Science of the Total Environment xxx (2009) xxx-xxx



Contents lists available at ScienceDirect

Science of the Total Environment



journal homepage: www.elsevier.com/locate/scitotenv

Selenium and trace element mobility affected by periodic displacement of stratification in the Great Salt Lake, Utah

Kimberly Beisner^{a,*}, David L. Naftz^b, William P. Johnson^c, Ximena Diaz^{c,1}

^a U.S. Geological Survey, 520 N. Park Ave., Tucson, Arizona, 85719, USA

^b U.S. Geological Survey, 2329 Orton Circle, Salt Lake City, Utah, 84119, USA

^c University of Utah, 135 South 1460 East, Salt Lake City, Utah, 84112, USA

ARTICLE INFO

Article history: Received 2 December 2008 Received in revised form 7 June 2009 Accepted 8 June 2009 Available online xxxx

Keywords: Selenium Great Salt Lake Hypersaline Seiche Brine layer Anoxic

ABSTRACT

The Great Salt Lake (GSL) is a unique ecosystem in which trace element activity cannot be characterized by standard geochemical parameters due to the high salinity. Movement of selenium and other trace elements present in the lake bed sediments of GSL may occur due to periodic stratification displacement events or lake bed exposure. The water column of GSL is complicated by the presence of a chemocline persistent over annual to decadal time scales. The water below the chemocline is referred to as the deep brine layer (DBL), has a high salinity (16.5 to 22.9%) and is anoxic. The upper brine layer (UBL) resides above the chemocline, has lower salinity (12.6 to 14.7%) and is oxic. Displacement of the DBL may involve trace element movement within the water column due to changes in redox potential. Evidence of stratification displacement in the water column has been observed at two fixed stations on the lake by monitoring vertical water temperature profiles with horizontal and vertical velocity profiles. Stratification displacement events occur over periods of 12 to 24 h and are associated with strong wind events that can produce seiches within the water column. In addition to displacement events, the DBL shrinks and expands in response to changes in the lake surface area over a period of months. Laboratory tests simulating the observed sediment re-suspension were conducted over daily, weekly and monthly time scales to understand the effect of placing anoxic bottom sediments in contact with oxic water, and the associated effect of trace element desorption and (or) dissolution. Results from the laboratory simulations indicate that a small percentage (1%) of selenium associated with anoxic bottom sediments is periodically solubilized into the UBL where it potentially can be incorporated into the biota utilizing the oxic part of GSL.

Published by Elsevier B.V.

1. Introduction

The Great Salt Lake (GSL) is a terminal lake located next to a large developing urban area which includes over 1.7 million people. The lake is divided into two distinct regions (North Arm and South Arm) by a railroad causeway completed in 1959. Lake circulation is restricted by the causeway, and typically the South Arm of the lake is stratified and characterized by the presence of a dense deep brine layer (DBL) originating from the North Arm (Madison, 1970). The North Arm brine is denser than the overlying South Arm brine and flows underneath and to the bottom of the South Arm where it gathers decaying organic matter falling through the water column and becomes anoxic forming the DBL.

The condition of stratification (meromixis) in the South Arm of the lake is maintained for annual time periods, punctuated with intermittent periods during which the stratification is not detected due to

* Corresponding author. Tel.: +1 520 670 6671x308; fax: +1 520 670 5592. *E-mail address:* kbeisner@usgs.gov (K. Beisner).

0048-9697/\$ - see front matter. Published by Elsevier B.V. doi:10.1016/j.scitotenv.2009.06.005

changes in freshwater input (Loving et al., 2000; Gwynn, 2002). Thermal and chemical stratification was observed for the entire study period from May 2006 through October 2007. The prolonged periods of meromixis are in direct contrast to freshwater lakes which typically experience annual turnover and complete water column mixing resulting from seasonal changes in thermal stratification (Hutchinson, 1957).

The South Arm of the GSL receives input from industrial, urban, mining, and agricultural sources within the 37,500 km² watershed supplying the lake. Most of the trace element contribution to the lake is anthropogenic (Domagalski et al., 1988). Studies of trace element concentration in the lake have characterized the UBL and DBL since construction of the railroad causeway (Stephens and Gillespie, 1976; Tayler et al., 1980). Previous studies have characterized the GSL as a self-cleaning system which removes metals through precipitation and sedimentation (Tayler et al., 1980). However, this characterization of the system as self-cleaning was based on a comparison of inflow concentration to lake concentration. A decrease in lake concentration compared to inflow concentration was demonstrated only for Cd, Cu and Zn, whereas other trace elements such as As and Se showed enhanced

¹ Present address: Department of Extractive Metallurgy, Escuela Politécnica Nacional, Quito, Ecuador.

lake concentrations relative to inflow concentrations (Tayler et al., 1980). More information is needed related to the sediment–water interaction to determine whether trace elements are permanently lost from the system due to sedimentation and precipitation or whether they may be periodically released back into the water column.

Recent interest has been focused on establishing a numerical standard for Se for the open waters of the GSL to protect avian wildlife. High levels of Se in water have been shown to cause malformations in bird embryos and chicks and may even lead to death (Ohlendorf et al., 1986). Selenium (and other trace elements) in sediments of the GSL may enter the food chain via brine shrimp (Artemia franciscana), which are filter feeders, and bioaccumulate as some birds using the GSL ingest brine shrimp as their diet (Utah Department of Environmental Quality, 2008). The load of Se to the GSL from surface water inflow over a period of 12 months from May 2006 to April 2007 was 1560 kg (Naftz et al., 2009). Approximately 10 kg/year of the total Se load to the GSL may come from seasonal re-saturation of shoreline sediments based on collection of shoreline sediments and laboratory leachate tests to determine the amount of Se released (Naftz et al., 2009). Removal of Se from the GSL is primarily controlled by volatilization, 1455 kg/year (Diaz et al., 2009a), and sedimentation accounts for removal of 624 kg/ year of Se (Oliver et al., 2009). Assuming that the Se load and removal mechanisms balance each other over an annual cycle, the residence time of Se in the GSL is on the order of about 3 to 5 years (Diaz et al., 2009b). However, although the removal values are within the range of error of the measured load, a slight statistical increase in Se over the period of study was observed indicating that there may be an unmeasured load of Se to the lake (Naftz et al., 2009).

Selenium is located directly below sulfur in group VI-A of the periodic table and therefore is chemically similar. Selenium can exist in four oxidation states: selenide [Se (-II)], elemental selenium [Se (0)], selenite [Se (IV)] and selenate [Se (VI)]. Under most natural, aqueous,

aerobic environmental conditions, Se exists as an oxyanion selenite (SeO_3^{2-}) or selenate (SeO_4^{2-}) (Masscheleyn and Patrick, 1993). Under reducing conditions Se (-II) is the dominant species and is often associated with an insoluble iron phase (Masscheleyn et al., 1990).

At the Saanich Inlet along the southeastern portion of Vancouver Island, Canada, selenite and selenate were present in the upper oxic waters, and organic selenide species became dominant in the anoxic hydrogen sulfide deep waters (Cutter, 1982). The stratification in the GSL is similar with the DBL characterized as anoxic and containing hydrogen sulfide. Selenium is also of concern to the ecosystem of the Salton Sea, California, dissolved water concentrations are $0.5-2 \mu g/L$ and lake bed sediment concentrations are 0.58-11 mg/kg (Schroeder et al., 2002). The Se values in the GSL fall on the low end of the range of Salton Sea concentrations.

The South Arm of the GSL contains an upper brine layer (UBL) characterized by oxidizing conditions and is in direct contrast to the reducing DBL below. Mobility of Se in each layer as well as in the lake bed sediment is likely to be influenced by the dominant species. Selenium flux from the sediment may be influenced by the redox conditions of the overlying water (Byron and Ohlendorf, 2006). Anoxic conditions (DBL) would favor reducing conditions that would promote Se association with insoluble iron phases while oxygenated conditions (UBL) would promote the opposite effect and release Se from the sediment into the overlying water as selenite or selenate (Masscheleyn and Patrick, 1993). Selenium enters the lake from surface water sources primarily in the dissolved phase (defined as water passing through a 0.45 µm filter) as selenate (average of 21% of the dissolved Se as selenite) (Naftz et al., 2009).

In contrast, arsenic typically exhibits the opposite effect to redox conditions compared to Se. Arsenite [As(III)] and arsenate [As(V)] are the two primary oxidation states of As. Under oxidizing conditions arsenate is the dominant species while arsenite is dominant under



Fig. 1. Great Salt Lake sampling locations (modified from Baskin (2005)).

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reducing conditions (Masscheleyn et al., 1991). Arsenite is relatively mobile under reducing conditions (Smedley and Kinniburgh, 2002). Various rates for oxidation of As have been documented; one study on oxygenation of As(III) in seawater showed slow rates of As oxidation (Johnson and Pilson, 1975), while another study found very rapid rates of As(III) oxidation in the presence of Mn oxides (Scott and Morgan, 1995).

Specific objectives of this study are to: (1) utilize temperature profiles as evidence of water-column movement; (2) utilize Acoustic Doppler Current Profiler (ADCP) profiles to trace movement of the DBL; and (3) utilize sediment laboratory extraction experiments to simulate observed water-column changes. Selenium is the focus of the study but other trace elements are also presented.

2. Methods

2.1. Field methods

Aqueous chemical and physical conditions were characterized in the field at 19 locations across the main body of GSL (Fig. 1). Depth profiles were collected at four stations (2267, 2565, 2767 and 3510) over 7 to 13 depths (varying by station), ranging from 0.2 to 8 m below the lake surface. The remaining stations were characterized at three depths (3, 6 and 8 m). Aqueous characteristics included temperature, specific conductance, pH, oxidation–reduction potential (ORP), and dissolved oxygen (DO), and were measured using an In-Situ Troll 9500. Density was determined in the lab from collected lake samples using an Anton Paar DMA 35 N density meter, and a salinity percent value was determined from the density value using the following equation:

$$Salinity(\%) = \frac{\left[(SG^*0.99823) / ((8^*T - T^2 + 132, 416) / 132, 432) - 1\right] / 0.63}{(SG^*0.99823) / ((8^*T - T^2 + 132, 416) / 132, 432)} *100$$
(1)

where SG is the specific gravity (density of the sample) measured in g/cm^3 and *T* is the temperature of the sample at time of density measurement measured in °C.

At sites 2565 and 3510, paired sediment traps were suspended in the water column attached to a stainless steel cable spanning the entire water column between a concrete weight at the bottom and a floating buoy just under the water surface. The sediment traps are 0.5 m-long clear acrylic cylinders which fit into fixed holders to ensure they stay upright within the water column. Temperature was measured using Onset brand thermistors (StowAway®, TidbiTTM, model #89419) attached to the stainless steel cable of the sediment trap apparatus. Temperature was measured at six depths spanning the interface between the DBL and UBL. Accuracy of the temperature sensors was ± 0.2 °C over the range of 0 to 55 °C. For site 2565, initial thermistor distances above the sediment-water interface were 1.8, 2.1, 2.5, 2.8, 3.2 and 3.5 m. In August 2006, the chain at the base of the site 2565 trap was shortened by 1 m to decrease the distance of each thermistor above the base by 1 m. For site 3510, thermistor distances above the sediment-water interface were 1.9, 2.2, 2.6, 3.0, 3.4 and 3.7 m. At both sites 2565 and 3510, thermistor spacing was increased to 0.5 m on September 28, 2006, to yield distances above the sediment-water interface of 1.0, 1.5, 2.0, 2.5, 3.0 and 3.5 m (Fig. 2). Thermistor readings were taken at 6-min intervals and were downloaded approximately monthly with an optical reader device that connects to a computer. Once the data had been offloaded from the thermistors, Boxcar® software was used to view the data and export the data files to Excel.

A SonTek® ArgonautTM-XR Acoustic Doppler Current Profiler (ADCP) was deployed June 2006 at site 3510 and in July 2007 at site 2565. The ADCP device was attached to the cylindrical concrete weight at the bottom of the sediment trap apparatus (Fig. 2). The device was retrieved monthly and the data were offloaded to a computer for detailed analysis. Data were recorded every 20 min with a sample averaging interval of 5 min. The data collected from the ADCP contains



Fig. 2. Schematic of the sediment trap apparatus including thermistors and ADCP bin spacing (far right values) after September 2006.

lake bottom temperature, horizontal and vertical current velocity, and current direction at 10 bins (intervals) within the water column above the lake bottom. The blanking distance of the ADCP sets the location of the first interval away from the physical ADCP device and combined with the depth of the concrete anchor the base of the first bin is 60 cm above the lake bottom. The spacing of the bins (in distance above the bottom of the lake) was 80 cm through 260 cm in increments of 20 cm from June 2006 through November 2006 at site 3510. Spacing was increased to 90 cm through 360 cm in increments of 30 cm after November 2006 at site 3510 and for all of the data collected at site 2565. All aqueous condition data were compared to weather measurements of wind speed, wind gust and wind direction recorded at Hat Island (HATUT) and maintained by MesoWest through the Department of Meteorology at the University of Utah.

Thirty bed sediment samples (ranging from 6.8 to 9.4 m in depth below the lake surface) were collected at 15 locations in the main body of GSL on May 31, June 2, 26 and 27, 2006, using an Eckman dredge (Fig. 1, GS sites). The sediment surface was typically coated with what appeared to be a dark organic-rich zone about 2-3 cm in thickness (referred to as ooze). Below the ooze layer the sediment (referred to as the mineral layer) was lighter in color and was primarily composed of sand sized particles along with other minerals which were not identified in this experiment. Ten samples (top 1-2 cm)were collected at 10 locations (GS1, GS4, GS5, GS8, GS9, GS11, GS12, GS14, GS18, and GS20) (locations GS3 and GS15 did not have an ooze layer), using a plastic spoon to remove the ooze off the upper part of the sediment core. Eight samples at sites GS4, GS9, GS10, GS11, GS13, GS18, GS19, and GS20 were composite sediments (mixture of ooze and underlying mineral sediment). The remaining 12 sediment samples (GS1, GS3, GS4, GS5, GS8, GS9, GS11, GS12, GS14, GS15, GS18, and GS20) were from the mineral layer. Composite, ooze, and mineral layer samples were collected in glass jars and kept on ice until transferred to a refrigerator where they were stored at 4 °C.

Water samples were collected in the field using a trace element collection procedure developed by the USGS (U.S. Geological Survey, 2006). Periodic blank samples and replicates were collected using certified inorganic blank water.

2.2. Laboratory methods

Water-quality and bed sediment samples were analyzed at the University of Utah Center for Water, Ecosystems, and Climate Sciences

(CWECS) laboratory facility by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) for Se and other trace elements (As, Cd, Co, Mn, Pb, Sb, and U).

Analyses of water samples were carried out using an Agilent 7500 ce mass spectrometer. Interferences were minimized by collision or reaction with gas in a collision cell. Selenium and As were analyzed using hydrogen gas in the collision cell, while analyses for the rest of the elements used helium as a collision cell gas. Indium $(7\mu g/L equivalent concentration)$ was used as an internal standard.

Dilution of GSL samples was required to prevent salt accumulation and consequent decrease of the ICP-MS signal. Minor elements, including Se, were diluted 50:1 or 30:1 by volume prior to being analyzed. Methanol (3%) and HNO₃ acid (ultra high purity, 0.1%) were used as a dilution matrix.

Sediment samples were digested using HNO₃ and HCl acid extraction and analyzed for total Se by ICP-MS at the CWECS laboratory facility. The extraction procedure does not dissolve silicates, because HF acid is not used, to avoid any possible damage to the ICP-MS quartz torch. Samples were diluted 20:1 and analyzed as described above. Maximum detection limit for Se was 0.01 mg/kg.

Upper brine layer water (15 g) collected from site 2267 in December 2006 was equilibrated with bed sediment (7.5 g) in a 50-ml

plastic centrifuge tube. The equilibration test was performed for subsamples from all 15 bed sediment sampling sites. In order to avoid direct addition of atmospheric oxygen to the sample, the bed sediment container was opened and a subsample was added to the UBL water in a nitrogen glove bag. In order to examine the influence of the availability of oxygen on Se remobilization into the UBL, two batch equilibration replicates were performed for each bed sediment sample, one with nitrogen, and the other with air, in the centrifuge tube headspace (25 ml). The centrifuge tubes were placed upright on a shaking table (130 rpm) for 24 h. Following equilibration, sample tubes were centrifuged at 5500 rpm for 3 min; if visible suspended material was still present, the sample was centrifuged again at 15,000 rpm for 45 min, and supernatant was removed and acidified to 0.8% nitric acid by volume. Major and trace element concentrations were analyzed by ICP-MS.

Analytical quality control was carried out using the EPA Multi-Media, Multi-Concentration, Inorganic Analytical Service for Superfund (ILM05.3) for ICP-MS, released on February 2004 and upgraded on January 2007 (EPA, 2004). The samples used for quality assurance/ quality control (QA/QC) included an initial calibration blank (ICB), interference check verification (ICV), a check standard (CRA), continuum calibration verification (CCV), and a continuum calibration



Fig. 3. Seasonal temperature variation at sites 2565 and 3510, with deep brine layer (DBL) present. Black line represents the temperature of the DBL (1.0 m above lake bottom) and grey line represents the temperature of the UBL (3.0 m above lake bottom).

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blank (CCB). For every 10 samples, a duplicate, spike, spike duplicate, serial dilution, CCV, and CCB were run.

Due to the hypersaline environment of the GSL, sediment concentrations reported from laboratory analysis need to be corrected for the salt mass and associated concentration present in the pore water of the sediment samples before freeze drying. The assumptions made in correcting for salinity were 17% salinity and uniform aqueous concentrations determined from DBL water analyses. Mass values for the salt correction were determined from sample weights before and after freeze drying.

3. Results and discussion

3.1. Water-column stratification

Water temperature in the GSL varies seasonally with highest temperatures observed in summer and lowest in the winter (Fig. 3). At sites 2565 and 3510 the water column is stratified due to the presence of the DBL. Temperatures in the UBL varied from -2 to 28 °C (a range of 30 °C), whereas, temperatures in the DBL varied from 1 to 27 °C (a range of 26 °C). Minimum temperature values occurred during early 2007 and are not shown on graphs in Fig. 3. During the summer, the DBL is cooler than the UBL and the contrast is reversed in the winter, when the DBL is warmer than the UBL. However, the temperature stratification was not observed from July through September 2006 due to the spacing of the thermistors, the spacing was changed at both sites in September 2006 (as described in the methods section) resulting in an abrupt change to

the true DBL temperature. The need for the spacing correction was due to a constant decrease in depth of the DBL corresponding to a decrease in lake gage height throughout the summer as evaporation exceeded fresh water inflow.

Water-column profiles show a distinct change in pH, specific conductance, oxidation reduction potential (ORP), and dissolved oxygen between the UBL and DBL (Fig. 4). The pH is slightly basic in the UBL (approximately 8.5) and becomes more neutral in the DBL (approximately 7.5). Specific conductance in the UBL is approximately 160,000 μ s/cm and increases over the brine layer interface to approximately 220,000 μ s/cm in the DBL. ORP is positive in the UBL (about 200 mV), indicating oxidizing conditions and becomes negative in the DBL (about -300 mV), indicating reducing conditions. Dissolved oxygen values varied over a range of 1 to 9 mg/L in the UBL, compared to DBL values which were <0.10 mg/L.

Profiles over time show a constant depth to the DBL from the lake surface at both sites 2565 and 3510, indicating changes in the altitude of the DBL interface, concurrent with surface lake level deviations. Surface lake level decreased 0.5 m during the summer during both years of study. Over the period of investigation, the thickness of the DBL at site 2565 ranged from 1.5 to 2.0 m and at site 3510 from 1.3 to 1.8 m. These findings are in contrast to USGS data from 1973–74, where the altitude of the DBL interface remained constant (Loving et al., 2000). However, the constancy of the DBL between 1973 and 1974 occurred prior to the construction of a breach in the causeway in 1984, which may have subsequently affected circulation in the lake. The elevation of the surface of the lake in the South Arm (measured at



Fig. 4. Water-column profiles at sites 2565 and 3510 collected November, 2006.

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Fig. 5. Current parameters at site 3510 detected by ADCP from June through September 2006 (a) horizontal current velocity (b) horizontal current direction and (c) vertical current velocity. Shaded box represents 25th through 75th percentile of data with center line representing the median and small square as the mean. Whiskers surrounding box represent 5th and 95th percentile. Outlying x symbols represent 1st and 99th percentile, while short dashes represent the minimum and maximum values.

the USGS Saltair gage 10010000) has varied over a wide range historically from 1277.5 m (1963) to 1283.7 m (1986) and may account for the periodic absence of stratification.

The average horizontal velocity of the DBL at site 3510 was 6.7 cm/s, moving in an average direction of 161° (southeast) from June through September 2006 (Fig. 5). During this period the average vertical velocity of the DBL was -0.88 cm/s. A negative value for vertical velocity implies a downward velocity vector, however the small average downward velocity value may be within the lower range of instrument accuracy and should not be interpreted as absolute. The horizontal velocity (Fig. 5a) and direction (Fig. 5b) varied over this time period in a similar pattern at all depths recorded. However, the vertical velocity showed a wider range for 80-cm and 160 through 220cm bins of the ADCP (Fig. 5c). The wide range of vertical velocity corresponds to the interface between the UBL and DBL.

At site 2565 the ADCP was deployed at the beginning of July 2007 and recorded data though the end of August 2007. The average horizontal velocity over this time period was 7.5 cm/s, moving in an average direction of 177° (southeast). During this time the average vertical velocity at site 2565 was -0.41 cm/s with the greatest range in vertical velocity occurring in the lowest 90-cm bin.

The density of the DBL in the northwest basin of the South Arm is greater than the density of the DBL in the southern basin of the South Arm. A decrease in density from north to south along the flow path of the DBL implies mixing of the DBL with the UBL. The observation that the DBL does not reach the south shore of the lake supports incorporation of the DBL into the UBL along the flow path of the DBL. The density of the DBL at sites 2565 and 3510 fluctuates over time but does not agree in the magnitude or direction of change between the two sites (Fig. 6). Lack of direct correlation of density between the two sites implies that mixing between the layers may vary spatially throughout the South Arm of the lake.

Periodic equilibration events punctuate the record of thermal stratification, such as during June 14–15, 2006, where the recorded temperatures at all depths suddenly become the same (Fig. 7a). Approximately 16 equilibration events were observed during the 16-month period, ranging in duration from 12 to 24h. The majority of the events occurred in spring and fall. These events were characterized by rapid onset and dissipation of the temperatures back to initial stratified conditions. All significant equilibration events were correlated to wind speeds greater than approximately 40 km/h (Fig. 7b). Lag time from dominant wind events was on the order of hours. The rapid onset and dissipation of the thermal equilibration events, and the fact that the equilibrated temperature is always that of the UBL regardless of which layer is colder (Figs. 7 and 8), suggests equilibration results from temporary displacement of the DBL.



Fig. 6. Deviation of density between sites 2565 and 3510 from November 2006 through October 2007. Solid line shows a 1:1 relation. Note all values at site 3510 are less than 2565 but do not show a linear relationship with time.

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Fig. 7. Temperature record from site 2565 showing (a) June equilibration event; tick marks represent midnight (MDT) and values represent distance above lake bottom; and (b) wind speed (black) and wind direction (grey circles) at Hat Island, Great Salt Lake.

The ADCP data show periods of time often associated with temperature equilibration events, such as that on October 18, 2006 (Fig. 8a), during which the horizontal direction of the DBL shifts suddenly (Fig. 8b). The incipient direction of horizontal flow indicates movement away from the North Arm along the long axis of the lake (towards the southeast). Associated with the change in horizontal direction is a substantial increase in the horizontal velocity, which occurs directly prior to the temperature equilibration event (Fig. 8c).

Thermal and chemical stratification of the South Arm of the lake was persistent over the time period of observation (May 2006 through October 2007). Historically, this stratification has been observed over annual to decadal time scales. However, no stratification was detected from 1992 to 1998 due to surface water inflow and causeway conveyance decrease (Loving et al., 2000). Results of previous work indicated that the DBL was resistant to mixing during periods of storm activity (Madison, 1970; Stephens and Gillespie, 1976). However, these studies were conducted before continuous short-term temperature monitoring devices were established in the water column. The periodic interruptions in temperature stratification recorded by continuous temperature sensors during this study suggest that movement of the DBL interface occurs in response to wind events at the surface of the lake.

One mechanism prevalent in lakes is a surface seiche which may set up an internal seiche within the DBL. A seiche is a prolonged oscillating wave in a body of water initiated by atmospheric effects such as wind (Hutchinson, 1957). In a stratified lake, a surface seiche that causes an increase in lake elevation on one end of the lake will cause the interface between the two layers to be tilted in the opposite direction. The tilting of the interface sets up an internal seiche.

Seiche events have been recorded on the GSL historically (Lin, 1977; Atwood, 2006) and also documented by changes in lake elevation at gaging stations that were active at the north and south ends of the South Arm of the lake. Currently, only the gage at the south end of the lake (Saltair) is active, but can still be used to record fluctuations in the surface elevation of the lake following sustained strong wind events characteristic of a seiche. Temperature equilibration events produced by seiches at site 3510 occurred hours after an increase in lake-level elevation at the Saltair gage. Gage stage increases from 0.15 to 0.3 m (0.5 to 1 ft) after a wind event, and oscillates after the initial surge around the initial lake-elevation value (Fig. 9).

3.2. Sediment resuspension

Paired sediment traps located at fixed locations within the water column show greater sediment accumulation in the lower trap (just above the DBL interface) than in the shallow trap (UBL) (Oliver, 2008). Sediment accumulation in the lower trap likely originated from the bottom of the lake or from suspended sediment in the DBL.

Shallow cores were collected at various sites throughout the lake and show the presence of ⁷Be in the upper 2 cm of the core (Oliver, 2008). ⁷Be ($t_{1/2}$ = 53.3 days) originates in the atmosphere and is used to indicate short-term deposition and/or mixing (Krishnaswami et al.,

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Fig. 8. Variations in parameters following a strong wind event, Great Salt Lake (a) temperature equilibration event at site 3510 associated with (b) a fluctuation in horizontal direction from the ADCP, and (c) a fluctuation in a horizontal velocity from the ADCP. Values are distance above lake bottom.

1980). The presence of this isotope in the top part of the core implies that the upper sediment was in contact with water recently in direct contact with the atmosphere (UBL) or from particle deposition from the UBL through the DBL to the bed sediment.

Total Se concentrations in bed sediment samples showed no spatial variation in either the ooze or mineral layer, or in the composite of the two (Fig. 10a). The average concentrations of the 10 sites combined for all elements analyzed were not statistically different between the ooze and mineral layers (averages overlapped within the range of one

standard deviation). The average Se concentration in the ooze layer was 2.0 ± 0.3 mg/kg, whereas the average Se concentration in the mineral layer was 1.8 ± 0.8 mg/kg. At 4 of 10 sites where ooze was present (GS 4, GS 5, GS 11, and GS 18), the Se concentration in the ooze was significantly greater than the corresponding Se concentration in the mineral layer (Fig. 10a). At site GS 14, however, the Se concentration in the mineral layer was substantially greater than the Se concentration in the ooze.

Arsenic showed a similar relation; at 5 of the 10 sites where ooze was present (GS 4, GS 5, GS 11, GS 18, and GS 20), the As concentration in the ooze was significantly greater than the corresponding As concentration in the mineral layer (Fig. 10b). The average concentrations of the 10 sites combined for all elements analyzed were also not statistically different between the ooze and mineral layers. Average As concentration in the ooze was 36.1 ± 16.3 mg/kg and 24.6 ± 15.4 mg/kg in the mineral layer. Selenium and As were both greater in the ooze than in the mineral layer at the same 4 sites (GS 4, GS 5, GS 11, and GS 18).

Other elements showed large spatial variability between the 10 sites for Cu, Pb, and U. The average Cu concentration in the mineral layer was $171.9 \pm 170.7 \text{ mg/kg}$ and $152.6 \pm 59.1 \text{ mg/kg}$ in the ooze. The average Pb concentration in the mineral layer was $90.3 \pm 95.0 \text{ mg/kg}$ and $54.3 \pm 15.3 \text{ mg/kg}$ in the ooze. The average U concentration in the mineral layer was $7.1 \pm 5.1 \text{ mg/kg}$ and $4.2 \pm 2.0 \text{ mg/kg}$ in the ooze.

3.3. Trace element mobility

Batch equilibration tests were performed to determine whether significant Se would be solubilized from bed sediment upon equilibration with UBL water (e.g., by resuspension or displacement of the DBL). Tests were conducted over day, weekly and monthly time scales to determine if Se released over longer periods of exposure with UBL water would be significant. The headspace of the week and month samples was air because there was not a statistically significant difference between the average Se concentration of the two headspace replicates in the 24-hour batch experiment. The only change to the procedure from the methods described in Section 2.2 was flushing the headspace of the sample once per day with air before the tubes were placed upright on the shaking table (130 rpm) for 5 min per day.

Percent Se solubilized (of extractible) over a 24-hour period varied spatially with no discernable pattern. The average percent Se solubilized in the samples with nitrogen gas headspace was $1.2 \pm 0.7\%$, whereas the average percent Se solubilized in the samples with air headspace was $1.2 \pm 1.4\%$. The maximum percent Se solubilized was from site GS 11 composite, with air headspace at 6.1% (Fig. 11a).

The amount of Se released during the week long experiment was $0.05 \pm 0.03 \,\mu\text{g}$. The amount of Se released in the batch test samples over a month of equilibration was $0.06 \pm 0.03 \,\mu\text{g}$ per 7.5 g of sediment. The corresponding percent Se solubilized was $2.4 \pm 1.1\%$ for the week long test and $3.0 \pm 1.1\%$ for the month long test (Fig. 11b and c).

Results for trace metals other than Se are shown in Fig. 11. Several elements show negative percent solubilized (of extractible), indicating that the element may have precipitated or adsorbed to a particle due to a change in oxidation state. For the week-long batch equilibration experiment, Pb had a negative average value for all samples analyzed, and Sb had negative value within the range of data. After the month-long batch equilibration experiment, As and Sb had a negative average value for all samples analyzed, and U had negative values within the range of data.

Solubilization of Se into the water column due to equilibration of anoxic sediment with UBL water may occur periodically, in response to wave-induced sediment resuspension and seiche-driven displacement of the DBL. The significance of these events to Se concentration is demonstrated by an example scenario based on observed sediment resuspension into the sediment traps. Since approximately 1 g of sediment is periodically resuspended into the sediment traps (3.6-cm radius), a 3.6-cm column of water can be expected to equilibrate with

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Fig. 9. Water-level fluctuation at the south end of the South Arm of the Great Salt Lake recorded at the USGS Saltair gage (10010000).



Fig. 10. Total concentrations of (a) Se and (b) As in bed sediment samples after salinity correction measured by ICP-MS following sediment digestion using nitric and hydrochloric acid.

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Fig. 11. Time series change in percent solubilized (amount of element present in water after experiment relative to amount released during digestion) from batch equilibration experiments for a variety of elements after (a) 1 day (b) 7 days and (c) 28 days. Shaded box represents 25th through 75th percentile of data with center line representing the median and small square as the mean. Whiskers surrounding box represent 5th and 95th percentile. Outlying x symbols represent 1st and 99th percentile, while short dashes represent the minimum and maximum values.

1 g of sediment. Assuming that the equilibrated column of water is 4 m in height, the resulting additional Se concentration from equilibration with anoxic sediment for site GS 11 (highest value site) is $0.0049 \ \mu g/L$.

The resultant additional Se concentration from the previous scenario is a negligible value compared to the average aqueous Se concentration of $0.5 \pm 0.08 \,\mu\text{g/L}$ measured in the lake (Diaz et al., 2009b). Site GS 11 represents the greatest potential for additional concentration based on batch test measurements. The average additional Se concentration contribution for samples with either air or nitrogen headspace is 0.0009 $\mu\text{g/L}$. The contribution from resuspension is therefore not likely to significantly increase the concentration of Se in the water column.

Solubilization of Se into the water column may also occur in response to shrinking of the DBL, because anoxic sediment present under the DBL may be put into direct contact with oxic UBL when the spatial extent of the DBL decreases. Lake level decreased from 1279.6 m in June 2006 to 1279.1 m in September 2006. During this period, the thickness of the UBL remained constant (as measured at sites 2565 and 3510), whereas the DBL thickness decreased by 0.5 m. This decrease in DBL extent corresponds to exposure of 96.214 km² (23,775 acres) of anoxic sediment to oxic UBL water, based on bathymetric data (Baskin, 2005).

The corresponding Se input to the lake (kg_{Se}) over a period of a month can be calculated if one assumes a maximum depth in the sediment from which Se is solubilized. Assuming this depth to be 2 cm yields a 2.34 cm^2 area for a sediment bulk density of 1.6 g/cm^3 , occurring over an area of 96.214 km². The corresponding load is 24.7 kg, which compared to the annual Se load to the lake from riverine inflow of 1560 kg (Naftz et al., 2009), is significant but not major. Furthermore, the load is based on a month-long equilibration study while the change in area of the DBL occurs over a period of several months. Also, the estimate is based on batch equilibration tests reflecting a 2:1 ratio of water to sediment conducted over a period of one month, whereas the larger water:sediment ratios and longer equilibration times in the field may yield larger Se inputs.

4. Summary

Over the period of study from May 2006 through October 2007, the DBL was present at two sampling sites located in the South Arm of the GSL. The density of the DBL in the northwest basin of the South Arm was greater than the density of the DBL in the southern basin of the South Arm. A decrease in density as the DBL moves in an average southeastern direction implies incorporation of the DBL into the UBL. Continuous temperature records at these two sites show periodic events where the temperature of the water column from 1 m to 3.5 m above the bottom of the lake suddenly equilibrates (becomes isothermal). The temperature equilibration events are associated with sustained wind speeds generally greater than 40 km/h. Surface seiches are also correlated with temperature equilibration events. The likely mechanism responsible for the temperature equilibration events is an internal seiche which temporarily tilts the UBL/DBL interface.

In addition to the short-term temperature equilibration events, the DBL decreased in depth by 0.5 m twice during the study period in response to a corresponding decrease in lake-surface elevation over a period of months. The decrease in lake bottom area covered by the DBL causes oxic UBL water to be placed in direct contact with the previously anoxic bed sediment.

The periodic thermal equilibration events do not appear to be long enough to introduce significant amounts of Se into the water column based on equivalent 24-hour batch equilibration tests. Decrease in area of the DBL may introduce approximately 25 kg of Se back into the water column based on a calculation from month-long batch equilibration results. However, this amount is not significant when compared to the external loading of Se from riverine inputs to the system.

Continuous monitoring of DBL spatial extent as well as traceelement concentration in the water column is needed. The monitoring will help ensure trace elements sequestered in anoxic lake bed

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sediments do not significantly increase bioavailable water-column concentrations and have an adverse effect on the GSL ecosystem.

Acknowledgements

Funding for this project was provided by the State of Utah Division of Water Quality and the U.S. Geological Survey. Use of brand names within this text is for identification purposes only and does not constitute endorsement by the University of Utah or U.S. Geological Survey. The manuscript was improved from technical reviews by Reed Green and Lawrence Spangler (USGS) and two anonymous journal reviewers.

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