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Inhibition of Precipitation and Aggregation of Metacinnabar (Mercuric Sulfide) by Dissolved Organic Matter Isolated from the Florida Everglades

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Precipitation and aggregation of metacinnabar (black HgS) was inhibited in the presence of low concentrations (≥3 mg C/L) of humic fractions of dissolved organic matter (DOM) isolated from the Florida Everglades. At low Hg concentrations ($\leq 5 \times 10^{-8}$ M), DOM prevented the precipitation of metacinnabar. At moderate Hg concentrations (5×10^{-5} M), DOM inhibited the aggregation of colloidal metacinnabar (Hg passed through a 0.1 μm filter but was removed by centrifugation). At Hg concentrations greater than 5×10^{-4} M, mercury formed solid metacinnabar particles that were removed from solution by a 0.1 μm filter. Organic matter rich in aromatic moieties was preferentially removed with the solid. Hydrophobic organic acids (humic and fulvic acids) inhibited aggregation better than hydrophilic organic acids. The presence of chloride, acetate, salicylate, EDTA, and cysteine did not inhibit the precipitation or aggregation of metacinnabar. Calcium enhanced metacinnabar aggregation even in the presence of DOM, but the magnitude of the effect was dependent on the concentrations of DOM, Hg, and Ca. Inhibition of metacinnabar precipitation appears to be a result of strong DOM–Hg binding. Prevention of aggregation of colloidal particles appears to be caused by adsorption of DOM and electrostatic repulsion.

Introduction

The toxicity of trace metals in natural waters depends on the aqueous speciation of those metals. As a soft metal, mercury interacts strongly with soft ligands such as thiols, sulfide, and other sulfur-containing ligands (*1*). In the presence of sulfide, mercury forms soluble mercury–sulfur complexes [e.g., $HgSH^+$, $Hg(SH)_2$, HgS_2H^-, HgS_2^{2-}] or insoluble mercuric sulfide (HgS) solids depending on the pH, sulfide, and Hg concentrations. Generally, formation of solid HgS is favored at low pH and low sulfide concentrations, while soluble

mercury–sulfur complexes are expected at high pH and high sulfide concentrations (*2–4*).

Mercuric sulfide occurs as two polymorphs: cinnabar (red HgS) and metacinnabar (black HgS). The solubility product of cinnabar is given as (*5*)

$$HgS_{red} + H^+ \leftrightarrow Hg^{2+} + HS^-$$

$$K_{sp} = 10^{-36.8} \ (20 \ °C, 1.0 \ M \ I)$$
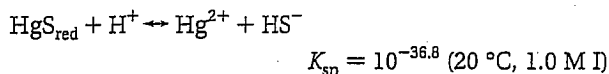
The solubility product of metacinnabar is $10^{-36.4}$. Formation of sulfide minerals from supersaturated solutions occurs in a sequence of steps including nucleation, growth of primary crystallites (usually few tens of nanometers in size), and aggregation of these microcrystals into larger (micron-sized) particles (*6*). Although metacinnabar should readily transform to cinnabar at ambient temperature (*7*), metacinnabar has been found to be the most common form in lab precipitation experiments and in natural environments (*8*, *9*). Formation of metacinnabar at low temperatures is attributed to a nonstoichiometric arrangement of Hg and S and the presence of impurities in HgS (*7*). Because of its low solubility, HgS is considered to be an important sink for Hg in sulfidic environments (*3*, *10*).

It is well-known that dissolved organic matter (DOM) complexes mercury and other trace metals and affects the surface-dependent geochemical processes such as particle growth, flocculation, coagulation, and dissolution (*11*, *12*). For example, DOM enhances the solubility of cinnabar, causing a significant release of mercury into solution (*13*). However, the effect of organic matter on the precipitation of cinnabar or metacinnabar has not been studied before. Because of the high affinity between mercury and sulfide, it is generally assumed that DOM has no effect on the formation of HgS and other Hg-sulfide complexes (*3*, *4*, *14*, *15*). While cinnabar and metacinnabar have been found to occur in sediments contaminated by known sources of mercury (*7*, *16*), there is no direct evidence for their presence in historically pristine sulfidic environments that are currently showing signs of mercury contamination.

In this laboratory study, organic matter isolated from the Florida Everglades was reacted with supersaturated solutions of mercury and sulfide. We observed that humic fractions (humic, fulvic, hydrophobic, and hydrophilic acids) of DOM inhibited the precipitation and aggregation of metacinnabar. Precipitation was inhibited at relatively low mercury concentrations ($\leq 5 \times 10^{-8}$ M), and aggregation of colloidal metacinnabar was inhibited at moderate mercury concentrations (5×10^{-5} M). The results presented here may have important implications for the geochemical modeling and bioavailability predictions of mercury in aquatic environments.

Methods

Isolation and Characterization of Organic Matter. The organic matter used in the precipitation experiments was isolated from various study sites in Water Conservation Area 2 in the northern Everglades, Florida, as a part of an ongoing study to understand the cycling of mercury in the Everglades. The study sites are designated F1 (26°21′35″ N, 80°22′14″ W), 2BS (26°09′49″ N, 80°22′41″ W), and E0 (26°22′17″ N, 80°21′05″ W). These sites were chosen because the nature and the concentration of organic matter were significantly different. For comparison, well characterized Suwannee River humic (SR–HA) and fulvic (SR–FA) acid standards obtained from the International Humic Substances Society (IHSS) were also

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TABLE 1. Experimental Conditions for Precipitation Experiments

expt no.	[Hg] (M)	[sulfide] (M)	[DOC]^a (mgC L^{-1})	other reactants (M)
1	5×10^{-5}	10^{-3}		pH 2–12
2	5×10^{-5}	10^{-3}	10	pH 1.5–12
3	5×10^{-5}	10^{-3}	0–10	
4	5×10^{-8}	10^{-4}	0–10	
5	5×10^{-6}	10^{-4}	10	
	5×10^{-5}	10^{-3}	10	
	5×10^{-4}	5×10^{-3}	10	
	5×10^{-3}	10^{-2}	10	
6	5×10^{-5}	10^{-3}		10^{-2} M chloride, 10^{-3} M each of
7	5×10^{-5}	10^{-3}	filtered water samples—F1 and 2BS sites	acetate, salicylate, EDTA, cysteine, and mercaptoacetate
8	5×10^{-5}	10^{-3}	filtered waters without polyvalent cations	
9	5×10^{-5}	10^{-3}	10	10^{-5}–10^{-2} M CaCl$_2$
	5×10^{-8}	10^{-3}	10	10^{-5}–10^{-2} M CaCl$_2$

^{a} The organic matter used in these experiments is F1 hydrophobic acid (F1—HPoA) except in the case of whole water samples.

used (17). DOM samples from the Everglades (collected in April 1996) were separated into hydrophobic acids (HPoA), hydrophilic acids (HPiA), hydrophobic neutrals (HPoN), and hydrophilic neutrals (HPiN) using the XAD-8/XAD-4 resin method (18). The hydrophobic acid fractions of F1 and 2BS samples (collected in July 1997) were further separated into fulvic acid (FA) and humic acid (HA) by precipitation at pH 1 (18). The humic acid fraction represents about 3–4% of the total hydrophobic acid fraction at F1 and 2BS sites.

Organic matter isolates were characterized in terms of elemental composition, acid site density, functional group content, specific UV absorbance, and molecular weight. It was confirmed that the levels of Hg in the isolates (7.7–13.2 ng/mg isolate) were not high enough to affect the availability of sulfide for HgS formation. Elemental composition was determined at Huffman Laboratories (Golden, CO) by the method described in Huffman and Stuber (19). Carboxyl group content was determined from the amount of base (0.1 M NaOH) used in titrating a hydrogen-saturated sample to pH 8.0 after appropriate blank subtraction (20). Quantitative information on various functional group contents of the isolates was obtained using a liquid- or solid-state carbon-13 nuclear magnetic resonance (^{13}C NMR) technique (21).

Specific UV absorbance (SUVA, L mgC^{-1} cm^{-1}) was measured on the isolates by dissolving a sample in distilled water and measuring dissolved organic carbon (DOC) concentration and UV absorbance (UVA). DOC concentrations were measured on an O. I. Corporation model 700 total organic carbon analyzer and the UVA on a Hewlett-Packard Model 8453 spectrophotometer. SUVA was calculated as the ratio between UV absorbance (cm^{-1}) at 254 nm and DOC concentration (mgC L^{-1}).

Number-average molecular weights of the isolates were determined by high-pressure size exclusion chromatography (HPSEC), using a Shimadzu LC-600 pump, a Shimadzu SPD-6A UV detector, and a Waters Protein-Pak 125 modified silica gel column according to the method of Chin et al. (22). The mobile phase consisted of 4 mM sodium phosphate buffer, adjusted to 0.1 M ionic strength by NaCl at a pH 6.8. Peaks were detected at a wavelength of 224 nm. The relative standard deviations from triplicate analyses of molecular weights were 10–12%.

Precipitation Experiments. Reagent-grade chemicals and distilled water were used in all the experiments. All samples were prepared under nitrogen in a glovebox. Each reaction vessel (125 mL Erlenmeyer flask) contained isolated organic matter, Hg(II) (as HgCl$_2$), and sulfide (as Na$_2$S·9H$_2$O) at concentrations given in Table 1. Precipitation experiments were conducted at variable organic matter (F1-HPoA) concentrations (experiments 3 and 4) and Hg concentrations

(experiment 5). The effects of various model ligands (chloride, acetate, salicylate, EDTA, cysteine, and mercaptoacetate) on precipitation were studied in experiment 6. These ligands were chosen because of the wide range of binding strength of these ligands for mercury complexation (13).

The effect of unfractionated DOM on metacinnabar formation was measured by adding Hg and sulfide to filtered water samples from F1 (DOC = 38.1 mg C/L) and 2BS (DOC = 16.9 mg C/L) sites collected using ultraclean sampling techniques (experiment 7). To study the effect of polyvalent cations on cinnabar precipitation, these water samples were passed through sodium-saturated cation-exchange resins (Dowex MSC-1-H) and then reacted with mercury and sulfide (experiment 8). In the case of isolated organic matter (F1-HPoA), the effect of polyvalent cations was studied by adding variable concentrations of CaCl$_2$ in the presence of sulfide and mercury (experiment 9).

All precipitation experiments were conducted in duplicate. DOM was added from stock solutions of isolates prepared in distilled water. Solutions containing Hg and DOM were sparged with nitrogen before adding sulfide. Dissolved oxygen concentrations, measured by a colorimetric method (CHEMetrics Inc.), were less than 6×10^{-7} M (10 ppb). Stock solutions (0.1 M) of sulfide were prepared weekly in distilled water sparged with nitrogen and kept anoxic. Sulfide solutions were not standardized because a large excess of sulfide (10^{-3} M) was present in these experiments as compared to mercury concentrations (5×10^{-5} M). After sulfide addition, the pH was adjusted to 7.0 ± 0.1 using dilute NaOH or HNO$_3$, except for experiments 1 and 2 in Table 1. Ionic strength was adjusted to 10^{-2} M using NaNO$_3$.

After sample preparation, flasks were closed tightly under nitrogen atmosphere with wet ground glass stoppers and electrical tape. The flasks were then gently shaken in an orbital shaker at 150 rpm. Kinetic experiments conducted up to 30 days indicated that precipitation reactions were complete in <2 h. Based on these results, samples were reacted for ~24 h. At the end of reaction time, samples were filtered using 0.1-μm polytetrafluoroethylene filters (Whatman). Mercury concentrations in filtrates were measured on a cold vapor atomic absorption spectrophotometer (Buck Scientific model 400A). The Hg detection limit for this instrument was 2.5×10^{-9} M.

In experiment 3 (Table 1), the sample was centrifuged at 18 000 rpm (RCF = 38 724) on a refrigerated (20 ± 2 °C) centrifuge (Sorvall RC-5B). The supernatant solution was sampled at 1-, 2-, 4-, 6-, and 8-h intervals and analyzed for Hg, which was operationally defined as "dissolved" Hg. The precipitate that settled in the tube, operationally defined as "colloidal" Hg, was analyzed by X-ray powder diffraction
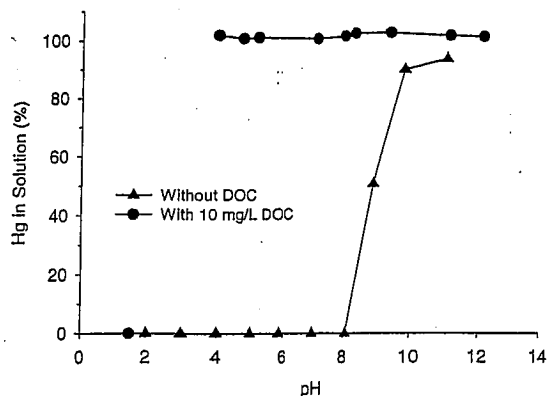
FIGURE 1. Effect of pH on the precipitation of metacinnabar (experiments 1 and 2 in Table 1): $[Hg]_{tot} = 5 \times 10^{-5}$ M; $[sulfide]_{total} = 10^{-3}$ M. Mercury concentration in solution is in the fraction that passes through a 0.1 μm filter.

(Cu $K\alpha$ radiation, Siemens D500). Electrophoretic mobility (EM) measurements (Brookhaven Instruments Zeta Plus) were made on metacinnabar that precipitated in the absence of organic matter (experiment 1) and the colloidal metacinnabar that settled in the centrifuge tube (experiment 3). EM measurements, made in triplicates at pH 7.0, were converted to ζ potential using the Smoluchowski equation (23).

Results

In the absence of dissolved organic matter, mercury combined with sulfide to form a black precipitate that was trapped on 0.1 μm filters. Analysis of the solid by X-ray diffraction spectroscopy indicated that it was predominantly metacinnabar, with one peak (at a d spacing of 3.15 Å) characteristic of cinnabar spectrum (24). Electrophoretic mobility measurements indicated that metacinnabar had a net negative surface with a ζ potential of -27.3 ± 2.3 mV. The precipitation of metacinnabar was rapid, with visible crystals forming in less than 1 h. Mercury was completely removed as metacinnabar (>0.1 μm) at pH 4–8, while greater than 90% of mercury passed through the filter at pH greater than 10 (Figure 1).

In the presence of 10 mg C/L organic matter (experiment 2, Table 1), 100% of Hg passed through the 0.1 μm filter at pH 4–12 (Figure 1). Mercury concentrations in filtered solutions (pH 7.0) monitored up to 30 days remained constant. Nearly 100% of mercury passed through the 0.1 μm filter even at relatively low DOC concentrations (≥ 3 mg C/L) (Figure 2). The amount of mercury passing through the 0.1 μm filter decreased as the total concentration of mercury increased. At a fixed organic matter concentration of 10 mg C/L (experiment 5 in Table 1), 100% of mercury passed through the filter at initial Hg concentrations $\leq 5 \times 10^{-5}$ M, about 30% passed through at 5×10^{-4} M, and no mercury passed through the filter at 5×10^{-3} M.

At an initial Hg concentration of 5×10^{-8} M (experiment 4), 100% of mercury ended up in the supernatant of the high-speed centrifugation (i.e., "dissolved" mercury), and no solids were settled by centrifugation. In the experiment that contained 5×10^{-5} M of Hg (experiment 3, Table 1), 100% of mercury passed through a 0.1 μm filter but was mostly removed as colloidal precipitate by centrifugation. The Hg concentration in the supernatant solution, measured after centrifuging for 1–8 h, was $12 \pm 4\%$ of the initial Hg concentration. The colloidal material that settled in the tube was identified as metacinnabar by X-ray diffraction. The colloidal metacinnabar had a zeta potential of -61.6 ± 4.8 mV at pH 7.0.

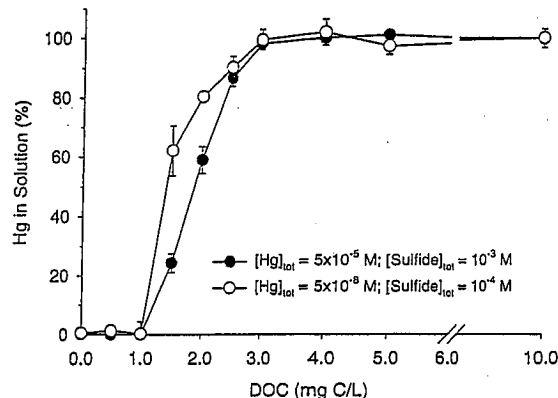**FIGURE 2.** Effect of DOC (F1-HPoA) concentration on the precipitation of metacinnabar (experiments 3 and 4): pH = 7.0 and $I = 0.01$ M. Mercury concentration in solution is in the fraction that passes through a 0.1 μm filter.

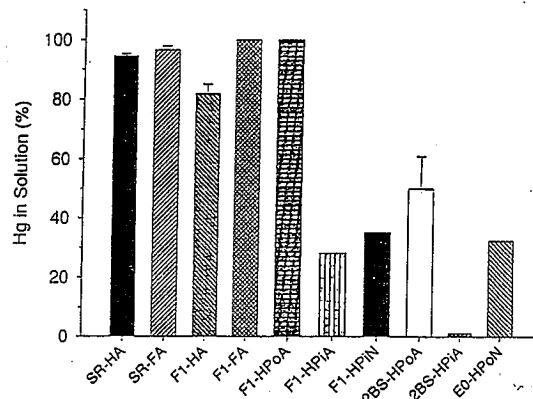**FIGURE 3.** Effect of different fractions of organic matter on the precipitation of metacinnabar: $[DOC] = 10$ mg C/L, $[Hg]_{tot} = 5 \times 10^{-5}$ M; $[sulfide]_{total} = 10^{-3}$ M; pH 7.0; $I = 0.01$ M. Mercury concentration in solution is in the fraction that passes through a 0.1 μm filter (sample key: HA: humic acids; FA: fulvic acids; HPoA: hydrophobic acids; HPiA: hydrophilic acids; HPiN: hydrophilic neutrals; HPoN: hydrophobic neutrals).

At fixed DOC (10 mg C/L) and mercury concentrations (5×10^{-5} M), different fractions of organic matter isolates had different effects on the amount of mercury passing through the filter. In the presence of hydrophobic organic acid, humic acid, and fulvic acid fractions, most of the mercury passed through a 0.1 μm filter. On the other hand, significant quantities of mercury were removed on the filter in the presence of the hydrophilic acid fractions (Figure 3). Metacinnabar precipitated and was removed on a 0.1 μm filter in the presence of most model compounds. In the presence of chloride, acetate, salicylate, EDTA, and cysteine, mercury was completely removed from solution by precipitation. About 15% of the mercury remained in solution in the presence of mercaptoacetic acid.

Mercury precipitated as solid metacinnabar (trapped on a 0.1 μm filter) when mercury and sulfide were added to whole water samples from F1 and 2BS sites (experiment 7) (Figure 4). After polyvalent cations were removed by cation-exchange resins (experiment 8), about 68% of the mercury passed through the 0.1 μm filter for F1 water and about 3% for 2BS water. Similarly, calcium promoted the aggregation of metacinnabar in the presence of organic matter isolates. In the presence of 5×10^{-5} M Hg and 10 mg C/L F1-HPoA, metacinnabar solids (>0.1 μm) formed when Ca^{2+} concentrations were greater than 10^{-4} M (Figure 5). When the initial Hg concentration was reduced to 5×10^{-8} M, precipitation occurred when Ca^{2+} concentrations were greater than 10^{-3} M.
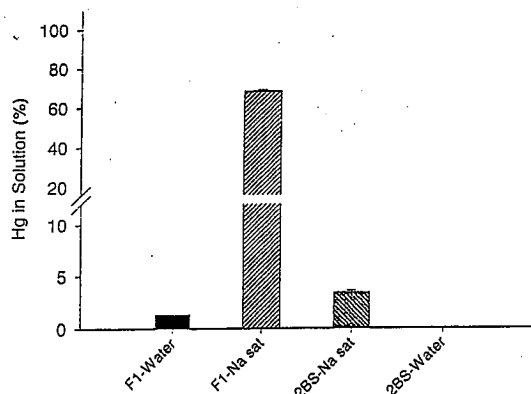
FIGURE 4. Precipitation of metacinnabar in the presence of whole water samples before and after removal of polyvalent cations through sodium saturated cation-exchange resins (CER) (experiments 7 and 8): $[Hg]_{tot} = 5 \times 10^{-5}$ M, $[sulfide]_{total} = 10^{-3}$ M. Mercury concentration in solution is in the fraction that passes through a 0.1 μm filter.
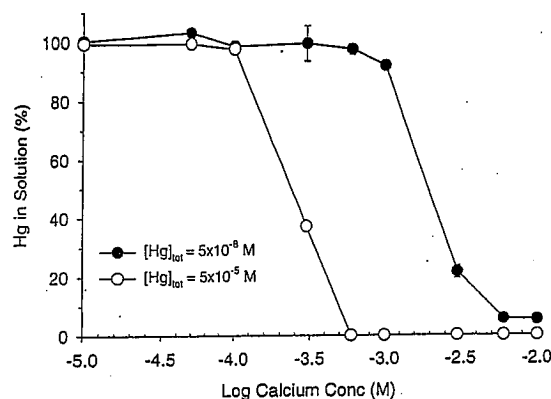

FIGURE 5. Effect of calcium concentration on the precipitation of metacinnabar at two different Hg concentrations (experiment 9): $[sulfide]_{total} = 10^{-3}$ M. Mercury concentration in solution is in the fraction that passes through a 0.1 μm filter.

Discussion

Thermodynamic Modeling. The speciation of mercury in aquatic environments is often predicted using thermodynamic models without considering the role of DOM (4, 15). We attempted to model the inorganic speciation of mercury using MINEQL$^+$ (25) under experimental and field conditions in the Everglades. The model uses log K values of 44.82 for metacinnabar and 45.19 for cinnabar for the reaction

$$Hg(OH)_2 + HS^- + H^+ \leftrightarrow HgS + 2H_2O$$
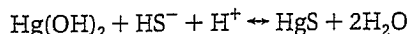
In simulations that contained no organic matter, 5×10^{-5} M Hg_{tot}, 10^{-3} M sulfide$_{tot}$, and pH 2–14, the model predicts that 100% of the Hg would occur as cinnabar (red HgS) solid. However, in our experiments, metacinnabar was the predominant species, and 100% of Hg was removed as metacinnabar at pH ≤ 8.0 (Figure 1). At pH ≥ 9.0, a significant amount of Hg remained in solution, possibly as HgS_2^{2-}.

To predict the speciation of mercury in the Florida Everglades (F1 and 2BS sites), the concentrations of the following components were measured in the field (Table 2) and used in MINEQL$^+$: H^+, Ca^{2+}, Mg^{2+}, Hg_{tot}, HS^-, Cl^-, and SO_4^{2-}. The model predicts that for the given conditions at F1, 100% of mercury would occur as cinnabar solid. This prediction does not change when there is a moderate change in pH, Hg_{tot}, or HS^- concentrations. When other parameters in Table 2 are kept constant, the model predicts that mercury would precipitate as cinnabar at pH 1–12, at mercury concentrations greater than 10^{-6} M, and at sulfide concen-

trations that are greater than mercury concentrations. The model thus predicts that, where sulfide concentrations are greater than mercury concentrations (as in most reducing, pristine environments), cinnabar would be the predominant species if the role of DOM is not considered.

Role of Dissolved Organic Matter. Formation of metacinnabar in the absence of organic matter is consistent with the extremely low solubility of HgS. However, in the presence of organic matter (F1-HPoA), mercury completely passed through the 0.1 μm filter under a wide range of pH conditions (pH 4–12). Mercury that passed through the filter could be in the form of DOM–Hg complexes or as colloidal metacinnabar that is smaller than 0.1 μm size. At low mercury concentrations ($<5 \times 10^{-8}$ M), most of the mercury appears to be complexed by organic matter ("dissolved" fraction), and colloidal HgS, if formed, is not removed under the centrifugation conditions used here.

It is generally believed that mercury (a soft metal) is strongly bound by sulfur-containing ligands (e.g., thiols) in organic matter (3, 10). The sulfur content in the isolated organic matter varied between 0.74 and 1.73% (dry weight, ash free) (Table 3). The reduced sulfur (as di- and polysulfide and thiol) content in F1-HPoA, analyzed by X-ray absorption near-edge structure spectroscopy (26), was about 28.7% of the total sulfur (1.73%) (Aiken et al., in preparation). At a DOC concentration of 4 mg C/L of F1-HPoA, for example, there is about 1.2×10^{-6} M of reduced sulfur. This is more than the amount needed to bind 5×10^{-8} M of Hg (100% of Hg was found in the "dissolved" state at this Hg concentration; Figure 2) if we assume a strong 1:1 binding between reduced sulfur and mercury. Dissolved Hg levels found in many freshwaters ($2-60 \times 10^{-12}$ M) (27) are much smaller than the experimental concentrations; therefore, it is likely that DOM would play an even more important role in preventing the precipitation of HgS in aquatic environments.

At moderate Hg concentrations (5×10^{-5} M), a small fraction (~12%) of Hg was found in the "dissolved" state, while a significant portion was found in the "colloidal" form. The colloidal metacinnabar that precipitated in the presence of organic matter had a more negative surface than the metacinnabar that formed in the absence of organic matter. This indicates strong adsorption of organic matter to the solid surface capable of overcoming the electrostatic repulsion between the metacinnabar surface and the DOM. Adsorption of organic matter could prevent the aggregation of HgS colloids through electrostatic repulsion (28). The growth of colloidal particles into larger crystals could also be suppressed by organic matter adsorption (29). Horzempa and Helz (28) obtained similar results for covellite (CuS). They showed that humic substances from marine environments stabilized colloidal sols of CuS and hypothesized that these interactions played a major role in the transport of copper in anoxic environments.

Generally, organic matter of higher molecular weight and higher aromaticity preferentially sorbs onto solid surfaces (e.g., iron oxides), resulting in the fractionation of dissolved organic matter (30, 31). When 5×10^{-3} M Hg, 10^{-2} M sulfide, and 10 mg C/L F1-HPoA were reacted, Hg was completely removed as solid HgS (>0.1 μm). In this reaction, the DOC concentration decreased by 45% and the UV absorbance decreased by 56%. The specific UV absorbance, which positively correlated ($R^2 = 0.81$, which is significant at the 95% confidence level) with the aromaticity (Table 3), was reduced from 0.062 ($\pm$0.003) to 0.049 ($\pm$0.002) L mgC^{-1} cm^{-1}, indicating preferential sorption and removal of more aromatic carbon.

Effect of Polyvalent Cations. While dissolved organic matter appears to impede the precipitation and aggregation of metacinnabar, polyvalent cations (e.g., Ca^{2+}) at sufficient concentrations favored aggregation even in the presence of

TABLE 2. Geochemical Characteristics of Surface Waters Collected (in July 1997) at Two Sites in Florida Everglades

parameter	units	F1 site whole water	F1 site Na-saturated[a]	2BS site whole water	2BS site Na-saturated[a]
Hg_{tot}[b]	M	1.25×10^{-11}	2.10×10^{-11}		
Ca^{2+}	M	1.64×10^{-3}	5.75×10^{-6}	9.36×10^{-4}	1.62×10^{-6}
Mg^{2+}	M	9.60×10^{-4}	1.48×10^{-6}	3.24×10^{-4}	3.70×10^{-7}
Cl^-	M	3.99×10^{-3}	c	1.14×10^{-3}	c
SO_4^{2-}	M	466×10^{-6}	c	68.7×10^{-6}	c
HS^-	M	1.1×10^{-6}	c	not detected	c
O_2	mg/L	0.32	c	3.35	c
pH	c	7.31	7.31	7.34	7.34
spec. conductance	μs	1072	c	443	c
DOC	mg/L	38.1	38.2	16.9	16.5
UV Abs_{254}	cm^{-1}	1.369	1.365	0.414	0.402
specific UVA ($\times 1000$)	L mgC^{1-} cm^{-1}	35.9	35.8	24.5	24.4

[a] Na-saturated: sample passed through a sodium-saturated cation-exchange resin column. [b] Total dissolved mercury concentration data from Mark Olson, USGS. [c] Not measured.

TABLE 3. Characteristics of Isolated Organic Matter Used in Precipitation Experiments

sample	elemental anal.[a] C (%)	elemental anal.[a] S (%)	carboxyl content[a] (meq/g)	aromatic C (NMR) (%)	specific UV abs. ($\times 1000$) L mgC^{-1} cm^{-1}	molecular wt (Daltons)
SR-HA	53.42	0.68	4.49	35.1	65.61	1399
SR-FA	53.46	0.56	5.50	22.9	37.02	1360
F1-HA[b]			3.80	25.2	57.56	1162
F1-FA	52.94	1.60	5.60	20.1	41.65	850
F1-HPoA	52.24	1.73	5.45	18.2	39.32	1031
F1-HPiA	47.69	1.63	5.41	13.1	27.97	832
F1-HPiN	55.99	0.74	2.17	12.0	14.01	
2BS-HPoA	52.25	1.23	5.09	15.4	31.70	953
2BS-HPiA[b]	47.32	1.55	3.07		23.93	862
E0-HPoN	54.68	1.12	3.91	12.4	34.62	964

[a] Analyzed on dried samples and reported here on an ash-free basis. [b] Not analyzed due to insufficient sample size.

DOM. For example, metacinnabar formed when mercury and sulfide were added to whole water sample from F1 site. When polyvalent cations were removed from the same water sample by passing through a cation-exchange resin, significant amount of mercury passed through a 0.1 μm filter (Figure 4). In the case of isolated organic matter, no mercury remained in solution (<0.1 μm) in the presence of F1-hydrophobic acid when calcium was added at significant concentrations (Figure 5). We observed a similar effect in the DOM-enhanced dissolution of cinnabar (13), where F1 and 2BS water samples enhanced the dissolution of cinnabar after the polyvalent cations were removed. Conversely, the dissolution of cinnabar by F1-HPoA isolates decreased significantly in the presence of calcium. From Figure 5, it could be expected that a large amount of polyvalent cations would be required to remove Hg as metacinnabar to the sediments in the presence of environmentally relevant DOM and Hg concentrations.

The negative effect of polyvalent cations on the precipitation of metacinnabar could be a result of complexation of these ions by the carboxyl groups in DOM, which could affect the charge density and the ability of organic matter to interact with the HgS surface. In cases where colloidal metacinnabar does form, calcium could also sorb on to the colloidal surface, blocking the active surface sites. We have shown that the surface of cinnabar becomes less negative through the sorption of calcium (13). Sorption of calcium and other polyvalent cations on metacinnabar surface could reduce electrostatic repulsion and thus favor aggregation.

Environmental Implications

This study demonstrates that dissolved organic matter could play an important role in the solubilization of mercury even in sulfidic environments. The results presented here suggest that the concentration and the nature of organic matter and the concentrations of mercury and polyvalent cations (e.g., Ca^{2+}) will dictate the extent to which metacinnabar formation and aggregation is inhibited in aquatic environments. It is interesting to note that the dissolved Hg concentrations in natural environments are measured on samples that are filtered by 0.1-, 0.2-, or 0.45-μm filters. Formation of colloidal metacinnabar (<0.1 μm) in our study suggests that some of the "dissolved" mercury measured in natural samples may actually be "colloidal" HgS that passes through these filters.

The mercury concentrations used in our precipitation experiments are much higher than the natural concentrations found in pristine environments, including the Florida Everglades. These high concentrations were chosen because of the high detection limit of our mercury analyzer and the presence of significant concentrations of mercury in the isolated organic matter. Future precipitation experiments need to be carried out with organic matter isolated by clean techniques and with mercury concentrations representative of pristine environments. However, if natural concentrations of DOM could prevent the precipitation of metacinnabar at mercury concentrations up to 5×10^{-8} M, then it is likely that DOM will inhibit metacinnabar precipitation in pristine environments. Inhibition of precipitation and aggregation of colloids could have important implications for mercury cycling and transport in many aquatic environments.

Acknowledgments

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