

Long-term monitoring of arsenic, copper, selenium, and other elements in Great Salt Lake (Utah, USA) surface water, brine shrimp, and brine flies

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Abstract This paper presents long-term monitoring data for 19 elements with a focus on arsenic (As), copper (Cu), and selenium (Se), in surface water (2002–2011), brine shrimp (2001–2011), and brine flies (1995–1996) collected from Great Salt Lake (GSL, Utah, USA). In open surface waters, mean (\pm standard deviation [SD]; range; n) As concentrations were 112 (\pm 22.1; 54.0–169; 47) and 112 $\mu\text{g/L}$ (\pm 35.6; 5.1–175; 68) in filtered and unfiltered surface water samples, respectively, and 16.3 $\mu\text{g/g}$ (\pm 5.6; 5.1–35.2; 62) dry weight (dw) in brine shrimp. Mean (\pm SD; range; n) Cu concentrations were 4.2 (\pm 2.1; 1.3–12.5; 47) and 6.9 $\mu\text{g/L}$ (\pm 6.6; 1.9–38.1; 68) in filtered and unfiltered surface water samples, respectively, and 20.6 $\mu\text{g/g}$ (\pm 18.4; 5.4–126; 62) dw in brine shrimp. Finally, mean (\pm SD; range; n) dissolved

and total recoverable Se concentrations were 0.6 (\pm 0.1; 0.4–1.2; 61) and 0.9 $\mu\text{g/L}$ (\pm 0.7; 0.5–3.6; 89), respectively, and 3.6 $\mu\text{g/g}$ (\pm 2.2; 1.1–14.9; 98) dw in brine shrimp. Thus, Se in open lake surface waters was most often in the range of 0.5–1 $\mu\text{g/L}$, and concentrations in both surface water and brine shrimp were comparable to concentrations measured in other monitoring programs for the GSL. Temporally, the statistical significance of differences in mean dissolved or total recoverable As, Cu, and Se concentrations between years was highly variable depending which test statistic was used, and there was no clear evidence of increasing or decreasing trends. In brine shrimp, significant differences in annual mean concentrations of As, Cu, and Se were observed using both parametric and nonparametric statistical approaches, but, as for water, there did not appear to be a consistent increase or decrease in concentrations of these elements over time.

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Introduction

This paper presents long-term monitoring data (more than one decade) for arsenic (As), copper (Cu), selenium (Se), and several other elements in surface water, brine shrimp, and brine flies collected from Great Salt Lake (GSL; Utah, USA) by the Kennecott Utah Copper Corporation (KUCC). GSL is the fourth largest terminal

lake in the world (Stephens 1990) and the largest hypersaline lake in North America (Felix and Rushforth 1979). The lake size and depth vary substantially due to annual and seasonal changes in inflow from precipitation, tributaries, and groundwater, and from losses through evaporation (UDEQ 2008). When the lake elevation is 1280 m, the lake is approximately 121 km long and 48 km wide and contains approximately 536 km of shoreline (UDEQ 2008). GSL is divided into two arms that are separated by a railroad causeway and embedded culverts. Because approximately 95 % of the freshwater flows enter the southern end of the lake, the salinity of the south arm is less than in the north arm (Post 1977). The salinity of the south arm, which is the focus of the monitoring data reported in this paper, has recently ranged from approximately 120 to 150‰ but has historically ranged from 56 to 280‰ (UDEQ 2008).

GSL supports a limited aquatic community due to its hypersaline conditions. The south arm hosts at least four species of bacteria (mainly *Halobacterium* and *Halococcus*), brine shrimp (*Artemia franciscana*), at least two species of brine flies (*Ephydra gracilis*, *E. hians*), and up to 20 algae species, primarily *Dunaliella viridis* and *D. salina* (Brix et al. 2004; Byron et al. 2011; Wurtsbaugh et al. 2011). The lake also provides important habitat for several avian species with, for example, approximately 25 % of all California gulls (*Larus californicus*) nesting on GSL and approximately 50 % of North America's eared grebes (*Podiceps nigricollis*) feeding in GSL (Conover and Vest 2009).

The eastern and southeastern portions of the lake are bordered by the larger Salt Lake City metropolitan area, which includes municipal and industrial point sources to the lake, as well as agricultural and urban runoff (Byron et al. 2011). Among the industries bordering the lake are the smelting and refining facilities for a copper mine operated by KUCC. A key constituent of this facility's wastewater discharge is Se, with historic concentrations as high as 300 µg Se/L (Brix et al. 2004) and current concentrations typically less than 27 µg/L. Recently, a site-specific water quality standard for Se was recommended (UDEQ 2008) and approved by the US Environmental Protection Agency (USEPA 2011). This standard is tissue-based and set not to exceed 12 mg/kg dry weight (dw) in bird eggs. KUCC has undertaken a long-term (14+years) monitoring program to evaluate potential impact of its operations on GSL water quality and to support development of the site-

specific water quality standard for Se. These data are compared to GSL monitoring data collected by the US Fish and Wildlife Service (USFWS), US Geological Survey (USGS), and local university scientists. The objectives of this paper are to synthesize and present the trace element monitoring data for GSL, including an analysis of temporal and spatial trends.

Methods and materials

The concentration data for As, Cu, Se, and other trace elements in GSL surface water and brine shrimp presented in this review were collected by KUCC from 1998 to 2011. In addition, KUCC collected limited Se data for brine flies sampled from the south shore of GSL in 1995 and 1996. For comparison, Se and other trace element concentration data were compiled for surface water (Marden 2008; Naftz et al. 2009), brine shrimp (Waddell et al. 1999, 2009; Marden 2008), and brine flies (Waddell et al. 1999, 2009). The data presented here focus on the south arm, also called Gilbert Bay. Important inputs to Gilbert Bay from the south shore of the lake include the KUCC 012 outfall, Lee Creek, Goggin Drain (the latter two primarily carry irrigation flow to GSL), and the Jordan River. KUCC's C7 Ditch was historically a source of Se to GSL but has not been used in more than 10 years. Accordingly, Se data for the C7 Ditch are not included here (data relative to the ditch and its discharge into GSL can be found in Brix et al. (2004)).

Sampling and analysis

GSL water samples were collected by KUCC from 2002 to 2011 (Fig. 1). The locations of the sampling stations were primarily selected in order to evaluate whether trace element concentrations in surface water and brine shrimp were greater nearer the KUCC discharge, while some stations were also selected to evaluate whether the Jordan River was a detectable source of Se to GSL surface water and brine shrimp. At some stations (stations 8, 10, and 16), both surface water and deep samples (below the halocline) were collected. All stations were not consistently sampled from 2002 to 2011; the most routinely sampled were open lake stations 1, 2, 4, 5, 8, 9, and 10 (Fig. 1). Accordingly, this set of stations was used for statistical analyses of temporal and spatial trends in

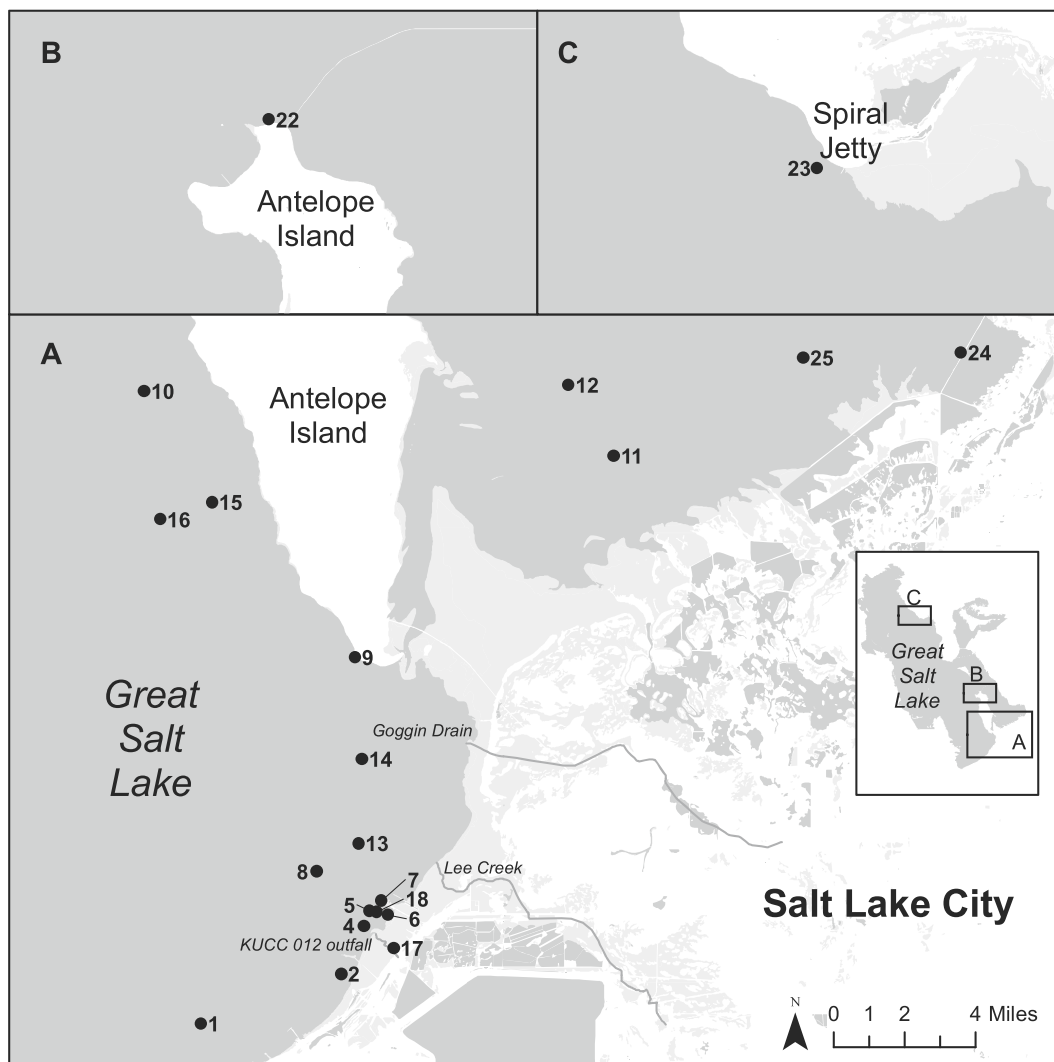


Fig. 1 Study area and KUCC sampling sites

surface water concentrations of As, Cu, and Se. In addition, surface water samples were selectively collected at Lower Lee Creek (tributary to GSL), drains and canals, and several ponds near the south shore of GSL.

Surface samples were collected in bottles placed under water with the cap then removed and replaced, while deep samples were collected into a bottle using a pump and silicone tubing. The majority of trace element analyses in water samples (unfiltered and filtered using a 0.45- μm membrane filter) were conducted by Frontier Geosciences Inc. (later Frontier Global Sciences Inc.; Seattle, WA). Arsenic and Se were analyzed by hydride generation-atomic fluorescence spectroscopy (HG-AFS), Al was analyzed by inductively coupled plasma

mass spectrometry (ICP-MS) with dynamic reaction cell (DRC) technology, Hg and MeHg were analyzed by cold vapor atomic fluorescence spectrometry (CVAFS), and the remaining elements were analyzed by ICP-MS.

Brine shrimp samples were collected by KUCC from 2001 to 2011. Brine shrimp samples were collected from the top two feet of the water using a dip net with a 150- μm mesh size. Brine shrimp samples were not separated by size or age. Brine shrimp analyses were conducted by the Geochemical & Environmental Research Group (GERG, Texas A&M University; College Station, TX), the Trace Element Research Lab (TERL, Texas A&M University; College Station, TX), and Laboratory

and Environmental Testing, Inc. (L.E.T., Inc., Columbia, MO). Arsenic and Se were analyzed by HG-AFS, total mercury by CVAFS, Pb by GFAA, and the remaining metals by ICP-MS. For all sample events, appropriate QA/QC procedures were applied, which included 10 % duplicate samples, blanks, spiked samples, and NTIS standards and reference samples.

Marden (2008) and Naftz et al. (2009) collected surface water samples for Se analysis from multiple sites in the south arm of GSL in 2006 and 2007. Details of the surface water sampling and analyses can be found in those reports. Water samples for dissolved Se analysis were passed through a 0.45- μm filter. Water samples from both studies were sent to Frontier Geosciences Inc. (Seattle, WA) for analysis of dissolved and total recoverable Se using hydride generation–atomic fluorescence (HG-AF).

The USFWS collected adult brine shrimp from Gilbert Bay in 1996, 1999, and 2000 and brine shrimp cysts from Gilbert Bay in 1996 and 1999 (Waddell et al. 2009). Details of the USFWS sampling and analysis of brine shrimp can be found in Waddell et al. (2009). Briefly, the 1996 brine shrimp samples were collected “offshore,” the 1999 samples were collected from a mixture of “offshore” and “onshore,” and the 2000 samples were collected “nearshore” proximate to the mouths of the historical C7 Ditch, Lee Creek, and Goggin Drain (see Fig. 5–1 in Waddell et al. (2009)). Brine shrimp samples were collected from the top 20–30 cm of the water surface by towing kick nets or plankton nets from a boat. Brine shrimp cysts were separated from adults with 500- and 106- μm stainless steel sieves (Waddell et al. 2009). The brine shrimp were digested in heavy-walled, screw-cap Teflon® Bombs with concentrated high purity nitric acid and, with the exception of As, Hg, and Se, chemical analyses were performed using inductively coupled plasma atomic emission spectroscopy (Waddell et al. 2009). Arsenic was analyzed using graphite furnace atomic absorption spectrometry (AAS), Se was analyzed using either graphite furnace or hydride generation AAS, and Hg was analyzed by cold vapor AAS (Waddell et al. 2009).

Marden (2008) collected brine shrimp from the south arm of GSL in 2006 and 2007. Details of the sampling and analysis of brine shrimp can be found in that report. Briefly, brine shrimp were collected

via horizontal or vertical plankton net hauls from 1–3-m and >7-m depths, which were then successively filtered through 850-, 500-, and 125- μm stainless steel sieves to obtain three age classes (nauplii/cysts, juveniles, adults). Samples were rinsed with prefiltered GSL water, placed in Whirl-pak® bags, and stored on ice. The samples collected in 2007 were considered by Marden (2008) as being more reliable based on modification to the sample preparation that was not conducted on the 2006 samples. Accordingly, we focused on the 2007 samples in the present paper. Selenium analyses were conducted by Laboratory and Environmental Testing, Inc. (L.E.T., Inc., Columbia, MO) using hydride generation–atomic absorption spectrometry (HG-AAS).

Limited Se data are also available for adult and larval brine flies collected by KUCC in June 1995 and August 1996 from Lee Creek and at the mouth of the C7 Ditch. Brine flies were collected using an aerial sweep net either along the shoreline or on floating debris in the water. Selenium concentrations were measured by TERL (Texas A&M University; College Station, TX) and analyzed by HG-AFS. In addition, trace element concentrations in brine fly larvae collected by the USFWS west and east of Antelope Island in 1996 are available (Waddell et al. 2009). Flies were collected using aerial sweep nets from moving vehicles along dike roads. The analytical methods for the 1996 brine fly larvae samples were the same as those summarized previously for brine shrimp.

Data analysis

Extended exploratory analyses were conducted to assess the effects of time (year, month), space (sampling location), and large-scale spatial factors (represented by lake elevation) on concentrations of As, Cu, and Se in surface water and brine shrimp. All statistical analyses were based only on the KUCC data due to the consistency of sampling techniques and locations, but data from the other studies (Waddell et al. 1999, 2009; Marden 2008; Naftz et al. 2009) were used as points of comparison. Relationships between concentrations in water and brine shrimp and effects on those relationships by time, space, and large-scale spatial factors were also explored. Although effects of all factors appeared to

contribute to variance in metal concentrations, the sampling design used to date was not consistent enough to allow for the development of a statistical model that accounted for all factors. Consequently, simpler models were created to test for effects of space and time that pooled data over the factors not being tested.

Annual and station mean concentrations of each element in water and brine shrimp were compared using analysis of variance (ANOVA) in SPSS (version 11.5), and homogeneity of variances was tested using Levene's test. As noted, only data from stations 1, 2, 4, 5, 8, 9, and 10 were used in these analyses. When differences between annual or station means were detected by ANOVA, Tukey's HSD post hoc multiple comparison test was conducted to determine which years differed. ANOVA was conducted using raw, log-transformed, rank-transformed, and rankit-transformed data, where use of rank and rankit transformations is equivalent to conducting a nonparametric ANOVA (Conover and Vest 2009). The same statistical methods were used to test for differences between months in surface water concentrations from GSL waters using data from 2005. This year was the only year with more than three samples from 3 months (June, July, September). Results were considered significant if $p < 0.05$. For concentrations below detection limits, the full detection limit was used in the statistics.

Translators for relating dissolved and total recoverable trace element concentrations in surface water were calculated as follows:

$$\text{Translator} = \frac{C_{\text{SW,D}}}{C_{\text{SW,TR}}} \quad (1)$$

where:

Translator	ratio of dissolved-to-total recoverable trace element concentration
$C_{\text{SW,D}}$	dissolved trace element concentration in surface water ($\mu\text{g/L}$)
$C_{\text{SW,TR}}$	total recoverable trace element concentration in surface water ($\mu\text{g/L}$)

Translators were not calculated if the trace element was U- or B-qualified (undetected or blank contamination, respectively) in either the filtered or unfiltered samples.

Finally, bioaccumulation factors (BAFs) were calculated for spatially and temporally colocated brine shrimp and dissolved surface water samples. The BAF was calculated as follows:

$$\text{BAF} = \frac{C_{\text{BS}}}{C_{\text{SW}}} \quad (2)$$

Where:

BAF	bioaccumulation factor (L/kg)
C_{BS}	trace element concentration in brine shrimp (mg/kg dry wt.)
C_{SW}	trace element concentration in surface water (mg/L dissolved)

Bioaccumulation factors can potentially be a tool for relating surface water concentrations of trace elements to concentration in food items, in this case brine shrimp, which may then be used as an indicator of potential dietborne toxicity. However, trace element BAFs may vary due to a variety of factors, including the magnitude of the dissolved concentration in surface water. Accordingly, it is important to understand this variability, which may vary spatially and temporally. Where sufficient data were available, relationships between trace element BAFs for brine shrimp relative to dissolved concentrations were evaluated.

Results and discussion

Monitoring results for surface water, brine shrimp, and brine flies are presented separately below. Concentrations of all elements monitored in surface water and brine shrimp are presented, but evaluations of temporal and spatial trends are focused on As, Cu, and Se.

Surface water

Mean dissolved and total recoverable concentrations for all elements analyzed for open waters of GSL, across all years, are provided in Fig. 2 (raw data and summary statistics are provided in Online Resource 1 and 2, respectively). Mean dissolved and total recoverable As concentrations in open GSL waters were both $112 \mu\text{g/L}$ with relatively low variability between stations and over

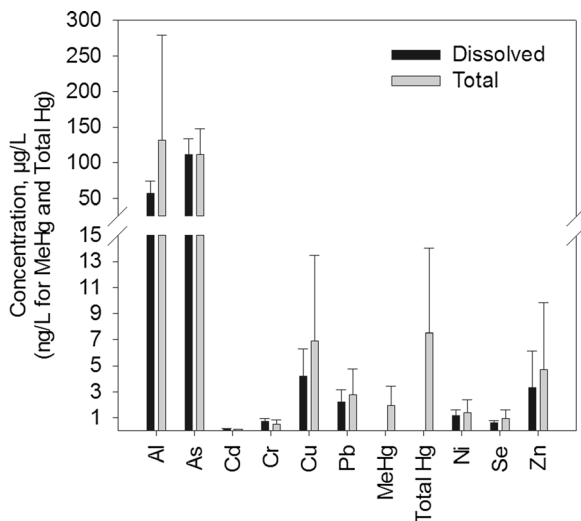


Fig. 2 Mean (\pm SD) dissolved and total recoverable element concentrations in surface water collected from open waters of the GSL by KUCC: 2002–2011. Dissolved methyl mercury (MeHg) and dissolved total mercury concentrations are not available

time. Mean dissolved and total recoverable Cu concentrations were 4.2 and 6.9 $\mu\text{g/L}$, respectively, with variability ranging by a factor of 10 and 20 for dissolved and total recoverable concentrations, respectively. Mean dissolved and total recoverable Se concentrations were <1 $\mu\text{g/L}$ in open GSL waters with relatively low variability. The annual mean dissolved Se concentrations, for example, ranged from 0.56 to 0.73 $\mu\text{g/L}$. For comparison, the minimum and maximum dissolved Se concentrations measured in 2006 and 2007 by Marden (2008) ranged from approximately 0.35 to 0.62 $\mu\text{g/L}$ and from approximately 0.25 to 0.84 $\mu\text{g/L}$ by Naftz et al. (2009). Considering that the concentrations are less than 1 $\mu\text{g/L}$, this is considered very good agreement.

Stations 1, 2, 4, 5, 8, 9, and 10 were consistently sampled over the same range of years, and these data were therefore the most useful for evaluating whether there were spatial differences in total recoverable and dissolved As, Cu, and Se concentrations (Fig. 3). Variance in station-mean concentrations was homogeneous for log-, rank-, and rankit-transformed total recoverable and dissolved concentrations of As, Cu, and Se except for raw total recoverable and dissolved concentrations of Se and total concentrations of Cu (Table 1). No significant differences between stations in mean concentrations were observed for any transformations of dissolved and total recoverable As, dissolved Cu, or total recoverable Se concentrations,

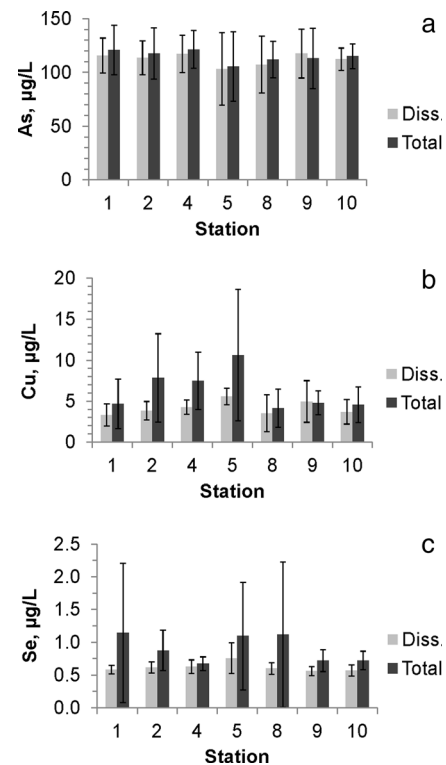


Fig. 3 Comparison of mean (\pm SD) dissolved and total recoverable a As, b Cu, and c Se concentrations in surface water between stations. Data from KUCC

or for rank- and rankit-transformed dissolved Se concentrations. Only raw and log-transformed dissolved Se concentrations and most transformations of total recoverable Cu indicated differences among stations (Table 1). For the most part, these results do not indicate significant differences among stations, except in total recoverable Cu. Although ANOVA indicates a difference among sites for Cu, the only station-to-station differences revealed by post hoc tests were differences between log- and rankit-transformed total recoverable Cu concentrations at stations 5 and 8 using Tukey's HSD test (no other tests pair-wise or group-wise post hoc tests indicated station-level differences).

Annual mean concentrations of dissolved and total recoverable As, Cu, and Se concentrations are provided in Figs. 4 and 5. Statistically significant differences ($p \leq 0.0063$) in annual mean concentrations of dissolved and total recoverable As, Cu, and Se concentrations between years were found using the nonparametric ANOVA (Table 1). The slopes of the relationships between the annual mean element concentrations versus time were not significant for

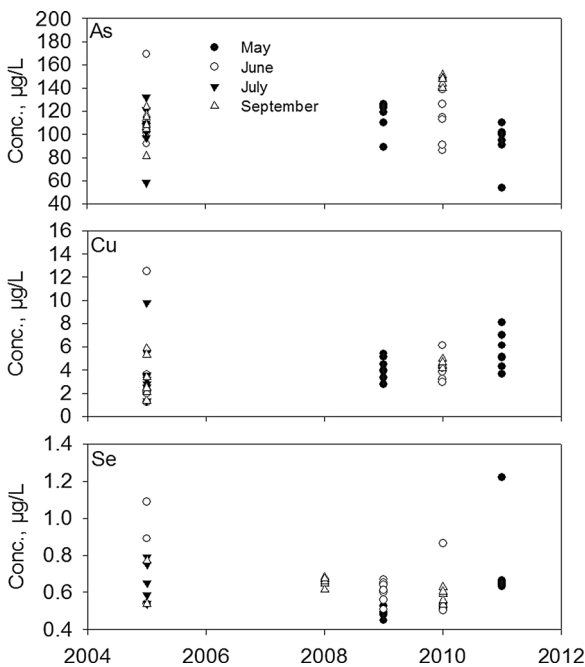


Fig. 4 Annual mean dissolved As, Cu, and Se concentrations in open GSL waters. Annual trend slopes not significantly different from zero ($p>0.05$) for each element. Data from KUCC

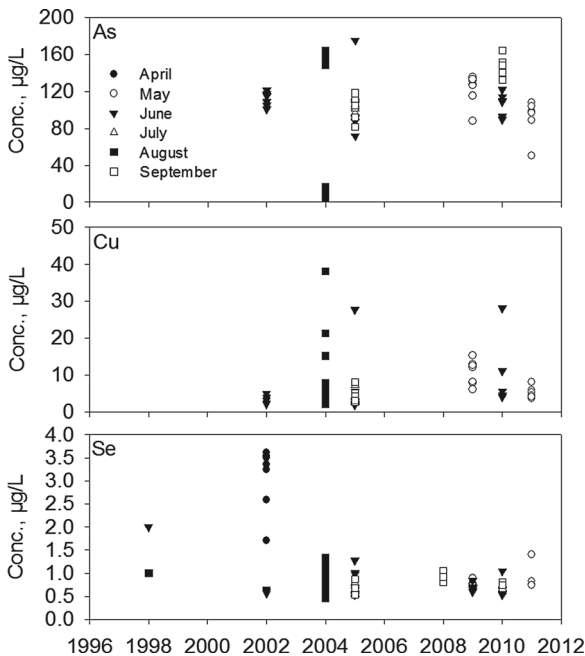


Fig. 5 Annual mean total recoverable As, Cu, and Se concentrations in open GSL waters. Annual trend slope significantly different from zero ($p=0.05$) for Se (see text), but not As or Cu. Data from KUCC

dissolved and total recoverable As, dissolved and total recoverable Cu, and dissolved Se (p values range from 0.21 to 0.93). However, the significance of the slope of annual mean total recoverable Se concentrations versus time was less clear for total recoverable Se. The slope of the regression using rankit-transformed total recoverable Se concentrations versus year was not significant ($p=0.59$), but the slope using log(10)-transformed total recoverable Se concentrations versus year was significant ($p=0.009$). The latter, though, was characterized by a very low R^2 value (0.075) and residuals indicating that a linear model is not valid (i.e., residuals were not homogeneous and were not randomly distributed). Accordingly, although the mean (\pm SD) total recoverable Se concentration of 1.8 ± 1.4 $\mu\text{g/L}$ in 2002 was more than two times greater than the annual means from all later years sampled, which ranged from just 0.67 to 0.89 $\mu\text{g/L}$, there was sufficient variability in the mean total recoverable Se concentration in 2002 that the slope was of questionable significance. The higher mean total recoverable Se concentration in 2002 was driven by the samples collected in April, which had Se concentrations ranging from 1.7 to 3.6 $\mu\text{g/L}$, compared to June samples that had Se concentrations ranging from 0.56 to 0.66 $\mu\text{g/L}$. April samples were not collected in any other years.

The data suggest that seasonal variability exists in the concentrations of at least some elements. For example, the highest total recoverable Se concentrations reported were measured in April 2002 (mean = 3.1 $\mu\text{g/L}$, range 1.7–3.6 $\mu\text{g/L}$). However, no samples were collected by KUCC (or by Marden (2008); Naftz et al. (2009)) in April of other years; so, we do not know if this observation tends to occur in other years and for dissolved Se concentrations. In 2005, when total recoverable and dissolved element concentrations were measured in samples collected in June, July, and September, no significant differences were found ($p>0.05$) in mean As, Cu, and Se concentrations between these 3 months. For comparison, Marden (2008) found that temporal trends in dissolved Se concentrations in the open GSL were variable in 2006 but that there was a positive linear relationship over time in 2007. Over the same general time period, Naftz et al. (2009) found that dissolved Se concentrations at four open GSL stations increased by 0.27 $\mu\text{g/L}$, on average,

Table 1 Summary statistics for dissolved-to-total recoverable translators for trace elements in surface and deep water samples collected from the Great Salt Lake

Analyte	Sample depth	Arithmetic mean	Standard deviation	Median	Min	Max	<i>n</i>	USEPA conversion factor ^a
Aluminum	Surface	0.47	0.17	0.48	0.06	0.79	21	-
	Deep	0.06	0.006	0.06	0.05	0.06	3	
Arsenic	Surface	1.01	0.13	0.98	0.56	1.41	50	1.000
	Deep	0.84	0.09	0.86	0.72	0.92	4	
Cadmium	Surface	0.95	0.24	0.94	0.53	1.50	30	0.994
	Deep	_b	_b	_b	_b	_b	_b	
Chromium	Surface	_b	_b	_b	_b	_b	_b	
	Deep	_b	_b	_b	_b	_b	_b	
Copper	Surface	0.77	0.50	0.75	0.22	3.21	49	0.83
	Deep	_b	_b	_b	_b	_b	_b	
Lead	Surface	0.89	0.34	0.86	0.13	2.04	48	0.951
	Deep	0.33	-	0.33	0.33	0.33	1	
Mercury (monomethyl) ^c	Deep	0.58	0.10	0.59	0.47	0.69	4	0.85
Mercury (total) ^c	Deep	0.68	0.12	0.66	0.57	0.81	4	
Nickel	Surface	1.10	0.55	0.97	0.52	2.24	9	0.990
	Deep	_b	_b	_b	_b	_b	_b	
Selenium	Surface	0.84	0.11	0.85	0.63	1.08	25	0.998
	Deep	0.41	-	0.41	0.41	0.41	1	
Zinc	Surface	0.99	0.73	0.77	0.16	2.89	25	0.946
	Deep	_b	_b	_b	_b	_b	_b	

Units are µg/L except ng/L for mercury (monomethyl and total)

^a The USEPA's conversion factors for saltwater metals criteria are provided here as a point of comparison (USEPA 2009). These conversion factors are derived from laboratory toxicity studies using "clean" synthetic seawaters

^b Statistics not available because the dissolved and/or total recoverable concentration was U- or B-qualified

^c Monomethyl and total mercury translators are not presented for surface samples because dissolved concentrations are not available

from May 2006 to August 2007 and that the increasing trend was statistically significant at all four stations (90 % confidence level; Mann-Kendall statistical test). Although KUCC did not collect water samples in 2006 and 2007, these positive trends were not reflected in the longer-term KUCC data subsequently collected from September 2008 to May 2011—the mean dissolved Se concentrations in 2008, 2009, 2010, and 2011 were 0.66, 0.56, 0.58, and 0.73 µg/L, respectively.

Lake elevation was evaluated as a potential indicator of long-term physical and chemical variability in GSL, as lake elevation may reflect temporal variability in freshwater inputs to GSL, dilution potential, and/or changes in salinity that may influence

trace element fate. However, As, Cu, and Se concentrations did not appear to show relationships with lake elevation that were consistent across all stations and chemicals (not shown). Concentrations in surface water were highly correlated with lake elevation at some stations, but the mechanism(s) that might explain this relationship is unclear at this time.

Summary statistics for dissolved-to-total recoverable translators are provided in Table 2. In water samples collected at the surface, As and Ni occur almost entirely in the dissolved fraction. The arithmetic mean translator for Zn (0.99) indicates that Zn mostly occurs in the dissolved fraction, although the arithmetic mean is skewed high relative to the

Table 2 Summary of statistical results for between-station and between-year comparisons of mean total recoverable and dissolved As, Cu, and Se concentrations in surface water

Test	As		Cu		Se	
	Diss.	TR	Diss.	TR	Diss.	TR
Between stations ^a						
<i>Significance (p values) for homogeneity of variances (Levene's) test</i>						
Concentration (raw)	0.32	0.30	0.54	0.01	0.02	<0.01
Rankit of concentration	0.14	0.23	0.52	0.23	0.91	0.31
Rank of concentration	0.24	0.41	0.43	0.40	0.99	0.43
Log of concentration	0.21	0.19	0.26	0.34	0.15	0.06
<i>One-way analysis of variance (ANOVA) testing for effects of site</i>						
Concentration (raw)	0.91	0.85	0.21	0.06	0.03	0.61
Rankit of concentration	0.98	0.81	0.10	0.02	0.24	0.73
Rank of concentration	0.98	0.84	0.06	0.04	0.39	0.63
Log of concentration	0.80	0.71	0.13	0.03	0.04	0.66
Between years						
<i>Significance (p values) for homogeneity of variances (Levene's) test</i>						
Concentration (raw)	0.42	<0.01	0.09	0.03	0.03	<0.01
Rankit of concentration	0.52	<0.01	0.04	0.05	0.01	<0.01
Rank of concentration	0.32	<0.01	0.08	0.01	<0.01	<0.01
Log of concentration	0.67	<0.01	0.01	0.06	0.05	<0.01
<i>One-way analysis of variance (ANOVA) testing for effects of year</i>						
Concentration (raw)	0.01	0.42	0.22	0.08	0.05	<0.01
Rankit of concentration	0.01	0.08	0.02	<0.01	<0.01	<0.01
Rank of concentration	<0.01	0.01	0.01	<0.01	<0.01	<0.01
Log of concentration	0.01	0.33	0.02	<0.01	0.02	<0.01

^a Stations 1, 2, 4, 5, 8, 9, and 10 (see Figs. 1 and 3)

Diss. dissolved, TR total recoverable

median translator (0.77), which reflects the influence of translators greater than 1.0 in some samples. Translators for Cd, Cu, Pb, and Se are somewhat lower, with arithmetic means of 0.95, 0.77, 0.89, and 0.84, respectively. Aluminum translators were lower than for other trace elements in both surface and deep water samples as might be expected due to mineral particles in the total recoverable samples. For Cr in surface and deep samples, as well as for Cd, Cu, Ni, and Zn in deep samples, translators could not be derived because all data were either U- or B-qualified. As a point of comparison, Table 2 also provides the USEPA's saltwater conversion factors for relating ambient water quality criteria from total recoverable concentrations to dissolved metal concentrations (USEPA 2009). Overall, the mean

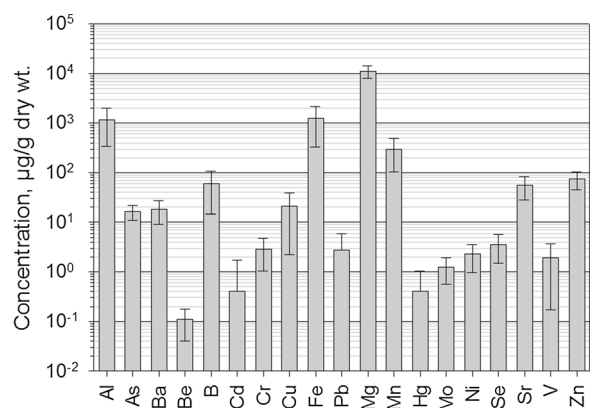


Fig. 6 Mean (±SD) element concentrations in brine shrimp collected from open waters of the GSL: 2001–2011. Data from KUCC

translators for most trace elements in surface samples are comparable in magnitude to the USEPA conversion factors, with the notable exception of Se, which has a translator (0.84) that is approximately 16 % lower than the USEPA's saltwater conversion factor (0.998) (Table 2).

Brine shrimp

Mean concentrations of 19 elements in KUCC brine shrimp samples, across all years, are provided in Fig. 6 (raw data and summary statistics are provided in Online Resource 3 and 4, respectively). The mean (\pm SD) As, Cu, and Se concentrations in brine shrimp, across all years, were 16.3 ± 5.6 , 20.6 ± 18.4 , and 3.6 ± 2.2 $\mu\text{g/g}$, respectively. For comparison, Waddell et al. (2009) measured mean (\pm SD) Se concentrations of 2.7 ± 0.52 $\mu\text{g/g}$ in brine shrimp adults collected from 1994 to 2000 and 1.6 ± 0.38 in brine shrimp cysts collected from 1996 to 1999, while Marden (2008) measured mean (\pm SD) Se concentrations of 4.32 ± 0.95 and $2.35 \pm$

2.42 $\mu\text{g/g}$ in adults and nauplii/cysts, respectively. Overall, therefore, brine shrimp Se concentrations measured during the KUCC monitoring program (which were not separated by size) are within the range of concentrations measured in other monitoring efforts.

As for surface water, stations 1, 2, 4, 5, 8, 9, and 10 were consistently sampled for brine shrimp over the same range of years, and these data were the most useful for evaluating whether there were spatial differences in As, Cu, and Se concentrations in brine shrimp (Fig. 7). Concentrations of As, Cu, and Se had homogeneous variances, and means did not differ significantly for As or Se (Table 3). For Cu, Tukey's HSD test found significant differences in

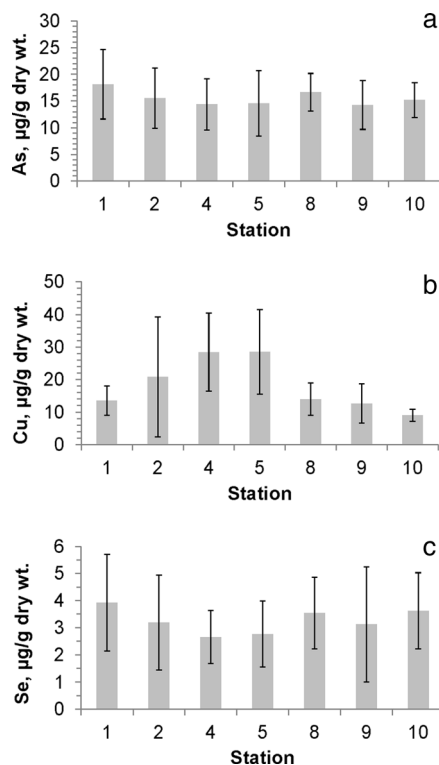


Fig. 7 Comparison of mean (\pm SD) **a** As, **b** Cu, and **c** Se concentrations in brine shrimp between stations. Data from KUCC

Table 3 Summary of statistical results for between-station and between-year comparisons of mean As, Cu, and Se concentrations in brine shrimp

Test	As	Cu	Se
Between stations^a			
<i>Significance (p values) for homogeneity of variances (Levene's) test</i>			
Concentration (raw)	0.69	0.04	0.65
Rankit of concentration	0.63	0.94	0.12
Rank of concentration	0.59	0.75	0.13
Log of concentration	0.64	0.77	0.29
<i>One-way analysis of variance (ANOVA) testing for effects of site</i>			
Concentration (raw)	0.78	0.01	0.40
Rankit of concentration	0.68	0.01	0.11
Rank of concentration	0.69	<0.01	0.08
Log of concentration	0.77	<0.01	0.16
Between years			
<i>Significance (p values) for homogeneity of variances (Levene's) test</i>			
Concentration (raw)	0.23	0.90	<0.01
Rankit of concentration	0.06	0.03	0.37
Rank of concentration	0.01	0.06	0.01
Log of concentration	0.10	0.27	0.47
<i>One-way analysis of variance (ANOVA) testing for effects of year</i>			
Concentration (raw)	<0.01	0.64	<0.01
Rankit of concentration	<0.01	0.03	<0.01
Rank of concentration	<0.01	0.02	<0.01
Log of concentration	<0.01	0.07	<0.01

^a Stations 1, 2, 4, 5, 8, 9, and 10 (see Figs. 1 and 7)

brine shrimp concentrations between station 10 and stations 5 and 4 using log- and rankit-transformed data, and between stations 10 and 5 using rank-transformed data.

In conducting a one-way ANOVA to test for differences among annual means in As, Cu, and Se concentrations, Levene's test found heterogeneous variances

for Cu and Se ($p < 0.043$ for both, either log(10)- or rankit-transformed) and homogeneous variances for As ($p = 0.072$ for rankit-transformed data and $p = 0.127$ for log(10)-transformed data). When using rankit-transformed data, all chemicals had significant annual differences ($p < 0.0005$ for As and Se, $p = 0.032$ for Cu; Fig. 8), but the annual means for Cu did not significantly differ when using log(10)-transformed concentrations ($p = 0.084$). Mean concentrations of both As and Cu were highest in 2002. While for As, post hoc tests found that 2010 and 2011 differed from 2002 and both 2004 and 2005 differed from 2011, no differences between years were found for Cu using post hoc testing. For Se, post hoc testing found that 2004 and 2005 were not equal to any other years (and all other years were not different from each other).

Bioaccumulation factors could be calculated for As, Cd, Cu, Pb, Se, and Zn based on spatially and temporally colocated concentrations measured in brine shrimp and filtered surface water samples. Consistent with other studies (McGeer et al. 2003; DeForest et al. 2007), BAFs for these trace elements tended to be inversely related to dissolved concentrations in surface water (Fig. 9). The slope of the relationship between the log element concentration in brine shrimp versus the log element concentration in filtered surface water was statistically significant ($p < 0.001$) for all elements except Pb ($p = 0.26$). On average, As is the least bioaccumulative of these six elements, with a geometric mean BAF of 128 L/kg dry wt. (range 55–204 L/kg), while Zn had the largest BAF, with a geometric mean of 26,700 L/kg dry wt. (range 6292–69,391 L/kg). For Se, the inverse relationship between BAF and dissolved concentration in surface water appeared to possibly be driven by a single data point with a highly dissolved Se concentration (43 $\mu\text{g/L}$ at station 19, in the vicinity of the Kennecott discharge); however, the slope was still highly significant ($p = 0.000002$) with this data point removed and only slightly different (-0.97 with the data point excluded versus -0.90 with the data point included).

Brine flies

Element concentrations in brine flies are limited to Se analyzed in brine flies collected from multiple locations from 1994 to 1996 (Online Resource 5). Selenium concentrations in adults ranged from 0.79

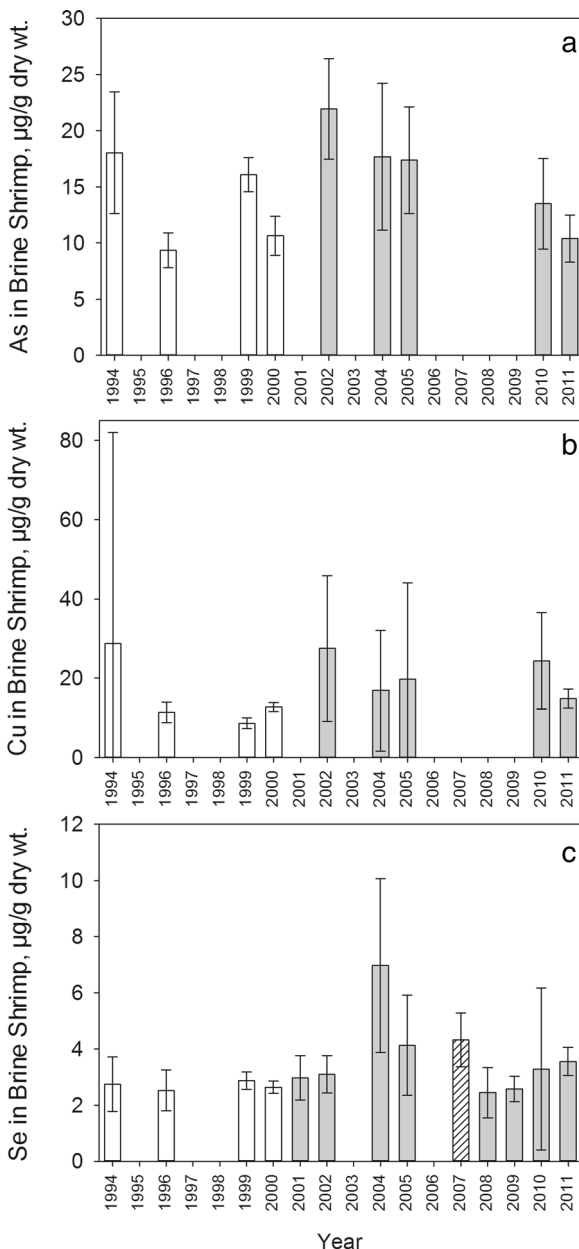
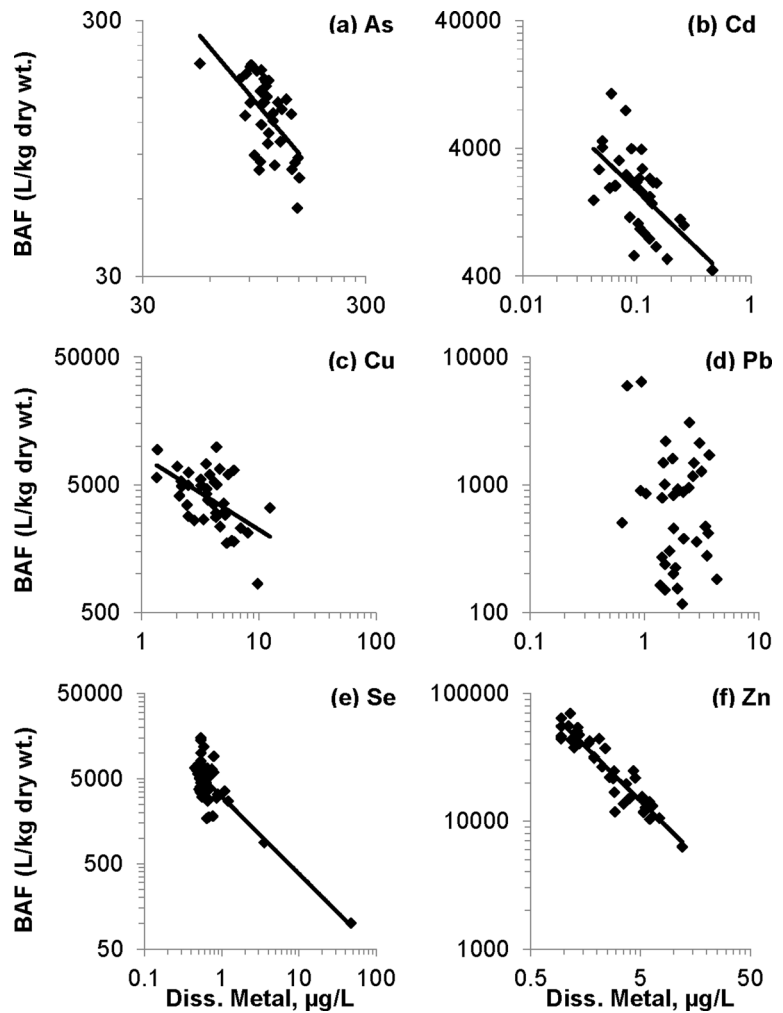


Fig. 8 Annual mean **a** As, **b** Cu, and **c** Se concentrations in brine shrimp. Gray bars = KUCC data; open bars = USFWS data; hatched bars = Marden (2008) data

Fig. 9 Relationship between bioaccumulation factors (BAFs) and colocated dissolved concentrations for **a** As, **b** Cd, **c** Cu, **d** Pb, **e** Se, and **f** Zn in brine shrimp. Regression line shown for significantly negative slopes ($p < 0.05$). Data from KUCC



to $2.6 \mu\text{g/g}$ and from 0.77 to $1.1 \mu\text{g/g}$ in larvae. These concentrations are comparable to, or less than, mean ($\pm\text{SD}$) Se concentrations that range from 1.6 to $4.3 \mu\text{g/g}$ in brine shrimp nauplii/cysts and adults (Online Resource 4).

Conclusions

Long-term monitoring of As, Cu, Se, and several other elements in GSL surface water and brine shrimp has been continuously conducted for more than 14 years. Annual mean concentrations of As, Cu, and Se in both surface water and brine shrimp are variable, with statistically significant differences between years sometimes being observed. There is

no clear evidence of either increasing or decreasing trends in As, Cu, or Se concentrations in surface water or brine shrimp.

Although the mean ($\pm\text{SD}$) total recoverable Se concentration of $1.8 \pm 1.4 \mu\text{g/L}$ in 2002 was more than two times greater than the annual means for all subsequent years sampled (0.67 to $0.89 \mu\text{g/L}$), there was sufficient variability in the mean total recoverable Se concentration in 2002 to obscure a statistically significant decreasing trend in 2002 relative to subsequent years. The higher mean total recoverable Se concentration in 2002 was driven by samples that were collected in April (first set of samples for the monitoring program), which had Se concentrations ranging from 1.7 to $3.6 \mu\text{g/L}$, compared to June samples that had Se concentrations ranging from 0.56 to $0.66 \mu\text{g/L}$. The higher Se concentration in

April may have reflected mobilization of Se during snowmelt, but April samples from other years are not available for comparison.

Seasonal variability in element concentrations may have influenced comparisons of annual mean concentrations, as surface water and brine shrimp samples were not always collected during the same months every year. However, when samples were collected during different months within the same year, statistical differences, at least for As, Cu, and Se, were not apparent. Finally, variability in trace element concentrations could not be clearly linked to large temporal-scale variability in the lake. Lake elevation, for example, which may simultaneously reflect temporal variability in freshwater inputs to GSL, dilution potential, and changes in salinity that may influence trace element fate, did not appear to explain variability in trace elements in GSL.

To better test hypotheses about spatial and temporal patterns in trace element concentrations, sampling designs for future monitoring should include consistent spatial and temporal sampling inside and outside the KUCC discharge area and across seasons to better assess long-term trends in annual mean concentrations.

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