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Arsenic speciation in Mono Lake, California: Response to seasonal stratification and anoxia

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Abstract—Mono Lake is a closed-basin, alkaline, hypersaline lake located at the western edge of the Great Basin in eastern California. We studied the distribution of arsenic (As) species in the water column of Mono Lake between February and November, 2002. This period captured the seasonal progression from winter mixing, through summer thermal stratification, to autumn overturn. Arsenic speciation was determined by ion chromatography-inductively coupled-plasma-mass spectrometry of samples preserved in the field by flash-freezing in liquid nitrogen. We found that arsenic speciation was dominated (>90%) by arsenate when oxygen was detectable. Once levels fell below 6 μmol/L O_2, arsenic speciation shifted to dominance by reduced species. Arsenate and arsenite co-occurred in a transition zone immediately below the base of the oxycline and low but significant concentrations of arsenate were occasionally detected in sulfidic hypolimnion samples. Thio-arsenic species were the dominant form of As found in sulfidic waters. Maxima of thio-arsenic species with stoichiometries consistent with mono-, di- and trithio-arsenic occurred in succession as sulfide concentration increased. A compound with a stoichiometry consistent with trithio-arsenic was the dominant As species (~50% of total As) in high sulfide (2 mmol/L) bottom water. Lower concentrations of total As in bottom water relative to surface water suggest precipitation of As/S mineral phases in response to sulfide accumulation during prolonged anoxia.

1. INTRODUCTION

Mono Lake is a closed-basin, alkaline (pH 9.8), hypersaline (~85 g/L) lake located at the western edge of the Great Basin in eastern California. Mono Lake is set in a region of active volcanism (Lajoie, 1968). Hot springs and geothermal activity are common in the watershed and the lake receives water from hydrothermal sources, resulting in naturally high concentrations of elements like arsenic. Previous studies (Maest et al., 1992; Oremland et al., 2000) have shown spatial and temporal variation in the speciation of arsenic and iron in Mono Lake. Oremland et al. (2004) have shown that arsenate serves as an important alternate electron acceptor for microbial respiration in the lake. The arsenite released by this process can be oxidized by other bacteria, resulting in a biogeochemical cycle similar to that of other metals and metalloids (Oremland et al. 2004). Arsenic is also incorporated into the Mono Lake foodweb. The only macrozooplankter in Mono Lake, the brine shrimp *Artemia monica,* contains ~15 μg/g dry weight total As, much of it in the form of various organic arsenicals (W. Cullen, personal communication).

Like many lakes, Mono Lake is subject to seasonal anoxia resulting from thermal stratification (Jellison and Melack, 1988; Melack and Jellison, 1998). Saline lakes are prone to longer periods of anoxia resulting from salinity stratification driven by interannual variation in local hydrology. This stratification prevents complete overturn and ventilation of the water column during winter (meromixis), allowing reduced species such as sulfide, ammonia and methane to accumulate to high concentrations in bottom water (Jellison and Melack, 1993a; Miller et al., 1993). Mono Lake recently experienced a period of meromixis lasting from 1995 to 2003 that resulted in the accumulation of sulfide, ammonia and other reduced compounds, including arsenic compounds, in the hypolimnion. This event provided an opportunity to study the interactions between arsenic and other redox species in the lake and especially to investigate the interactions between sulfide and reduced arsenic in natural waters. While previous studies have shown that arsenic is an important redox species in Mono Lake, their spatial and temporal resolution was limited and they did not address the possible formation of dissolved As-S complexes that have been shown to be important in alkaline, sulfidic model solutions (Wilkin et al., 2003).

Below we present an assessment of ion chromatography with anion self-regenerating suppression-inductively coupled plasma mass spectrometry (IC-ICPMS) as applied to the analysis of As species in Mono Lake water. We then present profiles of As species and of other relevant environmental variables, including Most Probable Number (MPN) estimates of the abundance of dissimilatory arsenate reducing bacteria, taken over a seasonal cycle at a station in the deepest portion of Mono Lake. We report on the distribution of thio-arsenic species in the lake and address the question of chemical equilibrium between the reactants. Finally, inventories of various constituents are calculated and compared to assess coupling between arsenic geochemistry and other biogeochemical processes in the lake.

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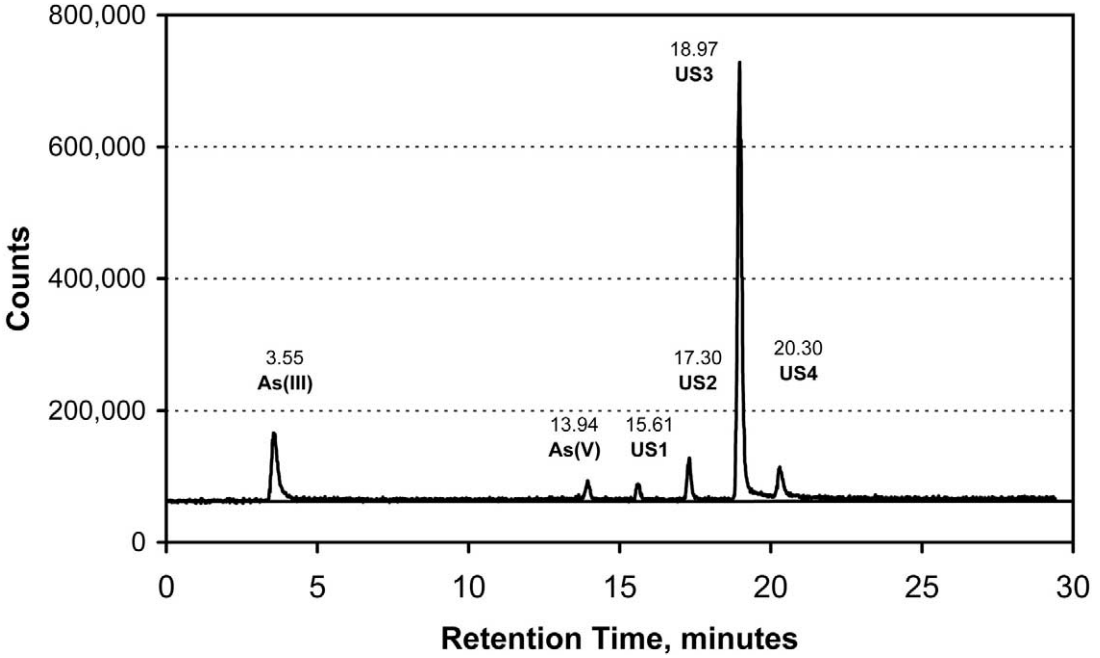

Fig. 1. Typical chromatogram of arsenic species in Mono Lake water showing peaks for arsenate (As[V]), arsenite (As[III]) and four unidentified thio-arsenic compounds (US1, US2, US3 and US4). The sample was from 30 m and was collected on 12 September 2002. Arsenic and sulfur in the separated species are determined on-line by measuring the arsenic signal at $m/z = 75$ ($^{75}As^{+}$) and sulfur signal at $m/z = 48$ (SO^{+}) as described in Wilkin et al. (2003).

2. MATERIALS AND METHODS

2.1. Sample Collection

The water samples used in this study were collected from the central basin of Mono Lake at Station 6 (37°57.822' N, 119°01.305' W; Station S30 in reports published before 2000) on February 12, March 18, April 23, May 13, June 19 (MPN only), August 6, September 12 and November 17 of 2002. Bathymetric charts of the lake are presented in a number of publications (cf. Jellison and Melack, 1993b) and at: http://geopubs.wr.usgs.gov/map-mf/mf2393/. Vertical profiles of temperature, pressure, conductivity, photosynthetically active radiation (PAR, 400–700 nm, Licor 2π sensor), turbidity (WetLabs C-Star transmissometer, 10-cm path length) and in vivo fluorescence (WetLabs WetStar fluorometer) were obtained with a SeaBird SeaCat profiler. Measurements were taken at ~0.1-m intervals, outliers were discarded, then the data were then block averaged over 0.5-m intervals. Oxygen profiles were obtained using a polarographic oxygen sensor (YSI) equipped with a Clark-type electrode. Water samples for chemical analyses were collected at discrete depths using a 5-L Niskin sampler equipped with a Teflon-coated spring. The interval between depths sampled varied, decreasing to 0.5 m in regions of sharp geochemical gradients.

Sulfide samples were drained from the Niskin sampler into 35-mL volume Quoropak glass bottles that contained a NaOH pellet (~0.5 g). The bottles were flushed with sample water (at least 2 volumes) and capped without introducing bubbles. Samples were stored on ice for <6 hr before analysis using an electrode that measures total free sulfide (ΣH_2S, Thermo-Orion Method #94-16). Subsamples (4.5 mL) were taken from each bottle using a gas-tight syringe and injected into 20 mL vials containing 5.0 mL of sulfide antioxidant buffer (Orion 941609). Standards ranging from 0.2 to 2000 μmol/L were prepared using 0.2 μm filtered, deoxygenated Mono Lake surface water. The electrode was immersed in the sample or standard, allowed to stabilize, and the millivolt signal was recorded. Sulfide concentrations in samples were calculated from regressions of data for standards.

Samples (~100 mL) for arsenic speciation were drained from the Niskin bottle into acid-washed, 250-mL, screw-cap, high-density polyethylene bottles, minimizing exposure to the atmosphere. February samples were immediately frozen in a dry ice/methanol bath and stored on dry ice until analysis. Since this procedure resulted in the loss of some of the reduced arsenic from bottom water samples (see below), subsequent samples were flash-frozen in liquid nitrogen as follows. As soon as a sample was drawn, the sample bottle was partially submerged in liquid nitrogen and swirled until the sample was frozen. Once the sample was frozen, the bottle was tipped to admit ~25 mL of liquid nitrogen, then capped. Volatilization of this liquid nitrogen purged atmospheric oxygen from the bottle; a 6-mm-diameter hole in the center of the screw-on cap vented the gas. Once most of the N_2 had vented, the bottles were sealed inside two Ziplock plastic freezer bags and placed in an insulated container with dry ice. The samples were maintained on dry ice until analysis, within a week of collection.

2.2. Arsenic Speciation

Arsenic speciation was determined using ion chromatography-anion self-regenerating suppression-inductively coupled-plasma-mass spectrometry (IC-ASRS-ICP-MS; Wilkin et al., 2003). The anionic arsenic species are separated on a high-capacity anion-exchange column under alkaline conditions using dilute NaOH (pH gradient of 12.3 to 13.0) as the eluant. The eluant was not deoxygenated; however, peaks were not smeared, (as would be expected if the As speciation was changing on the column), and all species are baseline-separated (see Fig. 1). The eluant is neutralized electrochemically after separation of arsenic species and before introduction into the nebulization system of the ICP-MS. Arsenic in the separated species is determined on-line by measuring the signal at $m/z = 75$ ($^{75}As^{+}$, corrected for potential spectral interferences from $^{35}Cl^{40}Ar^{+}$ by measuring $^{37}Cl^{40}Ar^{+}$ and $^{82}Se^{+}$ to account for the contribution of selenium to the signal at $m/z = 77$). As/S ratios for the peaks were determined by measuring sulfur at $m/z = 48$ (SO^{+}) as described in Table 2 of Wilkin et al. (2003). The samples were thawed at room temperature (air atmosphere), filtered through 0.22 μm pore size syringe filters and diluted with deionized water (oxic) as necessary. Typical detection limits of this instrument are 0.1 nmol/L (10 ng/L) arsenic per species; after sample dilution, method limits are on the order of 0.1 μmol/L. Quality assurance (QA) and quality control (QC) tests were run for each profile using samples taken