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Anthropogenic influences on the input and biogeochemical cycling of nutrients and mercury in Great Salt Lake, Utah, USA

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ABSTRACT

Despite the ecological and economic importance of Great Salt Lake (GSL), little is known about the input and biogeochemical cycling of nutrients and trace elements in the lake. In response to increasing public concern regarding anthropogenic inputs to the GSL ecosystem, the US Geological Survey (USGS) and US Fish and Wildlife Service (USFWS) initiated coordinated studies to quantify and evaluate the significance of nutrient and Hg inputs into GSL. A 6‰ decrease in $\delta^{15}\text{N}$ observed in brine shrimp (*Artemia franciscana*) samples collected from GSL during summer time periods is likely due to the consumption of cyanobacteria produced in freshwater bays entering the lake. Supporting data collected from the outflow of Farmington Bay indicates decreasing trends in $\delta^{15}\text{N}$ in particulate organic matter (POM) during the mid-summer time period, reflective of increasing proportions of cyanobacteria in algae exported to GSL on a seasonal basis. The C:N molar ratio of POM in outflow from Farmington Bay decreases during the summer period, supportive of the increased activity of N fixation indicated by decreasing $\delta^{15}\text{N}$ in brine shrimp and POM. Although N fixation is only taking place in the relatively freshwater inflows to GSL, data indicate that influx of fresh water influences large areas of the lake. Separation of GSL into two distinct hydrologic and geochemical systems from the construction of a railroad causeway in the late 1950s has created a persistent and widespread anoxic layer in the southern part of GSL. This anoxic layer, referred to as the deep brine layer (DBL), has high rates of SO_4^{2-} reduction, likely increasing the Hg methylation capacity. High concentrations of methyl mercury (CH_3Hg) (median concentration = 24 ng/L) were observed in the DBL with a significant proportion (31–60%) of total Hg in the CH_3Hg form. Hydroacoustic and sediment-trap evidence indicate that turbulence introduced by internal waves generated during sustained wind events can temporarily mix the elevated CH_3Hg concentrations in the DBL with the more biologically active upper brine layer (UBL). Brine shrimp collected during the summer/fall time periods contained elevated Hg concentrations (median concentration = 0.34 mg/kg, dry weight (dw)) relative to samples collected during the spring (median concentration < 0.2 mg/kg, dw). Higher Hg in brine shrimp during the summer and fall may reflect the higher proportion of adult brine shrimp during this time period, resulting in an increased time for bioaccumulation of Hg. Eared grebes (*Podiceps nigricollis*) consume brine shrimp from GSL during the fall molting period. Median Hg concentrations in eared grebe livers increased by almost three times during the 3–5 month fall molting period. Selected duck species utilizing GSL have consistently exceeded the US Environmental Protection Agency (USEPA) screening

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level for Hg (0.3 mg/kg Hg wet weight), resulting in the issuance of warnings against unlimited human consumption of breast muscle tissue.

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1. Introduction

The GSL, in the western United States, is a terminal lake with a surface area that can exceed 5100 km² (Fig. 1). The GSL ecosystem receives industrial, urban, mining and agri-

cultural discharge from a 37,500 km² watershed which includes over 1.7 million people. The open water and adjacent wetlands of the GSL ecosystem support millions of migratory waterfowl and shorebirds from throughout the Western Hemisphere (Aldrich and Paul, 2002). In

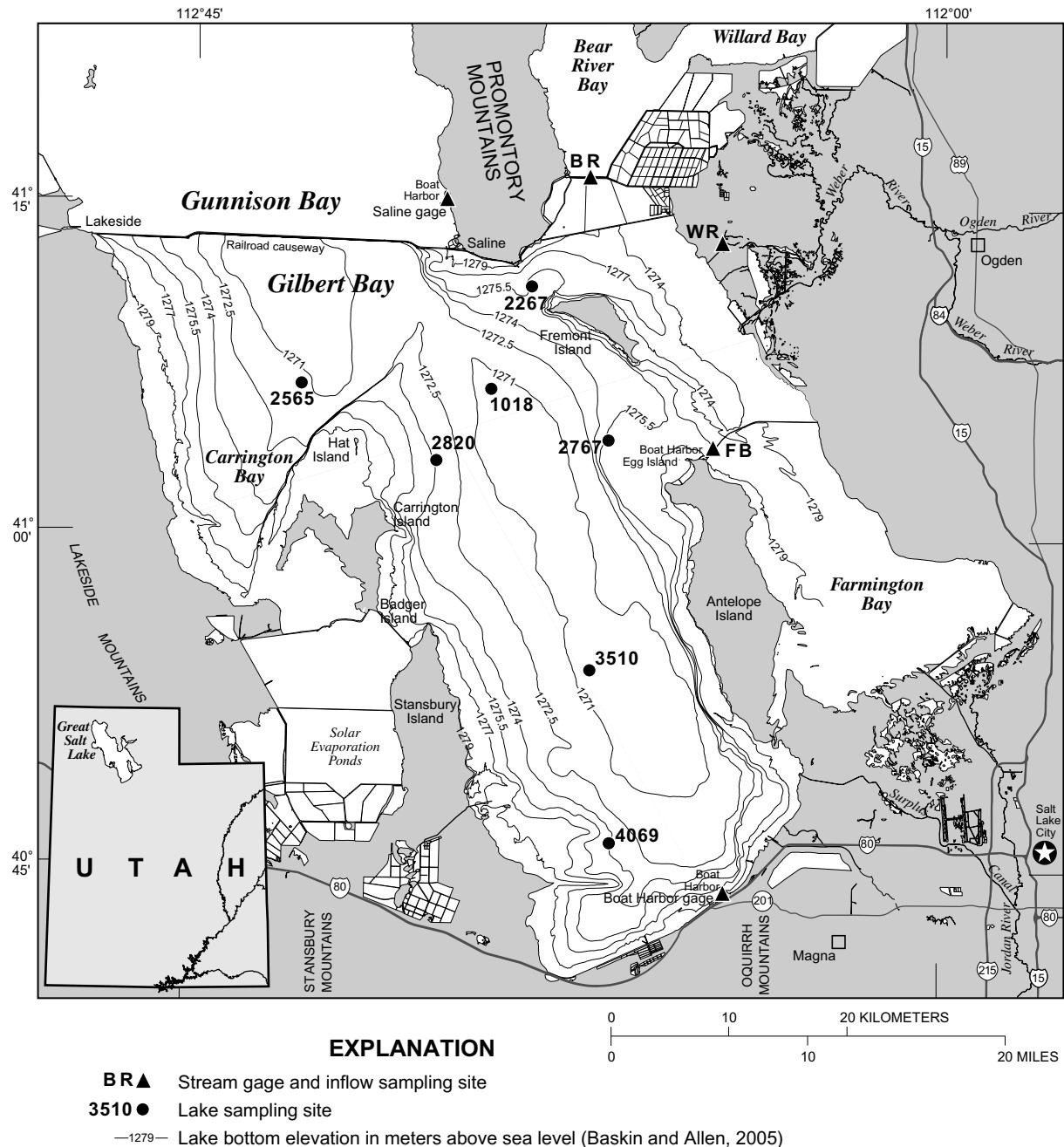


Fig. 1. Location of GSL and sites of stream gages and lake sampling points where nutrient, isotopic and Hg data were collected (Baskin and Allen, 2005).

addition to supporting migratory dependent waterbirds, the brine shrimp population residing in GSL supports a shrimp industry with annual revenues as high as 60 million US dollars (Isaacson et al., 2002). Other industries supported by GSL include mineral production (halite, K salts, Mg metal, Cl₂, MgCl₂ and nutritional supplements) and recreation that includes waterfowl hunting (Anderson and Anderson, 2002; Butts, 2002; Isaacson et al., 2002; Tripp, 2002). Natural oil seeps and actively produced and potential oil reserves are also found within and adjacent to the shoreline of GSL (Bortz, 2002; Hunt and Chidsey, 2002). Full production of these reserves has been limited by high production and refining costs; however, increasing trends in the market value of crude oil could strengthen the economical viability of these reserves.

Despite the ecological and economic importance of GSL, little is known about the input and biogeochemical cycling of nutrients and trace elements in the lake and how increasing anthropogenic pressures may affect this cycling. For example, increased watershed and airshed loading of Hg and other trace elements to GSL could negatively affect the migratory waterbirds and brine shrimp, which utilize the lake. Modifications in water circulation within GSL from the construction of causeways and other physical barriers could also change the geochemical conditions in parts of the lake. Changes in geochemical conditions (i.e., measurable dissolved O₂ transitioning to SO₄²⁻ reduction) could then affect the biogeochemical cycling and distribution of various trace elements and nutrients.

Domagalski et al. (1990) evaluated the geochemical response of a suite of trace metals (Fe, Mn, Cu, Pb, Zn, Cd, Co, Mo and V) to diagenetic processes in the bottom sediment of GSL. Results from this research found that most trace metals were associated with sulfide minerals in conjunction with decomposition of organic matter and production of H₂S in the near-surface sediment. Enrichment of Cu, Zn, Pb and Co in near-surface bottom sediment was attributed to anthropogenic sources in the GSL watershed. Most of the organic matter at the sediment/anoxic water interface was mineralized to CO₂ due to excess SO₄²⁻ in the system (Domagalski et al., 1990).

Work completed by Tayler et al. (1980) postulated that the GSL acts as a “natural disposal system” with respect to the immobilization of dissolved and suspended trace metals (Cu, Zn, Cd, Hg, Pb, Mo, Mn and Ag), and As and Se in the water column. Concentration factors (>1.0 indicates accumulation over inflow sources) for selected trace elements in the water column of GSL ranged from 0.1 for Cd to 2.5 for Se to 11.5 for As; however, industrial inflows were not considered during their calculations (Tayler et al., 1980). In general, the highest enrichments of these trace elements in GSL sediment were found in areas beneath the anoxic DBL, likely due to the production of sulfide and subsequent precipitation of insoluble metal sulfides.

From 1998 to 2001, the USGS conducted a water-quality and biological assessment within the GSL watershed (Waddell et al., 2004). Results from this study indicated that the majority of streambed sediment had concentrations of selected trace elements, which exceeded aquatic life guidelines for As, Cd, Cu, Pb, Hg, Ag and Zn in streams draining mine tailings and metal smelters. Elevated P con-

centrations were found in 12 of the 27 sampled streams in the GSL watershed.

Sediment cores collected by the USGS from the Farmington Bay area of GSL (Fig. 1) were used to reconstruct changes in the water quality entering GSL from the early 1700s to 1998 (Naftz et al., 2000). A 28-cm core indicated that deposition of contaminated sediment (elevated concentrations of Cd, Cu, Pb, Zn, N, organic C, and P) began sometime in the early to mid-1900s and became progressively greater in recently deposited sediment. The most contaminated sediment was deposited from 1979 to 1998. Prior to the early 1900s, uncontaminated sediment was deposited in Farmington Bay. The historical trends observed in the GSL core were attributed to the history of development in Salt Lake Valley.

In response to increasing public concern regarding contaminant input to the GSL ecosystem, the USGS and USFWS initiated studies to quantify and evaluate the significance of selected nutrient and trace-element inputs. Specific objectives of this paper are to (1) utilize stable isotopes of N in combination with particulate N and C data to evaluate seasonal and source term changes of nutrients to the brine shrimp population in GSL and (2) describe the distribution and biogeochemical cycling of Hg in the GSL ecosystem.

2. Methodology

2.1. Field methods

Field parameters (pH, water temperature, and specific conductance) were measured at inflow and lake sites using an In-Situ Troll 9500 multiparameter water-quality monitor. At a minimum, the high range specific conductance and standard pH probes were calibrated on a daily basis, prior to taking measurements. Temperature probe calibration was verified on an annual basis with a NIST certified thermometer. Semi-quantitative sulfide concentrations were determined on filtered (<0.45 µm) water samples with Chemetrics ampoules utilizing the colorimetric methylene blue method.

Water samples from river inflow sites analyzed for total particulate N (TPN) and total particulate C (TPC) were composited using the equal discharge increment (EDI) method (Wilde et al., 1999) at Bear River and Farmington Bay inflow sites and equal width increment (EWI) method (Wilde et al., 1999) at the Weber River site. River inflow samples were composited into a pre-cleaned churn splitter and processed on site. Water from the lake sites was collected at various depths using a peristaltic pump and flexible tubing that was weighted to minimize horizontal drifting. Within 6 h of sample collection TPN samples were filtered through a 25-mm glass fiber filter, encased in Al foil, and chilled at 4 °C until analysis. Bulk water samples collected for isotopic analysis of POM were stored frozen in field rinsed, 1-L polyethylene bottles until laboratory processing. Thawed samples were filtered through a 25-mm glass fiber filter. The accumulated particulates were scraped from the filter surface, transferred to a 30-mL plastic scintillation vial, and refrozen until isotopic analysis.

Because of potential contamination issues associated with the collection of whole water total Hg and CH₃Hg samples, special sample collection techniques were applied. Pre-cleaned Teflon tubing was used to pump lake water samples from various depths into pre-cleaned and double bagged Teflon bottles. Water samples were acidified with ultra-pure HCl after collection. During sample collection, personnel wore Tyvek suits and powder-free latex gloves to minimize potential sample contamination.

Brine shrimp were collected for isotopic analysis using a plankton net with a 155 µm mesh size. Samples were composited from the entire water column, excluding the DBL. The bulk brine shrimp samples were transferred into 30-mL plastic scintillation vials and chilled at 4 °C during field transport. Samples were frozen within 6 h of collection. Prior to laboratory analysis, the brine shrimp samples were thawed and the adults were selected from the bulk sample using forceps under a 0.7× power binocular microscope. Archived brine shrimp samples utilized for isotopic analysis were stored in a 10% formalin solution. Prior to isotopic analysis, the archived brine shrimp samples were placed on plankton netting (155 µm) and rinsed thoroughly with deionized water. The rinsed samples were then transferred to a 30-mL plastic scintillation vial and frozen until isotopic analysis. Previous work by Sarakinos et al. (2002) indicates limited effects of formalin on δ¹⁵N of preserved biota.

Eared grebes were sampled opportunistically in the south arm of GSL using a shotgun and steel shot. Age class was estimated by plumage and eye color. Each bird was weighed and the liver removed in the laboratory with decontaminated instruments and standard bird necropsy techniques. During 1997, approximately equal weight subsamples of livers were composited into three samples by collection site and analyzed for Hg. During 1998 and 2000, individual whole livers were submitted for Hg analysis.

Suspended sediment was collected from the water column to determine sediment deposition rates in GSL. Cylindrical sediment traps with a diameter of 7.3 cm were suspended on a stainless steel cable that was held vertical between a 115 kg cement bottom weight and a 0.5 m diameter buoy that was placed approximately 1 m below the water surface. Sediment traps were placed in both the UBL and at the DBL/UBL interface and deployed from 24 to 64 days between sampling intervals. During sampling, water was pumped out of each trap to within 3 cm of the accumulated sediment layer. The remaining water was then used to slurry the captured sediment into a pre-cleaned, wide-mouthed, 500-mL nalgene bottle. Prior to redeployment, each sediment trap was scrubbed with a nylon brush and rinsed with lake water. Samples were chilled to 4 °C for up to 8 h until they could be frozen at the on-shore laboratory. Each sample was freeze dried to determine captured sediment weights. Measured water density and associated salinity were used in combination with the wet vs. dry sample weights to correct the sediment weights for salt deposition during the freeze drying process.

A Sontek Argonaut-XR with an external battery pack, internal recorder, compass/tilt sensor, pressure sensor, and temperature sensor was deployed from a cement an-

chor in <9 m of water at the bottom of GSL for continuous measurement of water velocity and direction in horizontal and vertical planes using hydroacoustic technology. The equipment was programmed to collect data every 20 min with a sample averaging interval of 300 s. The multi-cell, vertical water velocity feature was activated to measure 10, 30-cm bins in the lower water column. Point velocity measurements throughout the water column were made using a 1200 kHz Rio Grande Acoustic Doppler Current Profiler (ADCP) manufactured by RD Instruments. The ADCP was deployed from the sampling boat and set up to collect data approximately once a second for >10 min at each site. The individual data from each site were then averaged together to compute the velocity and direction of flow throughout the water column over the sample collection period.

2.2. Laboratory methods

2.2.1. Nutrients

After removal from the water column by filtration onto a glass fiber filter, TPC and TPN were measured by high-temperature combustion with an Exeter Analytical elemental analyzer (USEPA, 1997b) at the USGS National Water-Quality Laboratory in Denver, Colorado. A total of five process blanks were analyzed for TPC and TPN. With the exception of one TPC sample collected on August 23, 2004, the process blanks were at or below the method detection limits.

2.2.2. Hg

All water analyses were performed at the USGS Hg Research Laboratory in Middleton, Wisconsin. Total Hg in whole water samples was determined using cold vapor atomic fluorescence spectrometry (CVAFS) (Olson and DeWild, 1999). The CH₃Hg in whole water samples was determined using distillation/ethylolation/gas-phase separation with CVAFS detection (DeWild et al., 2002). Primary standards for total Hg were obtained commercially and standardized and certified against a NIST standard reference material. No reference materials are currently available for CH₃Hg. Standards for CH₃Hg were prepared in the laboratory. Known reference samples were analyzed at the beginning of each analytical run, after every 10 samples and at the end of the run. Method blanks were prepared by adding SnCl₂ to 125 mL of Hg-free water and purging for 20 min to insure removal of any residual Hg. Method blanks were run periodically during each sample run and used to calculate the daily detection limit (DDL). The accepted value for the DDL is ≤0.04 ng/L. Matrix spikes were analyzed during each run or every 10 samples. Percent recovery of matrix spikes had to fall between 90% and 110% for the sample run to be accepted. Three field replicates and two process blanks were collected and analyzed for total Hg and CH₃Hg. Field replicate results were in close agreement, with replicates ranging from 3.0% to 5.5% for total Hg and 2.7% to 15.9% of the initial value for CH₃Hg. Process blanks had low total Hg (0.08 and 0.10 ng/L) and CH₃Hg (<0.04 ng/L) concentrations. Additional details on Hg laboratory methods and quality assurance and quality

control procedures can be found at <http://infotrek.er.usgs.gov/mercury/qa.html#B>.

Brine shrimp and eared grebe liver tissues were digested in heavy-walled, screw-cap Teflon bombs with concentrated high purity HNO₃. Bombs were heated for 2–8 h at an oven temperature of 130 °C and opened three times to release CO₂ gas build-up. After digestion, Hg was determined by CVAFS. During the analyses of brine shrimp tissue the following type and number of QA/QC samples were analyzed: laboratory blanks (3), laboratory replicates (3), matrix spikes (3), and reference materials (6). All procedural blanks were below 0.2 mg/kg (dw) and matrix spike recoveries were acceptable, ranging from 87% to 113%. During the analyses of eared grebe livers the following type and number of QA/QC samples were analyzed: laboratory blanks (4), laboratory replicates (4), matrix spikes (4), and reference materials (8). All procedural blanks were below 0.2 mg/kg (dw) and matrix spike recoveries were acceptable, ranging from 87% to 93%.

2.2.3. N isotopes

Brine shrimp and POM samples were freeze dried and ground to a fine powder. Sample aliquots were weighed into metal capsules (Sn capsules for brine shrimp; Ag capsules for POM) and closed. Carbonate was removed from the samples by vapor acidification (Yamamoto and Kayanne, 1995) and the capsules are crimped closed. Samples were analyzed for N isotopes using a Carlo Erba 1500 or 2500 elemental analyzer connected to a GVI Optima mass spectrometer located at the USGS National Research Program laboratory in Menlo Park, California. A working standard (EDTA) was analyzed in a size series, to bracket the expected sizes of the samples, at 10 sample intervals and used to correct the run for linearity, instrumental drift, isotope ratios, and elemental abundance. Ten percent of the samples were analyzed in duplicate and a blank consisting of an empty capsule was analyzed at the beginning and end of every run. Isotope ratio values for N are presented in the delta (δ) notation:

$$\delta^{15}\text{N} = \{[(^{15}\text{N})/^{14}\text{N}]_{\text{Sample}} / (^{15}\text{N})/^{14}\text{N}_{\text{Standard}}\} - 1\} * 1000, \quad (1)$$

where δ values are expressed as ‰ difference from the standard (atmospheric N). Precision for $\delta^{15}\text{N}$ in brine shrimp is $\pm 0.3\text{‰}$ and for POM is $\pm 0.4\text{‰}$.

3. Results and discussion

3.1. N isotopic variations in brine shrimp

Isotopes of N, C, and S can provide critical information about nutrient dynamics in aquatic environments (Kendall, 1998). Changes in the isotopic composition in various food web components in the GSL ecosystem may provide important insight into nutrient sources. Archived brine shrimp samples from four sites on GSL collected during 2000–2002 were analyzed for $\delta^{15}\text{N}$ composition (Fig. 2). Analyses of the archived samples indicate a 6‰ annual shift in $\delta^{15}\text{N}$. Early season brine shrimp samples collected during the spring have heavier isotopic signatures with

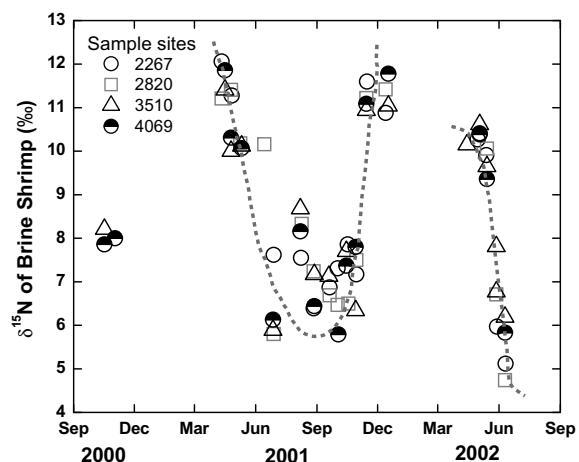


Fig. 2. Variation of $\delta^{15}\text{N}$ in archived brine shrimp samples collected from GSL, Utah. Note large seasonal trend in isotopic composition denoted by dashed lines.

$\delta^{15}\text{N}$ ranging from +12 to +13‰. The heavier $\delta^{15}\text{N}$ (>10 ‰) during this time period may be indicative of a food source supported by treated sewage or animal waste nutrient sources (Kendall, 1998).

Summer season brine shrimp samples (June through August) generally have lighter isotopic signatures with $\delta^{15}\text{N}$ ranging from +6‰ to +5‰ (Fig. 2). The lighter isotopic values observed during this time period are possibly indicative of higher proportions of food sources with a lighter isotopic composition. One possible source of isotopically light food in GSL is blue-green algae or cyanobacteria. Cyanobacteria fix atmospheric N and have a tightly constrained isotopic composition near 0‰ (Kendall, 1998; Goericke et al., 1994). For example, low $\delta^{15}\text{N}$ in bulk particulate and zooplankton samples collected in the East China Sea and North Pacific Ocean have been attributed to significant amounts of atmospheric N fixation (Goericke et al., 1994). Large blooms of cyanobacteria, composed primarily of *Nodularia*, have been observed in GSL (Farmington Bay) during the summer months (W. Wurtsbaugh, pers. comm., 2005). Brine shrimp samples collected from September through November return to heavier isotopic signatures, similar to the $\delta^{15}\text{N}$ observed in the spring, indicative of a return to a food source with a heavier isotopic composition.

In 2004, brine shrimp samples were collected from the same sites where archived brine shrimp samples had been collected (Fig. 3). Although similar shifts in $\delta^{15}\text{N}$ were observed in brine shrimp from sites 3510 and 2820, sites 2267 and 4069 exhibited smaller seasonal shifts in $\delta^{15}\text{N}$. The reason for smaller $\delta^{15}\text{N}$ shifts is unknown; however, they may be related to shifts in currents within GSL due to changes in river inflow to the lake. Early season disappearance of inflow from the Bear River to GSL in May 2004 due to the continuation of drought conditions in northern Utah (Wilkowske et al., 2003) may have prevented the supply of isotopically light food (cyanobacteria) to this area of GSL (site 2267). In contrast, both sites 3510 and 2820 are in proximity to outfall from Farmington Bay

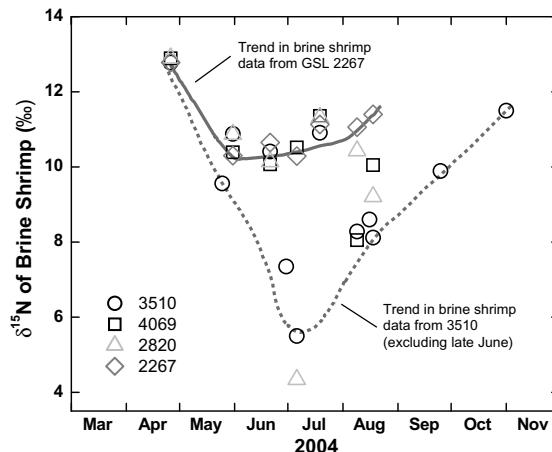


Fig. 3. Variation of $\delta^{15}\text{N}$ in brine shrimp samples collected from four sites on GSL during 2004.

and show a seasonal shift in $\delta^{15}\text{N}$, similar to the archived shrimp samples from previous years. Drought conditions observed during 2004 did not impact the outfall of Farmington Bay to GSL because of the likely high proportion of treated sewage effluent that contributes significant discharge source to GSL. The data indicate that isotopically light food sources from Farmington Bay (for example, cyanobacteria) may be significant to selected areas of GSL during these hydrologic conditions.

Part of the observed seasonal variation in $\delta^{15}\text{N}$ could be due to temporal changes in the relative proportions of different brine shrimp life stages (cysts, nauplius larva, nauplius, sub adult and adult). To address this possibility, three samples of live brine shrimp (undifferentiated) were separated from brine shrimp cysts and analyzed for $\delta^{15}\text{N}$. Based on the samples analyzed, there was less than a 1‰ difference in $\delta^{15}\text{N}$, with the brine shrimp cysts consistently having a lighter isotopic signal. After the cysts are open, the nauplius larva subsist on the yolk sac for approximately 12 h before feeding on the same food source(s) as the adult brine shrimp (Stephens, 2001). Given the similar isotopic composition between brine shrimp and brine shrimp cysts and utilization of the same food source(s) within 12 h of cyst opening, it is unlikely that the observed seasonal shifts in $\delta^{15}\text{N}$ are due to changing proportions of brine shrimp life stages.

3.2. N isotopic variations in POM

Samples for POM analysis were collected from inflow sites and site 3510 on GSL during 2004 to determine if there were seasonal trends in $\delta^{15}\text{N}$, similar to trends observed in brine shrimp samples. The POM samples collected at the outlet of Farmington Bay to GSL show a strong seasonal trend in $\delta^{15}\text{N}$ (Fig. 4) similar to the trends observed in the archived brine shrimp samples (Fig. 2). Decreasing trends in $\delta^{15}\text{N}$ in the POM during the mid-summer period are probably reflective of increasing proportions of cyanobacteria in the POM from Farmington Bay. In contrast, the $\delta^{15}\text{N}$ of POM from the Bear and Weber Riv-

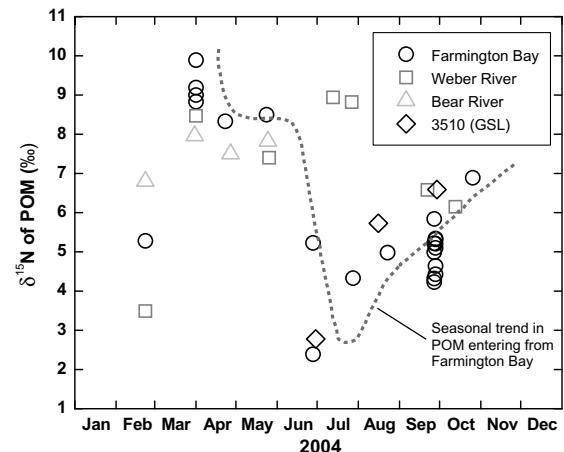


Fig. 4. Variation of $\delta^{15}\text{N}$ in POM samples collected from surface water inflow entering GSL compared to the $\delta^{15}\text{N}$ in POM collected from site 3510 located on GSL.

er inflows to GSL did not indicate a strong seasonal trend. Due to drought conditions in the GSL watershed during 2004, the Bear River did not contribute POM loads after June 2004 and discharge from the Weber River to GSL is small, with a mean daily discharge of 1.0 m³/s from April through September, 2004 (Enright et al., 2005).

The mole ratio of C:N in the POM collected from the river inflow sites were compared to the Redfield ratio to provide additional insights into seasonal changes in N sources entering GSL (Fig. 5). The Redfield ratio is the molar ratio between C, N and P of 106:16:1 that is relatively constant throughout the world's oceans and is reflective of the large influence that biota has on ocean chemistry (Redfield, 1958). In contrast to the Redfield ratio of ocean seston (C:N = 6.6), POM from terrestrial sources can have far different C:N ratios (Sterner and Elser, 2002). Terrestrial foliage C:N ratios are highly variable and can range from 7.5 to 225, reflective of extremely low N contents in these

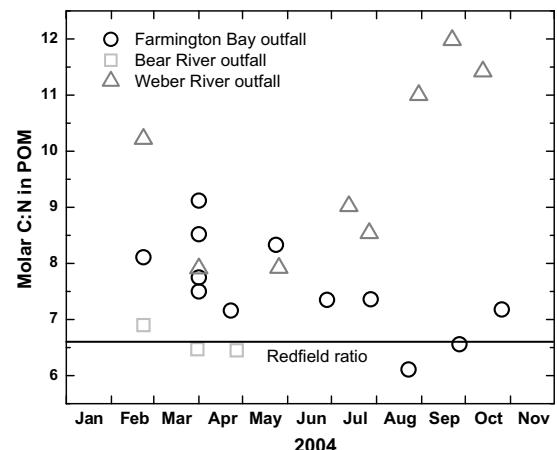


Fig. 5. Variation in the molar C:N of POM from river input to GSL during 2004 compared to the Redfield ratio (6.625).

materials (Sterner and Elser, 2002). The higher C:N ratio of POM composed of terrestrial material relative to POM produced within the water column can be used to understand the seasonal changes in $\delta^{15}\text{N}$ observed in POM entering GSL. With the exception of the Bear River inflow, the C:N ratio of POM during February through April is above the Redfield ratio, indicative of a higher contribution of terrestrial material to the POM in the outflow. This time period also coincides to the highest discharge from the Farmington Bay and Weber River outflows, creating the best potential for contribution of terrestrial materials during spring runoff events. From June through August, the C:N ratio of POM from Farmington Bay continues to decrease to ratios near the Redfield ratio, indicative of less contribution of terrestrial material to the POM and indicative of the increased activity of N fixation suggested by the depleted $\delta^{15}\text{N}$ in POM. During the same time period, the C:N ratio of POM in the outfall from Weber River increases substantially to over 11 (Fig. 5), indicative of increased proportions of terrestrial debris and confirmation of the low activity of N fixation suggested by the enriched $\delta^{15}\text{N}$ in POM from the Weber River.

Rates of N fixation were measured along an 18 km transect from Farmington Bay to the open water of GSL during September 2004 (J. Robinson, Utah State Univ., pers. comm., 2005). The rates of N fixation at both stations in Farmington Bay approached 2 $\mu\text{g/L/h}$ compared to rates of near zero for the open water of GSL. These results indicate that N fixation is only taking place in the relatively freshwater inflows to GSL and the lighter $\delta^{15}\text{N}$ in POM samples from GSL originate from less saline inflow sources and are not generated from N fixation in the more saline open water of GSL. Seasonal variations of POM $\delta^{15}\text{N}$ indicate that N-fixation rates in Farmington Bay may be higher from June through August. The predominance of isotopically light brine shrimp in specific areas of GSL during the summer (Fig. 3) may be due to a change in the phytoplankton community composition attributed to inflow from Farmington Bay.

3.3. Near-surface distribution of nutrients in GSL

During November and early December 2002 the spatial variations in the $\delta^{15}\text{N}$ of brine shrimp relative to inflow sources to the south arm of GSL were assessed. Distinct spatial trends in $\delta^{15}\text{N}$ of the brine shrimp samples were found and appear to be related to temporally consistent currents from major inflow sources to GSL (Fig. 6). Brine shrimp with relatively enriched $\delta^{15}\text{N}$ (+8.62‰ to +9.81‰) were found at inflow sources including the Bear River and Farmington Bay causeway breach and minor input sources along the southern margins of GSL that include Goggin Drain, Lee Creek and Kennecott Utah Copper Corporation (KUCC). The isotopically enriched brine shrimp extend west and SW of the Bear River and Farmington Bay inflow sources to sample sites west and north of Carrington Island. The enriched $\delta^{15}\text{N}$ found in brine shrimp around the inflow sources is consistent with the seasonal isotopic enrichment observed in both POM and brine shrimp during late fall time periods (Figs. 3 and 4). The data indicate that synoptic sampling and $\delta^{15}\text{N}$ analysis of brine shrimp dur-

ing specific time periods may give insight into persistent lake currents as well as seasonal changes in brine shrimp nutrient sources.

Initial lake current monitoring data from GSL appear to support the synoptic isotopic results. Current monitoring results collected during June 14, 2005 indicate a consistent near-surface (0–0.8 m) flow component moving in a westerly direction at site 2267 (Fig. 7), which is located NW of Fremont Island (Fig. 1). It is likely that this near-surface current represents a remnant inflow component from the Bear River. Because of water density differences, the relatively freshwater inflow from Bear River likely forms a thin layer over the more dense water from the main body of GSL. Based on the lake current profile observed during June 14, 2005, it is likely that this less saline layer can extend at least 10 km from the Bear River inflow to the south arm of GSL. The profile of specific conductance during the same time period also supports this conclusion, with a thin, less saline and higher pH water layer occurring between 0 and 0.8 m from the lake surface (Fig. 7). As the specific conductance increases and pH decreases below 0.8 m, the horizontal flow component reverses direction and increases in velocity. Continuous current measurements are not available at this site to evaluate the persistence of this freshwater layer; however, the persistence of ice in this area of GSL typically observed during the winter months supports the persistence of a thin freshwater layer originating as freshwater inflow from the Bear River.

3.4. Distribution and transport of Hg in GSL

Although Hg has been a known environmental pollutant for several decades, its presence in freshwater and marine environments continues to generate concerns related to biological exposure (King et al., 2000). Like many environmental contaminants, Hg bioaccumulates in organisms. The lipophilic nature of CH_3Hg makes it much more toxic to organisms than inorganic forms of Hg. The geographic, geochemical and hydrologic characteristics of GSL make it susceptible to Hg accumulation and toxicity, prompting the need for reconnaissance-level assessments of Hg in water, sediment and biota.

Atmospheric deposition is one of the major sources of Hg to aquatic environments (Krabbenhoft and Rickert, 1995). Geographically, GSL is located less than 600 km east and downwind of large atmospheric sources of Hg associated with Au ore processing facilities in eastern Nevada. From 1998 to 2001, stack emissions of Hg to the atmosphere from Au ore processing facilities in Nevada averaged 5520 kg/a (Jones and Miller, 2005). Nevada was the largest atmospheric Hg emissions source in western USA during 2001 and 2002 and the majority of these Hg emissions were from Au ore processing facilities (Jones and Miller, 2005). Although this study was not designed to identify the source of Hg to GSL, atmospheric Hg sources in the region, such as those emitted from Au mines in northern Nevada, may contribute Hg to GSL. The large surface area of GSL, (south arm = 1870 km² at a lake stage of 1279 m absl) (Baskin, 2005), and lack of an outlet may make GSL more susceptible to retaining local and regional atmospheric deposition of Hg.

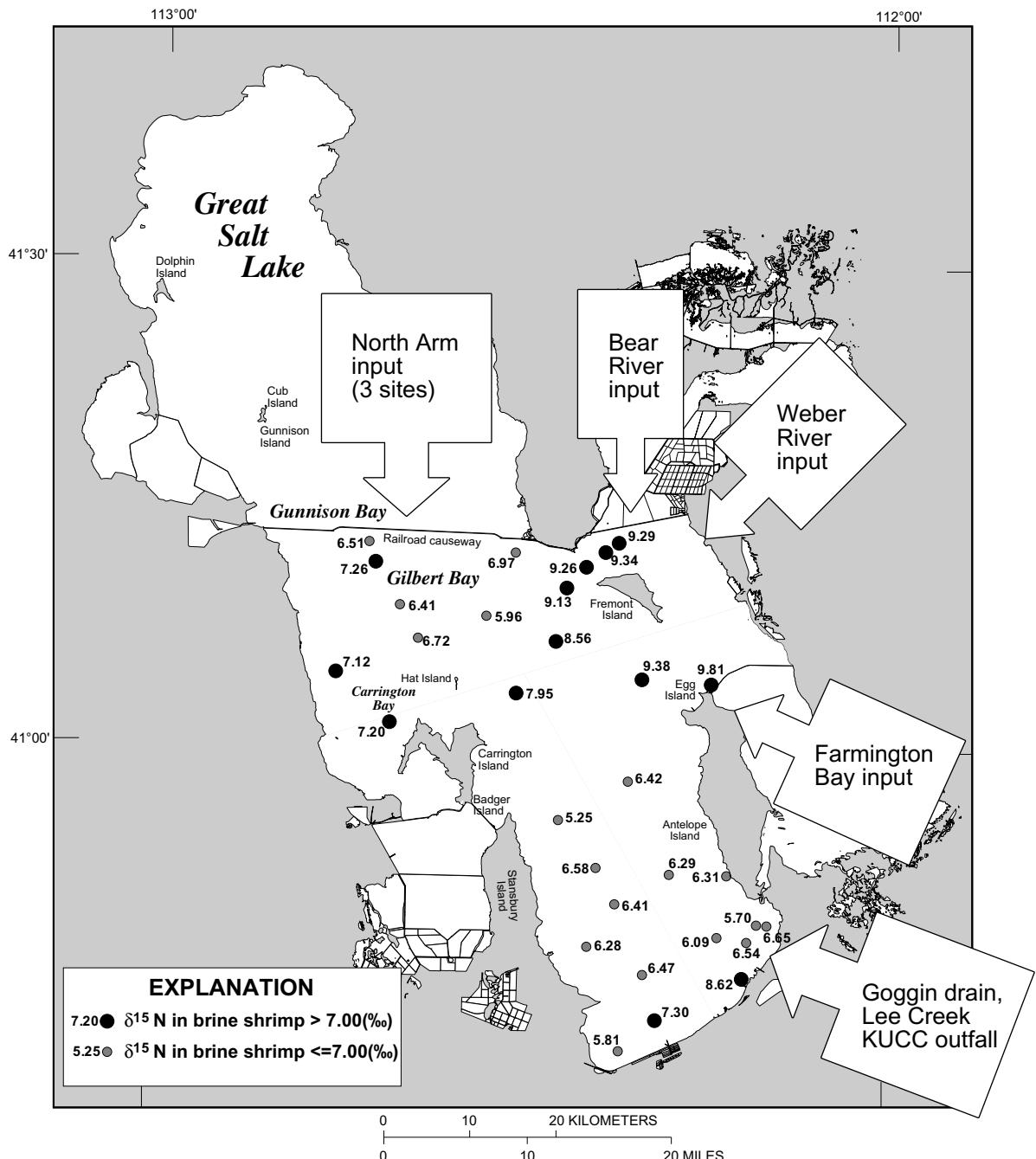


Fig. 6. Variation of $\delta^{15}\text{N}$ in brine shrimp collected from GSL during a synoptic survey in November and December 2002. KUCC is the abbreviation for Kennecott Utah Copper Corporation.

The high concentrations of Cl and Br in GSL may enhance the atmospheric deposition of Hg to the lake surface. Previous studies (Mason and Gill, 2005) have shown that the presence of halogens such as Br and Cl in the marine boundary layer (MBL) can act as oxidizing agents that will transform the relatively inert Hg^0 in the atmosphere to reactive gaseous Hg (RGHg). Once formed, RGHg has high deposition velocities and has been observed to be rapidly

removed from the atmosphere in polar locations relative to Hg^0 (Schroeder et al., 1998). The abundance of Br and Cl in the MBL above GSL may favor the formation of RGHg and enhance Hg deposition rates.

Once inorganic forms of Hg enter GSL, the physical and chemical conditions may be ideal for Hg methylation. Previous work has shown that marine sediment rich in organic matter and dissolved sulfide have rapid CH_3Hg

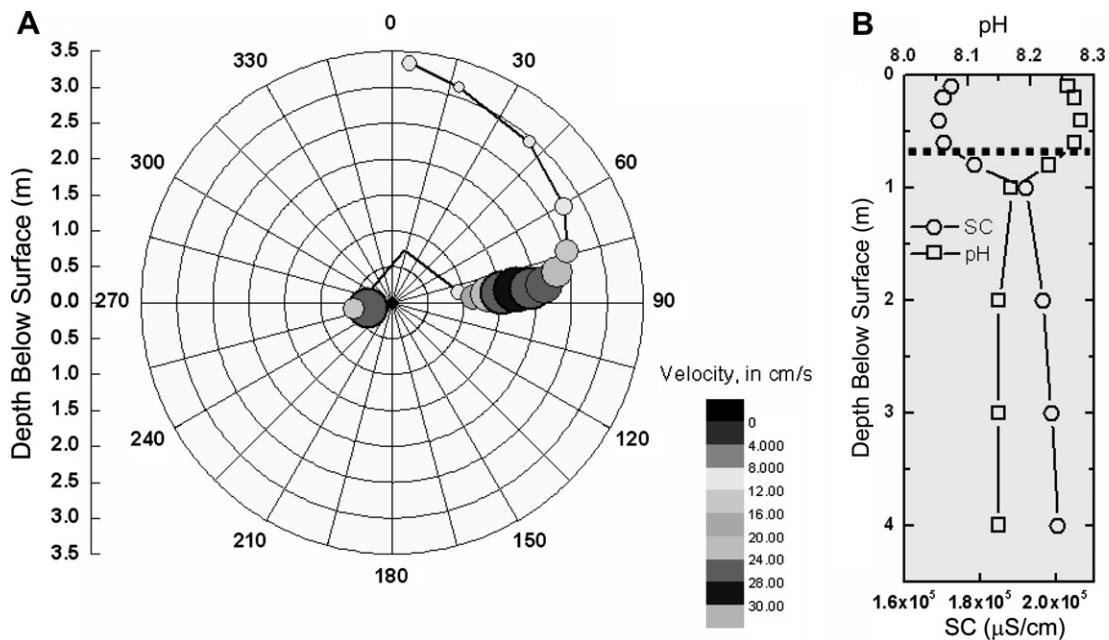
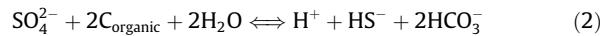


Fig. 7. Current velocity profile and direction with depth (A) and depth profile of specific conductance and pH (B) collected at GSL site 2267 during June 14, 2005. Dashed line in (B) indicates lower limit of less saline water layer.

production rates in conjunction with rapid rates of SO_4^{2-} reduction (King et al., 2000). Low dissolved O_2 saturation in hypersaline systems such as GSL can support high rates of SO_4^{2-} reduction. The SO_4^{2-} reduction rates measured in GSL were higher than 6000 nmol/cm³/day, one of the highest rates reported in a natural environment (Ingvorsen and Brandt, 2002). In laboratory experiments, King et al. (2000) determined that SO_4^{2-} reducing bacteria capable of acetate utilization in their metabolic pathways are the most efficient at methylating Hg. Acetate-utilizing bacteria (*Desulfobacter halotolerans* and *Desulfocella halophila*) capable of high methyl-Hg production have been isolated from sediment in the south arm of GSL (Ingvorsen and Brandt, 2002).

Human-induced modifications to water circulation in GSL may have increased the lake's capacity for SO_4^{2-} reduction and coincident methylation and demethylation of inorganic inputs of Hg. In 1959, completion of a railroad causeway across GSL separated the lake into two distinct hydrologic systems. More than 95% of the freshwater inflow is from the south arm of GSL, causing large differences in salinity between the northern and southern arms (Wold et al., 1997). This salinity contrast has created a density driven flow of highly saline water from the north to south arms through constructed openings in the railroad causeway and the permeable fill material (Loving et al., 2002). Because of the density differences between the water from south and north arms, a dense brine layer, denoted as the DBL, has formed in the south arm of GSL. The DBL is overlain by a less dense layer, denoted as the UBL. Due to the large density differences between the two layers, the DBL is not subject to annual turnover and becomes anoxic (Gwynn, 2002). Monitoring of the DBL at two sites from 2004 to 2005 found dissolved (0.45 µm pore size) sulfide

concentrations ranging from <0.1 to 40 mg/L. The chemical reaction for SO_4^{2-} reduction is



In GSL, this reaction is driven by a virtually infinite supply of SO_4^{2-} from the highly saline water and a continuous supply of dissolved organic C from brine shrimp, associated fecal material, and other organic detritus that are deposited into the DBL. Sulfide monitoring data indicate temporal variations in concentration. The lowest dissolved sulfide concentrations at both monitoring sites were found during late May and early June 2005, coincident with the highest annual lake stage in the south arm of GSL. The sulfide concentration at both monitoring sites shows a steady increase after early June. An explanation for the temporal changes in dissolved sulfide in the DBL is unknown, but could be a function of seasonal changes in recharge rates from the north arm water (introducing dissolved O_2) and changes in the flux rate of organic matter from the biologically active UBL.

Whole water samples were collected from GSL in 2003, 2005 and 2007 and analyzed for total Hg and CH_3Hg . The highest concentrations of total Hg were found in water samples collected from the DBL, ranging from 7 to >100 ng/L (Fig. 8), with a median concentration of 42 ng/L. A significant proportion (31–60%) of the total Hg in water samples from the DBL was comprised of CH_3Hg . Concentrations of CH_3Hg in the DBL ranged from 0.84 to >30 ng/L (Fig. 8), with a median concentration of 24 ng/L. Further confirmation of the elevated Hg in the DBL is provided by whole water samples collected by KUCC in 2005, where total Hg ranged from 66 to 97 ng/L and CH_3Hg ranged from 56 to 81 ng/L (K. Payne, KUCC, pers. comm.,

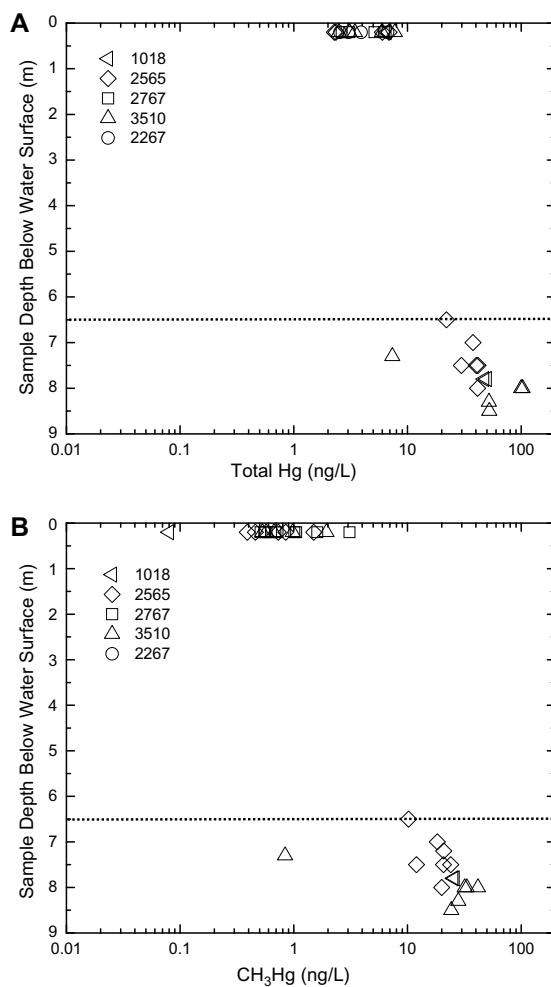


Fig. 8. Concentration of total Hg (A) and CH₃Hg (B) in whole water samples as a function of depth. Samples collected from five sites in the south arm of GSL during 2003, 2005, and 2007. Dashed line indicates approximate boundary between UBL and DBL.

December 2005). The KUCC data indicated a higher proportion of CH₃Hg/total Hg than samples collected and analyzed by USGS, ranging from 69% to 92%. The concentration of CH₃Hg measured in GSL is among the highest measured in surface water by the USGS Mercury Research Laboratory. For comparison, CH₃Hg in whole water samples collected from Maryland reservoirs ranged from 0.007 to 0.493 ng/L (Mason and Sveinsdottir, 2003).

Although the DBL is not subject to annual turnover and can persist for multiple annual cycles (Gwynn, 2002), the high concentrations of CH₃Hg could be potentially transferred to the biologically active UBL through vertical mixing during wind events. Fixed station monitoring of vertical water velocity at site 3510 (Fig. 1) using hydroacoustic equipment indicates periodic events that appear to mix the DBL with the UBL. It is likely that these are internal waves generated by sustained wind events on the lake. Internal waves are formed under stratified conditions and are generally much larger than surface waves, occurring specifically in the thermocline (Goldman and Horne,

1983), which in GSL is at the DBL/UBL interface. Turbulence introduced by internal waves can cause increased mixing across the thermocline and has been found in previous studies of other lake systems to provide a fresh supply of nutrients from the underlying hypolimnion to the thermocline.

Ten vertical bins, each 30 cm in length, were monitored for upward and downward vertical velocity at site 3510 (Fig. 9) with fixed station hydroacoustic equipment. Bin 5 was located at the thermocline and it was expected that this area would be most sensitive to internal waves. Internal waves were observed during selected time periods in September and October, 2006, and are characterized by cyclic upward and downward vertical velocities (Fig. 10). The September 9 internal wave set was preceded by a strong northerly wind event starting on September 8 at 1800 MDT with sustained wind speeds exceeding 32 km/h as measured at the Badger Island meteorological station. The October 1 and 2 internal wave set was preceded by a strong southerly wind event starting about 13 h prior to the propagation of internal waves. Sustained winds exceeding 22 km/h and gusting to 32 km/h at the Badger Island meteorological station preceded internal wave propagation during this event. Internal waves are not observed during calm conditions.

Additional evidence of mixing CH₃Hg enriched water from the DBL with the UBL is provided by sediment traps deployed at sites 3510 and 2565 (Fig. 1). Two pairs of sediment traps were deployed, one pair in the UBL, well above the DBL interface, and the second pair at the interface between the UBL and DBL. Only organic detritus was observed to accumulate in the upper sediment traps, with no mineral detritus being observed. Observable amounts of mineral detritus were deposited in the lower pairs of sediment traps at the DBL interface (Table 1). Deposition rates at site 3510 ranged from 0.0 to 0.1 g/cm²/a (shallow) and 0.0 to 1.1 g/cm²/a (deep). Sediment deposition rates at site 2565 were 0.0 g/cm²/a (shallow) and ranged from 0.0 to 2.0 g/cm²/a (deep). The mass differences between the upper and lower pairs of sediment traps indicate that the mineral detritus observed in the lower traps is from resuspension of bottom material instead of deposition of mineral detritus through the water column.

3.5. Bioaccumulation and biomagnification of Hg

Once in the biologically active zone, the CH₃Hg has a high potential for bioaccumulation and biomagnification (Burgess, 2005). Rates of CH₃Hg uptake are much greater than the corresponding elimination rates, resulting in higher CH₃Hg concentrations as the organism ages. Biomagnification of CH₃Hg has been found to increase between 10⁴ and 10⁶ times from water to phytoplankton (Burgess, 2005). To assess potential bioaccumulation and biomagnification of CH₃Hg in GSL, the total Hg concentration (dw) in both brine shrimp and eared grebe liver samples were determined intermittently from 1994 to 2000 in the south arm of GSL.

The total Hg concentration in 28 brine shrimp samples collected during the spring was less than the analytical reporting limit of 0.2 mg/kg (dw) (Fig. 11). Brine shrimp

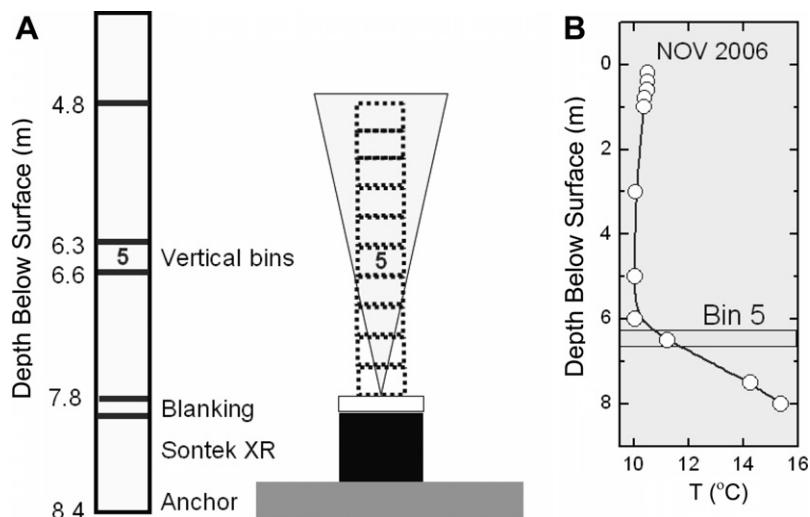


Fig. 9. Schematic diagram showing location of hydroacoustic equipment at site 3510 and depth intervals where discrete measurements of vertical velocity are determined (A) and vertical temperature profile relative to vertical velocity measurement bin 5 located at the thermocline and associated interface between the upper and deep brine layers (B).

samples collected during the summer and fall had a higher Hg concentration (median concentration = 0.34 mg/kg, dw), with 51 of 52 samples exceeding the average Hg concentration in shrimp of 0.16 mg/kg (dw) (USEPA, 1997a; converted from wet-weight data using 75% moisture). The higher Hg concentrations in brine shrimp during summer and fall time periods (Fig. 11) may indicate bioaccumulation of Hg in the aging population. Only brine shrimp cysts survive over the winter, therefore, the spring population is initially composed of nauplii and juveniles (Wurtsbaugh and Gliwicz, 2001). During the summer time period, the proportion of adults in the overall brine shrimp population begins to increase relative to the numbers of nauplii and juveniles. In the late summer and early fall, the nauplii and juveniles disappear and the adult brine shrimp dominate the population until the winter die off. The higher Hg concentrations found in the pooled brine shrimp samples collected during the summer and fall are likely the result of bioaccumulation of CH₃Hg in the aging brine shrimp population.

During the time when the aging brine shrimp population exhibit increasing Hg concentrations, a large population of eared grebes (for example, 1.5 million in 1997) from throughout North America use GSL during the molt migration beginning in August and continuing through December and January (Aldrich and Paul, 2002). The migration and molting habits of eared grebes make them an ideal population for the reconnaissance evaluation of Hg bioaccumulation. A small population of eared grebes also breeds and nests in the GSL system; consequently, there is an eared grebe population in all seasons except mid-winter. The seasonal changes in Hg concentration in eared grebe livers indicate bioaccumulation during the fall molting period when the grebes feed exclusively on brine shrimp. The median Hg concentration in eared grebe livers collected from 1997 to 2000 increases from 6.4 mg/kg (dw) in samples collected during the September early molt per-

iod, to more than 17 mg/kg (dw) in samples collected during December near the end of the molting period (Fig. 12). This trend suggests bioaccumulation of Hg; however, it may be complicated by changes in the liver size of eared grebes during their molting period. Additional data are currently (2006–2007) being collected by the USFWS and USGS to address this issue.

In response to elevated CH₃Hg levels in water samples from GSL, the State of Utah collected and analyzed breast tissue for total Hg from seven duck species that utilized GSL and surrounding wetlands in 2004 and 2005 (Utah Department of Health, 2005). These reconnaissance-phase analyses found that a number of the breast muscle samples exceeded the USEPA screening level of 0.3 mg/kg Hg (wet weight) the concentration at which limited human consumption of bird breast muscle is recommended (USEPA, 2000). Breast muscle tissue from Northern Shovelers and Common Goldeneye ducks consistently exceeded this screening level. Mercury concentration in one of the Northern Shovelers specimens exceeded 10 mg/kg. Median Hg concentrations in the other duck species were below the USEPA screening level; however, Hg levels in some of the Mallard specimens also exceeded the USEPA screening level. As a result of the reconnaissance-phase Hg assessment of the duck population in GSL, a health advisory was issued by the Utah Department of Health in September 2005 warning against unlimited human consumption of Northern Shoveler and Common Goldeneye ducks harvested from GSL. Additional breast muscle data from ducks utilizing GSL are currently (2006–2007) being collected by the State of Utah to further assess the extent of the potential Hg contamination.

4. Summary

Despite the ecological and economic importance of GSL, little is known about nutrient and Hg cycling within the

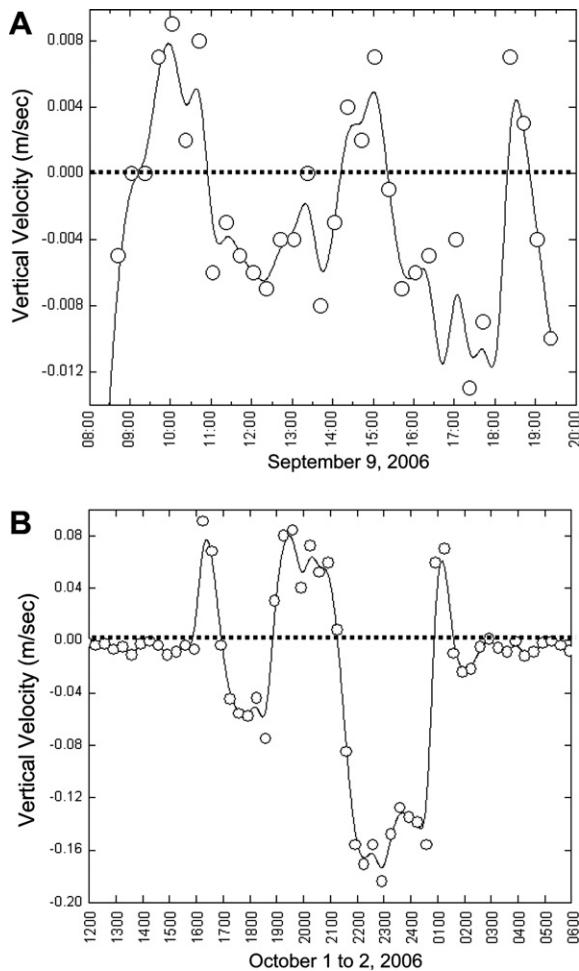


Fig. 10. Upward (positive) and downward (negative) vertical velocity measured at the interface between the DBL and UBL at site 3510 during two different time periods: September 9, 2006 (A) and October 1–2, 2006 (B). Dashed line indicates zero vertical velocity. The trend line was constructed using a spline polynomial function.

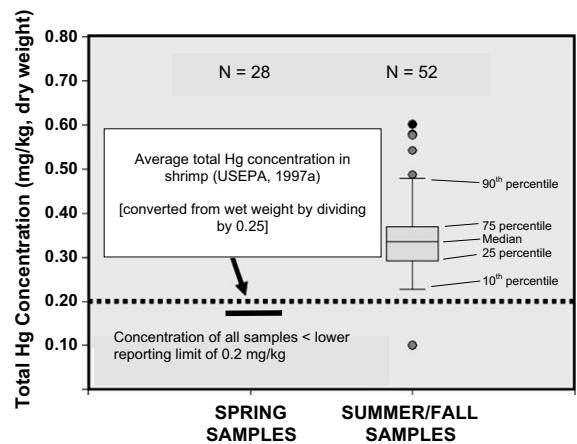


Fig. 11. Box plots showing the distribution of total Hg in brine shrimp collected from GSL during 1994–2000.

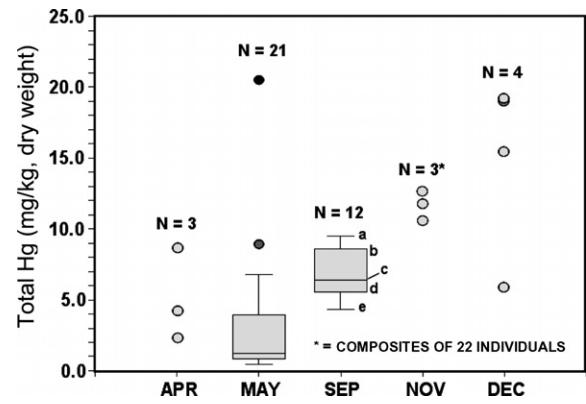


Fig. 12. Box and scatter plots showing the distribution of total Hg in GSL eared grebe livers collected from 1997 to 2000: (a) upper adjacent value up to 1.5 times the interquartile range (IQR); (b) 75th percentile; (c) median; (d) 25th percentile; (e) lower adjacent value up to 1.5 times the IQR. When $n \leq 4$, a scatter plot was used to represent the data distribution.

Table 1

Summary of mean sediment mass captured by paired traps at sites 3510 and 2565 during 2006, GSL

Site	Date of sediment collection	Deployment period (days)	Mean sediment mass (g)	Mean sediment deposition rate ($\text{g}/\text{cm}^2/\text{a}$)
3510-Shallow	7/27/06	30	0.0	0.0
3510-Deep	7/27/06	30	3.6	1.1
3510-Shallow	9/12/06	47	0.1	0.0
3510-Deep	9/12/06	47	0.1	0.0
3510-Shallow	11/03/06	52	0.4	0.1
3510-Deep	11/03/06	52	0.8	0.2
3510-Shallow	12/07/06	34	0.0	0.0
3510-Deep	12/07/06	34	0.0	0.0
2565-Shallow	5/26/06	64	0.0	0.0
2565-Deep	5/26/06	64	14.3	2.0
2565-Shallow	6/19/06	24	0.0	0.0
2565-Deep	6/19/06	24	0.9	0.3
2565-Shallow	7/28/06	63	0.0	0.0
2565-Deep	7/28/06	63	0.0	0.0
2565-Shallow	9/11/06	45	0.2	0.0
2565-Deep	9/11/06	45	0.6	0.1
2565-Shallow	11/01/06	51	0.0	0.0
2565-Deep	11/01/06	51	1.3	0.2

lake. Both nutrients and Hg have the potential to impact the ecological balance of GSL by a variety of biogeochemical processes. A 6‰ decrease in $\delta^{15}\text{N}$ observed in brine shrimp samples collected from GSL during summer time periods is likely due to the consumption of cyanobacteria produced in freshwater bays that mix with the lake. Cyanobacteria fix atmospheric N and have a tightly constrained isotopic composition near 0‰. Outflow from Farmington Bay indicates decreasing trends in $\delta^{15}\text{N}$ in POM during the mid-summer time period, reflective of increasing proportions of cyanobacteria in POM exported to GSL on a seasonal basis. The C:N molar ratio of POM in outflow from Farmington Bay decreases during the summer time period to values similar to the Redfield ratio (6.6 unitless), supportive of the increased activity of N fixation indicated by the $\delta^{15}\text{N}$ data. Although N fixation is only taking place in the relatively freshwater inflows to GSL, data indicate these same fresher water inflows influence large areas of the lake. Current, specific conductance, and pH profiling of the water column in GSL indicates the presence of a transient, near-surface, fresher water layer extending at least 10 km from freshwater inflow sources to GSL.

Completion of a railroad causeway in 1959, that separated GSL into two distinct hydrologic and geochemical systems, has created a persistent and widespread anoxic layer in the southern part of GSL. The DBL has been found to contain elevated CH_3Hg concentrations exceeding 30 ng/L. Hydroacoustic and sediment-trap evidence indicate that turbulence introduced by internal waves generated during sustained wind events can temporarily mix the CH_3Hg -rich DBL with the more biologically active UBL. Chemical analyses of Hg in brine shrimp, eared grebes and selected duck species utilizing GSL have indicated bioaccumulation and biomagnification of Hg. In September 2005, a health advisory was issued by the Utah Department of Health warning against unlimited human consumption of Northern Shoveler and Common Goldeneye ducks harvested from GSL.

Acknowledgments

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