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Contrasting arsenic cycling in strongly and weakly stratified contaminated lakes: Evidence for temperature control on sediment-water arsenic fluxes

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Abstract

Arsenic contamination of lakebed sediments is widespread due to a range of human activities, including herbicide application, waste disposal, mining, and smelter operations. The threat to aquatic ecosystems and human health is dependent on the degree of mobilization from sediments into overlying water columns and exposure of aquatic organisms. We undertook a mechanistic investigation of arsenic cycling in two impacted lakes within the Puget Sound region, a shallow weakly-stratified lake and a deep seasonally-stratified lake, with similar levels of lakebed arsenic contamination. We found that the processes that cycle arsenic between sediments and the water column differed greatly in shallow and deep lakes. In the shallow lake, seasonal temperature increases at the lakebed surface resulted in high porewater arsenic concentrations that drove larger diffusive fluxes of arsenic across the sediment-water interface compared to the deep, stratified lake where the lakebed remained ~10°C cooler. Plankton in the shallow lake accumulated up to an order of magnitude more arsenic than plankton in the deep lake due to elevated aqueous arsenic concentrations in oxygenated waters and low phosphate: arsenate ratios in the shallow lake. As a result, strong arsenic mobilization from sediments in the shallow lake was countered by large arsenic sedimentation rates out of the water column driven by plankton settling.

Keywords

arsenic; lakes; temperature

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Data

All original data presented in this manuscript have been submitted to the Pangaea data repository and are publicly accessible at <https://doi.pangaea.de/10.1594/PANGAEA.896037>.

1. Introduction

Arsenic is a carcinogen and neurotoxin naturally found in rocks, soils and sediments around the world (Smedley and Kinniburgh 2002). In the solid phase, it typically poses little risk to human or ecosystem health. However, when it is mobilized from the solid phase into air or water, biological exposure can occur, posing threats to the health of aquatic ecosystems (Chen et al. 2015) and to humans who may consume contaminated fish (Williams et al. 2006). Globally, lakebed sediments are contaminated by arsenic from pesticide application, mining, and a range of other industrial activities (Aurilio et al. 1994; Martin and Pedersen 2002; Durant et al. 2004; Chen et al. 2008; Whitmore et al. 2008; Barringer et al. 2011). Given the widespread nature of arsenic contamination in lakes and the ecosystem and human health threat posed by arsenic in lake water columns, it is important to understand the physical, chemical and biological processes involved in lacustrine arsenic cycling. These may include mobilization of arsenic from lakebed sediments into porewaters, flux of porewater arsenic to the overlying water column, arsenic uptake by the aquatic foodweb, and sequestration of arsenic out of the water column back into lakebed sediments. Previous studies have predominately focused on deep lakes in the Northern Hemisphere that experience summer stratification (Rodie et al. 1995; Smedley and Kinniburgh 2002); in these systems, the potential for mobilization of reduced arsenic species into hypolimnetic waters during seasonal anoxia has been relatively well-documented. However, few investigations exist for shallow lakes, yet the dominant processes and time-scales associated with arsenic mobilization, transport, and biotic uptake are expected to be different in shallow water bodies (Aurilio et al. 1994; Arnold and Oldham 1997), which tend to maintain well-mixed, oxic water columns throughout the year.

We undertook a mechanistic investigation of two lakes impacted by sediment arsenic contamination in the Puget Sound region in western WA— a shallow, weakly stratified lake (Lake Killarney) and a deep, seasonally stratified lake (Angle Lake). In this region, the former ASARCO copper smelter (1890 to 1986) released arsenic, associated with copper ore, through its emissions stack into the atmosphere (Glass 2003). Arsenic settled out downwind of the smelter across the landscape, contaminating surface soils and also lakebed sediments, which contain large amounts of legacy arsenic pollution (Gawel et al. 2014). Initial work on lakes in the impacted region has shown that this sedimentary arsenic may be mobilized into the overlying water column and enter the aquatic food web (Gawel et al., 2014; Barrett et al. 2018).

There are a range of physical, chemical, and biological factors likely to exert control on arsenic cycling in these contrasting study sites. In lakebed sediments, arsenic tends to be associated with iron-(hydr)oxide minerals, either sorbed to or co-precipitated with these minerals (Ferguson and Gavis 1972). Arsenic can be mobilized into porewaters through competitive ion desorption from sediment particles or by reductive dissolution of the Fe-oxide mineral (Smedley and Kinniburgh 2002). Reductive dissolution is mediated by microbes that, in anaerobic conditions, oxidize organic carbon by reducing Fe(III). Thus, a key control on arsenic mobilization is organic carbon, which fuels the reactions that consume oxygen and other electron acceptors, driving the system to iron-reducing conditions, as well as supplying ions such as phosphate that can mobilize arsenic from

sediment particles via competition for sorption sites. Additionally, because arsenic mobilization during dissimilatory iron reduction is a microbially-mediated process and microbial kinetics are impacted by temperature (Ratkowsky et al. 1982), temperature has potential to modify rates of arsenic release from sediments, as has been suggested by laboratory experiments with terrestrial soils (Weber et al. 2010).

Once mobilized into sediment porewaters, arsenic can be transported by molecular or turbulent diffusion into the overlying water column. The fate of arsenic within the lake water column largely depends on the mixing regime of the lake. Classically, elevated levels of arsenic are associated with anaerobic hypolimnetic waters that form during summer stratification (Aggett and O'Brien 1985; Azcue and Nriagu 1995; Senn et al. 2007; Barringer et al. 2011; Wei et al. 2011). In seasonally stratified lakes, arsenic generally remains trapped within the hypolimnion and is typically present in the reduced form as arsenite (Aurilio et al. 1994; Martin and Pedersen 2002; Durant et al. 2004; Barringer et al. 2011, 2007; Chen et al. 2008; Barrett et al. 2018). Of the lakes impacted by legacy arsenic contamination in the Puget Sound region, those that exhibited seasonal hypolimnetic anoxia had elevated dissolved arsenic in bottom waters at levels correlated to sedimentary arsenic concentrations (Gawel et al., 2014). Arsenate, the oxidized form of arsenic, is particle reactive and can be readily scavenged out of oxic water columns due to sorption onto settling particles and sediments (de Vitre et al., 1991; Dixit and Hering 2003; Tufano and Fendorf 2008). Thus, arsenic concentrations are typically low in oxic waters because of this particle reactivity (Smedley and Kinniburgh 2002). However, some shallow well-mixed lakes in our study region have also been shown to maintain high arsenic concentrations during summer months (Barrett et al. 2018). In unstratified or weakly stratified lakes, arsenic tends to be mixed throughout the oxic water column rather than being isolated in the hypolimnion (Martin and Pedersen 2002; Couture et al. 2010; Barrett et al. 2018).

A key outcome of the flux of arsenic in oxic lake water columns is increased potential for biological exposure to aqueous arsenic (Barrett et al. 2018). In oxygenated conditions, arsenic tends to be speciated as arsenate, a phosphate analog, which is mistakenly taken up by phytoplankton during phosphate transport (Rahman et al. 2012). This uptake of arsenic by phytoplankton is a critical entry point for arsenic into the aquatic food web as zooplankton and fish primarily accumulate arsenic through their diets (Chen and Folt 2000; Chen et al. 2000; Erickson et al. 2011). The uptake of arsenate by phytoplankton depends on the trophic status of the lake and the relative concentrations of arsenate and phosphate. When phosphorus is not a limiting nutrient, which can be the case in the early stages of blooms, algae will take up excess phosphorus ('luxury uptake'), resulting in enhanced arsenate uptake (Hellweger et al. 2003; Hellweger and Lall 2004). When phosphorus is a limiting nutrient, which is usually the case in summer, the rate of arsenate uptake is typically inversely proportional to the phosphate-to-arsenate ratio as the two species compete for uptake sites on cell membranes (Sanders and Windom 1980).

Multiple processes may remove arsenic from the lake water column. Arsenic taken up by plankton is returned to the sediments when the plankton die and settle from the water column. In seasonally stratified lakes, sulfide generation associated with prolonged anoxia can facilitate precipitation of arsenic-sulfide minerals (Moore et al. 1988; Harrington et al.

1998). Additionally, when stratification ends, mixing and oxygenation of the lake can result in both arsenic and iron oxidation, likely promoting scavenging of arsenate onto settling Fe-rich particles (Hartland et al. 2015). Hence, a range of physical, biological and chemical processes influence arsenic concentrations in lake waters, including temperature, mixing status, organic carbon availability, and phosphate concentrations. Ultimately, aquatic exposure to aqueous arsenic depends on the balance between the processes responsible for moving arsenic out of the sediment into the overlying water and the processes that remove arsenic from the water column. Our study demonstrates that the rates and amount of arsenic cycling between lakebed sediments and overlying lake water are dramatically different between shallow, weakly stratified lakes and deep, seasonally stratified lakes. Year-round *in situ* water column and sediment sampling in study lakes combined with laboratory experiments manipulating intact sediment cores suggests that temperature plays a fundamental role in arsenic mobilization under the different mixing regimes typical of deep and shallow lakes.

2. Methods

2.1 Study sites

Angle Lake and Lake Killarney are densely-populated urban lakes in the South Puget Sound lowlands (Figure S1) with arsenic-contaminated sediments from legacy pollution due to aerial emissions from the former ASARCO copper smelter in Ruston, WA, now designated the Commencement Bay/Nearshore Tidelands Superfund Site (Gawel et al. 2014). Angle Lake and Lake Killarney have similar concentrations of arsenic in lakebed sediments, but different mixing behaviors and levels of productivity (Table 1) (Barrett et al. 2018). Angle Lake is a deep, oligotrophic lake that experiences strong thermal seasonal stratification resulting in anoxic bottom waters, while Lake Killarney is a shallow eutrophic lake that generally maintains a well-mixed, oxic water column throughout the year (Figure S2).

Water, plankton, sediment, sediment trap, and porewater sampling was conducted from a boat at approximately the deepest point in each lake. Water, plankton, and sediment trap sample collection was carried out monthly in winter (Nov–Mar) and twice monthly in spring, summer, and fall (Apr–Oct) on a total of 29 dates between July 2016 and December 2017. Sediment and porewater sampling was conducted in summer 2016 (July–Oct), summer 2017 (Aug) and winter 2017 (Dec) (Table S1).

2.2 Water and plankton

Water and plankton sampling was carried out as reported in Barrett et al. (2018). Briefly, temperature and dissolved oxygen profiles were measured using a multi-parameter water quality probe (In-Situ smarTROLL MP). Unfiltered and filtered (0.45 µm Geotech cartridge filter) water samples were collected from four depths using a peristaltic pump into acid-washed polypropylene bottles. Samples for ICP-MS analysis were acidified with trace metal grade nitric acid (1% v/v). Filtered water samples for analysis of arsenic speciation were preserved with 0.5 mM EDTA in 10 mM acetic acid (Samanta and Clifford 2005). Water samples for determination of dissolved phosphorus concentrations were frozen until analysis on a Westco SmartChem 200 Discrete Analyzer (Standard Method 4500-P E).

Phytoplankton vertical net tows (20 μm) were collected from 1–2 m above bottom and stored in acid-washed polypropylene bottles on ice, then filtered through a 153 μm sieve to remove zooplankton and collected on pre-weighed 5 μm polycarbonate membrane filters (Millipore) in the laboratory. Phytoplankton samples were dried overnight (60°C) then subjected to a microwave (CEM MARS 5) total digestion protocol (modified EPA method 3015) using trace metal grade nitric acid in pressurized digestion vessels.

Total arsenic concentrations in water and phytoplankton samples were determined by ICP-MS (Agilent 7900, University of Washington Tacoma). Analytical accuracy was monitored using NIST 1640a (trace elements in natural water), which had a recovery of $107 \pm 12\%$ ($n = 10$) for arsenic. The phytoplankton digestion protocol was verified using BCR-414 (trace elements in plankton), which had a recovery of $95 \pm 7\%$ ($n=8$). The total method blank for analysis of phytoplankton arsenic was determined from blank filters; the method blank of 0.8 ng As ($n=3$) is equivalent to a concentration of $0.05 \mu\text{g g}^{-1}$ for the average phytoplankton sample weight (15 mg).

The speciation of arsenic in filtered water samples was determined at the Trace Element Analysis laboratory at Dartmouth College on an Agilent LC1120 liquid chromatograph, using an anion-exchange column (Hamilton PRP-X100), coupled to an Agilent 8900 triple quadrupole ICP-MS (Taylor and Jackson 2016). The eluent was 20 mM $(\text{NH}_4)_2\text{CO}_3$ at a flow rate of 1.1 mL min^{-1} with a column temperature of 35°C. Quality control included analysis of recoveries (reported for arsenate) from spikes ($89 \pm 5\%$, $n=4$) and calibration verifications using a secondary standard ($107 \pm 3\%$, $n=11$) run at intervals of one every 10–20 samples.

2.3 Sediment traps

Sediment trap design consisted of 2 ABS tubes (10 cm x 70 cm) to minimize turbulence (Bloesch and Burns 1980) covered with a ~1 cm mesh to deter large predators, with reducing couplings connected to 250 mL sample bottles. Traps were deployed at mid-depth (~7 m and ~2 m from bottom in Angle Lake and Lake Killarney, respectively) and near bottom (~1 m above bottom) in both lakes on each sampling date, and collected the following sampling date. In the laboratory, samples were pre-filtered through a 335 μm sieve onto a polycarbonate filter to exclude grazers and large, terrestrially-derived material. After drying at 60°C, samples underwent the total microwave-assisted digestion procedure described above and arsenic concentrations were determined by ICP-MS. The protocol was verified using NIST 2711a (Montana Soil II) with a recovery of $91 \pm 12\%$, $n = 6$. Method blanks were equivalent to a concentration of $0.03 \mu\text{g g}^{-1}$ for the average sample weight analyzed (30 mg).

2.4 Porewater

Passive diffusive samplers for porewater collection (peepers) were adapted from LaForce et al. (2000) and Thomas and Arthur (2010) with the addition of horizontal wings at the sediment-water interface for stabilization (Figure S2). The PVC peepers hold sample vials at 14 sampling depths across the sediment-water interface with a vertical resolution of 3.4 cm and 4 replicate vials per depth. Sample vials (LDPE, 5 mL) were filled with a de-oxygenated

reverse tracer solution (200 μM KBr) and covered with polysulfone membrane filters (0.2 μm). Vials were transported to the field with oxygen scavengers in sealed bags and placed in the peeper frame immediately prior to deployment. Peepers were positioned in sediments either by divers or by lowering with a line from the boat; the placement and orientation was verified at the start and end of deployment by camera. Peepers were typically deployed for 2 weeks (Table S1). After recovery, duplicate porewater samples were acidified in the laboratory for ICP-MS analysis of arsenic concentrations. Bromide concentrations were measured using an ion selective electrode. The reverse tracer was used to monitor equilibrium of the sample cell with surrounding porewaters and correct measured arsenic concentrations as in Thomas and Arthur (2010); the applied correction was <1% for all samples.

2.5 Sediment

Bulk surface sediment (top 10–20 cm) was collected using a grab sampler and analyzed for arsenic by total digest (microwave-assisted digestion followed by ICP-MS) and organic carbon content (loss on ignition).

Sediment cores were collected by *in situ* freezing for preservation of unconsolidated near-surface sediments and redox-sensitive solid phases of arsenic. The fiberglass freeze corer was built following the design of Rauch et al. (2006). The corer was filled with a dry ice/ alcohol slush and lowered vertically into the sediments for 10 min to freeze a sediment slab onto the steel plate (8 cm x 90 cm). Cores were covered in plastic wrap and stored on dry ice in the field, then sealed in vacuum bags with oxygen scavengers and stored frozen. Freeze cores were sectioned under a N_2 atmosphere in a glovebox using a hot knife. The top 10 cm was collected and allowed to thaw in gas-tight centrifuge tubes, then centrifuged at 4500 rpm for 30 min. The porewater was decanted and sediment samples were dried open in a desiccator under N_2 . When dry, the sediment was homogenized using a mortar and pestle in the glovebox, then split into duplicate samples of 100–300 mg.

The solid phase of arsenic in sediments was investigated using a 3-step sequential extraction protocol adapted from Loeppert and Inskeep (1996) and Keon et al. (2001): a phosphate-exchangeable fraction (PE) targeting strong adsorbed arsenic, a citrate-bicarbonate-dithionite (CBD) treatment targeting arsenic associated with iron oxides, and a microwave-assisted total nitric digestion targeting residual arsenic (R). For the first extraction step (PE), 1 M NaH_2PO_4 adjusted to pH ~5 with trace metal grade HCl was added to sediment samples in the glovebox with an extractant to sediment ratio of 100:1. The sample was tumbled for 16 hr, then centrifuged at 4500 rpm for 45 min. The extractant solution was decanted in the glovebox, syringe-filtered (0.2 μm), and acidified with ultra trace metal grade nitric (1% v/v). The procedure was repeated with another treatment of 1 M NaH_2PO_4 tumbled for 24 hours, followed by a wash with Milli-Q water tumbled for 30 min. For the second extraction step (CBD), sediment samples were heated in a water bath to 75–80°C with 1 M NaHCO_3 (0.5 mL) and 0.3 M sodium citrate (4 mL) in a clean hood. Two additions of sodium dithionite (0.1 g) were added to the slurries and stirred for 5 and 15 minutes, respectively. Samples were then centrifuged, decanted, filtered, and acidified as in the previous step, followed by two Milli-Q washes. Finally, residual sediment samples were dried on

polycarbonate filters and subjected to the total digestion procedure described above. Total method blanks were determined by the same procedures using extractant solutions only; blanks for all steps were <1% of average sample arsenic content given average sample mass (230 mg).

2.6 Sediment core temperature incubation experiment

Four gravity cores were collected from each study lake in January 2018. Small (~2 mm) holes were pre-drilled into CAB plastic core sleeves (5 cm x 76 cm) every 4 cm and covered with electrical tape. In the laboratory, the overlying water was syphoned off until the water level was consistent across all 8 cores (32 cm above the sediment surface). Using a syringe, vegetable oil (~ 5 mL) was added to the water surface to prevent gas exchange during the incubation period. Duplicate cores from each lake were placed in temperature-controlled chambers held at 10°C and 20°C. The overlying water in each core was sampled approximately weekly at 7 timepoints over the next 48 days. A needle and syringe was used to collect ~ 4 mL of sample through the pre-drilled hole closest to the surface of the sediment, angling the needle to collect water ~ 1 cm above the sediment-water interface. The samples were then syringe-filtered and acidified to 1% HNO₃ for ICP-MS analysis. At the final timepoint, 25 mL of water was also collected for spectrophotometric determination of sulfide concentrations by methylene blue method (Chemetrics Vacu-vials K-9503).

3. Results and Discussion

3.1 Sediment to Lake Water Arsenic Flux

Strong seasonal thermal stratification of the water column in Angle Lake led to depletion of dissolved oxygen (<0.2 mg L⁻¹) in bottom waters in summer, typically June-Oct (Figure 1). During these periods, elevated arsenic concentrations were observed below the thermocline in Angle Lake (Figure 1), indicating a sedimentary source of arsenic to the water column. Maximum observed bottom water concentrations varied interannually, reaching 56.3 µg L⁻¹ in Oct 2015 (Barrett et al. 2018), 35.3 µg L⁻¹ in Sept 2016, and 3.5 µg L⁻¹ in June 2017. In Lake Killarney, the water column remained relatively well-mixed throughout the year with only weak thermal stratification observed in the summer (Figure 1). Bottom waters were occasionally hypoxic (> 2 mg L⁻¹), as observed in July 2016 and June-Aug 2017. Despite the lack of a persistent hypoxic hypolimnion, sedimentary release of dissolved arsenic was also apparent in Lake Killarney as evidenced by elevated arsenic concentrations in bottom waters, with maximum observed concentrations of 29.6 µg L⁻¹ in Sept 2015 (Barrett et al. 2018), 52.7 µg L⁻¹ in May 2016, and 70.6 µg L⁻¹ in July 2017 (Figure 1). Comparison of filtered and unfiltered water samples revealed that arsenic was largely in the dissolved (<0.4 µm) phase throughout the water column in both Angle Lake (76 ± 21%) and Lake Killarney (72 ± 23%), suggesting that the sedimentary arsenic source to the water column was primarily a flux of aqueous arsenic from porewaters rather than re-suspension of arsenic-rich sediment particles.

Dissolved arsenic concentrations measured in porewaters collected from passive peeper samplers (Figure 2) reveal arsenic profiles across the sediment-water interface that also suggest a robust sedimentary source of arsenic to the water column in Lake Killarney and

seasonally in Angle Lake; profiles from Angle Lake in late summer suggest that a stable hypolimnion had allowed equilibration between bottom waters and sediment porewaters. Most notably, porewater arsenic profiles show marked differences between Angle Lake and Lake Killarney in the seasonal trends in maximum arsenic concentrations in sediment porewaters. In Angle Lake, average porewater arsenic concentrations remained relatively constant between winter ($38 \pm 5 \mu\text{g L}^{-1}$) and summer ($43 \pm 4 \mu\text{g L}^{-1}$ in 2016 and $38 \pm 6 \mu\text{g L}^{-1}$ in 2017). However, in Lake Killarney, large seasonal variation was observed in porewater arsenic, which increased from concentrations similar to those observed in Angle in the winter ($19 \pm 15 \mu\text{g L}^{-1}$) to $>1000 \mu\text{g L}^{-1}$ in summer (averaging $948 \pm 121 \mu\text{g L}^{-1}$ in 2016 and $714 \pm 238 \mu\text{g L}^{-1}$ in 2017). Similarly elevated porewater arsenic concentrations have been observed by previous researchers in suboxic sediment zones in highly contaminated lakes (Andrade et al. 2010; Toevs et al. 2008; Van Den Berghe et al. 2018). Due to the vertical resolution of the passive sampler ($\sim 3 \text{ cm}$), measured concentrations represent some spatial averaging that may overlook micro-scale heterogeneity within sediments that could contain localized maxima in porewater arsenic (Stockdale et al. 2009) and hence, maximum observed porewater arsenic concentrations reported here may be a conservative estimate. However, likely due to relatively high sedimentation rates at our study sites, peak arsenic concentrations in reported porewater profiles are typically represented by multiple sampling depths and the porewater arsenic profiles we observe are similar to those reported for contaminated lake sediments using higher-resolution techniques (e.g., Sun et al. 2016).

The elevated porewater arsenic concentrations in Lake Killarney during the summer created strong concentration gradients (dC/dz) across the sediment-water interface ($-0.15 \mu\text{g cm}^{-4}$ in July 2016 and $-0.10 \mu\text{g cm}^{-4}$ in August 2017); the gradient decreased significantly in the winter ($-1.7 \times 10^{-3} \mu\text{g cm}^{-4}$ in December 2017). Using these gradients, we calculated the flux density of arsenic from the sediments into the overlying water column due to molecular diffusion using a conservative Fickian transport coefficient $D = 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ (Hemond and Fechner 2014). The diffusive flux density for Lake Killarney was calculated to be $1300 \mu\text{g m}^{-2} \text{ d}^{-1}$ in July 2016 and $870 \mu\text{g m}^{-2} \text{ d}^{-1}$ in August 2017 (Table 2). By comparison, diffusive flux rates for arsenic in Angle Lake were 130 times less than that for Lake Killarney in July 2016 ($11 \mu\text{g m}^{-2} \text{ d}^{-1}$) and 60 times less than that for Lake Killarney in August 2017 ($14 \mu\text{g m}^{-2} \text{ d}^{-1}$). The largest diffusive flux of arsenic in Angle Lake occurred in December 2017 ($127 \mu\text{g m}^{-2} \text{ dy}^{-1}$) but this maximum rate was still 10 times less than peak summer rates in Lake Killarney.

Because Angle Lake remains thermally stratified throughout the summer, the lakebed environment experienced relatively little variation in temperature, warming only slightly from 4°C in winter to $9\text{--}10^\circ\text{C}$ in summer (Figure 1). By contrast, bottom water temperatures in Lake Killarney increased from a winter minimum of 4°C to a maximum summer temperature of 23°C . These seasonal trends in bottom water temperatures mirror those in porewater arsenic concentrations and suggest that temperature is a strong control on the variation in sedimentary arsenic mobility in Angle Lake and Lake Killarney. Increased microbial activity driven by elevated temperatures ($>20^\circ\text{C}$) is likely to promote arsenic release associated with the dissimilatory reduction of Fe-oxides. Porewater Fe concentrations (Figure S3) show increased mobilization of Fe from sediments in Lake

Killarney compared to Angle Lake during summer 2016 and 2017, consistent with faster, temperature-driven respiration rates leading to increased Fe-oxide dissolution.

By contrast, other differences in environmental parameters between the study sites are unlikely to explain observed trends in arsenic mobilization. Differences in dissolved oxygen concentrations in bottom waters and resulting redox status would likely preferentially promote arsenic mobilization from sediments in Angle Lake (with a seasonally anoxic hypolimnion) rather than Lake Killarney, which experiences only intermittent hypoxia in summer. Surface sediments in Angle Lake and Lake Killarney are both relatively rich in organic carbon (Table 1), available to fuel dissimilatory iron reduction and associated arsenic release. Concentrations of water-column phosphate, which has been shown to promote arsenic release into sediment porewaters (e.g., Sun et al., 2017), were consistently low ($<10 \mu\text{g L}^{-1}$) year-round in both lakes. Porewater phosphate concentrations (Figure S3), which promote arsenic desorption from sediments via competitive ion exchange, were similar in Lake Killarney and Angle Lake in 2016 and higher in near-surface sediments in Angle Lake in 2017. Although chemical extraction experiments on solid sediments (see discussion below) suggest that phosphate-driven desorption is likely to be an important mechanism mobilizing arsenic at our study sites, phosphate availability does not appear to be the main driver of trends in porewater arsenic concentrations.

To test the assumption that temperature is a primary driver of differences in porewater arsenic fluxes between Lake Killarney and Angle Lake in summer and responsible for seasonal variation in Lake Killarney, sediment cores from both lakes were collected and incubated at temperatures designed to approximate average summer bottom water temperatures in Angle Lake (10°C) and Lake Killarney (20°C) (Figure 4). When sediment cores were collected in January 2018, bottom water temperatures were 5.5°C and 6.1°C in Angle Lake and Lake Killarney, respectively. During the experiment, initial arsenic concentrations in water overlying sediment cores were similar for both lakes in the 10°C ($4\text{--}6 \mu\text{g L}^{-1}$ Angle; $3\text{--}4 \mu\text{g L}^{-1}$ Killarney) and 20°C ($4\text{--}18 \mu\text{g L}^{-1}$ Angle; $3 \mu\text{g L}^{-1}$ Killarney) treatments. During incubation at 10°C , neither lake showed any evidence of enhanced release of arsenic into the overlying water from sediments, with concentrations of $2\text{--}6 \mu\text{g L}^{-1}$ in Angle water samples and $2\text{--}5 \mu\text{g L}^{-1}$ in Killarney water samples throughout the experiment. However, during incubation at 20°C , core samples from both lakes displayed elevated arsenic concentrations in overlying waters within 7 days (averaging up to $104 \mu\text{g L}^{-1}$ in Angle and $119 \mu\text{g L}^{-1}$ in Killarney cores), indicating enhanced flux of arsenic from the sediments into the water column. Hence, despite potential variation in other geochemical parameters between cores, higher bottom-water temperature resulted in increased arsenic fluxes from the sediments of Angle Lake, very similar to the magnitude of observed mobilization from Lake Killarney sediments. The results of these laboratory experiments are consistent with field observations that suggest elevated bottom water temperatures are a primary driver of arsenic mobilization, increasing microbial respiration rates and promoting arsenic release during organic carbon oxidation. After initial increases in arsenic in the overlying water in the high-temperature treatments, concentrations decayed with time, presumably due to precipitation of arsenic-sulfide minerals. The decay was particularly noteworthy for the core from Angle, in which arsenic concentrations in overlying water

decreased within 15 days. In line with that observation, final sulfide concentrations were higher in the Angle core (48 ppm) than in the Killarney core (13 ppm) (Figure 4).

Arsenic is thought to be mobilized into porewaters via competitive desorption from iron-(hydr)oxides or as a result of dissimilatory iron reduction (Smedley and Kinniburgh 2002). A sequential chemical extraction protocol was used to evaluate the solid-state phase of arsenic in Angle Lake and Lake Killarney sediments to determine whether sedimentary arsenic solid phase at these sites was consistent with proposed mobilization mechanisms. The operationally-defined extraction steps target different pools of arsenic based on the type of association with sediment particles. The phosphate-exchangeable extraction (PE) releases absorbed arsenic and is designed to mimic sedimentary arsenic release via competitive-ion desorption (Keon et al. 2001). The iron-reduction extraction (CBD) releases arsenic co-precipitated with iron oxides (Loeppert and Inskeep 1996) and was followed by a total digestion procedure to quantify residual arsenic (R) in mineral phases presumed to be largely inaccessible by microbially-driven mechanisms. The relative amount of arsenic released from surface sediments (10 cm) during each extraction step is shown in Figure 3. The sum of arsenic recovered in sequential extraction steps was comparable to the arsenic concentrations measured by microwave-assisted total digestions of surface sediments collected by dredge (Table S2). In both lakes, a large proportion (40–70% of total) of sedimentary arsenic was released during the PE and CBD extractions, fractions that represent arsenic likely to be accessed during microbially-mediated processes in sediments. The fraction of sediment arsenic mobilized by the PE and CBD extractions was not significantly different (t-test, $p > 0.05$) in cores from Angle Lake ($42 \pm 4\%$, $n=6$) and Lake Killarney ($53 \pm 12\%$, $n=7$), indicating that temperature and not sediment arsenic mineralogy primarily drives differences in arsenic mobilization. This is consistent with the results of our laboratory temperature experiment in which similar peak arsenic concentrations from porewater fluxes were observed in cores from both sites under high temperature conditions.

3.2 Lake Water to Sediment Arsenic Flux

The large arsenic fluxes from contaminated sediments into the water column in Lake Killarney were countered by a downward particle-mediated arsenic flux that was estimated using sediment traps. On sampling dates when peepers were deployed, we compared the diffusive flux density for arsenic mobilized into overlying lake water to that of arsenic removed via sedimentation (Table 2). In Lake Killarney, the rate of arsenic transport out of sediment porewater into lake water due to molecular diffusion (the minimum possible flux rate out of the sediment) was greater than the rate of sedimentation during the summer months (July 2016 and August 2017). The opposite was true in December 2017 in Lake Killarney when sedimentation outpaced the upward flux. In Angle Lake, arsenic sedimentation was greater than the diffusive upward arsenic flux except in December 2017. Arsenic sedimentation flux density rates displayed a strong seasonal pattern in Lake Killarney (Figure 5). Sedimentation increased significantly at middle and bottom depths from summer into early autumn in 2016 and 2017, reaching maximum values of $2200\text{--}3100 \mu\text{g m}^{-2} \text{d}^{-1}$ in September. This increase was driven both by higher arsenic concentrations in the sediment trap samples collected and higher sediment trap mass accumulation during the

algal growth season (Figure S3). By contrast, arsenic sedimentation rates in Angle Lake were consistently low throughout the study period (Figure 5).

Comparison of sediment trap material and arsenic concentrations in phytoplankton biomass between lakes suggests that the primary mechanism for arsenic removal from the water column in Lake Killarney involved phytoplankton. Elemental analysis indicates (Table S3) that sediment trap organic material was consistent with phytoplankton macroelemental composition in small lakes (Sturner et al. 2008). The timing of the large flux of arsenic to the sediments during summer and early fall in Lake Killarney appears to be largely driven by high arsenic concentrations observed in phytoplankton biomass samples during this period (Figure 6). Phytoplankton arsenic concentrations in Lake Killarney reached 700–875 $\mu\text{g g}^{-1}$ in the warmer months in 2016 and 2017 compared to generally $<150 \mu\text{g g}^{-1}$ in the colder months and 15–170 $\mu\text{g g}^{-1}$ year-round in Angle Lake. These values were much higher than typically observed in freshwater green algae and diatoms ($<10 \mu\text{g g}^{-1}$) (Rahman et al. 2012 and references therein), groups that dominate phytoplankton communities in our study lakes (Barrett et al. 2018). However, comparable levels of phytoplankton arsenic bioaccumulation have been reported in other highly-contaminated freshwater systems (Caumette et al. 2011).

Bioaccumulation of arsenic in shallow, weakly-stratified lakes is a result of elevated arsenic in oxic waters, which results in spatial overlap between contamination and primary aquatic habitat and favors the speciation of arsenic as arsenate, a phosphate analog (Barrett et al. 2018). The high arsenic concentrations observed in phytoplankton in Lake Killarney may also be enhanced by a low ratio of phosphate to arsenate ($\text{PO}_4^{3-}:\text{AsO}_4^{3-}$). The availability of phosphate in freshwater lakes is often the limiting factor for algal growth, thus competition for phosphate has resulted in phosphate-specific uptake strategies in plankton. However, the chemical similarity of phosphate and arsenate results in arsenic uptake via competitive binding at phosphate transport sites (Rahman et al. 2012). Arsenic speciation was determined for filtered water samples from both lakes on five dates (Table S4). Phosphate concentrations in all samples from the oxic upper water column in both lakes were below the analytical detection limit of $10 \mu\text{g PO}_4\text{-P L}^{-1}$. Conservatively taking this P-detection limit as the dissolved phosphate concentration and the measured average arsenate concentration in the oxic water column, we calculated an upper limit on $\text{PO}_4^{3-}:\text{AsO}_4^{3-}$ molar ratios. In Lake Killarney, the highest possible $\text{PO}_4^{3-}:\text{AsO}_4^{3-}$ ratio was 2.5 and 1.7 (mol/mol) in Aug 2016 and July 2017, respectively, while the highest possible $\text{PO}_4^{3-}:\text{AsO}_4^{3-}$ ratio was 20–40 times higher in Angle Lake (Table 3). Using the average fraction of arsenate as a percentage of total dissolved arsenic from the five dates where arsenic speciation was determined (23% for Angle and 74% for Killarney), we can estimate the arsenate concentration and $\text{PO}_4^{3-}:\text{AsO}_4^{3-}$ ratio for all sampling dates during the study period. The average $\text{PO}_4^{3-}:\text{AsO}_4^{3-}$ ratio during the warmest months of July–September was 2.5 in Killarney, and 72 in Angle. Thus, arsenic uptake by phytoplankton in Lake Killarney may be enhanced by the abundance of arsenate relative to phosphate in this lake.

This greater arsenic bioaccumulation in plankton growing in waters with seasonally elevated aqueous arsenic concentrations appears to drive arsenic removal from the water column in Lake Killarney. Bulk surface sediments (Table 1) have arsenic concentrations up to an order of magnitude lower than near-bottom sediment trap material (Figure 5); hence sediment

resuspension cannot account for sediment trap arsenic observations. Additionally, in summer and early autumn when arsenic sedimentation rates were highest, advective fluxes such as stormwater runoff and wind-driven sediment resuspension are expected to be lowest. Arsenic concentrations in phytoplankton peak just prior to periods of high arsenic sedimentation (Figure 6). Although average phytoplankton arsenic concentrations were lower than those observed in sediment trap material (Figure S3) (26%, Jul-Oct 2016 and 2017), we hypothesize that arsenic was concentrated during plankton settling and decay through the preferential loss of carbon and other macronutrients, as has been observed with other particle-reactive trace elements (Twining et al. 2014). Zooplankton grazing on phytoplankton may also concentrate arsenic in settling fecal pellets (Davies 1978).

4. Conclusions

In our study lakes, bottom water and sediment temperatures appear to strongly regulate lake arsenic concentrations. Terrestrial-based studies conducted with flooded soils have demonstrated that arsenic mobilization increases with temperature (Cho and Ponnamperna 1971; Weber et al. 2010; Neumann et al. 2017). Our results suggest that arsenic mobilization within lakebed sediments are similarly sensitive to temperature, and that differences in lakebed temperatures between deep and shallow lakes drives much of the arsenic dynamics we observe in our study system. High lakebed temperatures in our shallow lake resulted in arsenic porewater concentrations that were more than an order of magnitude higher than those in our deep, stratified lake with similar levels of sediment arsenic. We estimate that these elevated porewater concentrations in the shallow lake drive large fluxes of aqueous arsenic into overlying waters, despite presumed attenuation by adsorption onto iron oxyhydroxides across a sediment-water interface that experiences only intermittent hypoxia. Although we estimated only diffusive fluxes from sediment porewaters acting to mobilize legacy arsenic contamination into the lake water column, turbulent transport would also likely play an important role in shallow lakes. Ongoing work at these sites will classify flow characteristics in shallow contaminated lakes to determine the importance of lakebed turbulent processes in sustaining elevated aqueous arsenic in the oxic water column.

Arsenic cycling was also significantly tied to phytoplankton abundance and arsenic uptake. Warmer temperatures and nutrient inputs drive algal growth, which in turn contributes organic carbon to lake sediments, fueling microbial metabolism responsible for dissimilatory iron reduction and arsenic release. Importantly, phytoplankton are also the primary vehicle for arsenic sedimentation to the lakebed. The plankton in Lake Killarney bioaccumulate arsenic to high concentrations in the summer when increased concentrations of aqueous arsenic are present in surface waters and phytoplankton competing for limited phosphorus potentially take up more arsenic as $\text{PO}_4^{3-}:\text{AsO}_4^{3-}$ ratios decline. As phytoplankton die and settle, or are grazed by zooplankton, arsenic is transported back to the sediment surface.

Hence, in shallow lakes, large fluxes of arsenic from sediments are coupled to high arsenic sedimentation rates. However, these relatively balanced fluxes appear to still result in seasonally high arsenic concentrations in oxic surface waters, likely due to asynchronous timing in the peak of these opposing processes. Lakebed temperatures in our shallow study lake began to warm in Mar-Apr and reach peak temperatures in early August, presumably

reflecting trends in microbial metabolism, which is supported by seasonal evolution in bottom-water aqueous arsenic concentrations. However, arsenic sedimentation rates, primarily driven by plankton bloom decay, peak in September, as evidenced by the timing of maximum arsenic fluxes measured in sediment traps.

Increased arsenic bioaccumulation in these shallow lakes has been observed at the base of the food chain (Barrett et al. 2018), indicating the potential for transfer up the aquatic food web and ultimately to humans. Hence, the risks to ecosystem and human health from legacy contamination may be greater in shallow lakes, where comparatively large fluxes cycle arsenic between water and sediment, supporting a reservoir of aqueous arsenic in surface waters under conditions that promote biotic exposure to and uptake of arsenic.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1. Temperature (°C), dissolved oxygen (mg L⁻¹), and arsenic (μg L⁻¹) in filtered (0.4 μm) water samples from Angle Lake (left) and Lake Killarney (right) between July 2016 and December 2017. Black points show individual samples. Note the difference in scale between panels; colorbars have been scaled to highlight range in values. Plots produced using Ocean Data View (Schlitzer 2010).

Figure 2.

Arsenic concentrations ($\mu\text{g L}^{-1}$) in bottom water and sediment porewater collected using peeper samplers in Angle Lake (left) and Lake Killarney (right) during summer (July-Oct) 2016, summer (Aug) 2017, and winter (Dec) 2017. In August 2017 in Lake Killarney, settling of the sampler during deployment resulted in a position ~10 cm deeper into the sediment than other dates and sample cup depths have been adjusted to reflect the location of the sediment-water interface on recovery. Error bars represent ± 1 SD on replicate samples.

Figure 3.

Percentage of arsenic released from surface sediment (1–10 cm) in sequential chemical extraction steps: phosphate exchange (PE), Fe-oxide reduction (CBD), and total digest of residual sample (R). Sediments collected by freeze coring in Angle Lake (A16 – Sept 2016; A17 – Aug 2017; AW – Dec 2017) and Lake Lake Killarney (K16 – July 2016; K17 – Aug 2017 (2 cores); KW – Dec 2017) with duplicate samples (A/ B or C/D) where sufficient sample mass allowed.

Figure 4.

Arsenic concentrations ($\mu\text{g L}^{-1}$) at the sediment-water interface in sediment cores from Angle Lake (solid symbols) and Lake Killarney (open symbols) incubated at 10°C (blue) and 20°C (red) over a 48-day experiment. Diamond symbols represent sulfide concentrations at the final timepoint. The symbol scheme for sulfide data is the same as for arsenic concentrations; the sulfide data points for both Killarney temperature treatments overlap. Error bars represent ± 1 SD on samples from duplicate cores. Where no error bar is shown, the error is contained within the symbol.

Figure 5.

Flux rates for arsenic sedimentation ($\mu\text{g m}^{-2} \text{d}^{-1}$) in sediment traps at mid-depth and near-bottom in Angle Lake and Lake Killarney. Note the difference in scale between the two panels.

Figure 6.

Arsenic concentrations in phytoplankton ($\mu\text{g g}^{-1}$) from Angle Lake and Lake Killarney between July 2016 and December 2017. Error bars represent ± 1 SD on samples from duplicate samples. Note the difference in scale between the two panels.

Table 1.

Characteristics of study sites.

	Angle Lake	Lake Killarney
average depth (m)	7.5	2.6
max depth (m)	15.8	4.5
lake area (km ²)	0.42	0.12
trophic status	oligotrophic	eutrophic
stratification	strong	weak
surface sediment [As] (µg g ⁻¹) ^a	208 ± 28 (n=2) ^b	206 ± 17 (n=2) ^b
surface sediment [Fe] (%) ^a	2.5 ± 0.2 (n=3)	1.2 ± 0.2 (n=7)
surface sediment organic C (%) ^b	27.5 ± 0.04 (n=2)	49.1 ± 0.4 (n=3)

^adetermined by microwave-assisted total digestion^b[Gawel et al., 2014]^cdetermined by loss on ignition

Table 2.

Comparison of flux estimates for arsenic remobilized from sediments to arsenic removal via sedimentation.

site	date	As flux from sediments ^a ($\mu\text{g m}^{-2} \text{d}^{-1}$)	As flux to sediments ^b ($\mu\text{g m}^{-2} \text{d}^{-1}$)
Angle Lake	Sept 2016	11	15.7
	Aug 2017	14	5.1
	Dec 2017	127	51
Lake Killarney	July 2016	1302	647
	Aug 2017	873	964
	Dec 2017	15	174

^a estimated from gradients across sediment-water interface in porewater peeper samples

^b estimated from near-bottom sediment trap arsenic fluxes

Table 3.

Phosphate:arsenate ($\text{PO}_4^{3-}:\text{AsO}_4^{3-}$ mol/mol) ratios in Angle Lake and Lake Killarney estimated using measured arsenate concentrations in oxic waters and minimum detection limit for phosphate ($10 \mu\text{g PO}_4\text{-P L}^{-1}$).

date	$\text{PO}_4^{3-}:\text{AsO}_4^{3-}$ (mol/mol)	
	Angle	Killarney
9 Aug 2016	52.9	2.5
3 Oct 2016	169.8	3.7
1 Feb 2017	105.2	5.3
3 Apr 2017	66.8	6.2
12 July 2017	64.0	1.7
2016–2017 summer (July–Sept) average ^a	72	2.5

^a arsenate concentrations calculated by applying average percentage As(V) from 5 dates on which arsenic speciation was determined to total filtered arsenic concentrations on all sampling dates