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Distribution of Selenium, Mercury, and Methylmercury in Surficial Missouri River Sediments

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Abstract Sediment deposition into Lewis and Clark Lake, an impoundment of the Missouri River, has caused substantial storage capacity reductions. Current proposals to hydrologically flush sediment would disturb river and reservoir sediment that may contain heavy metals. We quantified existing concentrations of selenium (Se), mercury (Hg), and methylmercury (MeHg) in surficial sediments upstream of and in Lewis and Clark Lake. We found elevated levels of Se (range 0.12–9.62 μg/g) and Hg (range 0.02–1.55 μg/g) at several sites throughout the study area; however, few sites contained levels of MeHg above detection limits. Sites with highest MeHg concentrations were found in Lewis and Clark Lake and ranged from below detection limit to 0.79 ng/g. We conclude that further investigation of sediment-sequestered contaminants in Lewis and Clark Lake should be conducted.

Keywords Selenium · Mercury · Methylmercury · Reservoir · Lewis and Clark Lake · Sediment

Sediment trapping in reservoirs leads to loss of water storage capacity that can affect power generation, flood control, and recreational services. Loss of reservoir storage can be mitigated through a variety of sediment abatement techniques including installation of sediment bypass channels, dredging, hydrologic sediment flushing through reservoir drawdown and high discharge, and dam decommissioning (Morris and Fan 1997). Deposition of 100,000 acre-feet (12,335 hectare-meters) of Niobrara River and Missouri River alluvia into the headwater area of Lewis and Clark Lake, the smallest and downstream most impoundment on the Missouri River, has occurred since the closing of Gavins Point Dam in 1957. Sedimentation in this reservoir has resulted in a 23% reduction of reservoir water storage capacity (USACE 2003) and threatens dam and reservoir services. Currently, proposals to flush these sediments from the reservoir using increased water releases from Ft. Randall Dam the next upstream dam from Gavins Point Dam, are favored over other forms of sediment abatement.

Concerns with flushing sediment out of a reservoir focus on the fact that water turbidity and suspended solids in and downstream of a reservoir can remain elevated for long periods of time during and after sediment flushing events (Morris and Fan 1997). These events can also redistribute sediment contaminants to downstream locations (Morris and Fan 1997). Likewise, sediment flushing in Lewis and Clark Lake could also lead to a period of resuspension of sediment contaminants in riverine portions upstream of Lewis and Clark Lake, in Lewis and Clark Lake, and in the Missouri River downstream of Lewis and Clark Lake. Specifically, presence of elevated mercury (Hg) and methylmercury (MeHg) levels in nearby wetlands (Schaap and Bartholomay 2006) and erosion of Se-containing shale bluffs that border the study area (Sando and Neitzert 2003) create a need for a pre-abatement investigation of concentrations of these metals in the sediments. These heavy metals are capable of bioaccumulation in biota and biomagnification through the food chain and are responsible for a variety of sub-lethal and lethal effects on fish and wildlife such as reproductive and growth impairment, teratogenesis, nervous system damage, and death in fish and wildlife species (Lemly 1993; Webb et al. 2006). Resuspension and increased bioavailability of sediment-

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sequestered contaminants is of particular concern due to presence of federally endangered species including pallid sturgeon *Scaphirinchus albus*, piping plover *Charadrius melodius*, and interior least tern *Sterna antillarum athalassos*. Our objective in this study was to describe the distribution of Se, Hg and MeHg in the area of Missouri River that would be impacted by Lewis and Clark Lake sediment flushing.

Materials and Methods

Collection of sediment took place in the Ft. Randall Dam (river kilometer (RK) 1,416) to Gavins Point Dam (RK 1,305) reach of the Missouri River (Fig. 1). We subdivided the study reach into three zones determined by geomorphology and hydrology. Zone 1 extended from Fort Randall Dam (RK 1,416) to the confluence of the Niobrara River and Missouri River (RK 1,360). Zone 2 extended from the confluence of the Niobrara River and Missouri River to the Sand Creek boat ramp at the headwaters of Lewis and Clark Lake (RK 1,334). This zone has high sediment loads due to alluvial input from the Niobrara River causing channel aggradation and a highly braided channel. Zone 3 extended from the Sand Creek boat ramp to Gavins Point Dam (RK 1,305) and contains the entire lacustrine portion of Lewis and Clark Lake. We collected five sediment samples from each of three sites within the three zones (Fig. 1).

Sample collection sites were selected based on a stratified random sampling design where collection sites were randomly selected from areas that appeared likely to harbor Se or MeHg (i.e., near shale bluffs likely to contain Se or in backwater areas likely to contain MeHg). Sediments were collected in 500 mL amber glass jars and frozen until they could be processed for analysis. Raw (wet) samples were extracted or digested and analyzed to avoid effects of volatile Hg and Se loss, and moisture content was determined gravimetrically on separate portions by drying in an oven at 110°C for 5 h. All concentrations were converted to dry weight equivalent. A value of one-half the detection limit was used for all non-zero values below the detection limit for calculating means.

Samples were extracted at room temperature using a method adapted from He Bin et al. (1998), derivatized using sodium tetraethylborate (NaBEt$_4$), and analyzed by purge and trap GC/MS using the procedure outlined in Mao et al. (2008). Briefly, 20 mL of 0.1 M pH 3.0 acetic acid-sodium acetate (HAc-NaAc) buffer solution and 1 mL of concentrated nitric acid (Trace Metal grade, Fisher Scientific, St. Louis, MO) were added to 0.5–3 g of sediment in a 40 mL amber glass vial. Vials were sealed with Teflon-lined caps, agitated for 1 min, and incubated in the dark at room temperature for 24 h. After extraction, 10 mL of clear supernatant was mixed with 10 mL of 0.1 M pH 5.0 HAc-NaAc buffer solution, and pH adjusted to near 5.0 with sodium hydroxide. Propylmercury chloride (10 ng, Pfaltz and Bauer, Waterbury, CT) was added as internal standard and S- Ethyl Dipropylthiocarbamate (EPTC) (Pestanal, Chemservice, Westchester, PA) as a surrogate, followed by 20 µL of freshly prepared 0.1 g/mL NaBEt$_4$ (Sigma–Aldrich, St. Louis, MO) in chilled water. The NaBEt$_4$ is pyrophoric and water-reactive and was therefore pre-weighed into septum vials in a nitrogen-flushed glove bag and stored at −20°C.

Derivatized extracts were analyzed on a model 4551 autosampler with a 4660 Eclipse purge & trap autosampler

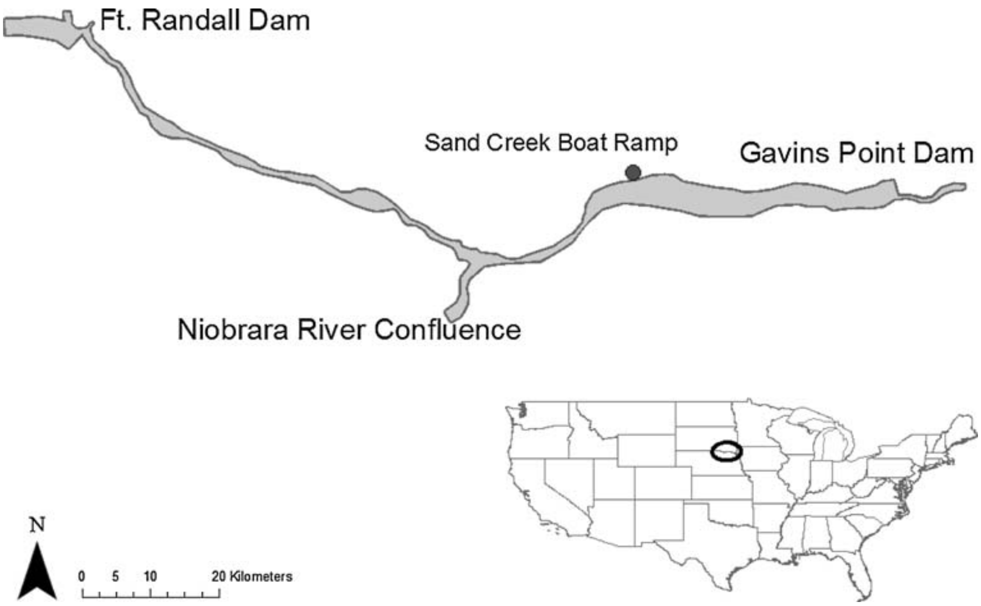

Fig. 1 Map of study area showing points of zone boundaries. *Zone 1* extends from Ft. Randall Dam downstream to the confluence of the Niobrara River. *Zone 2* extends from the confluence of the Niobrara River to the Sand Creek boat ramp. *Zone 3* extends from the Sand Creek boat ramp to Gavins Point Dam

(OI Analytical, College Station, TX) interfaced to an Agilent 5973 GC/MS (Palo Alto, CA). An OI #10 trap (8 nm Tenax/silica gel) was installed as adsorbent trap. The sample was purged with helium at 40 mL/min for 11 min at 30°C and followed by desorption at 190°C for 4 min. Chromatographic analysis was performed with 6890 N GC equipped with a 5,973 inert source quadrupole MS operating in selected ion monitoring (SIM) mode. An HP-1MS capillary column was used with helium as carrier gas at a flow rate of 6.5 mL/min. The column temperature was programmed as follows: 40°C for 1 min, increasing to 80°C at 10°C/min then increased to 175°C at 15°C/min and holding for an additional 5 min. The injection port was operated at 180°C and the detector port was operated at and 230°C. Calibration solutions were prepared using methylmercury chloride (Sigma–Aldrich, St. Louis, MO) at amounts ranging 0.10–1 ng, derivatized and analyzed at the same time as the samples. Based on the variation of a low-level fortified blank, the method detection limit (MDL) for MeHg was 0.20 ng/g (average recovery = 101 ± 9%).

Total mercury was determined using microwave digestion with nitric acid (Zhou et al. 1997) and detection by inductively coupled plasma-mass spectrometry (ICP-MS) using a cold vapor sample introduction system. Approximately 0.5 g of sample was weighed along with 5 mL trace metal grade concentrated nitric acid in Teflon digestion vessel, and then heated under pressure in a MARS XPress microwave digestion system (CEM Corporation, Matthews, NC) using 100% power (1,600 watts), 1,035 kPa (150 psi) 200°C for 5 min. The solution was then cooled and the contents were filtered with a Whatman #1810-047 low metal glass fiber. The filtered solution was then diluted with distilled deionized water to 50 mL and analyzed using a GV Instruments Platform XS ICP-MS (Manchester, UK) with a CETAC HGX-200 cold-vapor sample introduction system (Omaha, NE). Instrumental conditions were: 1,350 watts plasma RF, argon carrier gas 400 mL/min, nebulizer gas 450 mL/min. Stannous chloride (2.5% in 1 M hydrochloric acid) was metered into the cold vapor system at a rate of 1.0 mL/min. Mercury standards, prepared over the range from 0.10 to 2 ng/g were digested and analyzed with samples. The MDL for the total mercury (Hg) was 0.04 µg/g. Several samples of certified reference material (NWRI Great Lakes Sediment #WQB-1) were digested and analyzed by this method with an average measured concentration of 1.35 µg/g compared to a certified value of 1.09 ± 0.15 µg/g.

We used microwave digestion with aqua regia (75:25) hydrochloric: nitric acid for total selenium determination (Zhou et al. 1997). Hydride generation ICP-MS was used to minimize interferences from sample matrices (Moor and Kobler 2001). Approximately 0.5 g of sample was accurately weighed in a Teflon digestion vessel along with 3.5 mL concentrated trace metal grade nitric acid and 10.5 mL concentrated hydrochloric acid. Samples were heated at 100% power for 15 min, cooled, filtered and diluted as for Hg determination. A 5 mL aliquot of digest was mixed with 5 mL of concentrated hydrochloric acid for 10 min at 100°C to reduce selenium to +4 form, cooled to room temperature, and diluted with deionized water prior to analysis by hydride generation ICP-MS with the CETAC HGX-200. Sodium tetraborate was metered in the generator at a rate of 0.5 mL/min. Instrumental conditions were: 1,350 watts plasma RF, argon carrier gas 220 mL/min, nebulizer gas 650 mL/min. Selenium standards (0.1–10 ng) were reduced and analyzed at the same time as sample digests. The MDL for Se is 0.078 µg/g. The WQB-1 reference material was digested and analyzed with an average measured concentration of 0.80 µg/g compared to the certified value of 1.02 ± 0.17 µg/g.

Results and Discussion

Mean Se, Hg, and MeHg concentrations are summarized by site in Table 1. Mean Se concentrations ranged from 0.45 ± 0.32 µg/g at site 2.2 to 7.22 ± 1.90 µg/g at site 3.3.

Table 1 Site number, number of samples (N), mean ± SD (range) for sediment selenium (µg/g), mercury (µg/g), and methylmercury (ng/g) concentrations between Ft. Randall Dam and Gavins Pt. Dam on the Missouri River

Site	N	Selenium	Mercury	Methylmercury
1.1	5	0.94 ± 0.38 (0.50–1.55)	0.61 ± 0.55 (0.22–1.55)	*
1.2	5	1.09 ± 0.13 (0.96–1.31)	0.12 ± 0.04 (0.09–0.18)	*
1.3	5	2.37 ± 1.33 (0.91–3.83)	0.09 ± 0.03 (0.06–0.13)	*
2.1	5	2.57 ± 0.70 (1.94–3.73)	0.32 ± 0.39 (0.08–1.0)	0.11 ± 0.20** (0–0.47)
2.2	5	0.45 ± 0.32 (0.22–0.99)	0.05 ± 0.07 (0.02–0.17)	*
2.3	5	0.62 ± 0.36 (0.12–1.10)	0.10 ± 0.05 (0.07–0.18)	*
3.1	5	1.23 ± 0.37 (0.81–1.71)	0.13 ± 0.05 (0.07–0.18)	*
3.2	5	4.01 ± 2.22 (1.86–7.03)	*	0.26 ± 0.30** (0.05–0.79)
3.3	5	7.22 ± 1.90 (4.29–9.62)	0.06 ± 0.01 (0.05–0.08)	0.02 ± 0.17** (0–0.44)

Detection limit for selenium and mercury analyses was 0.05 µg/g and 0.2 ng/g for methylmercury analyses

* No values above detection limit

** Some values below detection limit

Sources of sediment Se throughout this reach are geologic; this reach of Missouri River is bordered by shale bluffs that contain elevated levels of Se (Ruelle et al. 1993). The highest Se concentrations were recorded from zone 3: the lacustrine portion of Lewis and Clark Lake. Surface sediments in this reach were largely composed of pulverized shale from erosion of bluffs along the reservoir shoreline. Similar concentrations of Se were found by Sando and Neitzert (2003) in zone 1 of the present study area.

Lemly (2002) described the sediment toxic effect threshold for Se in sediment as 2 µg/g. Mean sediment Se concentrations at four of the nine sites exceed this threshold. Lemly (1995) devised risk categories of Se entrance into the benthic food chain based on Se sediment concentration: >4 µg/g – high; 3–4 µg/g – moderate; 2–3 µg/g – low; 1–2 µg/g – minimal; and <1 µg/g – no hazard (Lemly 1995). Two sites contain mean sediment concentrations in the high risk category: both in Lewis and Clark Lake. Additionally, two sites fall within the low risk category and two sites in the minimal risk category, and three in the no hazard risk category. Sando and Neitzert (2003) also found maximum sediment Se concentrations in this study area to fall within the moderate to high risk categories as characterized by Lemly (1995).

Understanding the risk of sediment Se entering the food chain presently in addition to during and after sediment flushing is important for assessing the potential implications of sediment flushing for river biota. Maleffects of Se on biota, such as reproductive failure and teratogenesis, can occur at relatively low sediment Se concentrations (Lemly 1995). Levels of Se currently present in this reach of Missouri River may be sufficiently high to cause biological impacts on fish and bird species prior to remobilization of additional sequestered Se (Lemly 1995). Furthermore, despite the Solomon River Basin, KS having lower Se concentrations in water, sediment, invertebrates, and fish than those reported in this study, it was concluded that Se concentrations present posed a toxic hazard sufficient to cause reproductive failure in Se sensitive fish and bird species (May et al. 2008).

Mean total Hg concentrations ranged 0.02 ± 0.01 µg/g at 3.2–0.61 ± 0.55 µg/g at site 1.1. However, the highest mean MeHg concentration, 0.26 ± 0.31 ng/g was found at site 3.2 although this site was shown to have the lowest mean total Hg concentrations. Schaap and Bartholomay (2006) found that in sediments from wetlands adjacent to this reach of Missouri River, total Hg and MeHg concentrations were not directly related. However, sediment Hg concentrations have been shown to be positively associated with Hg levels in biota. For example, Huggett et al. (2001) found sediment and fish Hg concentrations were positively related in three North Mississippi Lakes containing fish with Hg concentrations greater than the United States Environmental Protection Agency's action level of 1 µg/g: the level of Hg in fish when fish consumption advisories are issued for waterbodies. Levels of total Hg found in our study were greater than those reported by Huggett et al. (2001).

River biota downstream of Gavins Point Dam would likely be the most impacted by sediment associated contaminants flushed from Lewis and Clark Lake. Flushing sediment from Lewis and Clark Lake is intended to resuspend millions of tons of sequestered sediment in the reach of Missouri River between Ft. Randall and Gavins Point dams as well as in the area below Gavins Point Dam. Local and downstream effects of sediment flushing may include increased Se, Hg, and MeHg concentrations in the water and increased bioavailability of the remobilized heavy metals for long periods of time (Morris and Fan 1997).

Assessment of Missouri River sediment between Ft. Randall Dam and Gavins Point Dam for additional elements and compounds is critical to understanding the biological impact of Lewis and Clark Lake sediment flushing. The findings of our study indicate that concentrations of Se, Hg, and MeHg in this reach of river may be sufficiently high to negatively impact Missouri River biota, particularly in the areas downstream of Lewis and Clark Lake that will receive flushed sediment. Sediment that has accumulated in Lewis and Clark Lake may also contain other elements and compounds that were not evaluated in this study that could also be injurious to native fauna. The potential for heavy metal-induced impacts on already declining populations of endangered river birds and fish emphasizes the need for more comprehensive assessments of sediment contaminants prior to sediment flushing.

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