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Mercury deposition and methylmercury formation in Narraguinnep Reservoir, southwestern Colorado, USA

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ABSTRACT

Narraguinnep Reservoir in southwestern Colorado is one of several water bodies in Colorado with a mercury (Hg) advisory as Hg in fish tissue exceed the 0.3 μg/g guideline to protect human health recommended by the State of Colorado. Concentrations of Hg and methyl-Hg were measured in reservoir bottom sediment and pore water extracted from this sediment. Rates of Hg methylation and methyl-Hg demethylation were also measured in reservoir bottom sediment. The objective of this study was to evaluate potential sources of Hg in the region and evaluate the potential of reservoir sediment to generate methyl-Hg, a human neurotoxin and the dominant form of Hg in fish. Concentrations of Hg (ranged from 1.1 to 5.8 ng/L, $n = 15$) and methyl-Hg (ranged from 0.05 to 0.14 ng/L, $n = 15$) in pore water generally were highest at the sediment/water interface, and overall, Hg correlated with methyl-Hg in pore water ($R^2 = 0.60$, $p = 0007$, $n = 15$). Net Hg methylation flux in the top 3 cm of reservoir bottom sediment varied from 0.08 to 0.56 ng/m^2/day (mean = 0.28 ng/m^2/day, $n = 5$), which corresponded to an overall methyl-Hg production for the entire reservoir of 0.53 g/year. No significant point sources of Hg contamination are known to this reservoir or its supply waters, although several coal-fired power plants in the region emit Hg-bearing particulates. Narraguinnep Reservoir is located about 80 km downwind from two of the largest power plants, which together emit about 950 kg-Hg/year. Magnetic minerals separated from reservoir sediment contained spherical magnetite-bearing particles characteristic of coal-fired electric power plant fly ash. The presence of fly-ash magnetite in post-1970 sediment from Narraguinnep Reservoir indicates that the likely source of Hg to the catchment basin for this reservoir has been from airborne emissions from power plants, most of which began operation in the late-1960s and early 1970s in this region.

1. Introduction

Mercury is a well-known and widespread environmental contaminant that affects land, lakes, reservoirs, and other water bodies in the USA and worldwide (NAS, 1978; Ullrich et al., 2001; USEPA, 1997). The U.S. Environmental Protection Agency (USEPA) indicated that, of the pollutants mentioned in the Clean Air Act, Hg has the greatest potential to affect human health (USEPA, 1997). All forms of Hg are potentially hazardous, have no biological function in humans, and any exposure to Hg is undesirable, but methyl-Hg (CH_3Hg^+) is potentially the most hazardous because it is a neurotoxin (Eisler, 1987; USEPA, 1997; WHO, 1990). Methylation of Hg is dominantly through the action of microorganisms, primarily by the action of sulfate reducing bacteria, which is most common in organic-rich sediment (Compeau and Bartha, 1985; Gilmour et al., 1992). Several studies have shown that Fe-reducing bacteria are also capable of methylating Hg (Alpers et al., 2013; Fleming et al., 2006; Kerin et al., 2006; Marvin-DiPasquale et al., 2014; Parks et al., 2013; Schaefer et al., 2014), although sulfate reducing bacteria are generally reported to be more dominant in the sediment column (Gilmour et al., 1992; Hammerschmidt and Fitzgerald, 2004; Marvin-DiPasquale and Agee, 2003). Methyl-Hg formation is most common in the sediment column, and because it is water soluble, it is transferred to the water column and then to biota, such as fish (NAS, 1978; USEPA, 1997). Studies of reservoirs have indicated that methylation of Hg is enhanced following the initial flooding of reservoirs, supply of nutrients and organic matter, reduction of oxygen supply producing anaerobic conditions, and supply and bioavailability of Hg (Bodaly et al., 1997; Bonzongo et al., 1996; Montgomery et al., 2000; TetraTech, 2001; Ullrich et al., 2001; Waldron et al., 2000). Human consumption of Hg contaminated fish is the most common pathway of methyl-Hg to humans (Clarkson, 1990) because generally more than 90%

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of Hg in fish is methyl-Hg (Fitzgerald and Clarkson, 1991; Rimondi et al., 2012; Ullrich et al., 2001; USEPA, 1997).

There are numerous natural and anthropogenic sources of Hg with the potential to contaminate air, land, and water, but of these, anthropogenic sources of Hg are the largest (Lamborg et al., 2002; Mason et al., 1994; NAS, 1978; USEPA, 1997). Burning of fossil fuels is the dominant anthropogenic source of Hg, and emissions from coal-fired power plants have been known as a significant source of atmospheric Hg for many years (USEPA, 1997). Deposition of Hg-bearing particulates emitted from various anthropogenic combustion point sources has been reported to lead to Hg contamination in local, regional, and remote lakes and other water bodies (Fitzgerald et al., 1998; Gray and Hines, 2006; Mason et al., 1994; USEPA, 1997). Several coal-fired power plants are located in the Four Corners region of the U.S. (Colorado, New Mexico, Utah, and Arizona) (Fig. 1). Two of the largest of these are the Four Corners (>11,000,000 MWH output) and San Juan (>14,000,000 MWH output) plants, both located about 80 km south of Narraguinnep Reservoir near Farmington, New Mexico (Fig. 1). Currently, there are 21 water bodies in Colorado with advisories recommending limited consumption of fish due to elevated concentration of Hg in fish tissue (CDPHE, 2012). Six of these advisories are located in the Four Corners area of Colorado including Narraguinnep, McPhee, Vallecito, Navajo, Echo Canyon, and Trotten Reservoirs. In addition, advisories for Hg in fish are widespread on water bodies in the Four Corners area such as Lake Powell in Arizona and Utah (AFGD, 2014; USEPA, 2014) and several lakes in northwest New Mexico, including Abiquiu Lake, Eagle Nest Lake, and El Vado Lake among others (NMDGF, 2012).

Geochemical research of water ways and reservoirs in the Four Corners region have attempted to evaluate sources of various land and airborne contaminants (Butler et al., 1995, 1997; Gray et al., 2005; Malm et al., 1990; TetraTech, 2001). Several studies have indicated that coal-fired power plants in the Four Corners area have likely emitted airborne particulates, which have been deposited to local land and water bodies (Gray et al., 2005; Malm et al., 1990; TetraTech, 2001; Wright, 2011; Wright and Nydick, 2010). Gray et al. (2005) studied historical deposition of Hg using sediment cores collected from Narraguinnep Reservoir and found an increase in Hg during the period that coal-fired power plants were in operation (about 1970 to present day) in the Four Corners region (Fig. 1). Wright and Nydick (2010) used wet deposition geochemical studies and back-trajectory analysis of climatic patterns that suggested that coal-fired power plants operating in the Four Corners region south of Mesa Verde National Park are likely an important source of Hg deposition in the park. However, these previous studies neither measured rates of Hg methylation in reservoirs with posted Hg advisories in the Four Corners area, nor attempted to identify the sources of particles in reservoir sediment, some of which may have been emitted from regional coal-fired power plants. Therefore, the objectives of this study were to determine (1) rates of Hg methylation and methyl-Hg demethylation in reservoir bottom sediment, (2) concentrations of Hg, methyl-Hg, organic carbon, and other trace elements in reservoir bottom sediment and pore water extracted from bottom sediment, and (3) the presence or absence of reservoir sediment particles that likely originated from coal-fired power plant emissions in the region.

2. Study area

The area of study was Narraguinnep Reservoir, a small reservoir, located just west of McPhee Reservoir, with a surface area of about 2.53 km^2 and a 23,000,000 m^3 storage capacity. The primary water supply for both reservoirs is the Dolores River (Fig. 1). Water flows from the Dolores River into McPhee Reservoir and then into Narraguinnep Reservoir. McPhee Reservoir acts as a sink for coarse sediment flowing from the Dolores River, but Dolores River water

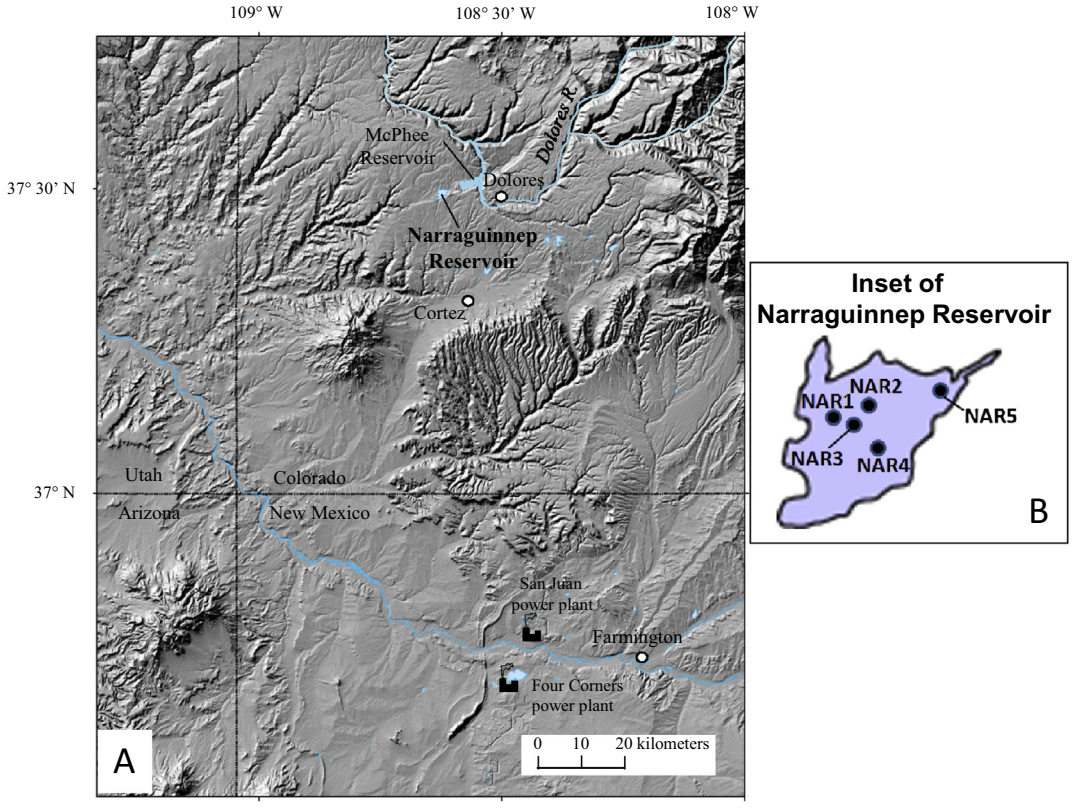

Fig. 1. (A) Location of study area. (B) Inset shows the location of sample sites in Narraguinnep Reservoir.