. Major and minor ions, metals and trace elements were quantified using inductively-coupled plasma-mass spectroscopy (ICP-MS) and atomic emission spectroscopy (ICP-AES) with a relative standard deviation (RSD) of $\pm 10\%$. The results for As, Fe, Mo, Ni and Se will be discussed here.

The $>2\ \mu\text{m}$ fractions of 15 air-dried DTMF samples collected during the 2005 drill program from the Deilmann ($n = 10$) and McArthur River ($n = 5$) and were subjected to energy and wavelength dispersive X-ray analysis (EDX and WDX) and to X-ray diffractometry (XRD) and Rietveld analysis for mineral quantification. Residual sulfides were estimated for 22 solid samples from the Deilmann ($n = 12$) and McArthur River ($n = 10$) tailings, selected from corehole 08-E8, using LECO combustion and a dilute HCl digest. The detection limit for total S was 0.01 wt%. At least one standard was analyzed with every 20 samples and as the last sample in a run to ensure no significant drift in the instrument. In addition, sample blanks and repeat samples were analyzed.

3.4. Pore fluid geochemistry

Pore fluid samples ($n = 165$) were extracted from tailings samples within 24 h of collection using piston squeezing. Tailings samples of approximately 500 mL were placed in the cylinder of the piston squeezer and subjected to a force of approximately 4300 kPa. Extracted pore fluids were collected into 60 mL syringes and filtered in-line ($0.45\ \mu\text{m}$ cellulose acetate membrane) to

Table 1
Sequential extraction method for U tailings.

Extraction step	Reagent	Extraction process	Reference
1. Water soluble	Nanopure water; 20 mL	1 h shake, 25 °C, 10 mL rinse	Donahue and Hendry (2003)
2. Exchangeable	1 M Mg(NO ₃) ₂ ; 15 mL	4 h shake, 25 °C, 10 mL rinse	Krishnamurti et al. (1995) [*]
3. Metal–organic complexes	0.1 M Na ₄ P ₂ O ₇ ; 10H ₂ O; 30 mL	20 h, 25 °C, 10 mL rinse	Krishnamurti et al. (1995) [*]
4. Easily reducible oxides	0.1 M NH ₂ OH·HCl in 0.01 M HNO ₃ ; 20 mL	30 min shake, 25 °C, 10 mL rinse	Krishnamurti et al. (1995) [*]
5. Amorphous oxides	0.2 M (NH ₄) ₂ C ₂ O ₄ adjusted to pH 3.0 with 0.1 M oxalic acid; 10 mL	4 h shake (in dark), 25 °C, 10 mL rinse	Krishnamurti et al. (1995) [*]
6. Primary crystalline oxides	0.2 M (NH ₄) ₂ C ₂ O ₄ adjusted to pH 3.0 with 0.1 M ascorbic acid; 25 mL	30 min, 90 °C, 10 mL rinse	Krishnamurti et al. (1995) [*]
7. Residual	HNO ₃ –HCl–HClO ₄ ;		

^{*} All samples were centrifuged for 10 min at 3000 rpm before and after rinse step.

mitigate interactions with the atmosphere. All samples were stored at 4 °C prior to analysis.

The pH and Eh was measured on the squeezed pore fluids immediately after piston squeezing. pH was measured using an Orion glass combination electrode (Model 9102BN) calibrated with pH 4, 7, and 10 buffers. Eh values were measured using a VWR Symphony redox Pt electrode (Model 14002-858) calibrated using a redox standard (424 mV, 25 °C).

Filtered pore fluids were immediately placed in glass containers and acidified with trace-grade HNO₃ for major cation, trace metal, and radionuclide analyses. Aliquots for major anions and alkalinity were collected, unpreserved, in 50 mL HDPE containers. As, Fe, Mo, Ni and Se were quantified using a combination of ICP-MS and ICP-AES with a RSD of ±8%.

Samples for As ($n = 21$) and Se ($n = 11$) speciation were collected in 20 mL HDPE containers from selected squeezed porewater samples taken from corehole 09-E2, then frozen unpreserved and analyzed within 7 d of collection from the DTMF. Inorganic and methylated As oxy- and thio-As species were determined by anion-exchange chromatography–inductively-coupled plasma–dynamic reaction cell–mass spectrometry (AEC–ICP–DRC–MS) using conditions similar to previously published methods (Wallschläger and London, 2008; Wallschläger and Stacey, 2007). Inorganic Se species were determined by AEC–ICP–DRC–MS, using previously published separation (Wallschläger and Roehl, 2001) and detection conditions (Wallschläger and London, 2004). Total As and total Se were determined by ICP–DRC–MS using O₂ (Planer-Friedrich et al., 2007) or CH₄ (Petrov et al., 2011), respectively, as the reaction gases.

3.5. Sequential extractions

Sequential extraction methods were used to aid in the identification of minerals and complexes controlling the distribution of EOCs (As, Fe, Mo, Ni, Se) in one fresh as-discharged tailings collected from the mill in April 2009 and five tailings samples collected from each of the McArthur River and Deilmann tailings in June 2008. Extractions were also conducted on pure phase samples of ferrihydrite, goethite, hematite and scorodite to define the associated distribution of Fe and As.

The sequential extraction method (Table 1) was based on that of Donahue and Hendry (2003) and Krishnamurti et al. (1995). This method fractionates oxide bound species into four distinct extractions: (i) the pyrophosphate leach for secondary mineral phases, (ii) the hydroxylamine leach for easily reducible metal oxide bound species, (iii) the ammonium oxalate–oxalic acid leach for amorphous mineral phases, and (iv) the ammonium oxalate–ascorbic acid leach for primary crystalline minerals. Water soluble and readily exchangeable extractions were added to distinguish elements associated with gypsum and other water-soluble phases. Finally, a HNO₃–HCl–HClO₄ leach was used to target the residual

minerals remaining in the tailings samples after the first six extractions. Samples were air dried for 24 h and lightly crushed with a mortar and pestle prior to testing. Four replicates were included for each individual sample and the resulting extract solutions combined prior to analyses. Approximately 1 g of sample was combined with the required solution in a 50 mL centrifuge tube and constantly agitated using a wrist-action shaker and by hand every 5 min if heating above room-temperature was required. After mixing, the samples were centrifuged, the supernatant decanted, and 10 mL of nanopure water added to the residue to wash any remaining reagents from the remaining tailings solids. The samples were centrifuged again and the rinse solution combined with the supernatant. All samples were filtered through a 0.45 μm cellulose–acetate syringe filter and collected into 125 mL and 20 mL polyethylene bottles for cation and anion analyses. Extracts were analyzed as described in Section 3.3.

3.6. Statistical analysis

Statistical analyses were conducted to determine the presence of significant vertical or lateral differences in the aqueous and solid phases between or within the Deilmann and McArthur River tailings. The calculated means of Deilmann and McArthur River solid and dissolved EOC data from different sampling dates within

Table 2
Thermodynamic data for As complexes with Al, Ca, Fe, Mg, and Mn added to the LLNL database in PHREEQC.

Species	Dissociation reactions	Log <i>K</i>
Whiting (1992)		
MgH ₂ AsO ₄ ⁺	Mg ²⁺ + H ₂ AsO ₄ [−] = MgH ₂ AsO ₄ ⁺	1.52
MgHAsO ₄	Mg ²⁺ + HAsO ₄ ^{2−} = MgHAsO ₄	2.86
MgAsO ₄ [−]	Mg ²⁺ + AsO ₄ ^{3−} = MgAsO ₄ [−]	6.34
MnHAsO ₄	Mn ²⁺ + HAsO ₄ ^{2−} = MnHAsO ₄	3.74
MnAsO ₄ [−]	Mn ²⁺ + AsO ₄ ^{3−} = MnAsO ₄ [−]	6.13
FeH ₂ AsO ₄ ⁺	Fe ²⁺ + H ₂ AsO ₄ [−] = FeH ₂ AsO ₄ ⁺	2.68
FeHAsO ₄	Fe ²⁺ + HAsO ₄ ^{2−} = FeHAsO ₄	3.54
FeAsO ₄ [−]	Fe ²⁺ + AsO ₄ ^{3−} = FeAsO ₄ [−]	7.06
NiHAsO ₄	Ni ²⁺ + HAsO ₄ ^{2−} = NiHAsO ₄	2.90
FeH ₂ AsO ₄ ⁺	Fe ³⁺ + H ₂ AsO ₄ [−] = FeH ₂ AsO ₄ ⁺	4.04
FeHAsO ₄ ⁺	Fe ³⁺ + HAsO ₄ ^{2−} = FeHAsO ₄ ⁺	9.86
FeAsO ₄	Fe ³⁺ + AsO ₄ ^{3−} = FeAsO ₄	18.9
AlH ₂ AsO ₄ ⁺	Al ³⁺ + H ₂ AsO ₄ [−] = AlH ₂ AsO ₄ ⁺	4.04
AlHAsO ₄ ⁺	Al ³⁺ + HAsO ₄ ^{2−} = AlHAsO ₄ ⁺	9.86
AlAsO ₄	Al ³⁺ + AsO ₄ ^{3−} = AlAsO ₄	18.9
Bothe and Brown (1999)		
CaH ₂ AsO ₄ ⁺	Ca ²⁺ + H ₂ AsO ₄ [−] = CaH ₂ AsO ₄ ⁺	1.30
CaHAsO ₄	Ca ²⁺ + HAsO ₄ ^{2−} = CaHAsO ₄	2.66
CaAsO ₄ [−]	Ca ²⁺ + AsO ₄ ^{3−} = CaAsO ₄ [−]	4.36

each corehole (E2, E6, E8) were not significantly different. As such, tailings samples were grouped as either Deilmann or McArthur River tailings for each corehole location regardless of collection date for subsequent statistical analyses. Descriptive statistical analyses were conducted on all datasets to determine if they were normally distributed. For normally distributed datasets, a one-way, completely randomized, analysis of variance (ANOVA) was conducted to determine any significant spatial differences (vertical or lateral), using a least significant difference method to compare means. For datasets not normally distributed, the logarithmic values were analyzed for normal distribution and a Kruskal-Wallis test conducted to determine any significant spatial differences.

3.7. Saturation indices

The saturation indices (SI) of carbonates, arsenates, Fe hydroxides, and sulfate minerals were calculated using the PHREEQC geochemical modeling program (Parkhurst and Appelo, 1999) and measured pH, Eh, and aqueous geochemical data from the squeezed, in-pit tailings samples. The Lawrence Livermore National Laboratory (LLNL) thermodynamic database was used for geochemical modeling because of its inclusion of As, Fe, Mo, Ni, and Se thermodynamic data; additional thermodynamic data for Fe, Al, Mn, Mg and Ca arsenate complexes were added to this database (Table 2).

4. Results and discussion

4.1. Solids geochemistry

The solid phase concentrations of As, Fe, Mo and Ni for as-discharged Deilmann and McArthur River tailings are summarized

Table 3
As-discharged solids geochemistry entering the DTMF from the Key Lake milling process.

Parameter	Units	Min	25th	Median	75th	Max	Mean	Std. dev.	n
<i>Deilmann tailings (<410 masl)</i>									
As	$\mu\text{g g}^{-1}$	1500	4300	5800	8250	19,900	6571	3386	47
Ca	$\mu\text{g g}^{-1}$	3800	31,500	35,100	43,500	55,000	36,803	9357	47
Fe	$\mu\text{g g}^{-1}$	n/a	n/a	n/a	n/a	n/a	n/a	n/a	0
Mo	$\mu\text{g g}^{-1}$	10.0	65.0	90.0	100	500	99.1	73.6	47
Ni	$\mu\text{g g}^{-1}$	1100	4930	6100	8045	17,500	6633	3185	47
<i>McArthur tailings (>410 masl)</i>									
As	$\mu\text{g g}^{-1}$	3.94	240	479	705	7650	633	912	83
Ca	$\mu\text{g g}^{-1}$	6260	42,000	49,300	58,600	94,700	50,612	15,641	85
Fe	$\mu\text{g g}^{-1}$	10.0	11,180	13,300	14,460	33,860	12,109	5506	71
Mo	$\mu\text{g g}^{-1}$	2.32	22.0	30.3	96.0	550	67.1	83.7	84
Ni	$\mu\text{g g}^{-1}$	10.0	477	585	752	2230	641	373	83

Table 4
Solids geochemistry summary for the McArthur and Deilmann tailings within the DTMF, collected from borehole locations E2, E6, and E8 between 2004 and 2009.

Parameter	Units	Min	25th	Median	75th	Max	Mean	Std. dev.	n
<i>Deilmann tailings (<410 masl)</i>									
As	$\mu\text{g g}^{-1}$	165	3838	5890	7798	14,100	5888	3009	93
Ca	$\mu\text{g g}^{-1}$	35.0	30,575	39,600	45,575	80,700	37,438	17,082	93
Fe	$\mu\text{g g}^{-1}$	4600	13,525	16,400	18,500	23,500	15,761	4136	93
Mo	$\mu\text{g g}^{-1}$	9.00	52.0	68.0	85.0	183	69.9	29.9	93
Ni	$\mu\text{g g}^{-1}$	243	4090	5850	8325	14,300	6134	3203	93
Se	$\mu\text{g g}^{-1}$	1.40	13.3	18.5	22.0	33.0	17.4	6.65	93
<i>McArthur tailings (>410 masl)</i>									
As	$\mu\text{g g}^{-1}$	0.70	188	322	610	1850	440	394	74
Ca	$\mu\text{g g}^{-1}$	130	6645	19,200	38,500	82,300	25,020	20,727	74
Fe	$\mu\text{g g}^{-1}$	990	4570	7500	11,300	15,700	7780	4165	74
Mo	$\mu\text{g g}^{-1}$	0.60	6.50	13.0	20.0	33.0	13.6	8.69	74
Ni	$\mu\text{g g}^{-1}$	1.60	232	451	769	2180	551	477	74
Se	$\mu\text{g g}^{-1}$	0.00	0.75	2.80	4.63	8.30	3.03	2.23	74

in Table 3. The concentrations of As, Fe, Mo, Ni and Se in the *in situ* DTMF tailings solids from coreholes E2, E6, and E8 are summarized in Table 4 and presented with depth in Fig. 3.

Significant decreases in solid phase As and Ni concentrations in tailings were observed between the as-discharged Deilmann and McArthur River tailings. These differences are attributed to the greater proportion of Ni- and As-bearing sulfides in the polymetallic Deilmann orebody. Conversely, Mo values remained relatively equal between the two as-discharged tailings types. A comparison between as-discharged and *in situ* solid phase concentrations for each tailings type indicated that measured As and Ni values have remained largely unchanged since deposition in the DTMF. However, significant differences in solid phase Mo concentrations were observed between the as-discharged and *in situ* Deilmann and McArthur River tailings.

The vertical differences in the distribution of As and Ni with depth in the DTMF tailings solids can be directly related to the metallurgical processes and neutralized, as-discharged mill-slurries which correspond with the quantities of Ni, As, Co, Cu, Fe-bearing sulfides in the different ores (Deilmann, McArthur River). A similar observation was also made for the different tailings layers, representing different ore bodies mined, in the RLITMF (Donahue and Hendry, 2003). A comparison of Fe concentrations was not possible because solid phase Fe concentrations were not measured prior to June 2002.

For *in situ* tailings concentrations there were no significant differences in As, Mo, and Ni concentrations laterally between coreholes E2, E6, and E8. However, significant differences were observed laterally for Fe and Se values between E6 and E8 in the McArthur River tailings. These differences were attributed to temporal heterogeneity in tailings deposition across the DTMF. This variability was also observed in the RLITMF (Donahue et al., 2000) where the overall mill process for leaching and

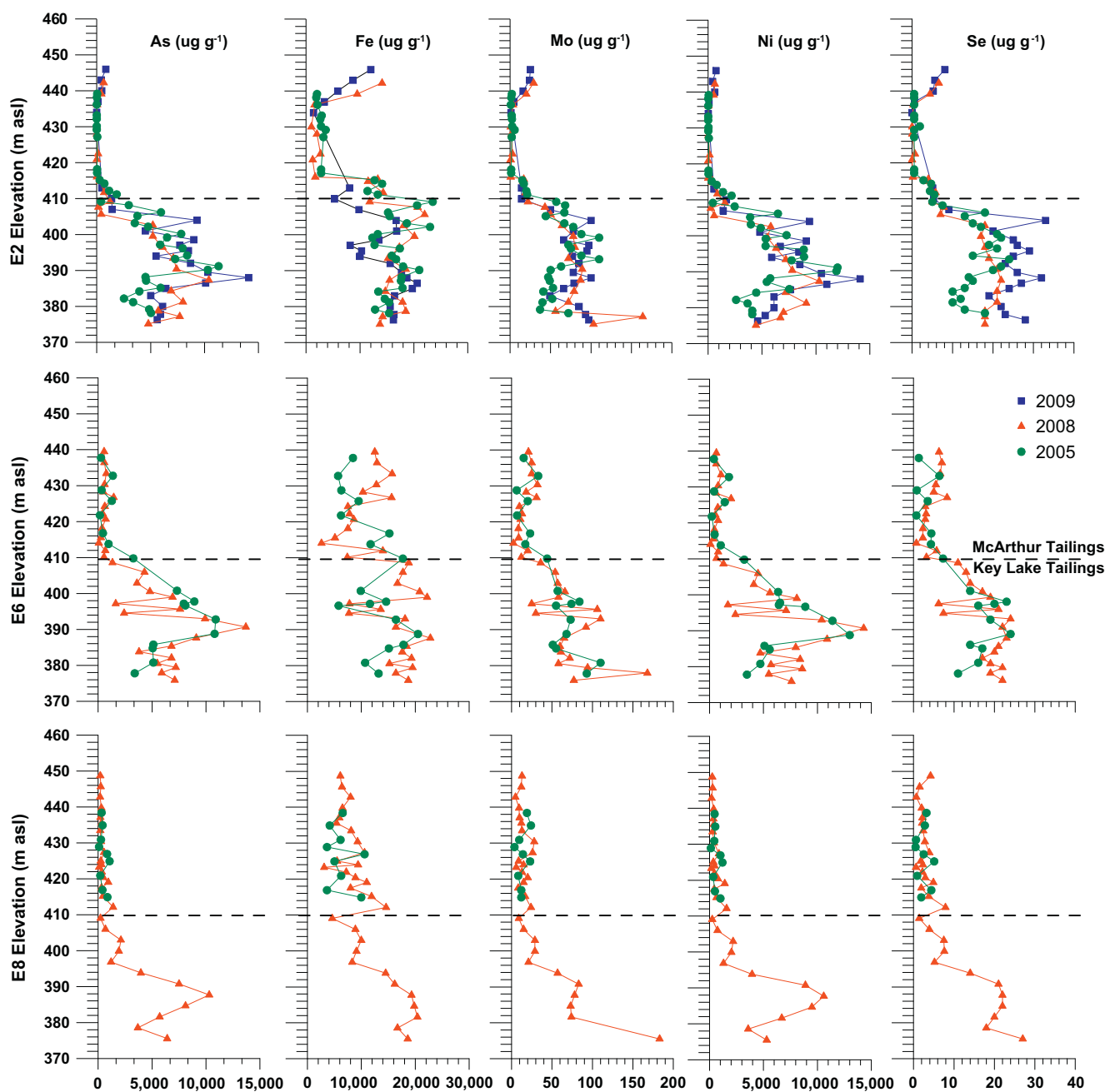


Fig. 3. Depth profiles for solid phase As, Fe, Mo, Ni and Se concentrations from corehole locations E2, E6, and E8. Collected between 2004 and 2009.

neutralization of the Rabbit Lake U ores is similar to that at Key Lake and the tailings are also deposited within an engineered in-pit tailings management facility; however, Rabbit Lake tailings are neutralized to approximately pH 8.5 and the DTMF tailings to 10.5 with slaked lime.

4.2. Element partitioning

Unpublished analyses of bulk Fe K-edge XANES spectra of tailings samples indicate that the presence of both pyrite and chalcopyrite (minor phases) in the Deilmann and McArthur River tailings, which is consistent with results obtained from electron microprobe analysis (Essilfie-Dughan et al., submitted for publication-b) as well as XRD analysis. Electron probe analysis (EMPA) as well as the XRD analysis by the authors also indicates the presence of

gersdorffite (NiAsS). These minerals have also been identified within the original U ores (Section 2.2), which indicates that the primary sulfide and arsenide minerals containing the EOCs are not completely solubilized during the milling process.

Major crystalline phases in the in-pit tailings, identified with XRD analyses, included quartz, gypsum, and phyllosilicates (muscovite, kaolinite, clinocllore) with minor amounts of sulfides (pyrite, chalcopyrite), goethite, and calcite. Moreover, mean sulfide values of 0.12 and 0.06 wt% were measured in the Deilmann ($n = 12$) and McArthur River ($n = 10$) tailings, respectively, and reflect the sulfide content in the leach residue of the corresponding ores. These identified mineral phases are typically associated with the crystalline gangue minerals (muscovite, kaolinite, goethite), residual minerals (sulfides, quartz), and water soluble phases (calcite, gypsum) in sequential extraction analyses (Krishnamurti

Table 5
Sequential extraction results for fresh, McArthur River, and Deilmann tailings. Summarized as percentage of total element sequestered in each of the 7 fractions analyzed.

Element	Tailings type	n	Water soluble	Exchangeable	Metal–organic	Easily reducible	Amorphous	Crystalline	Residual
As	Fresh tailings	1	1.1	3.6	30.2	1.3	55.2	2.5	6.0
	McArthur	5	1.5	5.1	31.8	5.6	38.6	2.3	15.0
	Deilmann	5	3.5	10.4	45.0	4.2	20.6	0.9	16.2
Fe	Fresh tailings	1	0.0	0.2	2.0	1.0	55.8	4.6	36.4
	McArthur	5	0.1	0.2	3.9	2.8	32.5	8.8	51.7
	Deilmann	5	0.0	0.1	6.4	2.6	30.7	12.1	48.2
Mo	Fresh tailings	1	29.0	7.6	13.3	1.2	20.9	15.0	12.9
	McArthur	5	10.7	5.9	37.1	3.5	19.1	11.4	12.2
	Deilmann	5	28.9	7.0	33.5	3.9	23.3	5.1	5.7
Ni	Fresh tailings	1	0.2	0.8	3.0	12.9	53.7	2.0	27.6
	McArthur	5	0.1	3.6	6.1	12.2	42.6	2.8	32.5
	Deilmann	5	0.1	1.3	8.5	11.8	35.0	3.1	38.4
Se	Fresh tailings	1	1.8	26.9	16.3	35.2	4.0	5.7	10.1
	McArthur	5	1.9	19.0	36.5	25.1	8.5	2.9	6.1
	Deilmann	5	10.3	24.8	26.0	11.5	11.7	3.8	11.0

et al., 1995). In a separate study, Fe K-edge X-ray absorption near edge structure (XANES) and X-ray absorption fine structure (XAFS) spectroscopic analyses (Essilfie-Dughan et al., submitted for publication-b), indicate the presence of both Fe(II) and Fe(III) in in-pit tailings samples, thereby supporting the presence of both ferrihydrite [Fe(III)(OH)₃] and primary Fe sulfide minerals (pyrite and chalcopyrite) in DTMF tailings solids. Previous laboratory and field-based studies (Fuller et al., 1993; Moldovan and Hendry, 2005; Mahoney et al., 2007) have demonstrated that ferrihydrite forms during progressive lime neutralization of the metallurgical raffinate solutions, during U ore processing.

Data from sequential extraction analyses of fresh, Deilmann, and McArthur River tailings indicate the majority of solid phase Fe is associated with the amorphous and residual phases with a lesser fraction associated with the crystalline phase (Table 5). The great amount of residual phase Fe was attributed to the presence of primary Fe minerals, such as sulfides, in the leach residue. Accordingly, the mean Fe solid phase concentration measured in the Deilmann tailings ($1.4 \times 10^4 \mu\text{g g}^{-1}$) was nearly twice that measured in the McArthur River tailings ($8.6 \times 10^3 \mu\text{g g}^{-1}$).

The majority of the recovered As and Ni in the Deilmann and McArthur River tailings was associated with the amorphous, metal–organic complexes, and residual phases (Table 5). Within the mill, initial oxic leaching (Eh \sim 600 mV) of the U ores and subsequent mill-based neutralization of raffinates with lime (Ca(OH)₂) would suggest that primary arsenide (As⁻¹) in sulfide minerals is liberated as biarsenate (HAsO₄²⁻). Similarly, Ni released from the Ni–As–S minerals should largely be sequestered as a Ni(OH)₂ solid phase or, to a lesser extent, as hydrated Ni arsenate phases (e.g. Cabrerite – (Ni,Co)₃(AsO₄)₂–8H₂O; Annabergite – Ni(AsO₄)₂–8H₂O). The pH of the tailings (\sim 10) is in the stability range of Theophrastite (Ni(OH)₂) and its presence has previously been identified in a mineralogical study of neutralized raffinate solution in an U mill (Mahoney et al., 2007). Recent micro-scale mineralogical studies, based on electron microprobe analysis and synchrotron-based micro-focusing X-ray fluorescence mapping and absorption spectroscopy, showed that some Ni is also adsorbed on ferrihydrite (Essilfie-Dughan et al., submitted for publication-b). Overall, the sequential extraction data suggests that secondary As and Ni precipitates or complexes dominate the tailings, with residual primary sulfides contributing a lesser amount.

The association of As with the amorphous phase extracts and prevalence of ferric iron oxides within the tailings (Essilfie-Dughan et al., submitted for publication-a) suggests it is associated with ferrihydrite through co-precipitation or adsorption to the surface. Due to the similarity in raffinate neutralization processes at Key

Lake and Rabbit Lake U mills, this association can be inferred to be the same as that studied by Moldovan et al. (2003), who indicated arsenate (HAsO₄²⁻) was associated with ferrihydrite. The considerable difference in amorphous phase Fe and As observed between the freshly discharged and *in situ* McArthur River tailings, relative to the older Deilmann tailings, suggests a decrease in ferrihydrite, due to a decrease in Fe associated with the amorphous fraction, with tailings age. The relative standard deviation (% RSD, Table 5) of the amorphous extraction results for Fe were 17%, 55%, and 35%, for the freshly discharged tailings, *in situ* McArthur River tailings, and *in situ* Deilmann tailings samples. These associations are, however, attributed to lesser amounts of Fe within the DTMF and the low resolution of the extraction techniques used, which preclude rigorous quantitative comparisons.

For both the Mo and Se sequential extraction results, the relative amount associated with each fraction was not well correlated to tailings age. Regardless of tailings age, Mo was shown to be primarily associated with the metal–organic complexes and easily reducible phases such as hydrous metal oxides, and with the readily mobilized water and exchangeable fractions (Table 6). Similarly, Se was also partitioned amongst several fractions with a majority in the metal–organic complexes and easily reducible phases, and substantial amounts associated with the exchangeable and residual phases (Table 6).

The substantial amounts of Mo and Se associated with the water and exchangeable fractions suggest weak adsorption to ferrihydrite, which formed during the milling process, and predominates within the mill slurries and DTMF tailings. Selenium and Mo are chalcophile and siderophile elements, respectively, with affinities for primary sulfides and Fe-bearing minerals (oxides, sulfides) co-located or associated with the original U ore bodies (Smirnov et al., 1983). The relatively small percentages of Se and Mo associated with the residual fractions suggest both were preferentially mobilized from sulfide phases during the milling process. With respect to Mo, the sequential extraction results broadly correspond with synchrotron and geochemical analyses that demonstrate Mo occurs as a complex with Fe, Ni and Ca in the tailings solids (Essilfie-Dughan et al., 2011).

4.3. Aqueous geochemistry

The median pH values measured in the as-discharged Deilmann and McArthur River mill slurries indicated no significant differences between tailings bodies (Table 6). Laboratory measured pH values were relatively constant between and within each corehole location and exhibited no significant differences between the

Table 6

Summary of the as-discharged dissolved concentrations reporting to the DTMF from 1996 to 2008.

Parameter	Units	Min	25th	Median	75th	Max	Mean	Std. dev.	n
<i>Deilmann tailings (<410 masl)</i>									
pH		8.81	9.53	9.86	10.1	11.1	9.83	0.48	45
As	$\mu\text{g L}^{-1}$	39.4	1853	3638	5088	8380	3693	2148	48
Ca	mgL^{-1}	7.30	603	636	684	981.0	613	157	48
Fe	mgL^{-1}	0.01	0.01	0.01	0.01	0.7	0.03	0.10	48
Mo	mgL^{-1}	0.72	19.0	22.80	28.2	47.0	23.2	9.03	48
Ni	mgL^{-1}	0.01	0.01	0.03	0.11	1.9	0.14	0.31	48
Se	mgL^{-1}	0.00	0.01	0.02	0.03	0.1	0.02	0.02	48
so ₄	mgL^{-1}	139	1500	1660	1819	2951	1638	415	48
<i>McArthur tailings (>410 masl)</i>									
pH		9.03	9.78	10.1	10.3	11.9	10.1	0.50	82
As	$\mu\text{g L}^{-1}$	7.80	90.2	129	262	1120	200	201	107
Ca	mgL^{-1}	230	596	643	672	845	634	76.7	107
Fe	mgL^{-1}	0.00	0.01	0.01	0.0	0.6	0.03	0.07	107
Mo	mgL^{-1}	0.01	3.24	3.96	4.7	11.3	4.16	1.72	107
Ni	mgL^{-1}	0.01	0.01	0.03	0.1	0.7	0.06	0.09	107
Se	mgL^{-1}	0.00	0.02	0.03	0.0	0.1	0.03	0.02	107
so ₄	mgL^{-1}	406	1531	1596	1653	2103	1574	229	107

Table 7

Summary of the DTMF porewater geochemistry from samples collected from coreholes E2, E6, and E8 during the 2004/05, 2008, and 2009 drill programs.

Parameter	Units	Min	25th	Median	75th	Max	Mean	Std. dev.	n
<i>Deilmann tailings (<410 masl)</i>									
pH		7.71	9.50	9.69	9.90	10.7	9.62	0.54	94
Eh	mV	-100	129	180	234	472	189	79.2	94
Alkalinity	mg L^{-1} (as HCO_3^-)	47.0	86.0	108	147	356	117	46.5	94
As		550	3670	5605	6270	14,100	3780	3618	94
Ca	mg L^{-1}	490	617	630	640	750	612	58.3	94
Fe	mg L^{-1}	0.00	0.01	0.01	0.01	0.26	0.01	0.02	94
Mo	mg L^{-1}	3.67	16.2	24.8	26.7	41.5	15.1	11.5	94
Ni	mg L^{-1}	0.02	0.03	0.03	0.04	0.13	0.04	0.02	94
Se	mg L^{-1}	0.02	0.04	0.05	0.05	0.08	0.04	0.02	94
SO ₄	mg L^{-1}	1410	1658	1800	1870	2200	1678	208	94
<i>McArthur Tailings (> 410 masl)</i>									
pH		7.63	9.49	9.82	10.0	10.5	9.62	0.71	65
Eh	mV	-64.0	177	221	263	472	220	84.4	65
Alkalinity	mg L^{-1} (as HCO_3^-)	44.0	78.0	122	154	230	119	50.1	61
As		6.30	288	470	680	2600	567	441	65
Ca	mg L^{-1}	260	561	623	640	670	597	70.2	65
Fe	mg L^{-1}	0.00	0.00	0.01	0.01	0.26	0.02	0.03	65
Mo	mg L^{-1}	0.29	2.65	3.99	4.98	8.85	4.13	2.00	65
Ni	mg L^{-1}	0.02	0.03	0.04	0.06	0.13	0.05	0.02	65
Se	mg L^{-1}	0.00	0.01	0.02	0.03	0.06	0.02	0.01	65
SO ₄	mg L^{-1}	1180	1440	1500	1600	1700	1518	116	65

in situ McArthur River and Deilmann tailings. Similarly, as-discharged pH values in both tailings types were statistically equal to *in situ* values. Historical Eh and alkalinity values were not available for the as-discharged tailings. Mean Eh values measured on extracted porewaters from the Deilmann and McArthur River tailings were 193 and 206 mV, which indicated that oxic conditions within these tailings were preserved through time (Table 7). Alkalinity (mg L^{-1} as HCO_3^-) averaged 116 and 119 mg L^{-1} in the Deilmann and McArthur River porewaters and no significant difference in concentrations was evident vertically between tailings types or laterally between boreholes (Table 7). The spatial and temporal uniformity between DTMF alkalinity values were attributed to the addition of excess lime during mill processing.

The mean as-discharged porewater concentrations of As, Ca, Fe, Mo, Ni, Se and SO₄ in the Deilmann and McArthur River are summarized in Table 6. Significantly greater As, Mo and Ni concentrations were measured in the Deilmann as-discharged porewaters than in those from the McArthur River tailings. In contrast, Se, Ca and SO₄ were statistically comparable amongst the two tailings types.

The porewater concentrations for pH, As, Fe, Mo, Ni, Se, Ca and SO₄ in the Deilmann and McArthur River tailings are summarized in Table 7 and selected parameters are illustrated in Fig. 4. The dissolved concentrations for all measured elemental constituents were significantly different between the two tailings types, with As, Mo, Se, Ca and SO₄ being greater in the Deilmann tailings and Ni and Fe greater in the McArthur River tailings (Table 7). Moreover, lateral differences were observed between two or more coreholes for As, Ca and SO₄ within the Deilmann tailings and for all constituents in the McArthur River tailings. Dissolved As concentrations were also significantly greater in the *in situ* porewaters for both tailings types compared to values measured in the as-discharged tailings porewaters, while Fe, Mo and Ni concentrations remained relatively unchanged (Tables 6 and 7).

Arsenic in the tailings was present primarily as As(V), with no detectable As(III) (Table 8). Mono-methyl As and traces of monothio As species were detected in the 09-E2 corehole samples. The observed presence of only As(V) in the 09-E2 samples is well correlated to the As speciation calculated using equilibrium thermodynamic modeling from the porewater Eh and pH values found

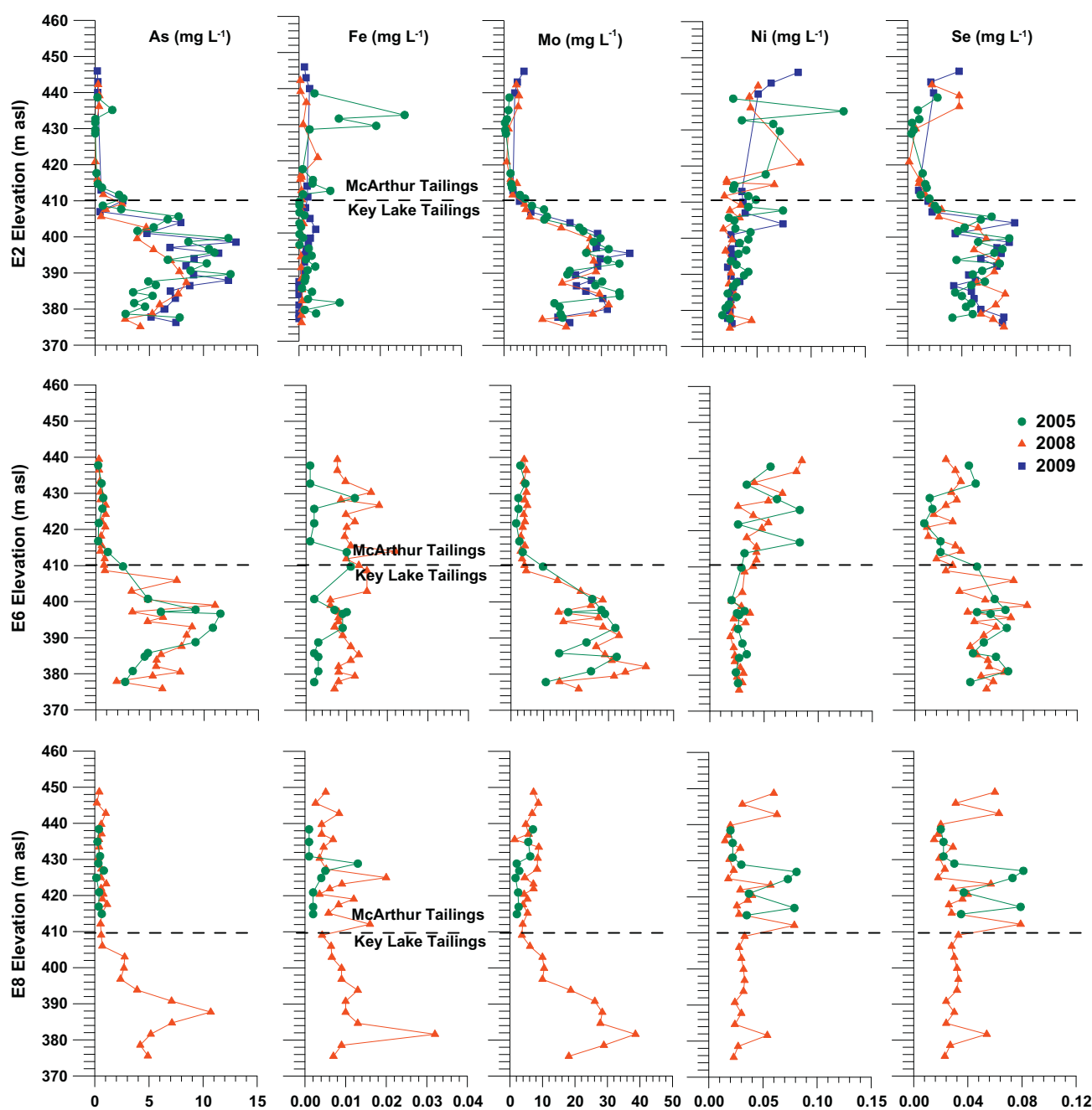


Fig. 4. Depth profiles for dissolved As, Fe, Mo, Ni and Se concentrations from corehole locations E2, E6, and E8. Collected between 2004 and 2009.

in 2008 and 2009 (Fig. 5). The processes leading to the formation of mono-methyl and mono-thio species could not be determined from the available dataset. However, methylated As species can form via either biotic or abiotic processes. Because microbes tend to produce dimethyl-As(V) species over monomethyl-As(V) species, the lack of dimethyl-As(V) in these samples suggests an abiotic methylation process (Hasegawa et al., 2001). Because the tailings contain residues of several organic chemicals containing methyl groups used in the metallurgical process, one or more of these could be the source of the methyl transferred to the inorganic As species. Monothioarsenate can be produced by the abiotic reaction of As(III) with sulfides (Wallschläger and Stadey, 2007). Given the tailings contain sulfides, this is a possible formation pathway for the observed traces of monothioarsenate. The absence of higher thioarsenates (di- to tetra-) may be explained by the low sulfide

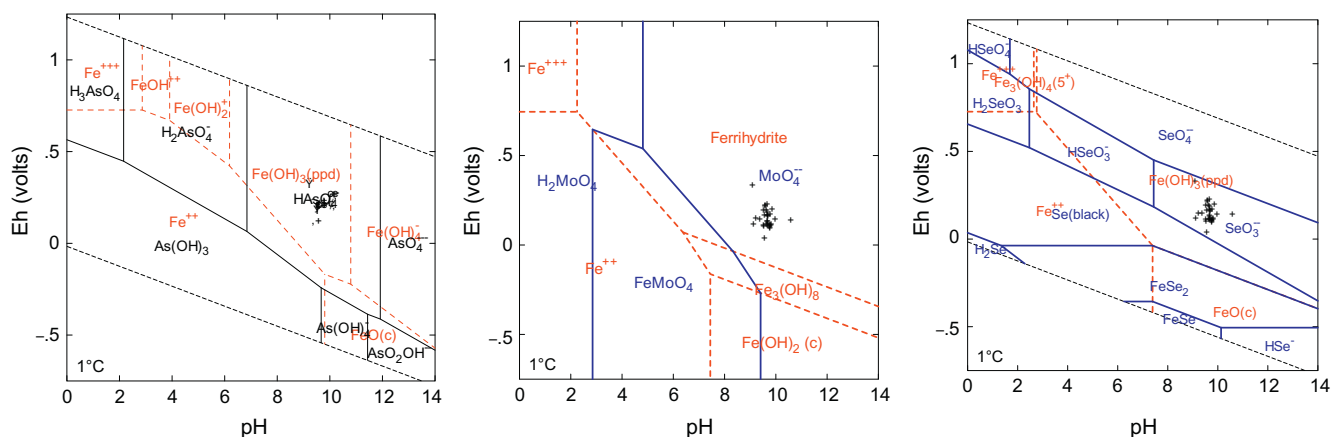
levels or inappropriate pH conditions (Planer-Friedrich et al., 2007) in the tailings.

Selenium speciation was dominated by Se(IV) and Se(VI) (Table 9). A small amount of selenocyanate (SeCN^-) was also measured and an unknown Se species in some of the porewater samples (Table 9). However, the measured speciation of Se as both Se(IV) and Se(VI) does not correspond well to the speciation distribution calculated from the porewater Eh and pH values using equilibrium thermodynamic modeling (Fig. 5). While the mechanism controlling this discrepancy between measured and calculated cannot be determined from the available data, it is potentially due to the same redox disequilibrium that is typical of As species. The identification of selenocyanate is based on chromatographic co-elution with a standard, but its formation/presence in this system is not clear at this time. It is assumed that SeCN^- is formed from elemental

Table 8

Dissolved As speciation for samples taken from corehole E2 in 2009. the fractions of the individual species are normalized to the sum of all measured species.

Sample ID	Depth (m)	Total As ($\mu\text{g L}^{-1}$)	As(III) (%)	As(V) (%)	Mono-methyl As (%)	Mono-thio As (%)
E2-GC01	446.0	203	0.0	66.2	33.8	0.0
E2-GC02	443.0	240	0.0	81.5	18.5	0.0
E2-GC03	440.0	227	0.0	77.6	22.4	0.0
E2-GC06	413.0	535	0.0	91.2	8.8	0.0
E2-GC07	410.0	2540	0.0	97.9	2.1	0.0
E2-GC08	407.0	438	0.0	55.5	44.5	0.0
E2-GC09	404.0	7910	0.0	93.4	6.6	0.0
E2-GC10	401.0	4770	0.0	82.5	17.5	0.0
E2-GC11	398.6	13,000	0.0	96.5	3.5	0.0
E2-GC12	397.1	6910	0.0	91.9	8.1	0.0
E2-GC13	395.5	11,400	0.0	96.5	3.5	0.0
E2-GC14	394.0	9140	0.0	94.7	5.3	0.0
E2-GC15	392.0	8380	0.0	91.8	8.2	0.0
E2-GC16	389.5	9080	0.0	94.6	4.3	1.1
E2-GC17	388.0	12,300	0.0	96.7	3.1	0.2
E2-GC18	386.5	8730	0.0	93.3	4.6	2.1
E2-GC19	385.0	6940	0.0	92.7	7.3	0.0
E2-GC20	383.0	7400	0.0	90.8	8.7	0.5
E2-GC21	380.0	6380	0.0	82.7	17.0	0.3
E2-GC22	377.8	5150	0.0	68.3	31.7	0.0
E2-GC23	376.3	7450	0.0	79.2	20.8	0.0

**Fig. 5.** Eh–pH diagrams for As, Fe and Se calculated using Eh and pH values collected from DTMF porewater samples in 2008 and 2009.**Table 9**

Dissolved Se speciation for samples from corehole E2 in 2009. The fractions of the individual species are normalized to the sum of all measured species.

Sample ID	Depth (m)	Total Se ($\mu\text{g L}^{-1}$)	Se(IV) (%)	Se(VI) (%)	Se–CN (%)	Unknown species (%)	Calculated Eh (mV)
E2-GC01	446.0	37.1	9.6	88.0	2.3	0.0	293
E2-GC06	413.0	13.8	42.5	49.3	8.2	0.0	276
E2-GC08	407.0	22.6	9.9	87.5	2.6	0.0	304
E2-GC10	401.0	41.3	21.3	71.9	2.9	3.9	312
E2-GC12	397.1	78.6	11.6	80.6	7.8	0.0	310
E2-GC14	394.0	46.3	32.5	58.8	3.9	4.8	315
E2-GC16	389.5	45.4	25.4	68.8	5.8	0.0	309
E2-GC18	386.5	38.0	23.0	71.3	5.7	0.9	314
E2-GC20	383.0	59.6	57.1	38.3	2.3	2.3	296
E2-GC22	377.8	80.1	38.0	59.1	2.9	0.0	263
E2-GC23	376.3	110	56.3	41.3	0.9	1.5	273

Se(0) and CN^- (Wallschläger and Bloom, 2001), and while the studied tailings may contain some Se(0), either introduced with the spent ore or formed *in situ* via reductive processes, it is not evident where the required cyanide comes from because it is not used in the milling process. One possible explanation might be the conversion of N compounds used in the metallurgical process to cyanide, although there is no experimental evidence to support this statement. Another possible explanation for the analytical observations could be the co-elution of a second unknown Se species with SeCN^- .

The nature or identity of the unknown Se species cannot be determined from the present data.

4.4. Aqueous geochemical controls

The geochemical conditions existing in the tailings and equilibrium with solid phases will control the fate of dissolved As, Fe, Mo, Ni, Se, Ca and SO_4 concentrations under present-day conditions. Equilibrium thermodynamic modeling under these present-day

Table 10
Saturation indices summary for geochemical modeling of DTMF porewaters collected from corehole E2, E6, and E8 during the 2004/05, 2008, and 2009 drill programs.

Phase	Log Ksp	Deilmann (<410 masl)		McArthur (>410 masl)	
		Average	Range	Average	Range
Ferrihydrite	5.65 ^a	-0.9	(-1.8)–0.2	-1.0	(-2.1)–1.0
Goethite	0.53 ^a	4.2	3.3–5.3	3.9	(-11)–6.1
Hematite	0.11 ^a	9.5	7.7–12	9.1	0.0–13
Gypsum	-4.48 ^a	0.0	(-0.1)–0.1	0.0	(-0.4)–4.6
Lime	32.58 ^a	-15	(-19)–(-14)	-15	(-20)–10
Calcite	1.85 ^a	1.8	0.3–2.4	1.9	0.3–2.3
Dolomite	2.51 ^a	2.3	(-0.4)–3.5	2.4	(-0.4)–3.6
Scorodite		-11	(-15)–(-6.4)	-12	(-16)–(-6.7)
Ca ₃ (AsO ₄) ₂	17.82 ^a	-3.2	(-3.9)–(-2.2)	-7.7	(-8.2)–(-5.9)
Mg ₃ (AsO ₄) ₂	-21.09 ^b	-7.7	(-11)–(-5.7)	-9.5	(-13)–(-7.3)
Ni ₃ (AsO ₄) ₂ ·8H ₂ O	15.7 ^c	-9.4	(-13)–(-7.5)	-9.4	(-17)–(-9.2)
MnHAsO ₄	-7.31 ^b	-5.9	(-7.2)–(-4.5)	-7.0	(-8.1)–(-4.3)
CaHAsO ₄ ·H ₂ O	4.79 ^d	-3.3	(-4.6)–(-2.6)	-4.3	(-6.0)–(-3.3)
Ca ₃ (AsO ₄) ₂ ·4H ₂ O	21.00 ^d	-1.0	(-4.6)–0.2	-3.1	(-11)–(-1.4)
Ca ₄ (OH) ₂ (AsO ₄) ₂ ·4H ₂ O	29.20 ^d	7.7	0.3–9.8	5.5	(-6.2)–8.3
Ca ₅ (AsO ₄) ₃ (OH)	38.04 ^d	0.4	(-6.9)–2.6	-2.6	(-16)–6.1
Ca ₅ (AsO ₃ OH) ₂ (AsO ₄) ₂ ·9H ₂ O Ferrarisite	31.49 ^d	-8.5	(-12)–(-6.3)	-10	(-24)–(-6.3)
Ca ₅ (AsO ₃ OH) ₂ (AsO ₄) ₂ ·9H ₂ O Guerinite	30.69 ^d	-7.7	(-11)–(-5.5)	-9.4	(-23)–(-5.5)
Ni(OH) ₂	12.75 ^a	-0.3	(-3.9)–0.7	-0.2	(-4.3)–1.1
Powellite – CaMoO ₄	-7.95 ^c	1.6	0.9–1.9	0.9	(-0.6)–1.3
NiMoO ₄	-11.14 ^c	1.7	0.1–2.5	0.7	0.4–1.4

^a LLNL database.

^b Lee and Nriagu (2007).

^c MINTeq database.

^d Bothe and Brown (1999).

geochemical conditions provides an indication of the current geochemical controls within the DTMF and between the Deilmann and McArthur River tailings bodies.

Within the mill, acids (H₂SO₄) and lime (Ca(OH)₂) used during initial ore leaching and raffinate neutralization led to excess dissolved SO₄²⁻ and Ca²⁺ within the as-discharged mill slurries and *in situ* tailings samples collected from the DTMF porewaters between 2004 and 2009 (Tables 7 and 8). Consequently, the porewaters are saturated with respect to gypsum in both the Deilmann and McArthur River tailings (Table 10), as evidenced by the presence of well-formed gypsum crystals in the DTMF solids (Essilfie-Dughan et al., 2011). In addition, calculated SI values suggest saturated to super-saturated conditions with respect to calcite and dolomite throughout the Deilmann and McArthur River tailings (Table 10). These conditions are attributed to the addition of lime during mill processing and the resulting alkaline pH conditions within the tailings.

Modeling suggests that ferrihydrite is slightly under-saturated in both the Deilmann and McArthur tailings (Table 10). Moreover, calculated SI values suggest super-saturated conditions for the more crystalline phases of goethite and hematite in the two tailings types (Table 10), which is expected as the system is near saturation with respect to ferrihydrite. Schwertmann et al. (2004) demonstrate the rate limiting transformation of ferrihydrite to goethite and hematite is dependent on both system pH and temperature, which increases with increasing temperature and pH. Further, Robins (1990) demonstrated that over time ferrihydrite should transform into the more crystalline phases of goethite and hematite. However, the persistence of near consistent Fe values within the DTMF in samples up to 12 a old, coupled with the presence of ferrihydrite in the corresponding solid samples (Essilfie-Dughan et al., submitted for publication-a), suggests that ferrihydrite formed during the milling process has remained stable. Langmuir (1997) indicates that pKsp values for ferrihydrite vary from 37 to 39, the value used in this study from the LLNL database is 36.3. Additionally, errors in pH measurement will also affect the calculated solubility of ferrihydrite. Therefore, it is likely that the system is at saturation with respect to ferrihydrite.

This observation is similar to those of previous studies that report ferrihydrite remaining stable over extended (up to 10-a) periods (Krause and Ettl, 1985; Dove and Rimstidt, 1987; Nordstrom and Parks, 1987; Moldovan et al., 2003). Fuller et al. (1993), Manceau (1995), and Waychunas et al. (1995) suggest that the incorporation of As into ferrihydrite (adsorption or co-precipitation), such as occurs in the DTMF, inhibits the transformation to goethite or hematite. Within the DTMF tailings, experiments on the effects of As sorption on the stability of ferrihydrite at approximately pH 10 demonstrates that arsenate sorbed onto ferrihydrite drastically decreases the rate of ferrihydrite crystallization (Das and Hendry, 2011). The authors suggest that ferrihydrite within these tailings (with Fe/As ratio greater than 4:1 as observed in the tailings) should remain stable for several tens of thousands of years at the low ambient temperatures (~2–3 °C) in the tailings. In the current study, a strong relationship exists between As and Fe molar concentrations in the solid phase samples collected from the DTMF, with average Fe:As ratios of 30:1 and 4:1 for the McArthur River and Deilmann tailings, respectively. The higher dissolved As concentrations measured in the Deilmann tailings are attributed to the lower Fe:As solid phase ratio. This observation was also made for the RLITMF, where dissolved As values > 1 mg L⁻¹ were associated with Fe:As ratios <5 (Donahue and Hendry, 2003).

Saturation index calculations suggest that scorodite (FeAsO₄·2H₂O) is undersaturated in the DTMF porewaters (Table 10). The precipitation of scorodite (FeAsO₄·2H₂O) at low pH gives way to the precipitation of ferrihydrite at near-neutral pH values (Moldovan et al., 2003; Chen et al., 2009). As a result, there is a lack of measurable scorodite within the DTMF (Essilfie-Dughan et al., submitted for publication-a). The super-saturation of a Ca-arsenate (Ca₄[OH]₂[AsO₄]₂·4H₂O; Table 10) suggests its possible existence in the tailings. However this mineral phase has yet to be identified experimentally in the DTMF solid phase. In keeping with the current study, Ca₄(OH)₂(AsO₄)₂·4H₂O was also identified as a saturated Ca-Arsenate in the RLITMF using thermodynamic modeling (Donahue and Hendry, 2003). A study by Bothe and Brown (1999) suggests that Ca₄[OH]₂[AsO₄]₂·4H₂O remains stable under alkaline

conditions similar to that in the DTMF. Donahue and Hendry (2003) postulate that Ca-arsenates could exert considerable control on the long-term dissolved As concentrations within the RLITMF, which is similar in geochemical conditions to the DTMF.

Although Ca–Fe arsenates (such as arseniosiderite and yukonite) have been identified in near neutral environments (Paktunc et al., 2003, 2004), such as waste mine dumps, mineralogical studies conducted on the solid tailings sample from the DTMF have indicated that the As is predominantly adsorbed on ferrihydrite (Essilfie-Dughan et al., submitted for publication-a). Moreover, both Ca–Fe arsenates are very often intimately associated with pharmacosiderite and less with other Fe(III)–arsenate systems, such as the DTMF in the current study. Finally, the solubility of arseniosiderite and yukonite have been reported in literature (Drahota and Filippi, 2009), thermodynamic data on their formation is lacking to adequately include them in the modeling conducted for this study.

Geochemical speciation results suggest that the majority of Mo in the DTMF porewater is present as MoO_4^- and that super-saturation conditions exist for powellite (CaMoO_4 and NiMoO_4 ; Table 10). Nickel speciation indicates undersaturated conditions for annabergite [$\text{Ni}(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}$] and near saturated results for theophrasite ($\text{Ni}(\text{OH})_2$) (Table 10), similar to the findings for the RLITMF which has tailings from comparable lime neutralization processes and as-discharged pH conditions (Donahue and Hendry, 2003).

5. Conclusions

Uranium mill tailings have been discharging into the DTMF since 1996. These tailings can be characterized by two geochemically distinct layers, the lower Deilmann tailings (<410 masl), and the upper McArthur River tailings (>410 masl). Generally, the observed differences between solids geochemistry in the Deilmann and McArthur River tailings can be attributed to the distinct composition of the original ore bodies from which they were derived. Solid phase As and Ni values have remained relatively unchanged over the lifespan of the DTMF, while Mo values decreased significantly between as-discharged and *in situ* measurements. The stability of Se concentrations could not be assessed as it was not measured in the as-discharged tailings.

The observed concentration profiles of aqueous phase As, Mo and Se were similar through the Deilmann and McArthur River tailings, with significantly greater values present in the Deilmann pore waters. For the purposes of predictive modeling of long-term transport of EOCs from the TMF to the surrounding groundwater, the mean *in situ* As, Ca, Fe, Mo, Ni, Se and SO_4 porewater concentrations can be used as source concentrations in the tailings, with values of 6.00, 623, 0.01, 22.6, 0.03, 0.05, and 1789 mg L^{-1} , respectively, in the Deilmann and 0.57, 597, 0.02, 4.13, 0.05, 0.02 and 1518 mg L^{-1} , respectively, in the McArthur River tailings. The inhibition effects of As sorbed on ferrihydrite suggest that under the temperature conditions in the TMF ($\sim 2\text{--}3^\circ\text{C}$), ferrihydrite should remain stable for much longer than 10 ka provided oxic conditions continue to prevail in the tailings.

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