



Speciation and toxicity of arsenic in mining-affected lake sediments in the Quinsam watershed, British Columbia



Maeve M. Moriarty^a, Vivian W.-M. Lai^b, Iris Koch^a, Longpeng Cui^c, Chris Combs^c, Eva M. Krupp^c, Jörg Feldmann^c, William R. Cullen^{b,*}, Kenneth J. Reimer^{a,*}

^a Royal Military College of Canada, Kingston, ON, Canada

^b University of British Columbia, Vancouver, BC, Canada

^c University of Aberdeen, Aberdeen, United Kingdom

HIGHLIGHTS

- The quantification of anthropogenic arsenic inputs into freshwater lakes must be done using multiple lines of evidence.
- Freshwater lakes within and outside of mine property show similar arsenic speciation, regardless of the total arsenic load.
- The amphipod *C. volutator* responds in a predictable manner to lake sediments and shows promise for arsenic toxicity testing.

ARTICLE INFO

Article history:

Received 7 March 2013

Received in revised form 23 May 2013

Accepted 1 July 2013

Available online xxxx

Editor: Gisela de Aragão Umbuzeiro

Keywords:

Sediment

Arsenic

Coal mining

Toxicity testing

XANES

Bioaccessibility

ABSTRACT

Anthropogenic arsenic inputs into fresh water lakes in the Quinsam watershed, British Columbia, were probed by using multiple methods of inquiry including sediment coring combined with ²¹⁰Pb dating, a principal components analysis of elemental composition of sediments, arsenic speciation, bioaccessibility, and toxicity testing. The quantification of arsenic inputs from anthropogenic sources was not trivial because a variety of processes redistribute the element throughout lakes. However, elevated arsenic and sulfate concentrations in Long Lake, a lake that receives arsenic from a seep, suggest that this lake is influenced by mine operations. X-ray absorption near edge structure (XANES) spectra reveal similar arsenic speciation for all sediments within the studied lakes. Bioaccessibility tests, which in this study were used to approximate the solubility and availability of arsenic to benthic organisms, indicate moderate bioaccessibility of arsenic in sediments (7.9–35%). Toxicity testing indicates that not all benthic organisms should be used for evaluating arsenic toxicity, and suggests that the amphipod, *Corophium volutator*, shows promise as a candidate for widespread use for arsenic sediment toxicity testing.

© 2013 Published by Elsevier B.V.

1. Introduction

The Quinsam watershed, British Columbia, is host to fresh water lakes that are within an area of coal mining. The physical and geochemical impacts of coal mining on lakes are mine-specific and can be wide ranging. For example, a study of 49 abandoned coal mines in the same geographic area found a variety of changes with sulfate, which is an indicator of the acid rock drainage that is a consistent metric of impact (Silva et al., 2011). Acid rock drainage can also lead to the release of arsenic if this element is present in the host ores or waste material. The degree to which coal mining activities have impacted lakes in the Quinsam watershed is unknown.

To determine impact from coal mining, or indeed any anthropogenic activities, the first step is often an examination of historical

and current arsenic concentrations, and comparisons to background sediment arsenic concentrations, which in Canada are generally low (up to about 10 mg·kg⁻¹) (CCME, 1999). Comparisons to guideline arsenic concentrations would also typically be made. Guidelines in Canada are based on increased mortality and decreased abundance of biota in sediments with elevated arsenic concentrations (CCME, 1999). Consequently, the Canadian Council of Ministers for the Environment (CCME) recognizes both a lower limit for sediment arsenic concentrations that will protect aquatic life from adverse effects, the interim sediment quality guideline (ISQG) of 5.9 mg·kg⁻¹; and a level beyond which severe effects on aquatic life are likely, the probable effect level (PEL) of 17 mg·kg⁻¹ (CCME, 1999). The same values have been proposed as working guidelines in British Columbia (BC) (Nagpal et al., 2006).

This approach has proved useful in assessing the arsenic impacts in sediments from an anthropogenic source in areas with little mixing or perturbation and where concentration gradients are

* Corresponding authors. Tel.: +1 613 541 6000x6161; fax: +1 613 541 6596.
E-mail address: reimer-k@rmc.ca (K.J. Reimer).

readily seen (e.g. Gault et al., 2003; Root et al., 2009). However, in freshwater sediments that may also have naturally elevated arsenic concentrations, the question of quantification of impact can be more challenging. A number of analytical tools are available to complement the analysis of total elemental concentrations. For example, the relative abundance of elements, or elemental makeup of sediments, is related to the sediment source and as a result, impacted sediments can be differentiated from background sediments using multivariate statistics, for example, a principal components analysis (PCA) (Shine et al., 1995; Singh et al., 2005; Zitko, 1994). Additionally, sediment coring can provide chronological evidence of deposition (Moore, 1988; Senn et al., 2007). These tools can be employed when high arsenic concentrations are encountered to determine source and may be useful for quantification of impact.

Guideline values do not take into account the chemical nature of the sediment, or the way in which arsenic occurs within it (arsenic speciation), even though the toxicity may vary according to the arsenic speciation. For example, arsenic bound to iron oxide hydroxides is more soluble and therefore more toxic than arsenic bound to sulfides (see Table 1). Most lake sediments probably host arsenic in an inorganic form (as either arsenite, As(III), or arsenate, As(V)) adsorbed mainly to iron oxide hydroxides or to a lesser extent to manganese and aluminum oxides (Fendorf et al., 2010). As(III) and As(V) are the usual end products of arsenic release to the environment by mineral weathering and oxidation processes (Fendorf et al., 2010). Arsenic can also be stored in sediment in a sulfidic (mineral) form from bulk transfer of mineralized arsenic, or from arsenic precipitation in sediments under reducing conditions (Root et al., 2009).

To quantify the environmental impact of arsenic enriched sediments resulting from coal mining activities, a very common approach is the use of toxicity testing with organisms like *Hyalella azteca* and *Chironomus* sp. Both of these organisms are common inhabitants of fresh water lakes, but they are tolerant of arsenic concentrations that are orders of magnitude higher (Liber et al., 2011) than guideline values. Therefore, it may be prudent to ascertain if other organisms are suitable for sediment toxicity testing.

The objectives of the present study were to determine whether quantification of anthropogenic inputs is possible in the studied lakes through a combination of coring, surficial sediment sampling and analysis; to determine the chemical nature of elevated arsenic in sediments near mining activities through the use of solid-state speciation X-ray absorption spectroscopic (XAS) methods; and to establish a method for evaluating the toxicity of the arsenic within these sediments, through the use of an amphipod *Corophium volutator*.

2. Methods

2.1. Study site description

The Quinsam watershed, a fish habitat for four species of salmon and two species of trout, is located near Campbell River on Vancouver Island, BC, Canada (Fig. 1 and Fig. S1 in supplementary data). No anthropogenic mining influences are anticipated to have affected Long

Lake prior to 1977 when exploration began in the area. These early operations included extracting a 20,000 t bulk sample near the south-east end of Long Lake. Open-pit mining adjacent to the south shore of Long Lake began in the mid-1980s and underground mining in the same region began in 1991. Coal wastes are stored near both Middle Quinsam Lake and Long Lake (QCC, 2009).

Underwater vegetation is sparse along the south side of Long Lake. The lake is potentially impacted by a number of industry-affected sources: settling ponds to the east of the northern tip of the lake and related drainage ditches; a quarry north of the east end of the lake; run off from exposed rock and tailings dumps; and water from the locally named Long Lake Seep in the southwest portion of the lake. The Long Lake Seep is influenced by groundwater flowing through high sulfur mine refuse contained in a subaqueous storage pond and also through abandoned underground mine workings in the area (see Fig. 1). There is also at least one underwater spring in Long Lake, located in the middle of the lake near the south shore.

2.2. Sample collection

Sediment samples were collected in 2008 and 2009 from Wokas Lake, Middle Quinsam Lake, No Name Lake and Long Lake, at locations shown in Fig. 1. Two surface (0–10 cm) sediment samples were collected at each site along the mid-line of the lake by using an Ekman grab and were combined for analysis. The same sampling plan was followed at Upper Quinsam Lake except for samples U2, U3 and U4, which were collected closer to the shore because of the depth of the lake. One lake sediment sample was collected downstream of the mine from Lower Quinsam Lake; this was considered sufficient since the primary purpose of the study was to ascertain effects on Long Lake. Four samples were collected from the Long Lake Seep: three samples representative of the soil in the area and another that appeared to be precipitated iron oxide underneath the flow of water into the lake. Two additional samples were collected from the stream flowing down a gully west of where the seep flows. Samples were kept cool (4 °C) until they could be frozen for storage. A subsample of each was freeze-dried, and ground using a mortar and pestle prior to analysis.

One high sulfur coal refuse sample (generated after lighter coal is extracted from bulk rock) was collected from the subaqueous storage area in Fig. 1. Six additional refuse samples were provided by the mine: three coarse and three fine refuse samples collected between 2007 and 2008. The coarse refuse (C1, C2, and C3) originated from a pit north of Middle Quinsam Lake.

Sediment cores (15–30 cm long) were collected in July 2011 from locations A–E in Fig. 1 by a diver using clear PVC piping, and one core (Core 1) was collected in April 2011 near Core C and used for speciation analysis. Cores were divided into 1 cm sections within 8 h of collection, frozen, and freeze-dried prior to analysis.

2.3. Total element content analysis

Sediment samples collected between 2008 and 2010 were analyzed at the ALS Chemex laboratory in North Vancouver, BC, which is accredited by Standards Council of Canada for all tests used in this study. All previously ground samples were sieved (<180 µm) and extracted using a standard aqua regia digestion, of 3:1 HCl:HNO₃ (v/v). A subset of these samples was extracted using a 4-acid digestion procedure similar to the ISO 14869-1:2001 method (described in Peña-Icart et al., 2011). In the present study, the samples were digested with HNO₃–HClO₄–HF to dryness, followed by leaching with HCl. Analysis of all digests was carried out for 51 (aqua regia) or 48 (4-acid digest) elements by ICP-MS.

Sediment cores were analyzed for arsenic using an Innov-X Model XT-440 Field Portable X-Ray Fluorescence (XRF) analyzer. The XRF was equipped with a high-resolution silicon PIN diode detector and Compton

Table 1

Arsenic (As) toxicities for *Corophium volutator* in various mineral forms (Cui et al., 2011). Bioaccessibility data are from Meunier et al., 2010a, 2010b; Liu et al., 2008; Kwan et al., 2001.

| Mineral form of arsenic | LD ₅₀ (sediment) (mg·kg ⁻¹) | LC ₅₀ (pore water) (mg·L ⁻¹) | Bioaccessibility (%) |
|--|--|---|----------------------|
| Arsenopyrite (FeAsS) | 1130–1330 | 0.54–0.64 | 0.36 |
| Orpiment (As ₂ S ₃) | 300–590 | 0.47–0.90 | Low |
| Realgar (As ₄ S ₄) | 220–510 | 0.42–0.95 | 0.6 |
| Iron–arsenic oxides | 30–55 | | 1–10 |

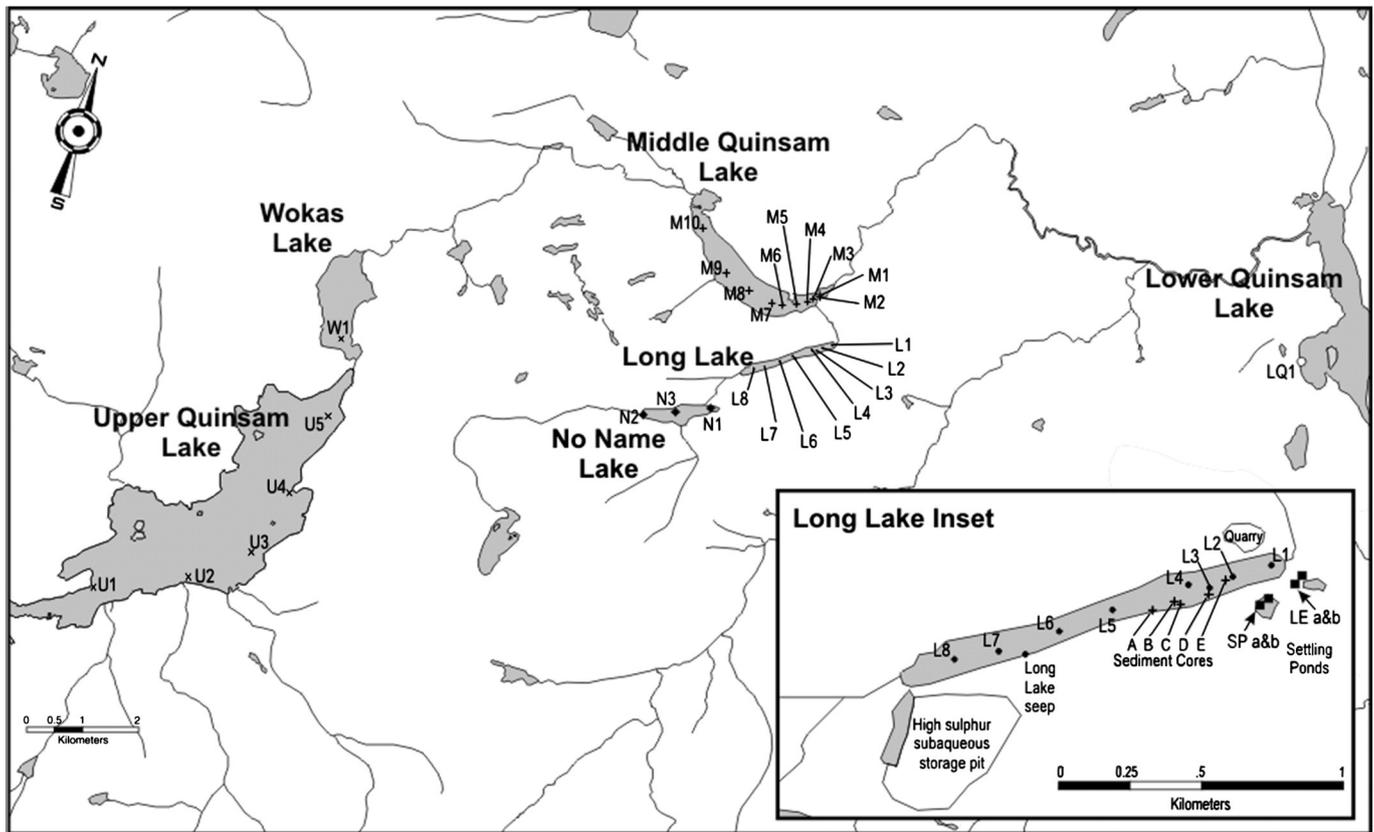


Fig. 1. Quinsam watershed sampling locations. L = Long Lake, LLE and SPC = Long Lake settling pond and culvert, N = No Name Lake, M = Middle Quinsam Lake, LQ = Lower Quinsam Lake, W = Wokas Lake, and U = Upper Quinsam Lake. Sediment cores A–E were sampled in July 2011; Core 1 (not shown on map, but from a location next to Core C) was sampled in April 2011.

normalization software. The XRF was factory calibrated for the analysis of arsenic using standard reference materials. This instrument is normally used for in-field analysis at a screening level (e.g., US-EPA SW846 Method 6200), but it was used in the present study because of its cost effectiveness and the large number of sediment core samples. To ensure that the results were fit for this purpose, quality control measurements were included: a MESS-3 sediment standard (National Research Council of Canada) and a SiO₂ blank were analyzed (<10 mg·kg⁻¹ arsenic) in each analytical batch test, and several samples were analyzed in duplicate within each batch. Samples from Core 1 were analyzed at ALS as described above (aqua regia method) to verify the XRF analysis and XRF values were on average within 12% of the accredited laboratory values (see supplementary data for more details). All samples were within laboratory QA criteria, and QA/QC data are included in the supplementary data.

2.4. Physiologically based extraction test (PBET)

The PBET method was adapted from Ruby et al. (1996) and Rodriguez et al. (1999). A liquid:solid ratio of 100:1 was used (dry weight), using the methods described in Koch et al. (2007b). Arsenic analyses were carried out using an X7 X-Series II, inductively coupled plasma mass spectrometer (ICP-MS) (Thermo Electron) using the collision cell mode. The detection limit (1 µg·L⁻¹) was based on the lowest concentration arsenic standard used in the calibration curve and is equivalent to 0.1 mg·kg⁻¹ sediment. Arsenic (*m/z* 75) was quantified using scandium, yttrium, indium, terbium, holmium and bismuth as internal standards to correct for instrument drift and matrix effects. Mass interferences from chloride were monitored as *m/z* 77(ArCl⁺) and

automatically corrected by the PLASMALAB™ software. All samples were within laboratory QA criteria and QA/QC data are included in the supplementary data.

2.5. Toxicity bioassay

C. volutator specimens were collected from non-contaminated River Ythan sediment (North East Scotland) (Cui et al., 2011). Test sediment L2 (628 mg·kg⁻¹ arsenic) was mixed with Ythan River sediment (5.4 mg·kg⁻¹ arsenic) in the following ratios: control (0%), 2%, 5%, 10%, 20% and 50%. Bioassay testing was carried out by using a modified 10 day static testing protocol in synthetic sea salt media (pH 7.0–7.2, salinity 22 g·L⁻¹, ~22 PSU) as previously described (Cui et al., 2011). Three replicates were prepared per concentration and 25 animals were added to each test-pot for the 10 day trial.

In a second experiment, three test sediments (N3, L4 and L8) were each mixed with Ythan River sediment in a ratio of 1:1 and exposed to *C. volutator* in the same manner. 40 animals were added to each test-pot and a control (Ythan River sediment as background) for the 10 day trial. Mortality was corrected using Abbott's formula (corrected mortality (%) = (P – P₀) / (100 – P₀) × 100, where P is the mortality of treated amphipods (%) and P₀ is the measured mortality in the controls) (see Fig. 2 and Fig. S4). The test amphipods were also analyzed for their total arsenic body burden and their inorganic arsenic fraction (Fig. 2).

The total arsenic concentrations of the amphipods were measured using ICP-MS after a nitric acid digestion. For inorganic arsenic the samples were measured with hydride generation-AFS using conditions that had been optimized for inorganic arsenic (As(III)) and

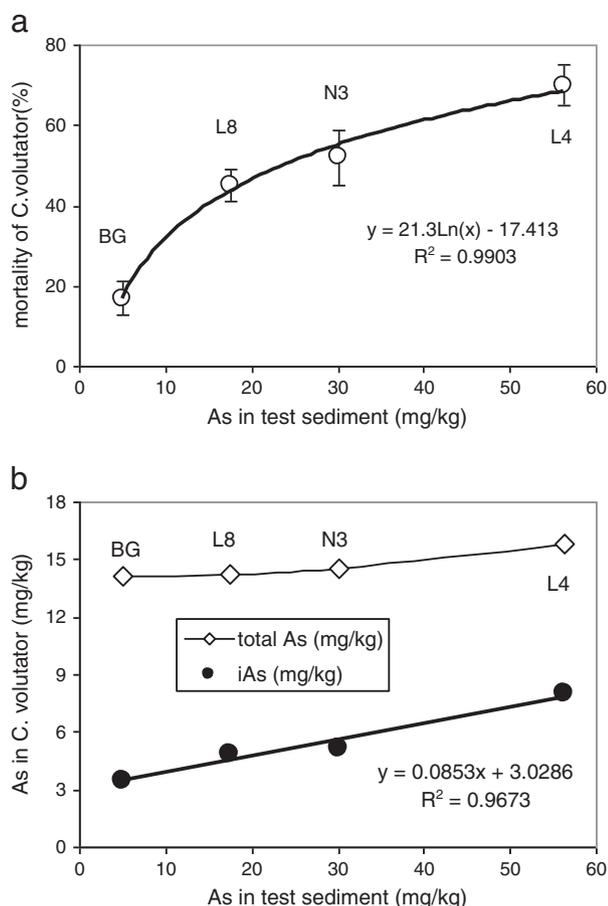


Fig. 2. Bioassay using *Corophium volutator* for sediment toxicity. The test sediments (Long Lake L4 and L8, and No Name Lake N3) were mixed 1:1 with control sediment (BG) and mortality was determined after 10 days. a) Mortality rate in %; each pot contained 40 amphipods. Error bars represent the SD for $n = 4$ for mortality; b) correlation of arsenic in test sediments and total and inorganic arsenic concentration (iAs) in test *C. volutator*.

As(V)). Under these conditions, hydride generation efficiency of DMA was <10% that of inorganic arsenic species. Hence, only the arsenic species that were hydride generation active, specifically inorganic arsenic species, were measured.

2.6. X-ray absorption near edge structure (XANES) analysis

X-ray analysis was performed at the Pacific Northwest Consortium X-ray Sciences Division (PNC/XSD) facility on the bending magnet beamline at sector 20 of the Advanced Photon Source (APS) in Argonne, Illinois, the set-up of which is described elsewhere (Smith et al., 2005). The Si(111) double-crystal monochromator for the BM line was calibrated using the first inflection point of the gold L_{III} absorption edge (11,919.7 eV). Dried (oven, 40 °C overnight for surface sediments; previously freeze-dried for core slices) samples were ground in a ball mill and prepared as four layers of powder on Kapton tape for analysis at room temperature. Wet samples were packed into sample holders between two layers of Kapton tape, and analyzed at 50 K. Fluorescence data were collected using a solid-state Ge(Li) detector. Five scans were collected for each sample and averaged before normalization to the edge jump. Examination of the XANES spectra from first to last in each set showed no beam damage to the samples.

XANES spectra of the arsenic K-edge were fit within -20 to $+30$ eV from arsenic's ionization energy, E_0 (11,868 eV) using

ATHENA software (Ravel and Newville, 2005). A reference gold foil was measured simultaneously with samples. Data were compared with linear combinations of reference compounds previously shown to distinguish between seven different groups of arsenic compounds based on the position of the main peak feature (Smith et al., 2005). Inorganic arsenite (As(III), As_2O_3) and arsenate (As(V), KH_2AsO_4) standards were used for the fitting: liquid for wet samples and solid for dried solids. All fits were constrained to sum to 100% of measured arsenic. The two peaks identified in samples correspond to As(III)-O (11,871.7 eV) and As(V)-O (11,875.3 eV) (see Fig. 3).

2.7. Sediment core dating

Freeze-dried and ground sediments (~ 1 – 2 g) were placed in centrifuge tubes and allowed to settle. Samples were then sealed with epoxy and allowed to equilibrate for three weeks. Sediments were counted on a digital, high purity germanium crystal spectrometer with lithium dif-fused electrodes (DSPEC, Ortec) and data processed at the Laboratory for the Analysis of Natural and Synthetic Environmental Toxins facilities in the University of Ottawa. ^{210}Pb (peak at 46.5 keV), ^{214}Pb (peaks at 295 and 352 keV; used to determine ^{226}Ra activity), ^{137}Cs (peak at 662 keV) and ^{241}Am (peak at 59.5 keV) were measured simultaneously. Spectra were analyzed using DOS-based software developed and provided by Peter Appleby (University of Liverpool, U.K.) which includes calculations for efficiency and corrections for self-absorption (Appleby et al., 2001). The sediment core was dated using the constant rate of ^{210}Pb supply (CRS) model. Similar results were obtained when a constant flux, constant sedimentation rate was used. Two ^{241}Am peaks were identified at 4.5 cm and 12.5 cm while one ^{137}Cs peak was identified at 4.5 cm (see Fig. 4 and Fig. S2).

2.8. Principal components analysis (PCA)

PCA allows for multivariate pattern recognition of the concentrations of inorganic elements in samples by examining their position on a reduced (usually two or three dimensional) plot. The axes of the plot are linear combinations of the original n variables.

The variables in this statistical analysis were selected from the determined concentrations of 51 elements: Ag, Al, As, Au, B, Ba, Be, Bi, Ca, Cd, Ce, Co, Cr, Cs, Cu, Fe, Ga, Ge, Hf, Hg, In, K, La, Li, Mg, Mn, Mo, Na, Nb, Ni, P, Pb, Rb, Re, S, Sb, Sc, Se, Sn, Sr, Ta, Te, Th, Ti, Tl, U, V, W, Y, Zn, and Zr. Non-detectable values were replaced with half the detection limit. Three elements – gold (Au), boron (B) and tantalum (Ta) – were not included because their concentrations were below detection limits in more than 50% of the samples analyzed.

Statistical analyses were carried out using Systat 12 software. The distribution of concentrations of each of the 48 variables (elements) in the 44-sample data set was examined and distribution for each variable was skewed (skewness ranged from -0.32 to 6.7). \log_{10} transformation reduced skewness (-3.1 to 1.6) and yielded more normal data distributions. Mean-centered, \log_{10} transformed data were subsequently used in the PCA (see Fig. S3).

3. Results

3.1. Sediment arsenic concentrations

The total arsenic content of grab samples of sediments from lakes in the Quinsam watershed was found to be as follows. Lakes upstream of impacted lakes were Upper Quinsam Lake and Wokas Lake and had a range of 3.9 to 45 $mg \cdot kg^{-1}$ arsenic ($n = 7$). Lakes within the mine property were No Name Lake ($n = 3$; range = 13 – 55 $mg \cdot kg^{-1}$ arsenic), Middle Quinsam Lake ($n = 10$; range = 6.5 – 34 $mg \cdot kg^{-1}$ arsenic) and Long Lake ($n = 8$; range = 26 – 630 $mg \cdot kg^{-1}$ arsenic). One sample was collected from downstream of the mine in Lower Quinsam Lake and it had 13 $mg \cdot kg^{-1}$ arsenic.

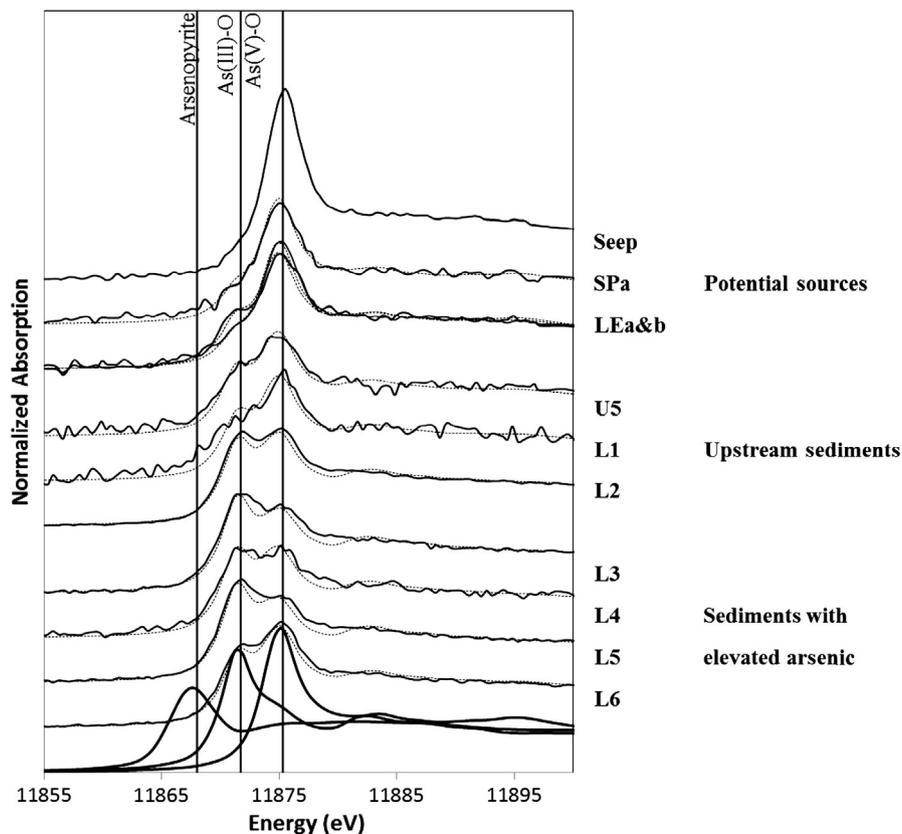


Fig. 3. XANES results of dried surface sediments from lakes in Quinsam watershed. Three arsenic standards are shown at the bottom: arsenopyrite, solid arsenite (As(III)-O) and solid arsenate (As(V)-O). Solid lines indicate collected data, and dotted lines indicate fit.

Refuse provided by the mine contained arsenic in a range of 4.8 to $10 \text{ mg} \cdot \text{kg}^{-1}$ ($n = 6$). A coal refuse sample collected from the subaqueous storage area in Fig. 1 contained $21 \text{ mg} \cdot \text{kg}^{-1}$ arsenic. A seep solid sample contained $420 \text{ mg} \cdot \text{kg}^{-1}$ arsenic.

Samples were compared using an analysis of variance (ANOVA $F(7, 33) = 11.33, p < 0.001$). Long Lake sediment and seep arsenic concentrations were found to be significantly higher than those in sediments from the upstream lakes, Middle Quinsam Lake, the mine settling pond and drainage ditch (pairwise comparisons using a Tukey's test ($p < 0.05$)). Long Lake sediments were also found to contain higher arsenic concentrations than coal refuse. In general, Long Lake sediment arsenic concentrations were highest near the seep (location indicated as Long Lake Seep in Fig. 1) and at the east end of the lake (see Fig. 1 and Table 2). A seasonally active surface water creek that flows over exposed rock and coal refuse before joining the seep was also investigated: sediment arsenic concentrations were $90 \pm 10 \text{ mg} \cdot \text{kg}^{-1}$ ($n = 3$).

The range of arsenic concentrations in Long Lake in the present study is similar to the range obtained by examining historical data available for Long Lake sediments (see supporting material for the rationale for comparison). These data consist of: results for one sediment sample collected from the deepest point of Long Lake sometime between 1982 and 1987 containing $197 \text{ mg} \cdot \text{kg}^{-1}$ arsenic (Rieberger, 1992); a number of sediment cores collected from Long Lake in 1983 with surficial arsenic concentrations of 50 – $1000 \text{ mg} \cdot \text{kg}^{-1}$ arsenic, increasing in concentration from west to east in the lake (Sneddon and Kelso, 1983); and a sediment sample from the east end of the lake containing $220 \text{ mg} \cdot \text{kg}^{-1}$ As (Nordin, 2006).

Three other lakes on Vancouver Island are reported to have elevated arsenic (Rieberger, 1992): Moat Lake ($490 \text{ mg} \cdot \text{kg}^{-1}$), Circllet Lake ($1300 \text{ mg} \cdot \text{kg}^{-1}$) and Lake Helen Mackenzie ($200 \text{ mg} \cdot \text{kg}^{-1}$). These

three lakes are distant from any mining sites and located within 10 km of each other within Strathcona Park, approximately 30 km southwest of the study area (Rieberger, 1992).

3.2. Arsenic bioaccessibility

Long Lake sediments, samples from nearby lakes, and surface samples from the mine site, were subjected to a PBET to assess arsenic bioaccessibility, which is the arsenic that is likely solubilized upon ingestion by humans (Ruby et al., 1996), and hypothesized in the present study to approximate the amount solubilized during the digestion of sediments by aquatic organisms. The method has not been "validated" through the comparison with animal (aquatic organism) testing, in the way similar tests have been "validated" to represent human bioavailability (e.g., Rodriguez et al., 1999). However the test was considered to be sufficiently meaningful for the purposes of the present study, which was to ascertain any differences in bioaccessibility that could potentially support any differences in arsenic speciation. The results are presented in Tables 2 and 3. Long Lake sediment arsenic bioaccessibilities ranged from 7.9% to 35% (mean = 19%) and one sediment sample from No Name Lake, which drains into Long Lake, was within this range: 8.5% arsenic bioaccessibility. Similar numbers were obtained for sediments from other lakes within the Quinsam watershed but remote from the mine, 16 – 49% arsenic bioaccessibility (mean = 28%). Similar numbers, between 5 and 30% , were obtained in a previous study of coal-impacted sediments when arsenic was extracted at room temperature into 0.25 M hydroxylamine chloride and 0.25 M HCl (Goldhaber et al., 2001).

Sediment samples from the mine site tailings pond drainage areas had 6.1 – 15% bioaccessibility (mean = 11%), and coarse and fine mine

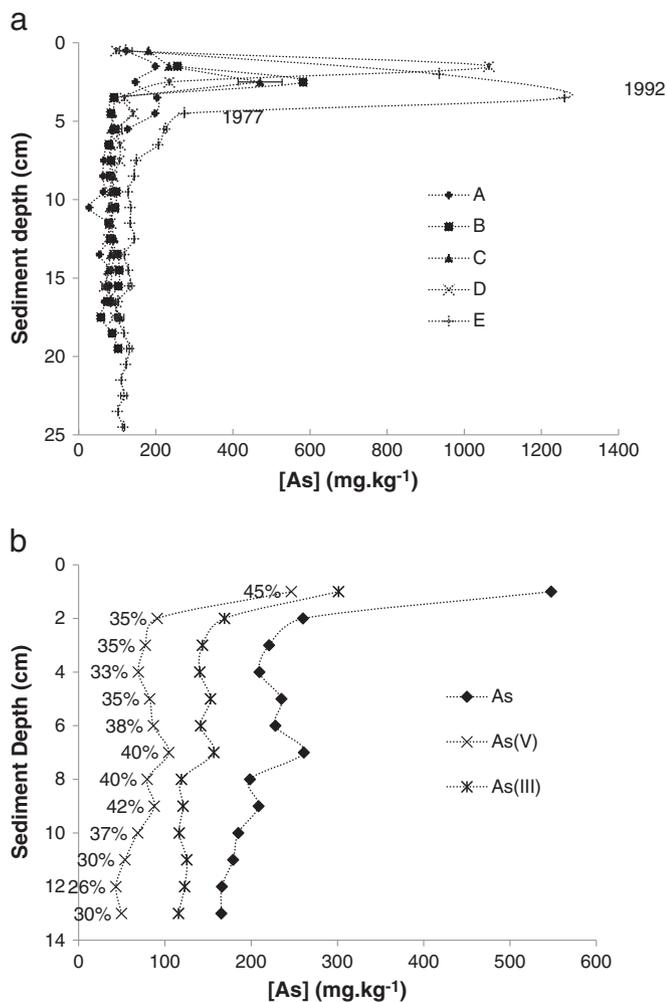


Fig. 4. Concentration of arsenic in sediment cores collected in (a) July 2011 (sediment cores A–E) and (b) April 2011 (Core 1) in the eastern half of Long Lake. Dating of core E was determined using ^{210}Pb . Speciation was obtained by XANES and percentages of As(V) (of the total As) are shown to the left of the As(V) values.

refuse had 23–55% bioaccessibility (mean = 37%) but the coal refuse from the subaqueous storage pit area had a lower bioaccessibility of 8.9%. The refuse provided by the mine (coarse and fine mine refuse) has a significantly higher arsenic bioaccessibility compared with both Upper Quinsam Lake and Long Lake sediments (ANOVA,

Table 2

Arsenic (As) concentrations in sediments from mine lakes (Long Lake (L), No Name Lake (N), and Middle Quinsam Lake (M)). Arsenic X-ray absorption near edge structure (XANES) results are for dried sediments; only As(V)–O and As(III)–O (fitted with solid standards) were found. Samples were forced to sum 100%. Values in italics are greater than the CCME guideline value of 5.9 mg·kg⁻¹.

| Sample ID | Water depth (m) | As(V)–O from XANES (%) | Bioaccessible As (%) | Bioaccessible As (mg·kg ⁻¹) | Total As (mg·kg ⁻¹) |
|-----------|-----------------|------------------------|----------------------|---|---------------------------------|
| L1 | 4.5 | 52 | 34 | 12 | 36 |
| L2 | 17 | 35 | 14 | 88 | 630 |
| L3 | 17 | 25 | 15 | 21 | 140 |
| L4 | 23 | 32 | 16 | 18 | 110 |
| L5 | 17 | 24 | 11 | 26 | 240 |
| L6 | 15 | 45 | 7.9 | 28 | 360 |
| L7 | 15 | | 35 | 9.1 | 26 |
| L8 | 5.0 | | 18 | 5.4 | 30 |
| N1–2 | 2.0 | | | | 13–55 |
| N3 | 12 | | 8.5 | 4.3 | 50 |
| M1–10 | 3.0–9.0 | | | | 6.5–34 |

Table 3

Arsenic (As) concentrations in sediments from the Quinsam watershed (Upper Quinsam Lake (U), Wokas Lake (W), and Lower Quinsam Lake (LQ)), and from mine solid samples: settling pond and drainage (SP and LE); coal refuse from high sulfur subaqueous storage area; refuse provided by the mine (coarse and fine refuse); and seep precipitate into Long Lake (Seep). Arsenic X-ray absorption near edge structure (XANES) results for wet and dried sediments (wet sample results are in brackets). Only As(V)–O and As(III)–O were found (wet samples fitted with liquid standards; dry samples with solid standards). Samples were forced to sum 100%. Values in italics are greater than the CCME guideline value of 5.9 mg/kg.

| Sample ID | As(V)–O from XANES (%) | Bioaccessible As (%) | Bioaccessible As (mg·kg ⁻¹) | Total As (mg·kg ⁻¹) |
|-----------------------|------------------------|----------------------|---|---------------------------------|
| U1–4 | | 16–48 | 0.82–2.1 | 3.9–13 |
| U5 | 50 (36) | 21 | 9.5 | 45 |
| W | | 19 | 1.7 | 9.1 |
| LQ | | 49 | 6.4 | 13 |
| SPa | | 12 | 2.5 | 21 |
| SPb | 77 (72) | 6.1 | 1.3 | 22 |
| LEa | 79 (45) | 12 | 2.6 | 22 |
| LEb | 65 (45) | 15 | 3.6 | 24 |
| Coal refuse | | 8.9 | 1.9 | 21 |
| Coarse refuse (n = 3) | | 30–55 | 2.0–3.8 | 4.8–10 |
| Fine refuse (n = 3) | | 23–38 | 1.6–2.9 | 6.5–7.6 |
| Seep | 100 | | | 425 |

$F(3, 23) = 4.852$, $p = 0.009$; Tukey's test pairwise comparison, $p = 0.012, 0.022$).

3.3. Toxicity testing

The marine amphipod *C. volutator* (Pallas) is tolerant of a wide range of salinity environments and exhibits both behavioral and mortality endpoints in response to contaminated sediments in bioassay tests (Traunspurger and Crews, 1996). Cui et al. (2011) recently used this amphipod to determine LD₅₀ values for three common arsenic sulfide minerals in sediments: arsenopyrite, realgar, and orpiment. They found that the response of the amphipod was arsenic specific and was related to the solubility of the mineral in the test medium (Table 1). In the present study, the only known contaminant that, in addition to arsenic, might have contributed toxicity in sediments was mercury. However, all mercury concentrations were lower than the CCME probable effect level for this element (0.486 mg·kg⁻¹), and two of the four tested sediments had concentrations less than the ISQG (0.17 mg·kg⁻¹). Thus we concluded that toxicity observed in the present study was attributable to arsenic.

The percent mortality data from a *C. volutator* toxicity test of Long Lake sediment L2, which has the highest arsenic concentration measured in a grab sample (630 mg·kg⁻¹), is illustrated in Fig. S4. The mean lethal arsenic dose (LD₅₀) value for the Quinsam sediment at the end of a 10-day exposure was calculated to be 42–52 mg·kg⁻¹ arsenic for this sediment (Fig. S4). Similar values (24–35 mg·kg⁻¹) were obtained using three different sediments (one from No Name Lake, N3, and two from Long Lake, L4 and L8), shown in Fig. 2a. These LD₅₀ values are approximately one order of magnitude lower than those determined for the arsenic sulfides (LD₅₀ values range from 220 to 1300 mg·kg⁻¹, Table 1) (Cui et al., 2011). This increase in toxicity is also reflected directly by the enhanced bioaccessibility of the arsenic in the sediment samples; L2 and L4 are approximately 10–20 times more toxic to *C. volutator* than arsenopyrite/realgar and they are approximately 20–40 times more soluble than the arsenic sulfides (Cui et al., 2011; Kwan et al., 2001; Meunier et al., 2010a). Although the bioaccessibility was not high (it averaged 15% for L2 and L4), the arsenic species in these two samples was 64% As(III), a compound well-known to be soluble, as well as toxic to a wide variety of organisms.

The increase in arsenic in the test sediments results in only a small increase in the total arsenic in the test animal (Fig. 2b), because the initial arsenic concentration in *C. volutator* from exposure to background sediment is already high ($14 \text{ mg}\cdot\text{kg}^{-1}$, Fig. 2b). This initial tissue body burden resulted from a sediment concentration of $5.4 \text{ mg}\cdot\text{kg}^{-1}$, less than the Canadian sediment quality guidelines for marine or freshwater sediments, and only 20% mortality was seen under these conditions. A linear relationship was found between the body burdens of inorganic arsenic stored in the *C. volutator* and the total arsenic concentrations in the sediments. Non-exposed *C. volutator* accumulate arsenic mainly in the form of organoarsenic species of which the non-toxic arsenobetaine is the main species. The additional exposure to soluble inorganic arsenic increases the inorganic arsenic burden significantly: *C. volutator* is unable to transform the inorganic arsenic into less toxic organoarsenic forms over the timescale of the experiment. This is similar to snails, clams, seaweed, mussels, and plankton from contaminated sites (Whaley-Martin et al., 2012, 2013; Caumette et al., 2011; Koch et al., 2007a). The linearity of this body burden from the exposure to different sediment samples with different arsenic concentrations suggests that the forms of arsenic in the different sediment samples are similar with respect to arsenic bioavailability, consistent with the finding of similar bioaccessibility numbers for these sediments. It further suggests that it is arsenic rather than other components of the sediments that is responsible for the increased mortality rate.

3.4. Arsenic speciation in surface sediments

Arsenic speciation was determined for selected dried sediments that contained arsenic concentrations sufficiently high for XANES analysis. These included samples from Long Lake (L1 to L6), the settling pond at the northeast corner of Long Lake (LEa and LEb, SPb), the seep, and one background lake, Upper Quinsam Lake (U5) (Tables 2 and 3). Inorganic arsenic bound to oxygen, with the arsenic in both oxidation states +5 and +3, was found to be the predominant arsenic form in all sediments analyzed. The effect of sediment drying on arsenic speciation was investigated in a subset of sediments (LEa and LEb, SPb and U5). The percentage of As(V)–O was found to increase upon drying by 5–34% (see Table 3), but a paired *t*-test did not indicate a significant difference in percent As(V)–O between wet and dried sediments (*t*-test, *df* = 3, *t* = –2.998, *p* = 0.06). Nevertheless, arsenic oxidation likely took place upon sample drying and storage, and may have included oxidation of dissolved arsenic in pore water. Rowland and coworkers noted that regardless of the collection and storage method used, substantial oxidation of arsenic in sediments was commonly observed over storage periods of weeks to several months (Rowland et al., 2005).

Although we initially hypothesized that some trends may be discernible in arsenic speciation and bioaccessibility results (e.g., materials that are less bioaccessible might have more mineral As–S forms; or As(V) forms might be less bioaccessible than As(III) forms), this proved not to be the case. Neither the bioaccessibility nor the speciation results varied sufficiently to allow for the discernment of any trends; that is, the sediments were fairly homogenous with respect to both bioaccessibility and speciation.

3.5. Arsenic in sediment cores

Five cores (16–24 cm long) were collected from the eastern section of Long Lake in order to examine arsenic concentrations with respect to sediment depth. The arsenic concentration peaked at 2–4 cm in all five cores (see Fig. 1 for core locations and Fig. 4a for core arsenic concentrations). One core, Core E, was dated using a constant rate of supply (CRS) ^{210}Pb model (dating results are shown in supplementary data Fig. S2) with a sedimentation rate ranging between 0.01 and $0.06 \text{ g}\cdot\text{cm}^{-2}\cdot\text{year}^{-1}$, and its arsenic concentration peaked at over $1200 \text{ mg}\cdot\text{kg}^{-1}$, corresponding to a date of 1991. Dating indicates that the sediment depth of 5 cm

corresponds to the first mine disturbance in 1977. Cores collected in 1983 (Sneddon and Kelso, 1983) contained between 12 and $140 \text{ mg}\cdot\text{kg}^{-1}$ arsenic at a 20 cm depth, increasing from west to east in the lake, and the cores in the present study, collected at the east end of the lake, contained between 65 and $120 \text{ mg}\cdot\text{kg}^{-1}$ arsenic in their deepest section (15–25 cm). The 1983 cores collected from the east of the lake contained $1010 \pm 90 \text{ mg}\cdot\text{kg}^{-1}$ arsenic (Sneddon and Kelso, 1983), consistent with current maximum sediment core arsenic values. However, there are some unexplained large variations in element concentrations particularly for manganese concentrations over a short time span (weeks) that tend to downgrade the value of the Sneddon and Kelso data (Sneddon and Kelso, 1983) (see supplementary data).

One core collected several months before the other cores but from the same location (Core 1) was analyzed for arsenic species by XANES and the results are displayed in Fig. 4b. The only species detected were As(V)–O and As(III)–O with no sulfide species even at depth. A slight increase in the proportion of As(III) was seen as the depth increased (55% As(III) at surface and 70% at depth), but no clear redox zones were detected; in particular a predominance of As(V) at surface was not seen. This contraindicates the idea that oxidation of As(III) to As(V) is taking place at the surface to a significant degree in this core.

3.6. Multi-element analysis

Sediments were analyzed for a suite of 48 elements and a PCA of these data was used to find trends (Fig. S3). In this case, the PCA resulted in eight factors that explain 91% of the variation in the data instead of the original 48 elements (variables); and the first two factors explain 51% of the variance in the data (28% and 23% for factors one and two, respectively) from lake sediments. The principal component values and scores for the first two factors which explain the most variation in data are plotted in the supplementary data, and give a general indication of sample grouping. Long Lake sediments, in particular L2–L6, are grouped together in the quadrant at the positive side of Factor 1 and Factor 2. They cluster together because of the high concentrations of elements commonly associated with coal: arsenic, mercury, lead and cadmium (Huggins et al., 2002). The concentrations of these elements, although generally higher than concentrations found in other samples, were mostly below sediment quality guidelines. Only some of the Long Lake mercury concentrations were above the CCME interim sediment quality guideline of $0.17 \text{ mg}\cdot\text{kg}^{-1}$, but none were above the probable effects level of $0.486 \text{ mg}\cdot\text{kg}^{-1}$. The concentrations of antimony and cadmium are statistically significantly higher in Long Lake sediments than in Upper Quinsam Lake sediments. Soils collected from around the seep cluster with coarse refuse and sediments collected from settling ponds associated with mine waste. The PCA suggests that the element concentrations of the Long Lake sediments may be unique to the watershed but do not match putative mineral sources of arsenic such as the sulfides realgar, orpiment, and iron pyrites.

4. Discussion

Long Lake has a number of tailings and settling ponds located along its south shore as well as exposed rock surfaces and tailings piles. The hydraulic gradient in the area flows in the northeast direction, and water flows into Long Lake from an area of abandoned underground workings and acid generating tailings located at the southwest corner of the lake (referred to as “the seep”). This water flows in at various locations. High sulfate levels have been measured both in the seep water and in Long Lake itself and are indicative of acid rock drainage (Silva et al., 2011).

High arsenic concentrations in surficial sediments in Long Lake were hypothesized to be associated with: (1) the direct input of arsenic bearing iron oxide hydroxides into the lake from point sources such as the Long Lake seep, the gully west of the seep, and surface

mine workings; and (2) the sorption of dissolved arsenic by freshly precipitated iron hydroxyl species. All Long Lake sediments from deep waters (>10 m) (with the exception of L7 upstream of the seep input) contain over 10% iron and the solid sample from the seep contained 45% iron, indicating that there is ample iron present for these processes to occur. The water from the seep and the associated seasonally active creek reaches Long Lake southwest of L6 and includes ground water and surface water flow from the vicinity of pits that store high sulfur coal wastes and abandoned mine workings. The arsenic entering Long Lake from various sources is then redistributed throughout the lake by sediment focusing.

Significantly higher values of arsenic concentrations are found in sediments from Long Lake when the concentrations are compared with neighboring lakes. However a PCA of 48 elements does not indicate a cluster of the suspected source (seep) samples with the deep Long Lake sediments despite the high arsenic concentrations found in both (see Fig. S3), suggesting that Long Lake sediments are not simply seep solids that have settled at the bottom of the lake.

Sediment cores have been used to trace the history of anthropogenic inputs of arsenic into sediments (Senn et al., 2007). In the current study, arsenic concentrations in surficial sediments are 10 times higher those in the background sediments found deeper in the cores, similar to findings from other impacted sites (Garcia-Sanchez and Alvarez-Ayuso, 2003; Gault et al., 2005; Goldhaber et al., 2001). The arsenic profile in the cores closely resembles that of a lake that received a pulse arsenic input in the 1960s (Senn et al., 2007).

In the current study, ^{210}Pb sediment core data were used to determine the depth at which sediments could have been impacted by mining activities. The results shown in Fig. 4a indicate that the elevated arsenic could be caused entirely by anthropogenic sources, based upon the length of time the mine has been in operation (historical documents indicate that Long Lake was first disturbed around 1977). Strong support for historic mining activity that would have released anthropogenic arsenic is provided by the sulfate levels in Long lake, which were below $40 \text{ mg}\cdot\text{L}^{-1}$ in the early 1980s and began to increase rapidly after open pit coal production began in the late 1980s, reaching around $120 \text{ mg}\cdot\text{L}^{-1}$ by the end of 1999 (the provincial water quality guideline for sulfate is $100 \text{ mg}\cdot\text{L}^{-1}$). Acid rock drainage from arsenic loaded iron pyrites would account for both the increase in sulfate and arsenic during this period, and test pads set up by the mine confirm this takes place in exposed residues (QCC, 2009).

Therefore, mine inputs are confirmed by high sulfate concentrations in the water, high total arsenic concentrations in lake sediments relative to background lakes, and high iron, as well as the clustering of Long Lake deep sediments separate from other lakes in the area.

Although anthropogenic arsenic should be buried over time if no new arsenic is introduced to the lake (Senn et al., 2007), diagenesis, or the physical and chemical cycling of sediment through natural processes (solubilization, recrystallization, bioturbation, etc.), can complicate the interpretation of sediment core profiles. In a study of Loch Lomond in the UK, which is a lake thought to have had no known anthropogenic arsenic inputs, diagenesis was suspected to be the source of arsenic concentrations found in surficial sediments that were >10 times higher than those found in sediments deeper in the cores (Farmer and Lovell, 1986). However, one Loch Lomond sediment did not have arsenic enrichment in its surficial sediments, nor did Lake Como sediments (Monticelli et al., 2011). In a study of remote lakes in the UK, Yang and Rose (2005) show that As enrichment begins at the same time historically as other elements and they trace it to anthropogenic inputs; for example, most of the arsenic in sediments deposited since 1860 in Loch Chon, about 6 km away from Loch Lomond, was attributed to anthropogenic input. Clearly the contribution of diagenesis to surficial arsenic enrichment is complex and difficult to quantify.

Arsenic can be enriched in surface sediments because it is a redox-sensitive element: it is dissolved in a reduced zone (producing As(III)) below the sediment–water interface, diffuse up the sediment

column, and become oxidized and then adsorbed to iron oxyhydroxides (Farmer and Lovell, 1986). Pore water speciation has been used to support this sequence, by showing mostly As(III) in deeper sediments, and barely detectable concentrations of predominantly As(V) in surface sediments (Farmer, 1994). In other studies of contaminated sites, mixtures of As(III) and As(V) have been found, both in pore water (Andrade et al., 2010), and in solid sediment samples (Toevs et al., 2008). The latter result is similar to the results obtained in the present study with mixtures of As(III) and As(V) through the length of the core. In the present study, the degree to which diagenesis would contribute to the elevated arsenic concentrations found in Long Lake is not clear, but diagenesis would exacerbate the problem into perpetuity; for example, it could lead to undesirable release of arsenic from sediment triggered by eutrophication (Martin and Pedersen, 2004).

A common method of evaluating the ecological effect of contaminated sediment is to conduct an integrated sediment study based on three lines of evidence (LOE): sediment chemistry, toxicity testing, and benthic invertebrate assessment. Organisms chosen for benthic invertebrate assessment should be chosen with care when analyzing arsenic toxicity, as some organisms are quite tolerant of arsenic contaminated sediments. One example of this effect is provided by the response of the amphipod *H. azteca*, and *Chironomus* sp., organisms that are commonly used in the multiple LOE approach. *H. azteca* is part of the native community of sediments at Long Lake but can tolerate high concentrations of arsenic relative to guideline concentrations, with an LD_{50} of $532 \text{ mg}\cdot\text{kg}^{-1}$ arsenic (Liber et al., 2011). When reared in Long Lake sediments, *H. azteca* experienced substantial mortality relative to a negative control (>50%) at six of fifteen of near shore stations and two of four deep stations in laboratory tests, and thus the results could not be attributed solely to arsenic sediment concentrations (Golder Associates Ltd., 2011). The ambiguous toxicity in the Long Lake toxicity testing is consistent with the known resilience of this organism to arsenic; all of the sediments tested in the Golder (2011) study were at arsenic concentrations below *H. azteca*'s LD_{50} of $532 \text{ mg}\cdot\text{kg}^{-1}$ arsenic (Liber et al., 2011). The potential resistance of *H. azteca* compared with other freshwater benthic invertebrates may be the reason for a higher PEL of $48 \text{ mg}\cdot\text{kg}^{-1}$ suggested for this organism (McDonald et al., 2000) compared with the PEL guideline value of $17 \text{ mg}\cdot\text{kg}^{-1}$, which is based on a range of benthic organisms (CCME, 1999).

Another amphipod, the marine amphipod *C. volutator*, is known to respond in a mineralogical-specific way to arsenic (Cui et al., 2011). The present study shows that it responds predictably to arsenic concentrations in Long Lake sediments and yields an LD_{50} of $45\text{--}52 \text{ mg}\cdot\text{kg}^{-1}$, when exposed to high arsenic sediment L2 ($630 \text{ mg}\cdot\text{kg}^{-1}$). The LD_{50} value is lower ($24\text{--}35 \text{ mg}\cdot\text{kg}^{-1}$) when sediments with lower arsenic content ($30\text{--}110 \text{ mg}\cdot\text{kg}^{-1}$) are used in the tests. In this latter experiment the inorganic arsenic uptake by *C. volutator* is linear with respect to the arsenic sediment concentration.

Thus it appears that *C. volutator* is more sensitive to arsenic than *H. azteca*, and might be more representative of the toxicity experienced by a range or general population of benthic organisms (such as those used to develop the sediment guidelines). *C. volutator* may be an appropriate amphipod when arsenic toxicity specifically is being investigated. However, because the tests are not conducted under the same conditions that would pertain in the fresh water environment, further work is required to determine the effect of the sediment or soil type. It may be best to regard the results with this organism as an indication of general toxicity rather than an indicator of toxicity in a specific setting. Future studies might also target a freshwater organism for toxicity testing that is more appropriate for arsenic.

5. Conclusion

Arsenic in lake sediments is primarily bound to arsenic iron oxyhydroxide species and speciation analysis in the present study, by

revealing a lack of arsenic-sulfide species and only inorganic As–O species, indicates that arsenic iron oxy hydroxide species are the likeliest form in Quinsam watershed lakes. Chemical analysis combined with PCA confirms that the elemental compositions of samples from a mine impacted lake (Long Lake) are unique to that lake. Dating of sediment cores in Long Lake revealed an increase of arsenic around the time mining operations began. This coincided with an increase in sulfate levels in the lake water. Overall the evidence indicates a mainly anthropogenic origin for the arsenic with a seep from abandoned underground workings being one of the sources. However, the possibility that diagenesis leads to some arsenic enhancement in surficial sediment cannot be ignored.

The test organism *C. volutator* could be a candidate for arsenic toxicity testing as it is capable of providing an estimation of the relative toxicity of the sediments but such tests will need further development before application to specific sites.

Author contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Acknowledgment

The 2008–2010 field programs were carried out by Dr. William R. Cullen and Vivian W.-M. Lai from UBC in the Quinsam watershed and mine site. They were assisted by Peter Winter, Barry Ross and Stan Goodrich from the Campbell River Environmental Committee (CREC) and personnel from the mine. Pacific Northwest Consortium X-ray Sciences Division (PNC/XSD) facilities at the APS, and research at these facilities, are supported by the US Department of Energy – Basic Energy Sciences, a Major Resources Support grant from NSERC, the University of Washington, Simon Fraser University and the Advanced Photon Source. Use of the Advanced Photon Source is also supported by the US Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract DE-AC02-06CH11357. Assistance at APS was provided by Dr. Robert Gordon. Mati Raudsepp, Department of Earth and Ocean Sciences, UBC, provided the X-ray powder diffraction and electron microscopy analyses. Funding was provided by the Canadian Water Network, and an NSERC Discovery Grant to KJR. The bioassay tests were funded by the TESLA research fund and the University of Aberdeen.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.scitotenv.2013.07.005>.

References

Andrade CF, Jamieson HE, Kyser TK, Praharaj T, Fortin D. Biogeochemical redox cycling of arsenic in mine-impacted lake sediments and co-existing pore waters near Giant Mine, Yellowknife Bay, Canada. *Appl Geochem* 2010;25:199–211.

Appleby PG, Last WM, Smol JP. Chronostratigraphic techniques in recent sediment. Tracking environmental change using lake sediments, vol. 1. Basin Analysis, Coring, and Chronological Techniques; 2001. p. 172–203.

Canadian Council of Ministers of the Environment (CCME). Canadian sediment quality guidelines for the protection of aquatic life: arsenic. <http://st-ts.ccme.ca/?lang=en&factsheet=9>, 1999. [accessed 15 May 2013].

Caumette G, Koch I, Estrada E, Reimer KJ. Arsenic speciation in plankton organisms from contaminated lakes transformations at the base of the freshwater food chain. *Environ Sci Technol* 2011;45:9917–23.

Cui L, Newcombe C, Urgast DS, Raab A, Krupp EM, Feldmann J. Assessing the toxicity of arsenic-bearing sulfide minerals with the bio-indicator *Corophium volutator*. *Environ Chem* 2011;8:52–61.

Farmer JG. Environmental change and the chemical record in Loch Lomond sediments. *Hydrobiologia* 1994;290:39–49.

Farmer JG, Lovell MA. Natural enrichment of arsenic in Loch Lomond sediments. *Geochim Cosmochim Acta* 1986;50:2059–67.

Fendorf S, Nico PS, Kocar BD, Masue Y, Tufano KJ. Arsenic chemistry in soils and sediments. In: Singh B, Grafte M, editors. *Synchrotron-based techniques in soils and sediments*. Elsevier Publishing; 2010. p. 357–78.

Garcia-Sanchez A, Alvarez-Ayuso E. Arsenic in soils and waters and its relation to geology and mining activities (Salamanca Province, Spain). *J Geochem Explor* 2003;80:69–79.

Gault AG, Polya DA, Lythgoe PR, Farquhar ML, Charnock JM, Wogelius RA. Arsenic speciation in surface waters and sediments in a contaminated waterway: an IC–ICP–MS and XAS based study. *Appl Geochem* 2003;18:1387–97.

Gault AG, Cooke DR, Townsend AT, Charnock JM, Polya DA. Mechanisms of arsenic attenuation in acid mine drainage from Mount Bischoff, western Tasmania. *Sci Total Environ* 2005;345:219–28.

Golder Associates Ltd. Interpretive report: 2010 Integrated Long Lake sediment assessment; 2011 [10-1421-0017].

Goldhaber MB, Irwin ER, Atkins B, Lee L, Black DD, Zappia H, et al. Arsenic in stream sediments of northern Alabama: U.S. Geological Survey miscellaneous field studies; 2001 [Map MF-2357].

Huggins FE, Huffman GP, Kolker A, Mroczkowski SJ, Palmer CA, Finkelman RB. Combined application of XAFS spectroscopy and sequential leaching for determination of arsenic speciation in coal. *Energy Fuel* 2002;16:1167–72.

Koch I, McPherson K, Smith P, Easton L, Doe KG, Reimer KJ. Arsenic bioaccessibility and speciation in clams and seaweed from a contaminated marine environment. *Mar Pollut Bull* 2007a;54:586–94.

Koch I, Sylvester S, Lai VW-, Owen A, Reimer KJ, Cullen WR. Bioaccessibility and excretion of arsenic in *Niu Huang Jie Du Pian* pills. *Toxicol Appl Pharmacol* 2007b;222:357–64.

Kwan SY, Tsui SK, Man TO. Release of soluble arsenic from realgar in simulated gastric juice. *Anal Lett* 2001;34:1431–6.

Liber K, Doig LE, White-Sobey SL. Toxicity of uranium, molybdenum, nickel, and arsenic to *Hyalella azteca* and *Chironomus dilutus* in water-only and spiked-sediment toxicity tests. *Ecotoxicol Environ Saf* 2011;74:1171–9.

Liu J, Lu Y, Wu Q, Goyer RA, Waalkes MP. Mineral arsenicals in traditional medicines: orpiment, realgar and arsenolite. *J Pharmacol Exp Ther* 2008;326:363–8.

Martin AJ, Pedersen TF. Alteration to lake trophic status as a means to control arsenic mobility in a mine-polluted lake. *Water Res* 2004;24:4415–23.

McDonald DD, Ingersoll CG, Berger TA. Development and evaluation of consensus-based sediment quality guidelines for freshwater ecosystems. *Arch Environ Contam Toxicol* 2000;39:20–31.

Meunier L, Wragg J, Koch I, Reimer KJ. Method variables affecting the bioaccessibility of arsenic in soil. *J Environ Sci Health A* 2010a;45:517–26.

Meunier L, Walker SR, Wragg J, Parsons MB, Koch I, Jamieson HE, et al. Effects of soil composition and mineralogy on the bioaccessibility of arsenic from tailings and soil in gold mine districts of Nova Scotia. *Environ Sci Technol* 2010b;44:2667–74.

Monticelli D, Pozzi A, Ciceri E, Giussani B. Interpreting complex trace element profiles in sediment cores from a multi-basin deep lake: the western branch of Lake Como. *Int J Environ Anal Chem* 2011;91:213–29.

Moore JN. Partitioning of arsenic and metals in reducing sulfidic sediments. *Environ Sci Technol* 1988;22:432–7.

Nagpal NK, Pommen LW, Swain LG. A compendium of working water quality guidelines for British Columbia. Environmental Protection Division, Science and Information Branch, British Columbia Ministry of Environment; 2006 [<http://www.env.gov.bc.ca/wat/wq/BCguidelines/working.html>, accessed 7 May 2013].

Nordin R. An evaluation of the sediment quality and invertebrate benthic communities of Long lake and Middle Quinsam Lakes with regard to local mining activity; 2006.

Peña-Icart M, Tagle MEV, Alonso-Hernández C, Hernández JR, Behar M, Alfonso MSP. Comparative study of digestion methods EPA 3050B (HNO₃–H₂O₂–HCl) and ISO 11466.3 (aqua regia) for Cu, Ni and Pb contamination assessment in marine sediments. *Mar Environ Res* 2011;72:60–6.

QCC. Volume 1. 2008/09 Annual Water Quality Monitoring and Reclamation Report: Covering Waste Management Permit PE-07008 and Reclamation Permit C-172, Reporting Period from April 01/08 to March 31/09, September; 2009.

Ravel B, Newville M. ATHENA, ARTEMIS, HEPHAESTUS: data analysis for X-ray absorption spectroscopy using IFEFFIT. *J Synchrotron Radiat* 2005;12:537–41.

Rieberger K. Metal concentrations in bottom sediment from uncontaminated BC lakes British Columbia. British Columbia: Water Management Division, Ministry of Environment; 1992.

Rodriguez RR, Basta NT, Casteel SW, Pace LW. An *in vitro* gastrointestinal method to estimate bioavailable arsenic in contaminated soils and solid media. *Environ Sci Technol* 1999;33:642–9.

Root RA, Vlassopoulos D, Rivera NA, Rafferty MT, Andrews C, O'Day PA. Speciation and natural attenuation of arsenic and iron in a tidally influenced shallow aquifer. *Geochim Cosmochim Acta* 2009;73:5528–53.

Rowland HAL, Gault AG, Charnock JM, Polya DA. Preservation and XANES determination of the oxidation state of solid-phase arsenic in shallow sedimentary aquifers in Bengal and Cambodia. *Mineral Mag* 2005;69:825–39.

Ruby MV, Davis A, Schoof R, Eberle S, Sellstone CM. Estimation of lead and arsenic bioavailability using a physiologically based extraction test. *Environ Sci Technol* 1996;30:422–30.

Senn DB, Gawel JE, Jay JE, Hemond HF, Durant JL. Long-term fate of a pulse arsenic input to a eutrophic lake. *Environ Sci Technol* 2007;41:3062–8.

Shine JP, Ika RV, Ford TE. Multivariate statistical examination of spatial and temporal patterns of heavy metal contamination in New Bedford Harbor marine sediments. *Environ Sci Technol* 1995;29:1781–8.

Silva LF, Wollenschlager M, Oliviera MLS. A preliminary study of coal mining drainage and environmental health in the Santa Catarina region, Brazil. *Environ Geochem Health* 2011;33:55–65.

Singh KP, Malik A, Sinha S, Singh VK, Murthy RC. Estimation of source of heavy metal contamination in sediments of Gomti River (India) using principal component analysis. *Water Air Soil Pollut* 2005;166:321–41.

- Smith PG, Koch I, Gordon RA, Mandoli DF, Chapman BD, Reimer KJ. X-ray absorption near-edge structure analysis of arsenic species for application to biological environmental samples. *Environ Sci Technol* 2005;39:248–54.
- Sneddon H, Kelso B. A data report on water quality of the receiving waters of the area around the proposed Quinsam coal development. Environment Canada, Environmental Protection Branch; 1983.
- Toevs G, Morra MJ, Winowiecki L, Strawn D, Polizzoto ML, Fendorf S. Depositional influences on porewater arsenic in sediments of a mining-contaminated freshwater lake. *Environ Sci Technol* 2008;42:6823–9.
- Traunspurger W, Crews C. Toxicity analysis of freshwater and marine sediments with meio- and macrobenthic organisms: a review. *Hydrobiologia* 1996;328:215–61.
- Whaley-Martin K, Koch I, Moriarty M, Reimer KJ. Arsenic speciation in blue mussels (*Mytilus edulis*) along a highly contaminated arsenic gradient. *Environ Sci Technol* 2012;46:3110–8.
- Whaley-Martin K, Koch I, Moriarty M, Reimer KJ. Arsenic speciation in edible periwinkles (*Littorina littorea*) by HPLC–ICPMS and XAS along a contamination gradient. *Sci Total Environ* 2013;456–457:148–53.
- Yang H, Rose N. Trace element pollution records in some UK lake sediments, their history, influence factors and regional differences. *Environ Int* 2005;31:63–75.
- Zitko V. Principal component analysis in the evaluation of environmental data. *Mar Pollut Bull* 1994;28:718–22.