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Distribution of total and methyl mercury in sediments along Steamboat Creek (Nevada, USA)

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Abstract

In the late 1800s, mills in the Washoe Lake area, Nevada, used elemental mercury to remove gold and silver from the ores of the Comstock deposit. Since that time, mercury contaminated waste has been distributed from Washoe Lake, down Steamboat Creek, and to the Truckee River. The creek has high mercury concentrations in both water and sediments, and continues to be a constant source of mercury to the Truckee River. The objective of this study was to determine concentrations of total and methyl mercury (MeHg) in surface sediments and characterize their spatial distribution in the Steamboat Creek watershed. Total mercury concentrations measured in channel and bank sediments did not decrease downstream, indicating that mercury contamination has been distributed along the creek's length. Total mercury concentrations in sediments (0.01–21.43 μg/g) were one to two orders of magnitude higher than those in pristine systems. At 14 out of 17 sites, MeHg concentrations in streambank sediments were higher than the concentrations in the channel, suggesting that low banks with wet sediments might be important sites of mercury methylation in this system. Both pond/wetland and channel sites exhibited high potential for mercury methylation (6.4–30.0 ng g^{-1} day^{-1}). Potential methylation rates were positively correlated with sulfate reduction rates, and decreased as a function of reduced sulfur and MeHg concentration in the sediments. Potential demethylation rate appeared not to be influenced by MeHg concentration, sulfur chemistry, DOC, sediment grain size or other parameters, and showed little variation across the sites (3.7–7.4 ng g^{-1} day^{-1}).

Keywords: Methyl mercury; Total mercury; Sediments; Methylation; Demethylation; Silver and gold mining; Sulfate reduction rate

1. Introduction

Steamboat Creek (SBC) terminates in the Truckee River, the water supply for landlocked Pyramid Lake. SBC has one to two orders of magnitude higher mercury concentrations in waters and sediments than those found in pristine environments, ranging from 24 to 419 ng/l in unfiltered water samples, and 0.3–10.2 μg/g in sediments (Lyons et al., 1998; Blum et al., 2001). Mercury in the creek is primarily derived from ore processing

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wastes (Smith, 1961; Thomas, 2003). In the late 1800s, mercury was used to amalgamate and extract gold and silver from the Comstock ores in the creek's headwaters, and it has been estimated that as much as 40 tons of mercury were released by this activity (Blum et al., 2001). Mercury has been distributed downstream by the creek's waters and during flooding events, and the creek is a constant source of mercury to the Truckee River (Thomas, 2003). In addition, water entering the creek that traverses the Steamboat Springs geothermal area is a source of natural mercury to the creek (Gustin et al., 1996; Coolbaugh et al., 2002; Thomas, 2003).

Much of the mercury found in aquatic systems is accumulated in sediments (Gilmour and Henry, 1991), and periodic wetting and drying of sediments has been shown to enhance MeHg production (Roulet et al., 2001). With plans for streambank restoration in Steamboat Creek and flood control measures along the Truckee River (US Army Corps of Engineers, 2001), information is needed on the distribution of mercury in Steamboat Creek, and the types of sedimentary environments that are favorable to MeHg production. In addition, current plans to construct wetlands at the confluence of Steamboat Creek and the Truckee River (US Army Corps of Engineers, 2001) may result in increased Hg methylation (Stamenkovic, 2003), as sites with elevated Hg concentrations may be flooded, and wetlands are known to be sources of MeHg (Zillioux et al., 1993; St. Louis et al., 1994; Morel et al., 1998).

The objective of this study was to determine: a) the concentrations of total mercury (THg) and MeHg in surface sediments and characterize their spatial distribution in the Steamboat Creek watershed, and b) the potential for benthic MeHg production and degradation at a subset of sites representative of a range of conditions along the SBC channel.

2. Study area

Steamboat Creek flows northeast 28 km from Washoe Lake to its confluence with the Truckee River (Fig. 1). The creek channel is within fluvial and glacial deposits, dominated by gravel-sized particles in the upper two thirds of the reach, and silt and clay sands in the downstream reach (Codega and WESTEC Inc., 1998). A number of ditches along SBC regulate the removal and transport of water for agricultural purposes. Water is diverted for irrigation and then returned after use, while several ditches deliver water from the Truckee River to the SBC channel. In addition, creek water has been impounded at several locations, decreasing the water velocity and significantly affecting water quality and sediment transport (Codega and WESTEC Inc., 1998; Thomas, 2003).

3. Methods

Surface sediment samples (0–5 cm) were collected from 13 sites in the Steamboat Creek watershed, as well as from two locations in the Truckee River upstream and three sites downstream of the confluence (Fig. 1). Samples were collected in November 2001 and August 2002 from the stream channel (below the water line), and streambank (wet sediments above the water line). Each sample consisted of three homogenized sub-samples (500 g) that were taken within a 5 m radius. All samples were stored in the refrigerator (ca. 5 °C) until analysis. Sediment THg in these samples was analyzed within 28 days using atomic absorbance spectrometry after digestion in aqua regia (Lechler et al., 1997) by Nevada Bureau of Mines and Geology. Replicate samples ($n=5$) yielded an average coefficient of variation (CV) of $14\pm14\%$.

Methyl mercury was measured in the sediment samples collected in August 2002. Subsamples for MeHg analysis were taken from the homogenized sample, placed in 10 ml glass vials and analyzed immediately (within 10 to 14 days of the sample collection; Horvat et al. (1993) demonstrated that MeHg was stable in fresh sediment stored in a refrigerator for up to 45 days). Sediment MeHg was determined by acidic bromide/methylene chloride extraction, aqueous-phase ethylation, isothermal GC separation and CVAFS detection (Bloom, 1989; Liang et al., 1994). Reagent blanks ($n=8$) were below the analytical detection limit (0.025 ng/l). Triplicate analysis of each sample yielded an average CV of $30\pm21\%$. Spike recoveries were $136\pm57\%$ ($n=5$). Dogfish muscle

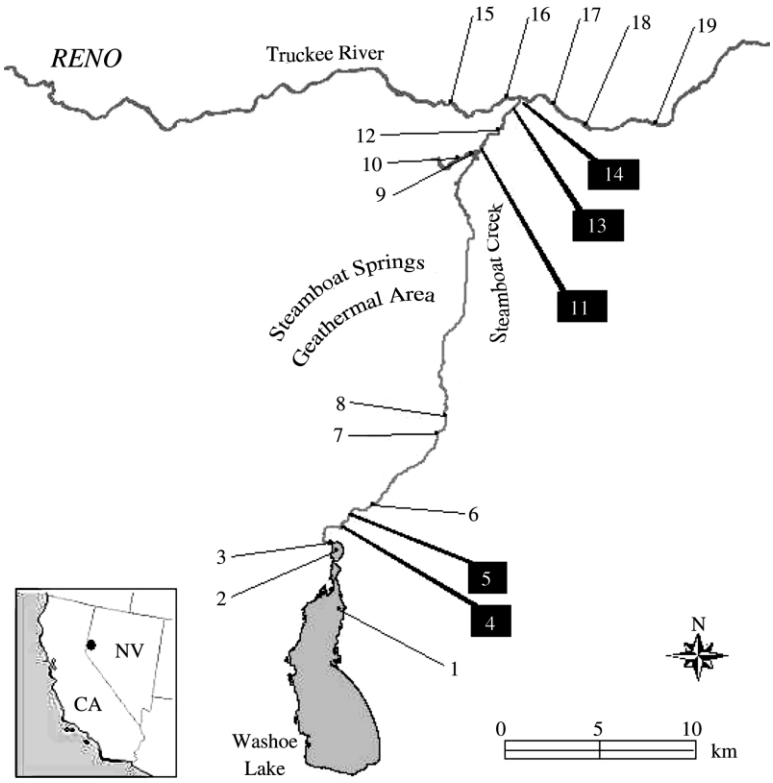

Fig. 1. Map of sampling locations for surface sediments along Steamboat Creek. Black boxes show sites that were also sampled in February 2002 for sediment cores. Numbers are explained in Table 1.

standard (DORM-2) was used as a quality control sample (cf. Marvin-DiPasquale et al., 2003), and measured concentrations were $120 \pm 19\%$ ($n = 13$) of the average certified value.

In early February 2002, surface sediment cores (0–5 cm) were collected to assess potential mercury methylation, MeHg degradation, and sulfate reduction rates in creek channel sediments. Two cores per site were collected using acid-cleaned polycarbonate core rings, and sediment was transferred to acid washed mason jars, double bagged in Ziploc® bags, stored on ice, and transported within 24 h to the US Geological Survey (USGS) facility in Menlo Park, CA. Sampling locations included: Frog Pond inlet (site 4; shallow, unvegetated pond with some groundwater input), Pagni Lane (site 5; deep channel allowing more water to pond up, some groundwater input), Rosewood Lakes outlet (site 11; slow water, wetland vegetation on the shores), Clean Water Way (site 13; significant agricultural runoff), and a small-scale constructed wetland at the Truckee Meadows Water Reclamation Facility (TMWRF, site 14; fed by SBC water and with SBC sediments) (Fig. 1).

Initial sediment processing for microbial rate assays and sediment geochemical characterization were conducted in an anaerobic (N_2 flushed) glove bag. Sediment samples were manually homogenized in a clean Ziploc® bag; subsamples were taken from this composite sample, weighed into the appropriate containers, and pore-water was collected by centrifugation. Radio labeled microbial assay incubations for MeHg production (amendment of 259 ng $^{203}HgCl_2$/g wet sediment) (Guimaraes et al., 1995), MeHg degradation (^{14}C-MeHg amendment 8.6 ng/g wet sediment) (Marvin-DiPasquale and Oremland, 1998) and microbial sulfate reduction (Jørgensen, 1978) were

Table 1
Total mercury in sediments [μg/g] collected along Steamboat Creek, Truckee River and tributaries in November 2001, and August 2002 (methyl mercury in parentheses, ng/g)

Site (ID number and name)	Stream channel [μg/g]		Streambank [μg/g]	
	Nov 2001	Aug 2002	Nov 2001	Aug 2002
(1) Washoe Lake	0.03	0.04 (0.03)	0.01	0.04 (0.54)
(2) Little Washoe Lake	8.53	0.13 (0.03)	1.31	0.05 (0.05)
(3) Washoe Lake Outflow	0.93	1.06 (0.59)	0.66	0.36 (0.68)
(4) Frog Pond	4.92	3.03 (0.24)	2.79	5.30 (0.43)
(5) Pagni Lane	0.85	1.06 (0.65)	3.86	21.43 (1.28)
(6) Laramie Lane	2.13	1.49 (0.27)	3.24	3.29 (0.50)
(7) Rhodes Road	0.79	2.67 (1.57)	2.37	3.39 (0.24)
(8) Towne Drive	1.22	1.12 (0.48)	1.24	1.34 (0.78)
(9) SBC at Mira Loma		1.31 (0.68)		16.03 (1.30)
(10) Ditch at Mira Loma	2.79	1.20 (0.74)	3.09	2.69 (1.63)
(11) Rosewood Lakes Outflow	0.21	2.37 (0.14)	0.06	0.74 (0.24)
(12) Airport Mitigation Site		0.16 (0.89)		0.09 (0.20)
(13) Clean Water Way	0.34	0.86 (2.98)	0.33	1.71 (0.96)
Truckee River upstream the confluence with SBC				
(15) Mayberry park	0.01	0.02 (0.14)	0.03	0.03 (1.54)
(16) Rock park		0.01 (0.12)		(0.18)
Truckee River downstream the confluence with SBC				
(17) Vista	0.02	0.02 (0.16)		
(18) Lockwood	0.19	0.05 (0.21)	0.19	0.19 (12.91)
(19) Painted rock	0.01	0.03 (0.22)	0.05	0.09 (0.96)

conducted in parallel and at 20 °C. Using this combined radiotracer approach provides a relative measure as to whether or not a particular location can be site of significant net MeHg production (Marvin-DiPasquale et al., 2003). Methylation rates in this study were calculated based only on the added ^{203}Hg and not normalized to ambient THg concentrations. Because amended and ambient concentrations were similar (0.6–5.5 times the ^{203}Hg amended amount), the calculated rates are thought to be representative of the in situ values.

Ancillary parameters measured included: sediment pH via electrode, sediment organic content as loss on ignition (LOI), bulk sediment acid-volatile and total reduced sulfur (Ulrich et al., 1997), porewater chloride and sulfate (Dionex, 1992), sulfide via electrode (Gilmour et al., 1998), dissolved organic carbon (DOC, Qian and Mopper, 1996), Fe^{2+} in porewater and solid phase Fe^{2+} and amorphous (poorly crystalline) Fe^{3+} (Lovley and Phillips, 1987), and crystalline Fe^{3+} oxides (Roden and Zachara, 1996).

Subsamples of the material sent to the USGS facility were analyzed within 7 days for MeHg and THg, as described above, at the Environmental Geochemistry Lab, University of Nevada, Reno. Total mercury for these sediments was quantified using a solid state Milestone™ Mercury analyzer (EPA method 7473). Calibration of the instrument was verified prior to and during analysis using National Institute of Standards and Technology certified reference materials (CRM): San Joaquin soil (# 2709) and Apple leaves (# 1515), and the variation about the mean concentration of the CRM was ±5%. All sediment samples were analyzed in triplicate, and average CV was 7.5±6.5%.

The strength of relationships between THg and MeHg concentrations in channel and bank sediments, and between methylation/demethylation rates and ancillary parameters were evaluated using Pearson correlation (Minitab® for Winows). Paired *t*-test was used to compare channel and bank THg concentrations on different sampling dates, and

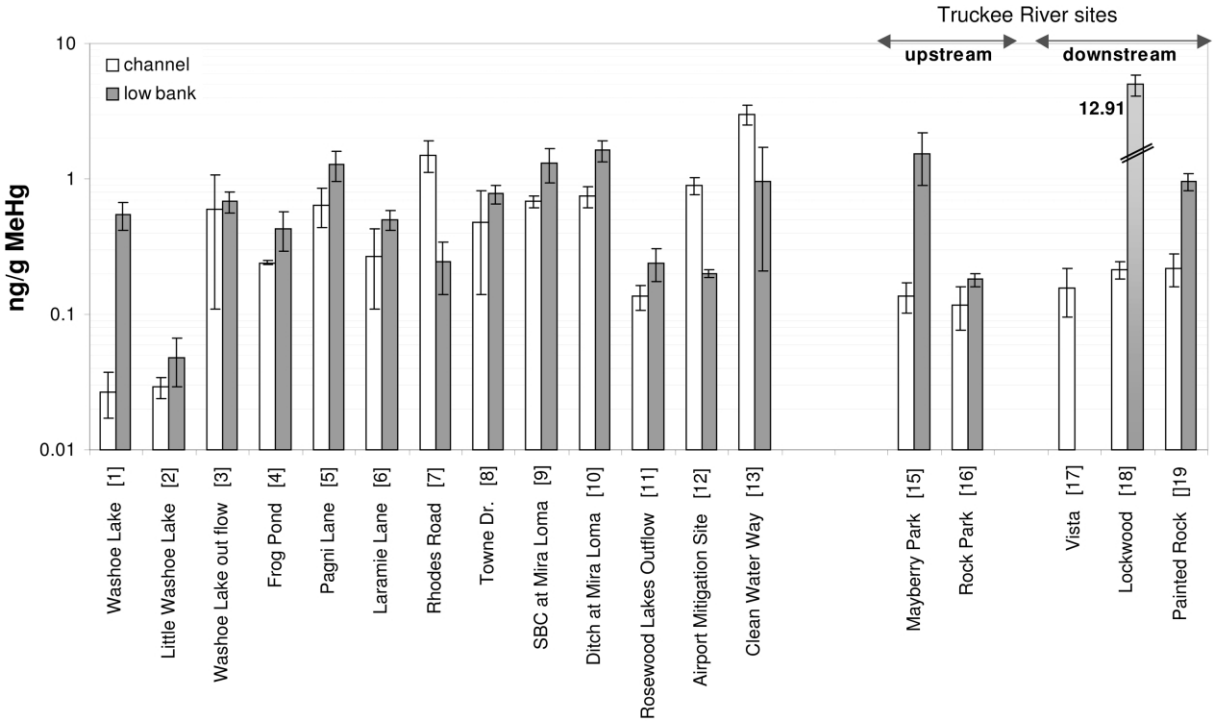

Fig. 2. Methyl mercury concentration in sediments [ng/g] collected in August 2002 along Steamboat Creek, and the Truckee River. Low bank sediments had higher MeHg concentrations than channel sediments at 13 out of 17 sites. The S.D. of triplicate measurements shown with error bars.

channel and bank MeHg concentrations measured in August 2002 samples (Minitab® for Windows).

4. Results

No temporal difference was detected for THg concentrations in channel ($P=0.42$), or in bank sediments ($P=0.25$) collected in November 2001 and August 2002 (Table 1). Overall, no spatial difference was observed between channel and bank sediments along SBC ($P=0.18$). Although no statistical difference was observed between channel and streambank sediment MeHg concentrations for the complete data set ($P=0.28$), the MeHg concentration was higher in streambank sediments than in channel sediments at 14 out of 17 sites (Table 1 and Fig. 2). Only at three sites (Rhodes Road, Airport Mitigation Site, Clean Water Way) were mean channel MeHg concentrations higher than the streambank sediment concentrations (Fig. 2). Percent THg as MeHg in channel sediments along SBC ranged from 0.01 to 0.07%, except for higher values at Airport Mitigation Site (0.55%) and Clean Water Way (0.35%). Similarly, percent MeHg in low bank sediments was low, ranging from 0.01 to 0.03% at all sites except Washoe Lake (1.24%). No correlation was found between MeHg and THg concentrations in channel sediments. However, MeHg and THg concentrations in bank sediments collected in August 2002 were correlated ($r=0.58$, $P=0.03$, $n=13$).

Samples collected from the Truckee River channel and bank showed a slight increase in THg and MeHg concentrations downstream of the confluence with SBC (Table 1). Low bank sediment collected at Lockwood, downstream of the confluence had the highest MeHg concentration of all the samples collected in August 2002, from channel or bank.

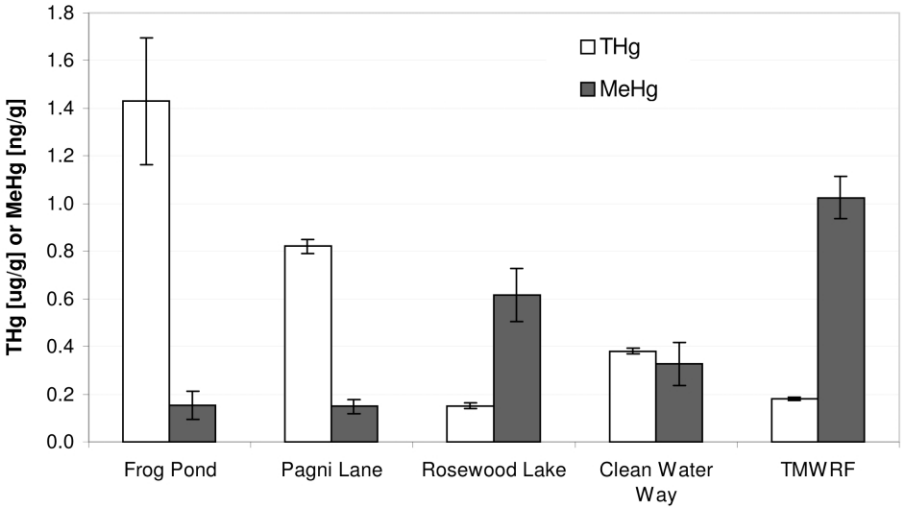

Fig. 3. Total mercury (THg) and methyl mercury (MeHg) in sediment cores collected in February 2002. There was a general decrease in THg concentrations from upstream to downstream, while MeHg showed the opposite trend. Error bars represent S.D. of triplicate samples.

A general decrease in THg concentrations in sediment cores collected in February 2002 was noted from upstream to downstream, while MeHg showed the opposite trend (Fig. 3). All sediment cores had pH close to neutral, while sediment organic content ranged from 0.87 to 5.63% LOI, and was lowest in coarse grained samples and higher in finer grain samples (Table 2).

Sediment potential MeHg production ranged from <0.08 to 30.0 ng g^{-1} dry sediment day^{-1} and MeHg degradation rates ranged from 3.7 to 7.4 ng g^{-1} dry sediment day^{-1} for the five cores (Table 2). The $^{14}CO_2/^{14}C$-total ratio was 0.96–0.99 across all sites, indicating that the oxidative pathway dominated MeHg degradation. Based on methylation/demethylation ratios (M/D), net

Table 2
Sediment pH, dry weight loss on ignition (LOI),% mercury as MeHg, potential MeHg production and degradation rates [ng g^{-1} dry sediment day^{-1}][a], methylation/demethylation (M/D) ratio, and sulfate reduction rates [nmol cm^{-3} dry sediment day^{-1}] in sediment cores collected in February 2002. S.D.'s ($n=2$) are given in parentheses

Site (core description)	pH	% LOI	% Hg as MeHg	Potential Hg methylation rate	Potential MeHg degradation rate	M/D ratio	Sulfate reduction rate
Frog Pond (coarse sand)	6.8	1.46	0.01%	24.1 (4.6)	3.7 (0.6)	6.46 (1.64)	98 (6)
Pagni Lane (coarse sand)	7.3	0.87	0.02%	<0.08[b]	4.4 (0.2)	0.02 (0.00)	35 (15)
Rosewood Lakes (fine sand and mud)	7.4	2.01	0.42%	30.0 (3.5)	6.1 (0.1)	4.93 (0.58)	299 (55)
Clean Water Way (fine sand)	7.3	2.47	0.09%	26.4 (0.6)	7.4 (0.0)	3.57 (0.08)	82 (14)
TMWRF (mud with organics)	7.4	5.63	0.58%	6.4 (0.0)	6.1 (0.2)	1.04 (0.04)	18 (6)

[a] rate assays were based on a 4 h incubation (kill control corrected) at 20 °C.
[b] detection limit.

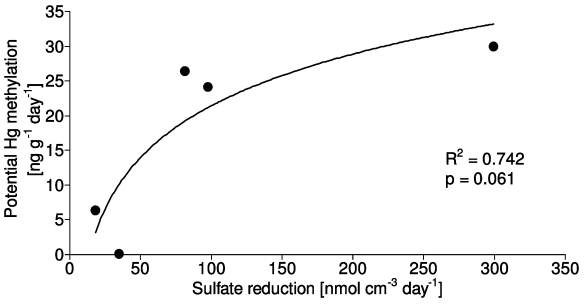

Fig. 4. Positive non-linear relationship ($y=10.7\ \ln x-28.1$) was observed between the microbial sulfate reduction rate and potential mercury methylation rate in sediment cores collected in February 2002 along Steamboat Creek.

MeHg degradation was observed only at Pagni Lane. Sulfate reduction rates ranged from 18 to 299 nmol cm^{-3} dry sediment day^{-1} (Table 2). A positive non-linear relationship was observed between the sulfate reduction and potential methylation rates for all watershed samples (Fig. 4).

TMWRF constructed wetland sediment core had the highest porewater concentrations of chloride, sulfate, sulfide and dissolved organic carbon (Table 3), as well as the highest total reduced sulfur in bulk sediment (Table 4). A trend of increasing porewater chloride and bulk sediment reduced sulfur (i.e. AVS, CRS and TRS) was noted in sediment moving from upstream to downstream. However, no relationship was found between these parameters and Hg-methylation, MeHg demethylation, or sulfate reduction rate.

Iron concentrations in bulk sediment were low for all cores, less than 3 mg/g and 5 mg/g for reduced and oxidized iron, respectively, with no distinct spatial trend (Table 4). In contrast, porewater iron was highest in the upper reaches of SBC, and 10–70 times lower in cores collected downstream (Table 3).

5. Discussion

Total mercury concentrations measured in Steamboat Creek channel and bank sediments did not decrease downstream, as it would be expected under the conditions of passive dispersal (i.e. hydraulic sorting of bed materials, and dilution by mixing of contaminated particles with 'clean' sediment, deposition and storage, and losses through chemical or biological uptake), and limited number of point sources (Miller, 1997). This suggests that mercury contamination has been distributed and stored along the creek's length during the 100 years since mining and ore processing. The high sediment THg concentration observed in Little Washoe Lake (8.53 μg/g, November 2001; Table 1), which had low water level at the sampling time, indicates that this area continues to be a significant source of mercury to the creek. Sections of the creek channel just downstream of Little Washoe Lake had the greatest mercury contamination reported in an earlier study (cf. Codega and WESTEC Inc., 1998). Total mercury concentration in sediments sampled from Little Washoe Lake in August 2002 was low (0.13 ng/g), reflecting the fact that the lake was full and the sample was taken from the shoreline that is rarely submerged.

The recorded THg concentrations (0.03–8.53 μg/g and 0.01–21.43 μg/g for channel and bank,

Table 3
Porewater parameters in sediments along SBC (February 2002): porewater content in sediments, chloride (Cl^-), sulfate (SO_4^{-2}), sulfide (S^{-2}), dissolved organic carbon (DOC), and reduced iron (Fe^{2+}). The deviation of $n=2$ replicate samples is given in parentheses

Site	Sediment porosity [ml/g]	Cl^- [μmol/l]	SO_4^{-2} [μmol/l]	S^{-2} [μmol/l]	DOC [μmol/l]	Fe^{2+} [μmol/l]
Frog Pond	0.42 (0.02)	1.1 (0.0)	69 (1)	<2[a]	86 (2)	76 (8)
Pagni Lane	0.39 (0.00)	0.6 (0.1)	128 (2)	37 (6)	200 (11)	76 (7)
Rosewood Lakes	0.60 (0.01)	3.0 (0.2)	658 (11)	<2[a]	111 (20)	2 (0.5)
Clean Water Way	0.57 (0.01)	4.6 (0.0)	404 (11)	<2[a]	126 (1)	1 (0.5)
TMWRF	0.74 (0.02)	40.5 (3.2)	42 165 (1285)	878 (434)	549 (50)	7 (0.6)

[a] detection limit.

Table 4
Sediment bulk density [g/cm^3 wet sediment], and bulk sediment parameters [per g dry weight] in samples along SBC (February 2002): acid-volatile sulfur (AVS), chromium reducible sulfur (CRS), total reduced sulfur (TRS), reduced iron (Fe^{2+}), amorphous oxidized iron ($_aFe^{3+}$), and crystalline oxidized iron ($_cFe^{3+}$). The deviation of $n=2$ replicate samples is given in parentheses

Site	Sediment bulk density	AVS [μmol S^{-2}/g]	CRS [μmol S^{-2}/g]	TRS [μmol S^{-2}/g]	Fe^{2+} [mg/g]	$_aFe^{3+}$ [mg/g]	$_cFe^{3+}$ [mg/g]
Frog Pond	1.77 (0.00)	0.4 (0.1)	0.2*	0.6 (0.1)	1.19 (0.03)	0.11 (0.00)	3.88 (0.45)
Pagni Lane	1.93 (0.02)	1.4 (0.0)	0.4 (0.0)	1.8 (0.0)	0.78 (0.01)	0.53 (0.04)	4.26 (0.11)
Rosewood Lakes	1.59 (0.02)	2.8 (0.5)	3.7*	6.5 (0.5)	1.78 (0.01)	0.45 (0.07)	2.31 (0.56)
Clean Water Way	1.57 (0.01)	23.3 (3.5)	15.4*	38.7 (3.5)	2.93 (0.01)	0.07 (0.02)	2.45 (0.88)
TMWRF	1.25 (0.04)	16.7 (10.3)	40.2 (2.8)	56.9 (10.6)	1.95 (0.02)	<0.005**	0.69 (0.08)

*$n=1$.
**detection limit.

respectively; Table 1) were similar to those observed previously for SBC channel (0.3–7.13 μg/g) and bank sediments (0.26–6.15 μg/g) (Blum et al., 2001). These concentrations are up to two orders of magnitude higher than the THg concentrations recorded for the canal sediments in the Florida Everglades (0.01–0.46 μg/g; Stober et al., 1995), where human health fish consumption advisories have been issued. Concentrations of THg in SBC sediments were comparable to concentrations in sediments of Carson River system, ranging from ~1.5 to 15.0 μg/g, which was also contaminated due to processing of Comstock ores (Chen et al., 1996; Miller et al., 1999).

At most sites sampled along SBC, average MeHg concentration in low bank sediments were higher than the average channel MeHg concentrations (Fig. 2). Since MeHg concentrations have been used as an analog for MeHg production (Gilmour et al., 1998; Benoit et al., 1999a), low banks with wet sediments may be an important site for mercury methylation in this system. Concentrations of MeHg in SBC channel (0.03–2.98 ng/g) and bank (0.05–1.63 ng/g) sediments were similar to concentrations measured previously in SBC sediments (0.2–2.8 ng/g; Blum et al., 2001), and up to an order of magnitude lower than the sediments from the mining impacted Carson River (approx. 2–28 ng/g; Chen et al., 1996).

Microbial sulfate reduction rates in sediment cores were 2.5–20 times lower than those recorded for the Florida Everglades across the nutrient transect (10–800 nmol cm^{-3} day^{-1}; Gilmour et al., 1998), but potential mercury methylation rates (Table 2) were similar or higher than the range reported across the trophic gradient in the Everglades (1–10 ng g^{-1} day^{-1}) that had been normalized to ambient THg concentrations (Gilmour et al., 1998). Although the observed positive nonlinear relationship between sulfate reduction and potential Hg methylation rate (Fig. 4) was based on only five sediment cores, there are findings that support this general trend in freshwater (Gilmour et al., 1992) and marine sediments (Choi and Bartha, 1994; King et al., 2001). Additionally, the cores with the highest methylation potentials had porewater sulfide concentrations below detection, indicating that sulfide concentration indeed might have been a limiting factor for Hg-methylation (Benoit et al., 1999b).

It is interesting that both pond/wetland and channel sites exhibited high potential for mercury methylation (Table 2), for higher rates would be expected at sites with slower water. The Frog Pond core had the lowest pH, yet exhibited a potential Hg methylation rate similar to that observed for the Rosewood Lakes and Clean Water Way cores (Table 2). The latter two sites had similar pH but higher potential Hg methylation rates than the sediment cores from Pagni Lane and TMWRF. This suggests that the pH in this case was not significantly influencing Hg methylation rates.

Geochemical factors that may have limited mercury methylation in the Pagni Lane and TMWRF cores are high porewater reduced sulfur and DOC concentrations (Table 3). Sulfide concentrations greater than 10 μM inhibit mercury methylation in sediments due to precipitation of HgS (Gilmour

et al., 1998), while DOC inhibits methylation due to the binding of free mercury ions (Winfrey and Rudd, 1990; Barkay et al., 1997). Sediment core from TMWRF constructed wetland had the lowest sulfate reduction rate in spite of the high porewater sulfate concentration, which was well above the optimal range of sulfate concentration for mercury methylation by SRB (200–500 μM; Gilmour and Henry, 1991).

Potential demethylation rates fell within a narrow range (Table 2), suggesting that demethylation was not driven by differences in MeHg concentration, sulfur chemistry, concentration of DOC, or other parameters that varied substantially among the five cores. Potential demethylation rates were more than two orders of magnitude lower than that observed for Florida Everglades peat sediments (Marvin-DiPasquale and Oremland, 1998). Previous research has indicated that potential methylation and demethylation rates vary with season (Korthals and Winfrey, 1987; Marvin-DiPasquale and Agee, in press). The analyzed sediments were collected in winter, and it is possible that this biased the active microbial community. A high $^{14}CO_2/^{14}C$-total ratio indicated the prevalence of oxidative demethylation at all sites (Oremland et al., 1995; Marvin-DiPasquale et al., 2000), which contributes to increased residence time for mercury (Marvin-DiPasquale and Oremland, 1998).

Since demethylation did not exhibit much variation, the observed differences in M/D ratios (Table 2) were most strongly affected by differences in Hg methylation rates. An exception was the core with the highest M/D ratio, Frog Pond inlet, which exhibited lower MeHg degradation potential (Table 2). MeHg mass balances for 2002 showed that Frog Pond was a source of MeHg to SBC during conditions of baseflow, and a sink during irrigation (Thomas, 2003). The same study showed that at most times Rosewood Lakes, the site with the second highest M/D ratio, were also a source of MeHg to the Creek (Thomas, 2003). A detailed study of net MeHg production in TMWRF constructed wetlands showed that this site was a sink for MeHg in winter, and source in other months (Stamenkovic, 2003), and it is likely that the sampling time (February) influenced the measured M/D ratio (just above one; Table 2).

The only site where M/D ratio indicated net MeHg degradation was Pagni Lane. Below detection mercury methylation potential, and the second lowest MeHg demethylation potential and sulfate reduction rate (Table 2) indicate that the overall microbial activity in the Pagni Lane core was lower than in other cores. This was presumably driven by the low sediment organic content (as LOI, Table 2), and competition with iron reducing bacteria. Iron reducing bacteria inhibit SRB through competition for carbon substrate in the presence of amorphous ferric oxyhydroxide (Lovley and Phillips, 1987), but they are able to obtain energy for growth from the reduction of crystalline Fe^{3+} oxides as well (Roden and Zachara, 1996). Both amorphous and crystalline Fe^{3+} pools were the largest in the Pagni Lane sediment core (Table 4).

6. Conclusions

Mercury contamination from historical mining activities in the Comstock period did not follow a passive dispersal model along the length of Steamboat Creek, and mercury contamination has been distributed and stored along the length of the creek. Low streambanks with wet sediments above the water line were identified as potentially important sites of mercury methylation. Although locations where the water flow was slower were expected to have higher potential methylation rates, channel sites exhibited potential for Hg methylation that was comparable.

Potential Hg methylation rates were positively correlated with sulfate reduction rates, while sites with the highest Hg methylation potentials had porewater sulfide concentrations below detection. This suggests that sulfur chemistry plays a major role in Hg methylation in this system. For this limited data set, MeHg demethylation rates did not appear to be influenced by MeHg concentration, sulfur chemistry, DOC, sediment grain size or other parameters that varied among the analyzed cores.

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References

Barkay T, Gillman M, Turner RR. Effects of dissolved organic carbon and salinity on bioavailability of mercury. Appl Environ Microbiol 1997;63:4267–4271.

Benoit JM, Gilmour CC, Mason RP, Heyes A. Sulfide controls on mercury speciation and bioavailability to methylating bacteria in sediment pore waters. Environ Sci Technol 1999a;33:951–957.

Benoit JM, Mason RP, Gilmour CC. Estimation of mercury–sulfide speciation in sediment pore waters using octanol-water partitioning and implications for availability to methylating bacteria. Environ Toxicol Chem 1999b;18(10):2138–2141.

Bloom NS. Determination of picogram levels of methylmercury by aqueous phase ethylation followed by cryogenic gas chromatography with cold vapor atomic fluorescence detection. Can J Fish Aquat Sci 1989;46:1131–1140.

Blum M, Gustin MS, Swanson S, Donaldson SG. Mercury in water and sediment of Steamboat Creek. Nevada: implications for stream restoration. J Am Water Res Assoc 2001;37(4):795–804.

Chen Y, Bonzongo JC, Miller GC. Levels of methylmercury and controlling factors in surface sediments of the Carson River system, Nevada. Environ Pollut 1996;92(3):281–287.

Choi SC, Bartha R. Environmental factors affecting mercury methylation in estuarine sediments. Bull Environ Contam Toxicol 1994;53(6):805–812.

Codega J, WESTEC Inc. Steamboat Creek Restoration Plan. Unpublished document prepared for the Washoe-Storey Conservation District. Reno, Nevada, 1998.

Coolbaugh MF, Gustin MS, Rytuba JJ. Annual emissions of mercury to the atmosphere from natural sources in Nevada and California. Environ Geol 2002;42(4):338–349.

Dionex. Installation Instructions and Troubleshooting Guide for the IONPAC AG4A-SC Guard Column/IONPAC AS4A-SC Analytical Column. Dionex Corporation Document No. 034528, 1992.

Gilmour CC, Henry EA. Mercury methylation in aquatic systems affected by acid deposition. Environ Pollut 1991;71:131–169.

Gilmour CC, Henry EA, Mitchell R. Sulfate stimulation of mercury methylation in fresh-water sediments. Environ Sci Technol 1992;26(11):2281–2287.

Gilmour CC, Riedel GS, Ederington MC, Bell JT, Benoit JM, Gill GA, Stordal MC. Methylmercury concentrations and production rates across a trophic gradient in the northern Everglades. Biogeochemistry 1998;40(2–3):327–345.

Guimaraes JRD, Malm O, Pfeiffer WC. A simplified radiochemical technique for measurements of net mercury methylation rates in aquatic systems near goldmining areas, Amazon, Brazil. Sci Total Environ 1995;175:151–162.

Gustin MS, Taylor GE, Leonard TL, Keislar TE. Atmospheric mercury concentrations associated with geologically and anthropogenically enriched sites in Central Western Nevada. Environ Sci Technol 1996;30(8):2572–2579.

Horvat M, Bloom NS, Liang L. Comparison of distillation with other current isolation methods for the determination of methyl mercury compounds in low level environmental samples. Anal Chim Acta 1993;281:135–1152.

Jørgensen BB. A comparison of methods for the quantification of bacterial sulfate reduction in coastal marine sediments. 1. Measurement with radiotracer techniques. Geomicrobiol J 1978;1:11–27.

King JK, Kostka JE, Frischer ME, Saunders FM, Jahnke RA. A quantitative relationship that demonstrates mercury methylation rates in marine sediments are based on the community composition and activity of sulfate-reducing bacteria. Environ Sci Technol 2001;35:2491–2496.

Korthals ET, Winfrey MR. Seasonal and spatial variations in mercury methylation and demethylation in an oligotrophic lake. Appl Environ Microbiol 1987;53(10):2397–2404.

Liang L, Horvat M, Bloom NS. An improved speciation method for mercury GC/CVAFS after aqueous phase ethylation and room temperature precollection. Talanta 1994;41(3):371–379.

Lechler PJ, Miller JR, Hsu L, Desilets MO. Mercury mobility at the Carson River Superfund Site, west-central Nevada, USA: interpretation of mercury speciation data in mill tailings, soils, and sediments. J Geochem Explor 1997;58:259–267.

Lovley DR, Phillips EJP. Rapid assay for microbially reducible ferric iron in aquatic sediments. Appl Environ Microbiol 1987;53:1536–1540.

Lyons WD, Wayne DM, Warwick JJ, Doyle GA. The Hg geochemistry of a geothermal stream, Steamboat Creek, Nevada: natural vs. anthropogenic influences. Environ Geol 1998;34(2–3):143–150.

Marvin-DiPasquale M, Agee J. Microbial mercury cycling in sediments of the San Francisco Bay-Delta. Estuaries (in press).

Marvin-DiPasquale M, Agee J, Bouse R, Jaffe B. Microbial cycling of mercury in contaminated pelagic and wetland sediments of San Pablo Bay, California. Environ Geol 2003;43(3):260–267.

Marvin-DiPasquale M, Agee J, McGowan C, Oremland RS, Thomas M, Krabbenhoft D, Gilmour CC. Methyl-mercury degradation pathways: A comparison among three mercury-impacted ecosystems. Environ Sci Technol 2000;34(23):4908–4916.

Marvin-DiPasquale MC, Oremland RS. Bacterial methylmercury degradation in Florida Everglades peat sediment. Environ Sci Technol 1998;32(17):2556–2563.

Miller JR. The role of fluvial geomorphic processes in the dispersal of heavy metals from mine sites. J Geochem Explor 1997;58:101–118.

Miller J, Barr R, Grow D, Lechler P, Richardson D, Waltman K, Warwick J. Effects of the flood on the transport and storage of sediment and mercury within the Carson River Valley, West-Central Nevada. J Geol 1999;107:313–327.

Morel F, Kraepiel A, Amyot M. The chemical cycle and bioaccumulation of mercury. Annu Rev Ecol Syst 1998;29:543–566.

Oremland RS, Miller LG, Dowdle P, Connell T, Barkay T. Methylmercury oxidative degradation potentials in contaminated and pristine sediments of the Carson River, Nevada. Appl Environ Microbiol 1995;61(7):2745–2753.

Qian J, Mopper K. Automated high-performance, high-temperature combustion total organic carbon analyzer. Anal Chem 1996;68(18):3090–3097.

Roden EE, Zachara JM. Microbial reduction of crystalline iron(III) oxides: Influence of oxide surface area and potential for cell growth. Environ Sci Technol 1996;30:1618–1628.

Roulet M, Guimarães J-RD, Lucotte M. Methylmercury production and accumulation in sediments and soils of an Amazonian floodplain – effect of seasonal inundation. Water Air Soil Pollut 2001;128:41–60.

Smith GH. The history of the Comstock Lode, 1850–1920. Nevada Bur Mines Geol Bull 1850;37:41–47.

Stamenkovic J. Mercury methylation in constructed wetlands and distribution in sediments, Steamboat Creek. Thesis, University of Nevada, Reno, 2003.

St. Louis VL, Rudd JMW, Kelly CA, Beaty KG, Bloom NS, Flett RJ. The importance of wetlands as sources of methyl mercury to boreal forest ecosystems. Can J Fish Aquat Sci 1994;51:1065–1076.

Stober QJ, Jones RD, Scheidt DJ. Ultra trace mercury in the Everglades ecosystem, a multi-media canal pilot study. Water Air Soil Pollut 1995;80:991–1001.

Thomas BA. Characterization of total and methyl mercury in Steamboat Creek, Nevada and implications for the Truckee River. Thesis, University of Nevada, Reno, 2003.

Ulrich GA, Krumholz LR, Suflita JM. A rapid and simple method for estimating sulfate reduction activity and quantifying inorganic sulfides. Appl Environ Microbiol 1997;63(4):1627–1630.

US Army Corps of Engineers. Section 206 Preliminary Restoration Plan, Steamboat Creek. Final Report 2001.

Winfrey MR, Rudd JWM. Environmental factors affecting the formation of methylmercury in low pH lakes. Environ Toxicol Chem 1990;9:853–869.

Zillioux EJ, Porcella DB, Benoit JM. Mercury cycling and effects in freshwater wetland ecosystems. Envron Toxicol Chem 1993;12:2245–2264.