Science of the Total Environment 640–641 (2018) 454–465

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Geochemical modeling of mercury speciation in surface water and implications on mercury cycling in the everglades wetland

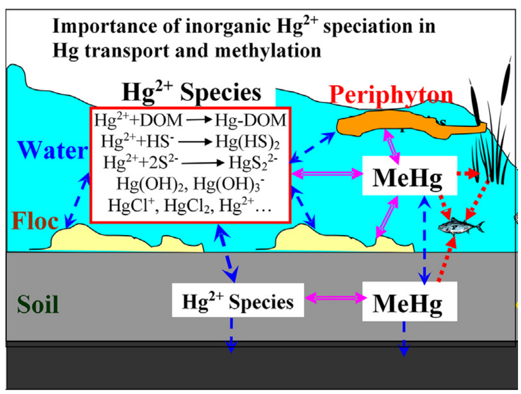
Ping Jiang [a], Guangliang Liu [a,b], Wenbin Cui [a], Yong Cai [a,c,*]

[a] Department of Chemistry & Biochemistry and Southeast Environmental Research Center, Florida International University, Miami, FL 33199, USA
[b] Institute of Environment and Health, Jianghan University, Wuhan, China
[c] State Key Laboratory of Environmental Chemistry and Ecotoxicology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing, China

HIGHLIGHTS

- Geochemical modeling of speciation of inorganic mercury (iHg) in Everglades water
- Even at low levels sulfide complexation with Hg to form HgS_2^{2-}, $HgHS_2^-$, and $Hg(HS)_2$
- Hg-DOM complexes prevalent without considering sulfide
- Relation of distribution of Hg-S and Hg-DOM species to methyl Hg production and fate

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 16 February 2018
Received in revised form 28 April 2018
Accepted 17 May 2018
Available online xxxx

Keywords:
Mercury speciation
Geochemical modeling
PHREEQC
Everglades wetland

ABSTRACT

The geochemical model PHREEQC, abbreviated from PH (pH), RE (redox), EQ (equilibrium), and C (program written in C), was employed on the datasets generated by the USEPA Everglades Regional Environmental Monitoring and Assessment Program (R-EMAP) to determine the speciation distribution of inorganic mercury (iHg) in Everglades water and to explore the implications of iHg speciation on mercury cycling. The results suggest that sulfide and DOM were the key factors that regulate inorganic Hg speciation in the Everglades. When sulfide was present at measurable concentrations (>0.02 mg/L), Hg-S complexes dominated iHg species, occurring in the forms of HgS_2^{2-}, $HgHS_2^-$, and $Hg(HS)_2$ that were affected by a variety of environmental factors. When sulfide was assumed nonexistent, Hg-DOM complexes occurred as the predominant Hg species, accounting for almost 100% of iHg species. However, when sulfide was presumably present at a very low, environmentally relevant concentration (3.2×10^{-7} mg/L), both Hg-DOM and Hg-S complexes were present as the major iHg species. These Hg-S species and Hg-DOM complex could be related to methylmercury (MeHg) in environmental matrices such floc, periphyton, and soil, and the correlations are dependent upon different circumstances (e.g., sulfide concentrations). The implications of the distribution of iHg species on MeHg production and fate in the Everglades were discussed.
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1. Introduction

Elevated levels of mercury (Hg), especially methylmercury (MeHg), have been measured in fish and wildlife in the Everglades, a subtropical

* Corresponding author at: Department of Chemistry & Biochemistry and Southeast Environmental Research Center, Florida International University, Miami, FL 33199, USA.
E-mail address: cai@fiu.edu (Y. Cai).

https://doi.org/10.1016/j.scitotenv.2018.05.216
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wetland ecosystem located in South Florida, United States, over the last few decades (Jordan, 1990; Ware et al., 1990; Lange et al., 1994; Fleming et al., 1995; Duvall and Barron, 2000; Scheuhammer et al., 2007; Rumbold et al., 2008). Despite extensive studies on Hg contamination in the Everglades (Cleckner et al., 1998; Gilmour et al., 1998; Liu et al., 2008; Li et al., 2012), much remains unclear about how elevated levels of Hg in fish and wildlife are accumulated in this system (Lange et al., 1994; Hurley, 1998). One of the particular concerns is the lack of study that deals with the speciation of inorganic Hg (iHg), whether being dissolved Hg ions (or neutral species) or bound to particles and organic matter, and the effect of these Hg species on Hg transformation (e.g., methylation).

In aquatic environments, iHg is present primarily as various inorganic and organic Hg(II) complexes plus elemental Hg (Hg(0)) (Cai et al., 2012). The common inorganic Hg(II) compounds in freshwater include $Hg(OH)_2$, HgOHCl, and $HgCl_2$, and in seawater Hg-chloride complexes prevail (e.g., $HgCl^+$, $HgCl_2$, $HgCl^{3-}$, and $HgCl_4^{2-}$), besides Hg-sulfide complexes if sulfide is present (Morel et al., 1998; Ullrich et al., 2001)(Morel et al., 1998). However, most iHg would be complexed with dissolved organic matter (DOM) in natural freshwater because of the strong association of Hg with DOM particularly the thiol groups (-RSH) within DOM (Reddy and Aiken, 2001). As some iHg species may be more bioavailable to Hg methylating bacteria (e.g., sulfate and iron reducing bacteria), the relative distribution of dissolved iHg species may influence MeHg production in aquatic ecosystems, as reported previously (Benoit et al., 1999; Najera et al., 2005). It would be helpful to know the distribution patterns of iHg species (e.g., what species are present at what percentages) for a better understanding of aquatic Hg cycling in Florida Everglades. Since it is practically impossible to use analytical techniques to determine all inorganic Hg species present through complexing with inorganic and organic ligands in aqueous phase, geochemical modeling provides a good alternative method to examine the distribution of Hg species (Shaw et al., 2006; Navarro et al., 2009).

Geochemical models such as WATEQ (WATer Equilibrium), MINEQL (MINeral EQuiLibrium), MINTEQ (MINEQL+WATEQ), and PHREEQC (pH and REdox EQuilibria in C) are frequently used thermodynamic studies of Hg speciation (Caruso et al., 2008; Liem-Nguyen et al., 2017; Meng et al., 2018). For example, thermodynamic modeling of the chemical speciation of Hg(II) and MeHg in boreal wetlands was performed using the Solgaswater (WinSGW), with a special focus on the effects of complexation of Hg species with organic thiols, inorganic sulfides, and polysulfides, and the results suggest the dominance of NOM-associated thiols on Hg speciation (Liem-Nguyen et al., 2017). In the stratified water column of Offatts Bayou (Galveston Bay, Texas), $HOHgHS^0$, HOHgHS(DOM), $HgSHS^{2-}$, and HgS_2^{2-} were suggested to be major species of mercury (Han et al., 2007). Even for the Everglades, a few studies have attempted to use models such as WHAM (Windermere Humic Aqueous Model) and PHREEQC for Hg speciation (Reddy and Aiken, 2001). These studies suggest that the complexes of Hg and sulfide dominate with measurable sulfide concentrations, while Hg-DOM complexes play a major role in the surface water with low sulfide concentrations. In sulfidic pore water in the Everglades, neutral HgS^0 species was shown as a major species of iHg during $MINEQL^+$ simulations and this species was suggested to be related to Hg methylation through bacterial uptake by passive diffusion (Benoit et al., 1999).

Water levels is a key factor controlling the environmental conditions and thus affecting Hg cycling in the Everglades. Anoxic conditions may change with water level variations due to the presence of dikes, levees, and other landscape features in this wetland mosaic, which may affect Hg methylation. The water chemistry in the Everglades varies significantly depending on locations, and a decreasing gradient from north to south for nutrient (e.g., nitrogen and phosphorus), sulfate, and DOM is generally present (Stober et al., 2001). As a result of variations in water chemistry, Hg speciation is expected to differ from location to location in the Everglades. The complexity and variations in Hg speciation across this wetland may not be completely reflected in studies performed for localized areas, and ecosystem-wide research on Hg species distribution are warranted for this purpose. The objective of this study is to understand how geochemical factors such as pH, Eh, and inorganic and organic ligands (e.g., sulfide and DOM) affect iHg speciation and the implications of iHg species distribution on Hg cycling in the Everglades, through modeling iHg speciation using PHREEQC. The distribution of inorganic Hg species in surface water throughout the entire Everglades was examined by geochemical modeling for different R-EMAP sampling sites. The patterns of inorganic Hg species distribution are related to MeHg levels in environmental matrices to examine how inorganic Hg species potentially affect the production and fate of MeHg.

2. Methods

2.1. Data sources

To examine Hg speciation at the ecosystem scale, datasets containing concentrations of Hg and related geochemical parameters are needed. The U.S. Environmental Protection Agency (EPA) Everglades Regional Environmental Monitoring and Assessment Program (R-EMAP), which samples the entire Everglades freshwater marsh and generates a massive dataset for concentrations of iHg, MeHg, and a variety of biogeochemical parameters, provides a unique data source suitable for ecosystem-wide Hg speciation modeling. The data used for this study are mainly from the dataset generated in the R-EMAP Phase III sampling in 2005. The R-EMAP Phase III sampling was conducted at 109 randomly selected stations in the dry season (May) and 119 in the wet season (November) in the four management units of the Everglades, namely Arthur R. Marshall Loxahatchee National Wildlife Refuge (LNWR or Water Conservation Area 1, WCA-1), Water Conservation Areas 2 and 3 (WCA-2 and WCA-3), and Everglades National Park (ENP) (Fig. 1). The dataset includes most model input parameters including total mercury (THg), MeHg, and a large number of biogeochemical parameters such as pH, dissolved oxygen, sulfide, and dissolved organic carbon (DOC).

2.2. Geochemical modeling

The PHREEQC program from U.S. Geological Survey (USGS), where the acronym PHREEQC stands for PH (pH), RE (redox), EQ (equilibrium), and C (program written in C), was used to provide thermodynamic simulations of iHg speciation in Everglades surface water using the concentrations of Hg and other geochemical parameters determined in the R-EMAP Phase III sampling. Among all the sampling locations, there are 69 stations in May and 113 in November that contain all necessary data suitable for modeling, and the iHg speciation was examined for these locations. The modeling was performed as three scenarios based on the concentrations of sulfide. For the stations with sulfide concentrations reported (>0.02 mg/L), the reported values were used in the modeling. For the stations without detectable sulfide reported, a scenario representing low sulfide was modeled by assigning a sulfide concentration of 3.2×10^{-7} mg/L, while the other scenario with presumably sulfide non-existence was done by setting sulfide concentration to 0 mg/L. This treatment for sulfide and special considerations for some other geochemical parameters and Hg-ligand complexes were described in detail below.

It should be pointed out that we modeled iHg speciation for each of these sampling stations and then examined the differences in iHg speciation among these stations. Although the spatial patterns of iHg species distribution were examined, we did not include any transport schemes for Hg species in the model. We used this treatment mainly based on two considerations. One reason is that the Everglades is a wetland with very slowly moving sheet flow through the system driven by water levels in Lake Okeechobee and local rainfall (Stober et al., 2001). The other consideration is that the R-EMAP employed a probability

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