

# Geochemical cycling of mercury in a deep, confined aquifer: Insights from biogeochemical reactive transport modeling

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## Abstract

Total dissolved mercury concentrations ( $Hg_T$ ) were measured in groundwaters collected along a flow path within a deep, confined aquifer (i.e., the Carrizo Sand) in southeastern Texas, USA, along with major solutes, pH, and redox sensitive parameters that include dissolved iron species [Fe(II), Fe(III)] and sulfide [S(-II)] concentrations. Mercury concentrations range from below detection ( $<0.43 \text{ pmol kg}^{-1}$ ) to close to  $8 \text{ pmol kg}^{-1}$ , and increase 6-fold along the first 13 km of the flow path, coincident with the region of the aquifer where dissimilatory Fe(III) reduction buffers the redox conditions. With groundwater flow beyond the Fe(III) reducing zone and into the region of the aquifer dominated by sulfate reduction, the dissolved  $Hg_T$  concentrations decrease by close to a factor of 3. Dissolved  $Hg_T$  is positively correlated with dissolved Fe(II) concentrations ( $r = 0.61$ ), and to a lesser extent with dissolved organic carbon (DOC) concentrations ( $r = 0.54$ ), and inversely related to both pH ( $r = -0.56$ ) and dissolved S(-II) concentrations ( $r = -0.41$ ), although this latter relationship is not statistically significant. Solution complexation modeling indicates that Hg is chiefly complexed with dissolved sulfide and that organic complexes with Hg are generally negligible. Biogeochemical reactive transport modeling demonstrates that the distinct zones of high Fe(II) followed by high S(-II) groundwaters observed along the flow path are consistent with microbially mediated Fe(III) reduction followed by  $SO_4^{2-}$  reduction that occurs sequentially along the flow path. Furthermore, the modeling suggests that Hg is released to Carrizo Sand aquifer groundwaters by dissimilatory reduction of the Fe(III) oxides/oxyhydroxides (goethite and hematite), which are common in the aquifer, occurring as coatings on sand grains (chiefly quartz). Subsequently, the model suggests that Hg is removed from Carrizo Sand groundwater further down gradient along the flow path by adsorption onto goethite and hematite. Adsorption onto, or co-precipitation with, Fe-sulfide minerals like mackinawite, sorption onto sedimentary organic matter, and/or precipitation of  $HgS_{(s)}$  may also play important roles in Hg removal from Carrizo Sand groundwaters.

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## 1. INTRODUCTION

Mercury (Hg) is recognized as a toxic trace metal that has been widely dispersed globally owing to anthropogenic activities including the burning of fossil fuels (e.g., coal), incineration of medical and municipal wastes, and chlor-alkali production, among other industrial activities (Fitzgerald and Lamborg, 2003). The geochemistry of Hg in

natural waters is complex owing in part to its redox chemistry, which leads to the formation of various redox species that include elemental ( $Hg^0$ ) and oxidized, ionic forms ( $Hg^+$ ,  $Hg^{2+}$ ). In addition, Hg forms aqueous complexes with chloride and sulfide ions, binds strongly to dissolved organic matter, and occurs as methylated forms in natural waters (Fitzgerald, 1979; Gill and Bruland, 1990; Dyrssen and Wedborg, 1991; Porcella, 1994; Paquette and Helz, 1997; Benoit et al., 1999a,b; Jay et al., 2000; Haitzer et al., 2002, 2003; Lamborg et al., 2003; Ravichandran, 2004). In particular, monomethylmercury ( $CH_3Hg^+$ ), which is generally referred to as methylmercury (MeHg),

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is a neurotoxin that is known to bioaccumulate across trophic levels in aquatic environments (Ullrich et al., 2001; Fitzgerald and Lamborg, 2003). The chief exposure route of Hg to human populations is via the consumption of fish, and the majority of this Hg (~95%) is methylmercury (Porcella, 1994; Fitzgerald and Lamborg, 2003).

The vast majority of studies concerning Hg in aquatic environments have focused on surface waters, including the oceans, estuaries, and lakes (e.g., Fitzgerald and Lyons, 1975; Gill and Fitzgerald, 1987; Mason et al., 1993; Watras et al., 1995; Bonzongo et al., 1996; Mason and Sullivan, 1997; Lyons et al., 1999, 2006; Conaway et al., 2003). Remarkably little effort, however, has been directed at investigating Hg in groundwater flow systems. Furthermore, the existing studies of Hg in groundwaters have involved relatively shallow, unconfined aquifers in direct contact with overlying surface water bodies, and have commonly focused on investigating the exchange of Hg across groundwater/surface water boundaries (e.g., Krabbenhoft and Babiarez, 1992; Barringer et al., 2005; Bone et al., 2007; Creswell et al., 2008; Bagnato et al., 2009). To the best of our knowledge, there have been no investigations of the geochemical cycling of Hg in deep, confined regional-scale aquifers.

Consequently, in this study we present total dissolved Hg concentrations ( $Hg_T$ ) for groundwaters from the confined, regional-scale Carrizo Sand aquifer in southeastern Texas. These data are employed along with major solute compositions and other geochemical parameters to develop a one-dimensional, biogeochemical reactive transport model for Hg in the Carrizo Sand aquifer that accounts for both aqueous and surface complexation reactions as well as changing redox conditions. The biogeochemical reactive transport model is subsequently applied to the Carrizo Sand aquifer system to develop a more comprehensive understanding of the processes that control Hg cycling and transport in deep, regional aquifer systems.

## 2. CARRIZO SAND AQUIFER

The portion of the Carrizo Sand aquifer studied is located within the Gulf Coastal Plain of southeastern Texas, USA (Fig. 1). The aquifer outcrops along a sand ridge that roughly parallels the Texas coast, and dips towards the southeast. Groundwater is recharged along the sand ridge and subsequently flows southeast down the structural dip of the aquifer towards the Gulf of Mexico.

The aquifer is composed of unconsolidated, mostly fine- to medium-grained, Eocene quartz sand with minor amounts of clay minerals, lignite, calcite, Fe oxides, and pyrite (Pearson and White, 1967; Hamlin, 1988; Basu et al., 2007). The aquifer sands are commonly coated with Fe(III) oxides/oxyhydroxides (i.e., goethite and hematite) mixed with fine grain clay minerals (chiefly kaolinite and illite; Basu et al., 2007). The Carrizo Sand is confined from below by the underlying massive clay layers and mudstones of the Lower Wilcox Formation, and from above by the overlying clays and shales of the Recklaw Formation (Castro and Goblet, 2003). In deeper portions of the aquifer (i.e., outside the study area) upward leakage of

groundwaters along faults has been documented (Hamlin, 1988; Stute et al., 1992; Castro, 2004; Castro and Goblet, 2005; Dutton et al., 2006). Within our study area essentially all of the groundwater within the Carrizo Sand aquifer represents meteoric recharge from the outcrop area (Alexander and White, 1966; Cowart and Osmond, 1977).

From the outcrop area in Atascosa County towards the south in McMullen County the thickness of the Carrizo Sand varies from 100 to 360 m, showing an increase along the flow path (Castro et al., 2000). The porosity of the aquifer is estimated to range from ~30% to 40% (Pearson and White, 1967). Radiocarbon analysis indicates that groundwater age increases from ~5000 years near the outcrop area in northern Atascosa County to ~30,000 years in southern McMullen County (Pearson and White, 1967). Based on  $^{14}C$  data, Pearson and White (1967) estimated the groundwater flow velocity to be approximately  $2.4 \text{ m a}^{-1}$  at a distance of roughly 16 km down gradient from the recharge zone, and  $1.6 \text{ m a}^{-1}$  50 km further down gradient. These flow velocities agree well with estimates based on hydrogeologic data that indicate the groundwater flow velocity near where the aquifer first becomes confined (i.e., in the vicinity of the KS-1 well; Fig. 1) is approximately  $7\text{--}8 \text{ m a}^{-1}$ , but decreases to  $\sim 0.8 \text{ m a}^{-1}$  at a distance of 57 km further down gradient (Pearson and White, 1967). Stute et al. (1992) determined similar groundwater flow velocities for the flow path and reported an average groundwater flow velocity of  $2 \text{ m a}^{-1}$ . The decrease in groundwater flow velocity likely reflects leakage to overlying aquifers that principally occurs along faults located further down gradient (e.g., Hamlin, 1988; Castro and Goblet, 2003, 2005; Dutton et al., 2006).

Previous investigations demonstrate that the composition of groundwater along the studied flow path is controlled by calcite and possibly halite dissolution, oxidation of organic matter and pyrite, precipitation of Fe(III) oxides/oxyhydroxides in shallow portions of the aquifer (e.g., in the recharge zone; Fig. 1), Fe(III) and  $SO_4^{2-}$  reduction in deeper parts of the aquifer, and chemical weathering of Al-silicate minerals further down gradient (Pearson and White, 1967; Hamlin, 1988). A number of investigations report distinct zones along the studied flow path where Fe(III) reduction followed by  $SO_4^{2-}$  reduction appear to buffer the in situ redox conditions (e.g., Hamlin, 1988; Haque and Johannesson, 2006; Tang and Johannesson, 2006; Basu et al., 2007; Willis et al., 2011). The changing redox conditions along the studied flow path were subsequently shown to influence the concentrations and speciation of a number of trace elements including As, Sb, Se, W, and the rare earth elements within the groundwaters (Haque and Johannesson, 2006; Tang and Johannesson, 2006; Basu et al., 2007; Dave and Johannesson, 2008; Willis et al., 2011).

## 3. METHODS

### 3.1. Groundwater sampling and analysis

All sample bottles (Teflon<sup>®</sup> and HDPE), field containers (LDPE), Teflon<sup>®</sup> tubing, and lab-ware were rigorously

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