



Mercury concentrations, speciation, and isotopic composition in sediment from a cold seep in the northern Gulf of Mexico



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ABSTRACT

Total-Hg, monomethylmercury (MMHg), and mercury isotopic composition was determined in sediment from a cold seep and background sites in the northern Gulf of Mexico (nGoM). Total-Hg averaged 50 ng/g ($n = 28$), ranged from 31 to 67 ng/g, and decreased with depth (0–15 cm). MMHg averaged 0.91 ng/g ($n = 18$), and ranged from 0.2 to 1.9 ng/g. There was no significant difference for total-Hg or MMHg between cold seep and background sites. $\delta^{202}\text{Hg}$ ranged from -0.5 to -0.8‰ and becomes more negative with depth ($r = 0.989$). Mass independent fractionation ($\Delta^{199}\text{Hg}$) was small but consistently positive (0.04 – 0.12‰); there was no difference between cold seeps ($\Delta^{199}\text{Hg} = +0.09 \pm 0.03$; $n = 7$, 1SD) and background sites ($\Delta^{199}\text{Hg} = +0.07 \pm 0.02$; $n = 5$, 1SD). This suggests that releases of hydrocarbons at the cold seep do not significantly alter Hg levels, and that cold seeps are likely not major sources of MMHg to nGoM waters.

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1. Introduction

Mercury (Hg) is a persistent, mobile and highly toxic heavy metal pollutant with a complex biogeochemistry that varies with its chemical form (speciation) and redox state (Mason et al., 1994; Fitzgerald and Lamborg, 2004). It exists in various inorganic and organic forms in the environment, most notably elemental Hg (Hg^0), oxidized divalent/ionic Hg (Hg^{2+} : which is typically complexed with various ligands and has a strong affinity for sulfides and organic matter), organometallic Hg (of which MMHg is of particular interest), and particle-bound-Hg (PBM), which may include the previous forms. MMHg is a neurotoxin that readily biomagnifies up the aquatic food chain (e.g., Porcella, 1994; Clarkson, 1990). Because MMHg is almost completely absorbed in the gastrointestinal tract and transported throughout the body, consumption of contaminated fish can lead to severe poisoning in both humans and wildlife (Wren, 1986; Clarkson, 2002).

The main source of MMHg in the oceanic environment is believed to be in situ production by natural processes (Fitzgerald et al., 2007). Mercury can become methylated by a number of biotic and abiotic means, with biological methylation likely dominating in the environment (Fitzgerald et al., 2007; Mills et al., 2003; Nikolaus et al., 2003). A variety of organisms are capable, under certain conditions, of transforming Hg^{2+} to MMHg. Among these, sulfate reducing and Fe-reducing bacteria (SRB) are believed to

be the most important (Fitzgerald and Lamborg, 2004). The main source of MMHg in open ocean water is not clear but likely involves, to some extent, methylation by microbes in low oxygen microenvironments within particulate organic matter during remineralization processes (Wang et al., 2012; Sunderland et al., 2009). In addition, submarine hydrothermal vents, where both elevated concentrations of Hg and SRB have been found, have been hypothesized as a deep marine source of MMHg (Kraepiel et al., 2003; Lamborg et al., 2006). However, Hg is apparently quickly sequestered near the vents and deep waters near the vents are not typically elevated in Hg so they are likely not a significant source of MMHg to the oceans (Lamborg et al., 2006; Fitzgerald et al., 2007). In contrast, little is known about mercury at cold seeps; as far as we are aware there have been no published studies of Hg at these sites.

The northern Gulf of Mexico (nGoM) is a diverse marine system that supports a vital fishery along the southern coast of the United States. The nGoM has numerous cold seeps, areas at the bottom of the water column where fluids containing hydrocarbons (crude oil and natural gas) and other constituents are released from geologic structures below (Sassen et al., 2004; Lapham et al., 2008). These seeps mostly occur along faults and fissures created by sedimentary, salt-driven tectonics (Lapham et al., 2008; Kennicutt et al., 1988). As upwelling fluids reach the sediment–water interface, entrained gases may become crystallized into gas hydrates or escape through bubble plumes or mud volcanoes (Dimitrov, 2003; Milkov, 2004). It is well known that cold seeps, where there are high rates of sulfate reduction and anaerobic hydrocarbon oxidation, support

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a diverse community of chemosynthetic organisms and microbial populations (e.g., Brooks et al., 1987; Fisher et al., 2000; Lanoil et al., 2001; Lloyd et al., 2006). The seeps are also responsible for carbonate reefs and chimneys, which represent the degradation and complete mineralization of hydrocarbons in a natural system (Roberts and Aharon, 1994).

Cold seeps have been an active area of new discovery and research since the 1980s (Paull et al., 1984); however, little is known about the biogeochemical cycling of Hg at cold seeps. Of particular interest is whether they serve as significant sources of MMHg to Gulf waters and its ecosystem. Given that cold seeps have a thriving microbial community capable of methylating Hg, and have an additional geologic source of Hg (Hg is present in the gases and fluids continually evolved from cold seeps), it is plausible that significant amounts of MMHg may be produced at these sites. Indeed, the chemical environment in cold seeps include areas with low redox potentials and the presence of hydrocarbons, conditions that are ideal to facilitate the growth of microbial organisms that can methylate Hg such as SRB and anaerobic methanotrophic archaea (Stokke et al., 2012; Levin, 2005). The source of the Hg in the petroleum system is not well known but general hypotheses include: (1) Hg liberated in the earth's crust driven by heat and pressure that migrates as a vapor to the traps in which oil and gas accumulate (Wilhelm et al., 2001), and (2) Hg that is co-deposited with the original organic matter making up the petroleum.

Typically, elemental Hg is the dominant species detected in natural gas, gas condensates and crude oil but dimethyl-Hg and mercuric halides may contribute trace amounts to the total Hg concentration (Wilhelm et al., 2001). Most crude oils processed in the US have relatively low Hg levels (<10 ng/g) (Wilhelm et al., 2007); in the Gulf of Mexico, the average concentration of total-Hg in crude oils was 2.1 ng/g from seven different oil streams (Shafawi et al., 1999). Elemental Hg concentrations in natural gas are highly variable but have been reported to range from 1 to 200 ng/g (Ryzhov et al., 2003). About 20–30 tons of Hg is recovered from natural gas by the European Union every year (UNEP, 2011). Thus, natural seepage of the petroleum system at cold seeps could provide a significant source of elemental Hg to the deep-water Hg budget.

Recently, mass dependent fractionation (MDF) of the seven stable isotopes of Hg has been demonstrated for geological processes (e.g., Smith et al., 2005) and biological processes (e.g., Kritee et al., 2007). In addition, mass independent fractionation (MIF) has been shown to occur for photochemical processes (e.g., Bergquist and Blum, 2007). As a result, Hg isotopic fingerprints have been used as a diagnostic tool to discriminate among Hg sources (e.g. Biswas et al., 2008). For cold seeps, the Hg isotopic composition may differ between cold seep and background sediments due, in part, to: (1) a different proportion of Hg sources (geologic “from below” and deposition “from above”), (2) different levels of biological activity (and associated biotic transformations of Hg), and (3) varying redox conditions and sequestration of Hg as cinnabar (HgS_{solid}).

The main objective of the present study was to determine if there are differences in mercury (total-Hg, MMHg, and Hg isotopic composition) between cold seep and background (control) sites to assess whether cold seeps are significant sources of Hg and MMHg to the nGoM deep marine environment. Here we report results for sediment from three different locations from the Woolsey Mound cold seep complex and from two background areas off the coast of Louisiana.

2. Materials and methods

2.1. Site descriptions

Sediments were obtained from 5 different locations in the nGoM off the Louisiana coast southeast of Grand Isle, LA, USA

(Fig. 1). Background sites were designated as Hg-1 and Hg-2, and cold seep sites as Hg-3, Hg-4, and Hg-5 (Fig. 2). Table 1 provides GPS coordinates and depths for each sampling site. The average water depth was 868 m. The samples stem from one of the most studied cold seeps in the GoM, Woolsey Mound in Mississippi Canyon 118. The site serves as a seafloor observatory for the long-term study of gas hydrates. Seismic surveys of the sub-bottom geology have been conducted and near-surface accumulation and seepage of the petroleum hydrocarbon system are well known (Simonetti et al., 2013, and references therein). Extensive coring programs have been conducted for lithologic logging and many have been subsampled for geochemical and microbial analysis (Bowles et al., 2011; Lapham et al., 2008). The rates and distribution of sulfate reduction and methane flux have been mapped and detailed habitat maps provide information on the distribution and locations of various chemosynthetic organisms. In addition, Woolsey Mound is also located relatively close to the Deepwater Horizon/Macondo Well incident, approximately 10 nautical miles to the north-northwest.

2.2. Core collection and handling

Samples were collected by the Mississippi Mineral Resources Institute (MMRI) using a box corer. MMRI has extensive experience studying and sampling Woolsey Mound. The samples contained macro- and micro-organisms that confirm that they were from the cold seep. On board the ship, two punch cores were collected from each box core using acid washed polycarbonate tubes. Cores for sites 1, 2 and 3 were 15 cm in length, cores 4 and 5 were 23 cm in length. The tubes were labeled (including direction), placed into a plastic bag, followed by an outer non-UV penetrable amber seal tight bag. Cores were stored upright in a freezer on the ship and delivered to the University of Mississippi on dry ice within 72 h. Cores were thawed in a laminar flow clean bench and divided using a titanium knife. Cores 1, 2 and 3 were divided into three 5 cm intervals, and cores 4 and 5 were divided into four equal intervals of about 5.75 cm in length. The sections were transferred into pre-cleaned 250 mL wide-mouth amber glass jars with PTFE-lined caps (I-Chem; VWR Scientific), homogenized using a Teflon coated spoon, and stored in a freezer until analysis. Samples were allowed to air dry in a laminar flow clean bench prior to analysis.

2.3. Analytical methods

Because the aim of this study was simply to compare mercury speciation and isotopic composition between cold seep and background sites, redox measurements, high resolution depth profiles,

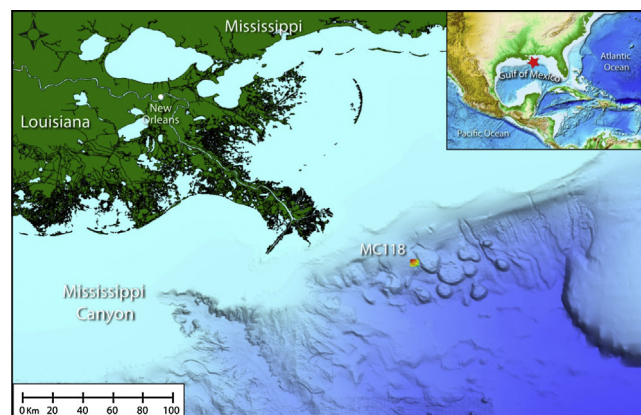


Fig. 1. Map showing the general sampling location (MC118) off the Louisiana coast in the Gulf of Mexico.

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