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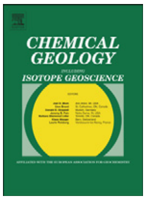

Tracing mercury seawater vs. atmospheric inputs in a pristine SE USA salt marsh system: Mercury isotope evidence

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ABSTRACT

Salt marshes can be a significant source of MeHg in coastal marine organisms, however the sources and cycling of Hg in salt marsh sediments, and in coastal environments in general, remain unclear. We analyzed surface and cored sediments from a salt marsh and adjacent upland sand dune in Cabretta Island, Georgia, USA, for total mercury (Hg_T), Hg isotopes and trace metal concentrations to better constrain the sources of Hg in this coastal environment. Hg_T concentrations are lower in the upland sands (1–6 ng/g) than in the marsh sediments (6–16 ng/g). Hg_T shows a positive correlation with total organic content (TOC) and increasing proportion of fines in the sediments. Trace metal concentrations also show a positive correlation with Hg_T in the marsh sediments regardless of chemical affinity (i.e. chalcophile, siderophile or lithophile). All these data are consistent with surface adsorption (either directly on to sediments or on to organic matter) as a dominant mechanism of Hg and metals accumulation in the marsh sediments. The surface sediments show significant mass independent fractionation (MIF) of odd Hg isotopes: the upland dune sands have zero to slightly negative Δ^{199}Hg (−0.07‰ to −0.14‰) and the marsh surface sediments have positive Δ^{199}Hg (0.48‰ to 0.79‰). As in the surface samples, well-sorted sand layers in the cored sediments have low Hg concentrations and zero to slightly negative Δ^{199}Hg, whereas fine particle-rich layers have higher Hg concentrations and positive Δ^{199}Hg values. In the absence of any evidence for MIF of Hg isotopes by bacteria mediated methylation–demethylation reactions, the observed Hg isotope differences between marsh and upland sands can be explained by different sources of Hg. We suggest that local atmospheric Hg deposition dominates the Hg budget in the ombrotrophic upland sand, while the positive MIF in the marsh sediments are consistent with Hg dominantly of seawater origin. While in situ processes, like photoreduction and evasion can overprint the Hg depositional isotope signature, their effect on the sediments is currently unconstrained. Nevertheless, our data show that Hg isotopes can delineate different sources of Hg in a pristine coastal environment and at small spatial scales. Thus natural background isotope variability should be assessed as a baseline when Hg isotopes are used as tracers of Hg in anthropogenically-influenced sites.

1. Introduction

Mercury is a toxic metal that accumulates in the environment, and anthropogenic inputs of mercury have increased concentrations in many systems that are problematic for humans and animals. Mercury is considered a global pollutant because elemental Hg can be transported over long distances in the atmosphere and makes its way into the ecosystem, where once methylated, it biomagnifies (USEPA, 1997; National Academy of Sciences, 2000). In any toxic metal cycle, the role of salt marshes is critical as they represent the interface between terrestrial and oceanic ecosystems. Salt marshes are often termed the “kidneys of the earth” (Mitsch and Gosselink, 1986) because they are natural sinks for environmental contaminants such as metals deposited from tidal water, the atmosphere and the surrounding catchment. Wetlands and salt marshes have often been used in pollution control and anthropogenic waste treatment (Dunbabin and Bowmer, 1992; Odum et al., 2000). However, salt marshes are also known sources of nutrients, bacteria, and other dissolved constituents (Ba, CH_4, Fe, U, As, Cu) to coastal water (Moore, 1997; Shaw et al., 1998; Charette and Buesseler, 2004; Charette et al., 2005; Charette and Sholkovitz, 2006; Paytan et al., 2006).

Salt marshes have been shown to be sources of net mercury methylation and export to estuaries and coastal waters (e.g. Mitchell and Gilmour, 2008 and references therein), with the potential to adversely affect coastal ecosystems and fisheries. However, it is unclear whether Hg in salt marshes, particularly in environments away from direct anthropogenic inputs is derived primarily from atmospheric deposition, or from seawater that is tidally circulating in the marsh. If salt marsh dominantly methylates seawater-derived Hg,

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then this has implications for the mass balance and cycling of total Hg vs. methyl-Hg, i.e. a salt marsh may simply act as a methylating Hg source, while at the same time sequestering Hg from seawater. To this extend, the study in the Bay of Fundy salt marsh (Hung and Chmura, 2006), suggested that the main source of mercury in those salt marsh sediments was indeed seawater, and not atmospheric deposition.

Mercury accumulation and potential release of Hg from salt marsh sediments can be a complex function of different physicochemical conditions and it depends on organic matter (Benoit et al., 1998; Mason and Lawrence, 1999; Hammerschmidt et al., 2004; Fitzgerald et al., 2007; Hollweg et al., 2009), the presence of Fe and Mn oxides, hydroxides (Rasmussen, 1994) and sulfides (Andersson et al., 1990) as well as grain size distribution. Mercury can bind to the sediment organic fraction through adsorption, ion exchange, co-precipitation and chelation (Andersson, 1979; Schuster, 1991), and these processes are enhanced in fine-grained sediments (Williams et al., 1994). Under anoxic conditions, Hg co-precipitates with sulfides, but if conditions become oxidizing Hg can be mobilized and subsequently released from such sediments (Gambrell, 1994; Williams et al., 1994).

Recently, the discovery of isotope fractionation of Hg has opened a new avenue for identifying sources and helps put additional constrains in the cycling of mercury in the environment. Mass dependent fractionation (MDF) and mass independent fraction (MIF) of mercury isotopes have now been observed in a variety of natural materials, including meteorites (Lauretta et al., 2001), hydrothermal systems (Smith et al., 2005, 2008; Sherman et al., 2009) mine waste (Stetson et al., 2009), crustal rock samples (Smith et al., 2008), arctic snow (Sherman et al., 2010), biological samples (Bergquist and Blum, 2007; Jackson et al., 2008; Das et al., 2009; Senn et al., 2010) sediments and coal (Jackson et al., 2004; Foucher and Hintelmann, 2006; Biswas et al., 2008; Ghosh et al., 2008; Jackson et al., 2008; Foucher et al., 2009; Gehrke et al., 2009; Feng et al., 2010; Lefticariu et al., 2011). Experimental studies have confirmed field-based interpretations and have begun to provide constraints on the mechanisms and type of Hg isotope fractionation for processes such as bacterial methylation/demethylation and photoreduction.

Hg isotopes have also provided important information on the sources of Hg in estuarine sediments. For example, the Hg isotope compositions of San Francisco bay wetland sediments have revealed two dominant anthropogenic sources of Hg related to gold mining (Gehrke et al., 2011a), and the spatial correlation of Hg isotopes between those sediments and near-shore fish was taken as evidence that Hg in local fish is sourced from local sediments (Gehrke et al., 2011b). A similar conclusion was reached in the lake Baikal region (Perrot et al., 2010). Also, the mercury contents in the surface sediments of Idrijca River, Socă/Isonzo River and Gulf of Trieste were attributed to variable mixing (ranging from >90% to <50%) between anthropogenic sources (Idrija mercury mine, western Slovenia) and natural sources (marine Hg from Adriatic Sea) (Foucher et al., 2009).

While the above studies have shown the potential of Hg isotopes to trace Hg pathways in the coastal environment, they have dealt mostly with significantly anthropogenically-impacted environments. While contaminated sites are an obvious priority for research, we currently lack a full understanding of Hg isotope systematics in natural coastal environments, away from local point sources. Here we present a combined Hg isotope and trace metal study of sediments from the salt marsh and adjoining sandy upland from Cabretta Island, a Holocene barrier island off the coast of Georgia, USA, with the goal of delineating seawater vs. atmospheric deposition sources of Hg in a pristine SE USA salt marsh system. The only sources of Hg in this barrier island are net atmospheric deposition (including any by seaspray due to the proximity to the ocean) and Atlantic seawater inundating the marsh during high tide. We will show that the marsh and adjoining sandy upland have significantly different Hg–isotope (both MDF and MIF) and trace metal systematics, broadly consistent with a seawater origin of Hg in the marsh, and local atmospheric deposition for the sandy upland and we will further discuss the mechanisms that can lead to the observed isotope systematics.

2. Study area and sample selection

Cabretta Island is a Holocene barrier island on the seaward side of Sapelo Island, Georgia, on the USA eastern seaboard (Fig. 1a, b) (Pomeroy and Wiegert, 1981). The island consists of a sandy beach, sandy upland and a salt marsh. The Cabretta salt marsh is connected to the ocean by a tidal creek, and it is isolated from Sapelo island to the west by the creek and N and S inlets. Stratigraphy was previously determined with sediment cores collected along a beach–marsh transect (Wilson et al., 2011). Attempts to date of the top-most sample (~30 cm depth) from the marsh core using Pb-210 and Cs-137 methods (Sharma et al., 1987) showed no excess radiogenic nuclides suggesting pre-industrial or older time of deposition for the marsh sediments at depth (Willard Moore, pers. comm.).

Beneath the sandy upland there is a fresh water lens (Wilson et al., 2011). This fresh water lens is entirely ombrotrophic, therefore total atmospheric deposition (wet and dry, including that of seaspray) should dominate any Hg inputs on the upland and presumably the underlying sand sediments. The salt marsh is dominated by typical *Spartina alterniflora* vegetation. A large part of the marsh is inundated daily by semi-diurnal tides. Therefore the source of Hg in the marsh should be a combination of total local atmospheric deposition and seawater that floods the tidal creek during high tide. The transition zone between the marsh and the sandy upland is marked by an area of sparse vegetation dominated by *Salicornia* spp., indicating higher salinities than seawater due to infrequent seawater inundation and subsequent evaporation. Sapelo island is part of the Mercury Deposition Network (MDN), of the National Atmospheric Deposition Program. The network's sampling site (site "GA33") is located 4.5 km S–SE of our study area. The total Hg wet deposition for the GA33 was calculated at 7.2 μg/m^2 for year 2011, based on data from the MDN (accessed on-line January 2012), and we assume similar deposition for our study transect.

We collected surface sediments along the beach–salt marsh transect (Fig. 1c) by scooping the top 2 cm of undisturbed sediment in pre-cleaned polystyrene tubes. All sampling locations were free of overlying vegetation. We augmented the data with sediments recovered from two cores (labeled TT-2 in the marsh and TT-4 in the sandy upland) from the Wilson et al. (2011) study, in order to better understand and constrain the Hg distribution and isotope variability in the sediments as a function of physiographic division and depth. The marsh core (TT-2) is 4 m deep and was collected within the salt marsh from an area that is typically inundated by the adjacent creek water during diurnal tides. The top part of the core consists of marsh mud which grades into a mixture of silt and clay followed by a thick layer of silt, clay and sand mixed in variable proportions. The sandy upland core (TT-4) is 1.5 m deep. The top ~1.2 m of the core consists mostly of well-sorted quartz sand. The bottom 0.3 m of the core (1.2–1.5 m) transitions to a mixture of silt and mud, as also evidenced by the increased proportion of fines (operationally defined here as <62 μm size particles) in the sediment. This bottom layer can be traced to the marsh surface through inspection of other cores along the transect (Fig. 1c). We interpret this feature as the surface of a paleomarsh that has been covered by the transgressing barrier island.

The cores were collected by vibracoring in 3-inch casing, which resulted in some sediment compaction on the top part of the sediment column. The shallowest part of the sandy upland core and plant root zone (~10–20 cm) was not collected. For labeling purposes, we labeled the depth increments starting at 0-cm (for TT-4) at the top of the recovered core, but it should be understood that the top of the core does not represent the actual surface, rather 10–20 cm bellow