Geochemistry of Mercury (Hg) in the Northeastern Gulf of Mexico after the *Deepwater Horizon* Oil Spill

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Introduction

Due to its strong reactivity towards environmental conditions as well as its long residence time in the atmosphere (0.5-2 years), mercury Hg pollution is a concern even in remote areas. Specific attention has to be paid to aquatic ecosystems, since seafood consumption is the major way of exposure to Hg for humans. This is because, once it enters water systems, Hg can be converted by microorganisms to an organic form (monomethylmercury, MMHg), a highly bioaccumulable Hg compound [1]. Due to its importance for U.S. fisheries, the Gulf of Mexico (GoM) is a key area to study the biogeochemistry of Hg. The measurement of stable Hg isotopic composition in natural samples now allows to track Hg sources and transformations in the environment [2]. Our study aimed to identify the main processes that affect the cycle and the bioaccumulation of Hg in the GoM, and to evaluate the role (direct or indirect) of the *Deepwater Horizon* oil spill (DWH) in Hg bioavailability for the food webs.

Experimental

Fish and atmospheric samples were collected during several field campaigns from 2010 to 2013 and were freeze-dried, ground and extracted with acid mixtures for further analysis. Atmospheric samples were collected via Au-traps or filters that were then combusted and the Hg was trapped in solution for further analysis. Hg compounds (iHg and MMHg) concentrations in samples were measured via Gas Chromatography-Atomic Fluorescence Spectrometry (TekranSeries2700®), and total Hg isotopic composition was measured with a Neptune multi-collector ICPMS (Thermofinnigan®) coupled to a Cold Vapor Generator (HGX-200, CETAC®).

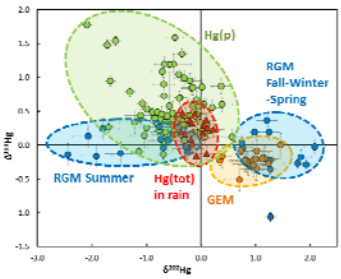

Figure 1. Hg Isotopic signatures of particulate Hg (Hg(p)), reactive gaseous mercury (RGM), gaseous elemental mercury (GEM) and total Hg in rain.

Results and Discussion

Different Hg compounds from the atmosphere, collected near Pensacola, FL, showed atmospheric background concentrations and revealed compound-specific isotopic signatures, which allowed us to identify several atmospheric Hg transformations, such as Hg(II) photoreduction in-aerosols (+MIF, see Fig. 1). Tilefish (*Lophalatilus chamaleonticeps*) were caught along the shelf-break of the northeastern GoM. Fish that were caught close to the DWH showed significantly lower Hg and MMHg levels in their muscle and liver than fish caught farther away (Fig. 2). We hypothesize the Mississippi plume, as well as microbes that are also involved in oil degradation, to limit MMHg bioavailability for organisms. A significant correlation was observed between Hg concentrations and δ^{202}Hg, as well as systematic offset in δ^{202}Hg between muscle and liver, hence we identify *in-vivo* MMHg degradation as an important process.

Conclusions

Our study confirms the ability of Hg isotopes to be a powerful tracer of Hg cycling in the environment. Hg isotopic composition in the atmosphere allowed us to constrain Hg sources (mostly atmospheric deposition from global Hg mixing) in the coastal northeastern GoM, whereas Hg isotopic composition archived in fish showed specific features and indicates that MMHg can be demethylated both in the water column (before going to the food webs) and *in-vivo*. The role of the DWH in changing fish feeding ecology/rate may significantly affect the fish response to Hg exposure and should be investigated.

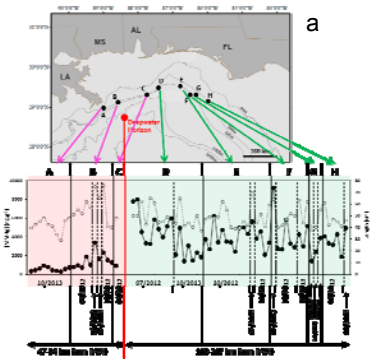

Figure 2. (a) Locations of sampling stations for Tilefish and (b) MMHg concentrations (ng Hg per gram of muscle) and fish length for the 8 sampling stations during different sampling campaigns (April, July and October 2012 and 2013).

Acknowledgements

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References

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[2] Bergquist, B.A. and J.D. Blum, Elements, **5**, 353-357 (2009).