

Mercury(II) Sorption to Two Florida Everglades Peats: Evidence for Strong and Weak Binding and Competition by Dissolved Organic Matter Released from the Peat

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The binding of mercury(II) to two peats from Florida Everglades sites with different rates of mercury methylation was measured at pH 6.0 and 0.01 M ionic strength. The mercury(II) sorption isotherms, measured over a total mercury(II) range of $10^{-7.4}$ to $10^{-3.7}$ M, showed the competition for mercury(II) between the peat and dissolved organic matter released from the peat and the existence of strong and weak binding sites for mercury(II). Binding was portrayed by a model accounting for strong and weak sites on both the peat and the released DOM. The conditional binding constants (for which the ligand concentration was set as the concentration of reduced sulfur in the organic matter as measured by X-ray absorption near-edge structure spectroscopy) determined for the strong sites on the two peats were similar ($K_{\text{peat,s}} = 10^{21.8 \pm 0.1}$ and $10^{22.0 \pm 0.1}$ M⁻¹), but less than those determined for the DOM strong sites ($K_{\text{dom,s}} = 10^{22.8 \pm 0.1}$ and $10^{23.2 \pm 0.1}$ M⁻¹), resulting in mercury(II) binding by the DOM at low mercury(II) concentrations. The magnitude of the strong site binding constant is indicative of mercury(II) interaction with organic thiol functional groups. The conditional binding constants determined for the weak peat sites ($K_{\text{peat,w}} = 10^{11.5 \pm 0.1}$ and $10^{11.8 \pm 0.1}$ M⁻¹) and weak DOM sites ($K_{\text{dom,w}} = 10^{8.7 \pm 3.0}$ and $10^{7.3 \pm 4.5}$ M⁻¹) were indicative of mercury(II) interaction with carboxyl and phenol functional groups.

Introduction

The accumulation and toxicity of mercury in higher organisms depend strongly on the abundance of methylmercury. The production of methylmercury by methylation of the mercuric ion, Hg²⁺, is mediated by sulfate-reducing bacteria. Ligands and sorbents that complex Hg²⁺ strongly inhibit methylation and reduce mercury bioaccumulation and toxicity (1). Recent studies in the Florida Everglades have

focused on the complexation of mercury(II) by sulfide and polysulfide species (2–4) and organic matter (5, 6, 32). Inverse correlations of sediment methylmercury concentrations and production rates with sulfide concentrations at sites in the northern Everglades led Gilmour et al. (2) to attribute differences in mercury methylation rates to the formation of mercury(II) sulfide complexes. The ability of dissolved organic matter fractions isolated from these sites to enhance the dissolution and prevent the precipitation of cinnabar (HgS(s)) and strongly bind aqueous mercury(II) at low ratios of mercury(II) to dissolved organic matter suggested to Ravichandran et al. (5, 6) and Haitzer et al. (32) that organic matter complexation of mercury(II) may also slow the rate of methylation.

In reduced sediments, where mercury methylation primarily occurs, both sulfide and organic matter are present, with organic matter in both the aqueous and solid phase (as peat). Most equilibrium speciation calculations indicate that sulfide complexation and HgS(s) precipitation control mercury(II) concentrations in anoxic environments, while organic matter dominates mercury(II) speciation only in oxic (sulfide-free) environments (7, 8). These conclusions are typically based on mercury(II)–organic matter binding constants that are either (i) estimated by comparison to mercury(II) binding by organic thiols (9) or (ii) measured at mercury(II) concentrations far greater than those found in most ambient surface waters. To address this lack of certainty concerning the affinity of organic matter for mercury(II), we measured the mercury(II) binding strength of two peats from the northern Everglades. One of the peats was collected from a site where methylation rates are high; the other was collected from a site where methylation rates are low (2). Given the difference in methylmercury abundance at the two sites, we hypothesized that the peat at the high methylation rate site would have less affinity for mercury(II) (i.e., mercury(II) would be more bioavailable) and that the difference in mercury(II) affinity could be correlated to a difference in the peat composition.

For mercury(II) binding, one of the key parameters of organic matter composition is the sulfur content. Mercury, a soft metal, binds strongly to soft ligands such as thiols (RSH). For many years, researchers speculated on the potential role of reduced sulfur functional groups in organic matter in binding mercury(II) (9–13). Recently, the abundance of reduced sulfur functional groups in natural organic matter has been probed by X-ray absorption near-edge structure (XANES) spectroscopy (5, 14–16). Using XANES and extended X-ray absorption fine-structure (EXAFS) spectroscopy, Xia et al. (17) found direct evidence of mercury(II) binding by thiol, disulfide, and disulfane functional groups in combination with carboxyl and phenol functional groups. Similarly, Hesterberg et al. (18) showed that mercury(II) binding to organic matter was dominated by interactions with reduced sulfur functional groups at low mercury(II)/reduced sulfur ratios and by interactions with oxygen-containing functional groups at high mercury(II)/reduced sulfur ratios. With mercury(II) binding constants for thiol-containing organic acids as high as $10^{34.5}$ M⁻¹ for mercaptoacetic acid (19), complexes of mercury(II) with reduced sulfur functional groups in organic matter should be strong. Recently measured mercury(II) binding constants of up to $10^{32.2}$ M⁻¹ (pH 3.2, ionic strength 0.44 M, ligand concentration set as the reduced sulfur concentration as measured by XANES spectroscopy, proton exchange modeled as mercaptoacetic acid) for sorption to organic matter in soils (20) and $10^{23.2}$ L kg⁻¹ (pH 7.0, ionic strength 0.1 M) for a hydrophobic

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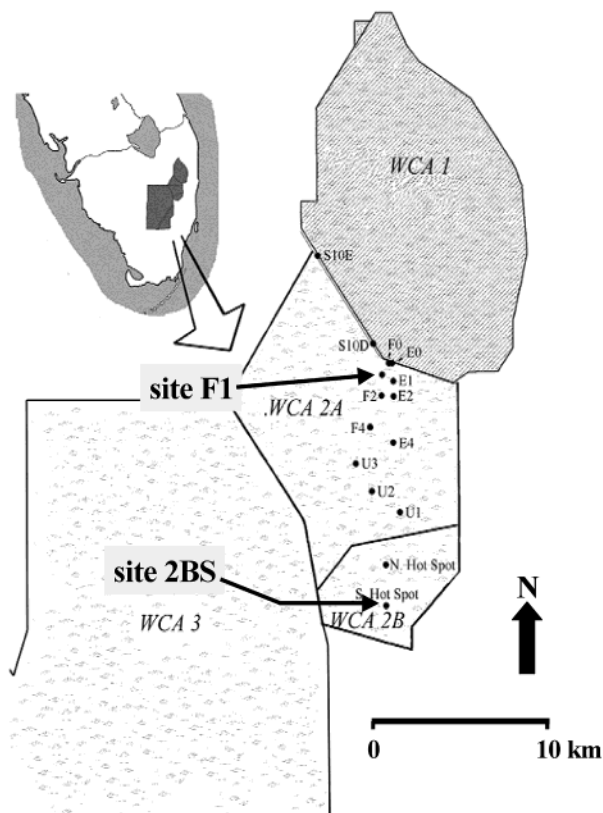


FIGURE 1. Map of the Florida Everglades showing the sampling sites used for this study (F1 and 2BS) and other studies and the Water Conservation Area (WCA) boundaries.

acid fraction isolated from the Everglades (32) indicate that competition with inorganic sulfide species may occur if mercury(II) concentrations do not exceed the concentration of strong mercury(II) binding sites in organic matter.

Materials and Methods

Peat. Peat samples were collected from two sites in the Florida Everglades, F1 and 2BS (Figure 1). Site F1 is located in northern part of Water Conservation Area 2A (26°21'35" N, 80°22'14" W). Site 2BS is located in southern part of Water Conservation Area 2B (26°09'17" N, 80°22'41" W). Water quality at these sites differs notably in dissolved oxygen, organic matter, and sulfide concentrations, the sediment concentration of methylmercury (2), and the reactivity of dissolved organic matter (DOM) with cinnabar (5, 6) (Table 1).

Peat was sampled from the two sites using a brass 230 mesh sieve to scoop material from the upper 10 cm of the peat layer. The peat samples were placed into precleaned 1-L glass jars with Teflon-lined lids and shipped overnight on ice to the U.S. Geological Survey in Boulder, CO. In the laboratory, the -14/+270 mesh (53 μm -1.41 mm) size fractions of the peat samples were isolated by rinsing through brass sieves with high-purity water (resistivity > 18 Mohm cm^{-1}) and freeze-dried (Virtis Unitop 600L). The dried peat was further separated with brass sieves into a -100/+150 mesh (75-104 μm) size fraction for use in the sorption experiments.

The 75-104 μm fractions of the peats were characterized by elemental composition, mineralogy, carbon functional group content, and major ion and mercury(II) content. Elemental composition (organic and inorganic C, H, N, O, S, and ash) was determined at Huffman Laboratories (Golden, CO) by a variety of techniques (22). Mineralogy was determined by powder X-ray diffraction (XRD; Cu-K α radiation,

TABLE 1. Water Quality Characteristics of the F1 and 2BS Sites in the Florida Everglades in July 1997 (21)

parameter	units	site F1	site 2BS
pH		7.3	7.4
specific conductance	$\mu\text{S cm}^{-1}$	1100	440
Mg^{2+}	mM	0.96	0.32
Ca^{2+}	mM	1.6	0.94
Cl^-	mM	4.0	1.1
SO_4^{2-}	μM	470	69
$\text{H}_2\text{S}_{\text{total}}$	μM	0.22	0.063
O_2	μM	10	100
Hg_{total}	pM	13	21
dissolved organic carbon	mg C L^{-1}	38	17
UVA ^a	cm^{-1}	1.37	0.41
SUVA ^a	$\text{L (mg C)}^{-1} \text{cm}^{-1}$	0.036	0.024
CH_3Hg^b	mol kg^{-1}	1.4×10^{-9}	1.3×10^{-8}

^a Ultraviolet light (254 nm) absorption (UVA) and specific ultraviolet light absorption (SUVA). ^b Total methylmercury sediment concentrations reported by Gilmour et al. (2).

$1.2^\circ 2\theta \text{ min}^{-1}$, $10-90^\circ 2\theta$; Scintag PAD V). Carbon functional group content was measured by solid state ^{13}C -nuclear magnetic resonance (^{13}C NMR; Varian Chemagnetics CMX, 200 MHz, 5.0 ms contact time, 4.5 μm pulse width). Acidometric titrations were performed on 0.5 g L^{-1} peat suspensions in 1.0 M NaNO_3 . The suspension was acidified to pH 2.0 with HNO_3 and sparged with helium for 15 min to remove inorganic carbon. NaOH solution (0.1 M) was added and pH was recorded at 60 s intervals. Carboxyl and phenol content are reported for the pH ranges of 2 to 8 and 8 to 10, respectively. Major ion content (Na^+ , NH_4^+ , K^+ , Mg^{2+} , Ca^{2+} , Cl^- , NO_3^- , SO_4^{2-}) was determined for a 40 mg L^{-1} peat suspension in high-purity water by ion chromatography (Dionex DX-120; 0.2 to 1.0 $\mu\text{eq L}^{-1}$ detection limits). The amount of mercury(II) leaching from the peat under experimental conditions was determined for a 40 mg L^{-1} suspension in 0.01 M NaNO_3 by cold vapor atomic fluorescence spectroscopy (CVAFS; P. S. Analytical, Merlin; 1.0 pM detection limit). The total mercury(II) content of the peat was determined by nitric acid/potassium dichromate and sulfuric acid/potassium permanganate digestion and CVAFS (22).

Mercury(II) Sorption Experiments. Batch sorption experiments were conducted in suspensions of 40 mg L^{-1} peat in high-purity water. The suspensions were contained in glass flasks cleaned by soaking for 2 h in 10% HNO_3 and 10% HCl . Ionic strength was set at 0.01 M by addition of NaNO_3 and pH was adjusted to 6.0 ± 0.1 by addition of trace metal-grade HNO_3 and NaOH solutions. The peat was equilibrated at pH 6.0 for 2 h before mercury(II) addition. Mercury(II) was added from 0.05, 0.5, and 5 mM $\text{Hg}(\text{NO}_3)_2$ stock solutions in 4 wt % HNO_3 to give total mercury(II) concentrations of 4×10^{-8} to 2×10^{-4} M. The lower end of the range was set just above the mercury(II) detection limit of cold vapor atomic absorption spectroscopy (CVAAS; Buck Scientific 400A, 0.5 nM detection limit); the upper end was limited by $\text{HgO}(\text{s})$ solubility. After mercury addition, the pH was readjusted to 6.0 ± 0.1 . The flasks were sealed with ground glass stoppers and mixed for 12 h on a rotating wheel at 4 rpm at $22 \pm 2^\circ\text{C}$. A preliminary kinetics experiment showed that sorption equilibrium was reached during the first hour of mixing (22). All experiments were performed in triplicate.

Mercury(II) Analysis. After mixing, the peat was allowed to settle for 10 min, and a 60-mL aliquot of solution was removed with a polypropylene syringe. The aliquot was

TABLE 2. Composition of the F1 and 2BS Peat Samples (75–104 μm Size Fraction)

property	units	site F1	site 2BS	detection limit
C	wt % ^a	50.9	51.9	0.05
H	wt %	4.9	5.5	0.05
O	wt %	38.9	37.3	0.1
N	wt %	3.58	4.05	0.01
S	wt %	1.79	1.27	0.01
ash	wt % ^b	5.4	18.0	0.1
aliphatic I (0–62 ppm)	C% ^c	30.0	39.4	
aliphatic II (62–90 ppm)	C%	18.9	18.2	
acetal (90–110 ppm)	C%	9.0	7.4	
aromatic (110–160 ppm)	C%	26.8	20.2	
carboxyl (160–190 ppm)	C%	12.4	11.2	
ketone (190–230 ppm)	C%	3.0	3.5	
carboxyl	meq g ⁻¹	5.1	6.4	
phenol	meq g ⁻¹	0.9	1.1	
total Hg	nmol g ⁻¹	0.70 \pm 0.05	0.90 \pm 0.05	

^a Elemental compositions reported as percentage of organic mass (corrected for ash). ^b Ash fraction reported as percentage of total mass of peat. ^c ¹³C NMR functional group composition reported as percentage of total carbon.

TABLE 3. Major Ion and Dissolved Organic Matter Concentrations Released from the F1 and 2BS Peat Samples (75–104 μm Size Fraction) into the Experimental Solution (40 mg L⁻¹ Peat, 0.01 M NaNO₃, pH 6.0)

property	units	site F1	site 2BS	detection limit
Na ⁺	M	3 \pm 1 \times 10 ⁻⁵	2 \pm 1 \times 10 ⁻⁵	5 \times 10 ⁻⁷
K ⁺	M	1 \pm 0.4 \times 10 ⁻⁵	5 \pm 3 \times 10 ⁻⁶	2 \times 10 ⁻⁷
NH ₄ ⁺	M	bdl	2 \pm 0.2 \times 10 ⁻⁶	9 \times 10 ⁻⁷
Mg ²⁺	M	bdl	4 \pm 0.4 \times 10 ⁻⁶	5 \times 10 ⁻⁷
Ca ²⁺	M	2 \pm 0.2 \times 10 ⁻⁵	8 \pm 4 \times 10 ⁻⁶	3 \times 10 ⁻⁷
Hg(II)	M	bdl	bdl	1 \times 10 ⁻¹²
Cl ⁻	M	1 \pm 0.6 \times 10 ⁻⁵	6 \pm 3 \times 10 ⁻⁶	8 \times 10 ⁻⁷
NO ₃ ⁻	M	bdl	1 \pm 0.3 \times 10 ⁻⁶	2 \times 10 ⁻⁷
SO ₄ ²⁻	M	8 \pm 2 \times 10 ⁻⁷	6 \pm 3 \times 10 ⁻⁷	3 \times 10 ⁻⁷
dissolved organic carbon	mg C L ⁻¹	0.9 \pm 0.2	1.2 \pm 0.3	0.2
UVA ^a	cm ⁻¹	0.020 \pm 0.004	0.020 \pm 0.004	
SUVA ^a	L (mg C) ⁻¹ cm ⁻¹	0.024 \pm 0.008	0.020 \pm 0.008	

^a Ultraviolet light (254 nm) absorption (UVA) and specific ultraviolet light absorption (SUVA).

filtered through a polysulfone membrane (0.45 μm , Gelman Supor Acrodisc 25) into a glass beaker and mixed with trace metal-grade concentrated acids (H₂SO₄, 5.0 mL; HNO₃, 2.5 mL) and KMnO₄ (5 wt % solution, 15.0 mL). The solution was allowed to oxidize for 15 min before adding K₂S₂O₈ (5 wt % solution, 8.0 mL) and heating in a water bath at 95 °C for 2 h. After cooling, a NH₄OH·HCl (12 wt %)/NaCl (12 wt %) solution (6 mL) was added and agitated by hand until the KMnO₄ was completely reduced (determined by solution clarity). Mercury(II) was measured in this solution by CVAAS. The concentration of mercury(II) associated with the peat was determined by difference between the total mercury(II) added and mercury(II) in the aqueous phase.

Dissolved Organic Matter Analysis. The solution phase was also tested for DOM content following the sorption experiments by dissolved organic carbon (DOC) measurements and ultraviolet light spectroscopy. For DOC measurements, samples were filtered through polysulfone membranes (0.45 μm) and measured as total organic carbon (Oceanography International 700). Ultraviolet light absorption was measured at a wavelength of 254 nm (UVA; Hewlett-Packard 8453). The absorbance calibration curve was adjusted for nitrate absorbance with a 0.01 M NaNO₃ solution. Specific UVA absorbance (SUVA; L (mg C)⁻¹ cm⁻¹) was determined as the ratio of the UVA absorbance and the DOC concentration. Insufficient DOM was released from the peat samples under the experimental conditions to allow for more detailed characterization of the DOM released from the peat.

Control Experiments. Both the glass flasks and polysulfone filters were checked for adsorption of mercury(II) in experimental solutions (0.01 M NaNO₃, pH 6.0, 1 mg C L⁻¹ DOM, 5 \times 10⁻⁷ M Hg(II)). The hydrophobic acid fraction isolated from water at the F1 site (5, 6) was used as the DOM. Isolation procedures were described in Ravichandran (21). Mercury(II) losses of less than 1% were measured for the glass flasks and filters.

Results

Peat Characteristics. The 75–104 μm fraction of the F1 peat contains more sulfur than the 2BS peat (Table 2). The aliphatic carbon content of the 2BS peat is considerably higher than that of the F1 peat, while the F1 peat contains more aromatic carbon. The organic matter contents of the peats are 94.6% (F1) and 82.0% (2BS). XRD revealed quartz and calcite in the F1 peat and quartz only in the 2BS peat. The peats released small amounts of major ions, about 1 mg C L⁻¹ DOM, and less than picomolar concentrations of mercury(II) to the experimental solutions (Table 3). A total of about 30 pM of mercury(II) was present in the amount of peat added to the experimental solutions (about 6 nmol of Hg/g of peat). The elemental and functional group compositions of the peat and the SUVA of the DOM released by the peat are similar to those measured for the corresponding DOM sampled at these sites (5, 6).

Mercury(II) Sorption to Peat. Mercury(II) binds strongly to the peat fractions from the F1 and 2BS sites (Figure 2). The

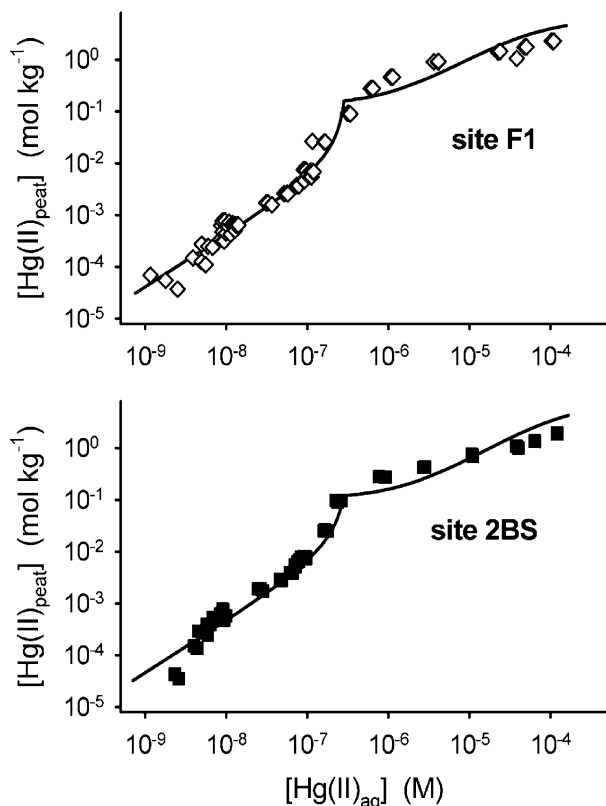


FIGURE 2. Mercury(II) sorption to F1 and 2BS peat fractions (75–104 μm) at pH 6.0, ionic strength 0.01 M NaNO_3 , and 40 mg L^{-1} peat. Fits of double site model using parameters in Tables 4 and 5 are shown as lines for each peat.

data at the lowest mercury(II) concentrations show greater uncertainty because the aqueous concentration of mercury(II) was approaching the CVAAS detection limit (0.5 nM). The sorption isotherms are similar if the entire range of aqueous mercury(II) concentrations is considered (a t-test shows no significant difference ($p > 0.05$) between the F1 and 2BS isotherms). However, significant differences exist for mercury(II) binding by the two peats over narrow ranges of aqueous mercury(II) concentration—the F1 peat binds more mercury(II) around $[\text{Hg(II)}]_{\text{aq}} = 10^{-6}$ M, while the 2BS peat binds more mercury(II) around $[\text{Hg(II)}]_{\text{aq}} = 10^{-8}$ M. Significant variability in mercury(II)–peat binding is more apparent by examination of the mercury(II)–peat distribution coefficients as a function of aqueous mercury(II) concentration (Figure 3). Distribution coefficients (K_d) were calculated as

$$K_d = \frac{[\text{Hg(II)}]_{\text{peat}}}{[\text{Hg(II)}]_{\text{aq}}} \quad (1)$$

with $[\text{Hg(II)}]_{\text{peat}}$ as the concentration of mercury(II) bound to the peat (mol kg^{-1} ; determined by difference between total and aqueous mercury(II)) and $[\text{Hg(II)}]_{\text{aq}}$ as the concentration of mercury(II) remaining in the aqueous phase (M). Viewed as K_d versus aqueous mercury(II) concentration, considerable scatter is apparent in the F1 isotherm at $[\text{Hg(II)}]_{\text{aq}}$ less than 10^{-8} M (Figure 3). We consider these low mercury(II) data as less reliable because $[\text{Hg(II)}]_{\text{aq}}$ is approaching the CVAAS detection limit. In the 2BS isotherm, the data at low $[\text{Hg(II)}]_{\text{aq}}$ are less scattered, but still considered less reliable.

Release of Dissolved Organic Matter from the Peat. During the experiments, the peat fractions consistently released about 1 mg C L^{-1} DOM (Figure 4). The amount of

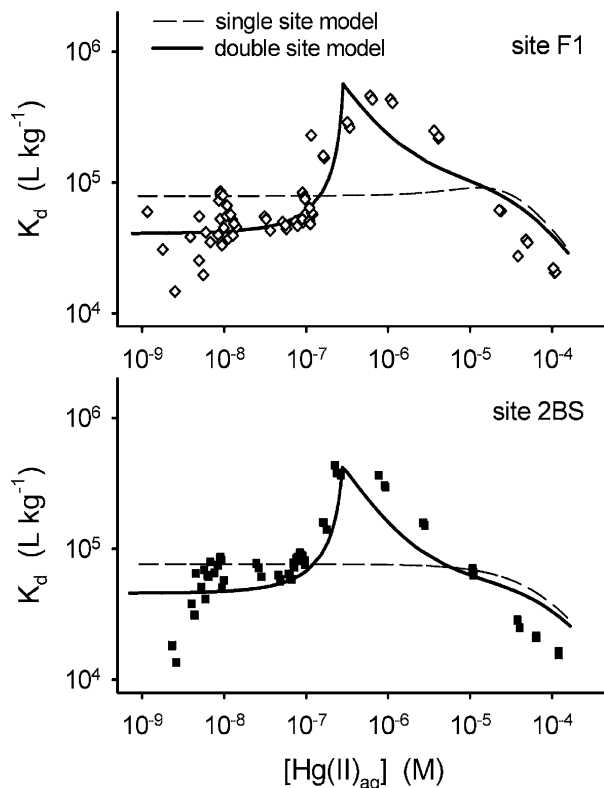


FIGURE 3. Mercury(II) distribution coefficients as a function of aqueous mercury(II) concentration for peats from sites F1 and 2BS. Single site and double site models were used to fit these data with the parameters in Table 4 to produce the conditional binding constants in Table 5.

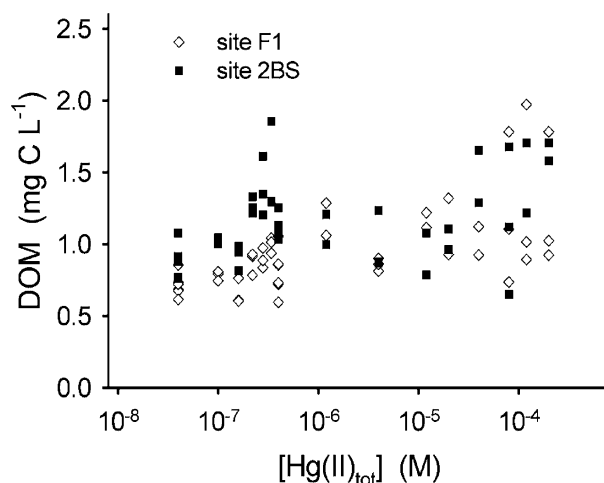


FIGURE 4. Dissolved organic carbon released from F1 and 2BS peat fractions during mercury(II) sorption experiments, pH 6.0, ionic strength 0.01 M NaNO_3 , and 40 mg L^{-1} peat.

DOM released did not depend significantly on the amount of total mercury(II) in the experiment.

Discussion

Mercury(II)–Peat Sorption Isotherms. The Everglades F1 and 2BS peats strongly sorbed mercury(II). Distribution coefficients ranged from $10^{4.1}$ to $10^{5.7}$ L kg^{-1} . Similar mercury(II) distribution coefficients have been measured for other natural sorbents containing high concentrations of organic matter. Hurley et al. (8) measured distribution coefficients of $10^{4.8}$ to $10^{5.7}$ L kg^{-1} for total mercury sorption to suspended particles at the F1, 2BS, and other sites in the

TABLE 4. Mercury(II) Complexation with Peat and Dissolved Organic Matter (DOM) in Single Site and Double Site Models and with Hydroxide and Chloride

model	reactions	fixed parameters		fitted parameters
		site F1	site 2BS	
single site	$\text{Hg}^{2+} + \text{peat}^- = \text{Hg-peat}^+$	$[\text{peat}]_{\text{tot}} = 2.4 \times 10^{-4} \text{ M}$	$[\text{peat}]_{\text{tot}} = 3.0 \times 10^{-4} \text{ M}$	K_{peat}
double site ^a	$\text{Hg}^{2+} + \text{dom}^- = \text{Hg-dom}^+$	$[\text{dom}]_{\text{tot}} = 8.3 \times 10^{-6} \text{ M}$	$[\text{dom}]_{\text{tot}} = 1.1 \times 10^{-5} \text{ M}$	K_{dom}
	$\text{Hg}^{2+} + \text{peat}_s^- = \text{Hg-peat}_s^+$	$[\text{peat}_s] = 6.4 \times 10^{-6} \text{ M}$	$[\text{peat}_s] = 4.8 \times 10^{-6} \text{ M}$	$K_{\text{peat},s}$
	$\text{Hg}^{2+} + \text{peat}_w^- = \text{Hg-peat}_w^+$	$[\text{peat}_w] = 2.4 \times 10^{-4} \text{ M}$	$[\text{peat}_w] = 3.0 \times 10^{-4} \text{ M}$	$K_{\text{peat},w}$
	$\text{Hg}^{2+} + \text{dom}_s^- = \text{Hg-dom}_s^+$	$[\text{dom}_s] = 2.83 \times 10^{-7} \text{ M}$	$[\text{dom}_s] = 2.78 \times 10^{-7} \text{ M}$	$K_{\text{dom},s}$
	$\text{Hg}^{2+} + \text{dom}_w^- = \text{Hg-dom}_w^+$	$[\text{dom}_w] = 8.3 \times 10^{-6} \text{ M}$	$[\text{dom}_w] = 1.1 \times 10^{-5} \text{ M}$	$K_{\text{dom},w}$
both models ^{b,c}	$\text{H-peat} = \text{H}^+ + \text{peat}^-$	$\log K_{a,\text{peat}} = -4.25$		
	$\text{H-dom} = \text{H}^+ + \text{dom}^-$	$\log K_{a,\text{dom}} = -4.25$		
	$\text{Hg}^{2+} + \text{OH}^- = \text{HgOH}^+$	$\log \beta = 10.42$		
	$\text{Hg}^{2+} + 2 \text{OH}^- = \text{Hg}(\text{OH})_2^0$	$\log \beta = 21.5$		
	$\text{Hg}^{2+} + 3 \text{OH}^- = \text{Hg}(\text{OH})_3^-$	$\log \beta = 20.6$		
	$\text{Hg}^{2+} + \text{Cl}^- = \text{HgCl}^+$	$\log \beta = 7.1$		
	$\text{Hg}^{2+} + 2 \text{Cl}^- = \text{HgCl}_2$	$\log \beta = 13.73$		
	$\text{Hg}^{2+} + 3 \text{Cl}^- = \text{HgCl}_3^-$	$\log \beta = 14.7$		
	$\text{Hg}^{2+} + 4 \text{Cl}^- = \text{HgCl}_4^{2-}$	$\log \beta = 15.4$		
	$\text{Hg}^{2+} + \text{Cl}^- + \text{OH}^- = \text{HgOHCl}$	$\log \beta = 18.0$		

^a Subscripts "s" and "w" refer to strong and weak sites, respectively. ^b Equilibrium constants for hydroxide and chloride complexation reactions for $I = 0$ corrected for $I = 0.01$ by Davies equation (29). ^c For all equilibrium calculations, $\text{pH} = 6.0$ and $[\text{Cl}^-] = 1.0 \times 10^{-5} \text{ M}$.

northern Everglades at total mercury concentrations in the 10–30 pM range. Bloom et al. (23) measured a mean distribution coefficient of $10^{4.89 \pm 0.43} \text{ L kg}^{-1}$ for inorganic mercury binding to estuarine sediments. Mercury(II) is bound to such sorbents, as well as aquatic and soil organic matter, more strongly than all other bivalent metals (24–26).

The distribution coefficients vary considerably over the range of mercury(II) concentrations. If mercury(II) were binding only to the peat, we would expect a Langmuir isotherm—a linear change in the amount of mercury(II) sorbed with the amount of mercury(II) remaining in solution up to a maximum mercury(II) binding capacity. However, the isotherms are not linear and a clear mercury(II) binding capacity (saturation of binding sites) is not reached. At the upper end of the isotherms, the $\text{HgO}(\text{s})$ solubility limit, the mercury(II) concentration in the peat is about 1 mol kg^{-1} (Figure 2), or about 2 meq g^{-1} , still below the total acid functional group content of these peats by about a factor of 3 (Table 2). At the lower end of the isotherms, shifts in the slope of the isotherm indicate that the peat is not the only ligand competing for mercury(II). These shifts are more apparent in the plot of K_d versus aqueous mercury(II) concentration (Figure 3). DOM released from the peat is the most likely candidate for this competing ligand. Other researchers have noted that DOM affects metal binding to peat soils (26–28).

Effect of Dissolved Organic Matter Released From the Peat. Our measurements of mercury(II) binding by the Everglades F1 and 2BS peat fractions were complicated by the unavoidable release of organic matter from the peat fractions. The resulting levels of DOM, about 1 mg C L^{-1} (Figure 4), caused nonlinearities in the mercury(II)–peat isotherms similar to the “s-shaped” isotherms observed by Yin et al. (28) for mercury(II) sorption to soils containing up to 5% organic matter. The “s-shaped” isotherms were caused by the binding of mercury(II) by DOM rather than by peat at low mercury(II) concentrations.

We were able to measure the amount of organic matter released by the peat, but we could not explicitly account for its effect on mercury(II) speciation, unlike other ligands with known mercury(II) binding constants present in the experimental solution (e.g., hydroxide, chloride). We know that the hydrophobic acid fractions of organic matter in the Everglades waters at these sites are highly reactive with mercury(II). These hydrophobic acids (nearly all fulvic acids)

can enhance the dissolution of cinnabar ($\text{HgS}(\text{s})$), an extremely insoluble solid (5), and prevent cinnabar precipitation in the presence of 1.0 mM total sulfide (6). Therefore, in constructing an equilibrium model of mercury(II) speciation in these peat/DOM systems, we included DOM as a ligand in solution and sought to determine the mercury(II)–DOM binding constants in addition to the mercury(II) binding constant of the peats.

Equilibrium Model of Mercury(II) Speciation. To estimate mercury(II) binding constants for the peat fractions and the released organic matter, we formulated equilibrium models of the mercury(II)–peat–DOM system and used them to fit the mercury(II) isotherms. We progressed from a system with two single site ligands (a single mercury(II) binding site on both the peat and DOM) to a system with two double site ligands (a strong and weak mercury(II) binding site on both the peat and the DOM) to achieve the best fit of the model to the isotherms.

The first attempt at modeling the $\text{Hg}(\text{II})$ –peat–released DOM binding considered mercury(II) inorganic speciation and mercury(II) binding to a single site in both the peat and the released DOM (Table 4). Chloride concentration was set at $1.0 \times 10^{-5} \text{ M}$ to represent the amount of chloride leached from the peat (Table 3). Proton exchange by the peat and DOM was modeled with a single $\text{p}K_a$ determined by acidometric titration of the peat fractions (22). The total peat site concentration was set as the product of the peat concentration (40 mg L^{-1}), and the total acid functional group concentration for each peat fraction (Table 2). The total DOM site concentration was set using the average DOC concentration (Table 3) and the carbon content and total acid functional group concentration for the hydrophobic acid fractions isolated from the F1 and 2BS sites (F1, 52.2% carbon, 6.2 meq g^{-1} ; 2BS, 47.3% carbon, 5.8 meq g^{-1} (5)).

The equilibrium binding constants providing the best fit of the model to distribution coefficient data (Figure 3) were found using a Newton–Raphson iterative solution and optimization techniques in Microsoft Excel. The best fit of the single-site ligand model did not portray accurately the range of distribution coefficients corresponding to the mercury(II) isotherm data. The best fit yielded binding constants for peat and DOM (Table 5) similar to those for mercury(II) binding by carboxyl- and hydroxyl-containing organic acids (e.g., oxalic acid, $10^{10.56} \text{ M}^{-1}$; phenol, $10^{8.24} \text{ M}^{-1}$ (19)).

TABLE 5. Conditional Equilibrium Binding Constants Resulting from the Best Fits of the Models to the Mercury(II) Isotherm Data

model	parameters fit	conditional binding constants ^a	
		site F1	site 2BS
single site	K_{peat}	$10^{12.1 \pm 0.1}$	$10^{11.6 \pm 0.1}$
	K_{dom}	$10^{12.8 \pm 0.2}$	$10^{9.0 \pm 2.6}$
double site	$K_{\text{peat,s}}$	$10^{22.0 \pm 0.1}$	$10^{21.8 \pm 0.1}$
	(K_{RSHg^+})	($10^{26.0}$)	($10^{25.8}$)
	$K_{\text{peat,w}}$	$10^{11.8 \pm 0.1}$	$10^{11.5 \pm 0.1}$
	$K_{\text{dom,s}}$	$10^{23.2 \pm 0.1}$	$10^{22.8 \pm 0.1}$
	(K_{RSHg^+})	($10^{27.2}$)	($10^{26.8}$)
	$K_{\text{dom,w}}$	$10^{7.3 \pm 4.5}$	$10^{8.7 \pm 3.0}$

^a Conditional binding constants for reactions in Table 4 with strong sites as reduced sulfur concentration measured by XANES spectroscopy for $K_{\text{peat,s}}$ and $K_{\text{dom,s}}$; with organic thiols ($\text{RSH} = \text{RS}^- + \text{H}^+$, $\text{p}K_a = 10$; $\text{RS}^- + \text{Hg}^{2+} = \text{RSHg}^+$) for K_{RSHg^+} (shown in parentheses without errors). Errors in conditional binding constants reported as a variation in the binding constant resulting in a 5% variation in the fitting criterion.

Incorporating Strong and Weak Binding Sites. To improve the ability of the model to fit the mercury(II) isotherm data, we considered strong and weak binding sites on the peat and DOM—a double site model (Table 4). For both the peat and DOM, we assumed that the strong binding sites consisted of reduced sulfur functional groups and the weak binding sites consisted of carboxyl and phenol functional groups. Thus, the strong site concentrations were estimated as the reduced sulfur content of the peat and DOM, and the weak site concentrations were estimated as the carboxyl and phenol site density as determined by titration.

For the peat and DOM, we assumed that the reduced sulfur content was equal to the reduced sulfur content of hydrophobic acid fractions of the aquatic organic matter from the same sites (site F1, 28.7%; site 2BS, 30.4%; determined by XANES spectroscopy; reduced sulfur defined as thiol and di- and polysulfide moieties (21)). Accounting for the total sulfur content of the peat (Table 2) and the concentration of peat used in the experiments (40 mg L^{-1}), the peat strong site concentrations were estimated as $6.4 \times 10^{-6} \text{ M}$ for F1 peat and $4.8 \times 10^{-6} \text{ M}$ for 2BS peat. We furthermore assumed that the DOM released from the peat had the same total sulfur content as the hydrophobic acid fractions from the same sites, resulting in DOM strong site concentrations of $2.83 \times 10^{-7} \text{ M}$ for F1 DOM and $2.78 \times 10^{-7} \text{ M}$ for 2BS DOM. The peat and DOM total acid functional group concentrations were the same as those used in the single site model (Table 4). The total mercury/reduced sulfur ratio ranged from about 0.006 to 30 for the site F1 peat and about 0.008 to 40 for the site 2BS peat.

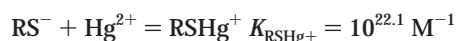
The double site model fit the distribution coefficient data much better than the single site model (Figure 3). The salient feature of the model fits is a sharp peak at about $[\text{Hg(II)}]_{\text{aq}} = 3 \times 10^{-7} \text{ M}$. At aqueous mercury(II) concentrations below this peak, mercury(II) binding to the peat is relatively weak; above this peak, binding of mercury(II) to the peat is relatively strong over the next order of magnitude of aqueous mercury(II) concentration. This peak corresponds to the concentration of strong sites on the DOM ($[\text{dom}_s]$; Table 4). At aqueous mercury(II) concentrations less than the strong site concentration of the DOM, the DOM competes with the strong peat sites for mercury(II). The strong DOM sites are filled as the aqueous mercury(II) concentration approaches $[\text{dom}_s]$. At aqueous mercury(II) concentrations above $[\text{dom}_s]$, the strong peat binding sites dominate the mercury(II) speciation, resulting in the highest K_d values. As aqueous mercury(II) concentrations approach the solubility of HgO(s) , the mercury(II)–peat distribution coefficients decrease as the strong peat sites are filled and the abundant weak

sites on both the peat and DOM begin to bind mercury(II).

With the strong site concentrations of both the peat and DOM set by the XANES spectroscopy results for the hydrophobic acid fractions of the F1 and 2BS aquatic organic matter, the double site model predicts DOM strong site binding constants ($K_{\text{dom,s}}$ of $10^{23.2}$ and $10^{22.8} \text{ M}^{-1}$, respectively) slightly stronger than peat strong site binding constants ($K_{\text{peat,s}}$ of $10^{22.0}$ and $10^{21.8} \text{ M}^{-1}$, respectively) (Table 5). This result is required for the model to predict the lower K_d values measured at low aqueous mercury(II) concentrations (Figure 3). An alternative modeling approach of specifying uniform strong site binding constants of $10^{22.0} \text{ M}^{-1}$ for both the peat and DOM and fitting the strong site concentration was attempted. This model predicted uniform K_d values over the lower aqueous mercury(II) concentration range, resulting in a poor fit with the isotherms. Only a model with strong sites on the DOM outcompeting strong sites on the peat can account for the lower K_d values at the low aqueous mercury(II) concentrations. One explanation for $K_{\text{dom,s}} > K_{\text{peat,s}}$ could be greater conformational flexibility for DOM relative to peat—greater flexibility could increase the probability of bidentate Hg(II) complex formation by the released DOM.

Strong and Weak Conditional Binding Constants. The double site model fit produces conditional binding constants that correspond well with the expected nature of the strong and weak binding sites. The binding constants for the strong sites on the peat and DOM range from $10^{21.8}$ to $10^{23.2} \text{ M}^{-1}$ and the fitting errors for the strong site binding constants are very small (Table 5). Assuming that the strong sites are organic thiol functional groups (RSH), we can correct these binding constants for proton exchange by the thiols ($\text{RSH} = \text{RS}^- + \text{H}^+$). Typical organic thiols possess $\text{p}K_a$ values of approximately 10 (9). At the experimental pH of 6.0, the concentration of deprotonated thiols would be 10^{-4} of the total thiol concentration. Applying this factor to the strong site concentration of the peat and DOM gives conditional binding constants that are greater by a factor of 10^4 , resulting in a range of strong site binding constants of $10^{25.8}$ to $10^{27.2} \text{ M}^{-1}$ for an RSHg^+ complex (designated K_{RSHg^+} in Table 5).

This range of binding constants falls in the range of binding constants estimated and measured for mercury(II) binding by thiol-containing organic acids (e.g., thiosalicylic acid, $10^{25.70} \text{ M}^{-1}$; 2,3-dimercaptopropanol, $10^{26.60} \text{ M}^{-1}$ (19)), but higher than the binding constant estimated by Dyrssen and Wedborg (9) for a mercury(II)-organic thiol (RSHg^+) complex:



Higher binding constants have also been reported by Skyllberg et al. (20), who measured binding constants of $K_{\text{RSHg}^+} = 10^{31.6}$ to $10^{32.2} \text{ M}^{-1}$ for mercury(II) sorption to peat soils (proton exchange of the reduced sulfur sites was accounted for by mercaptoacetic acid acidity constants). The Dyrssen and Wedborg (9) binding constant estimate appears to define the low end of strong mercury(II) complexation, with only a single thiol participating in the complex. On the basis of EXAFS spectroscopy results (17), Skyllberg et al. (20) attributed the strength of their binding constants to bidentate complexation by aliphatic thiol and oxygen-containing functional groups. The wide range of strong mercury(II) binding involving organic thiols spans the range of mercury bound by single RSH groups (9), by bidentate aromatic and aliphatic thiols and phenols (e.g., thiosalicylic acid, 2,3-mercapto-propanol), or by bidentate aliphatic thiols and phenols or carboxyls (17, 20). None of the binding constants measured for organic matter equal that of mercaptoacetic acid ($10^{34.5} \text{ M}^{-1}$; aliphatic thiol and carboxyl).

The binding constants for the weak sites on the peat are $K_{\text{peat,w}} = 10^{11.5}$ and $10^{11.8} \text{ M}^{-1}$ with small fitting errors (Table 5). The binding constants for the weak DOM sites are $K_{\text{dom,w}}$

= $10^{7.3}$ and $10^{8.7}$ M⁻¹. The fitting errors on these estimates are relatively large, indicating that the model fit to the data is insensitive to $K_{\text{dom,w}}$. The fit of $K_{\text{dom,w}}$ to the distribution coefficient data is based on only a few data points at high aqueous mercury(II) concentration, hence the insensitivity of the fit. The binding constants for these weak sites correspond fairly well with mercury(II) binding constants for carboxylic and phenolic ligands (e.g., oxalic acid, phenol). No ligands containing only oxygen functional groups have binding constants as high as the binding constant range for the strong peat and DOM sites.

Environmental Implication. Recent studies examining the effects of mercury(II) speciation on methylation have focused on inorganic sulfur species as controls of free mercury(II) (3, 4, 30, 31). The presence of strong mercury(II) binding sites in the Florida Everglades peat indicates that the peat will compete with inorganic sulfur species for mercury(II). The abundance of reduced sulfur functional groups in the peat are well in excess of total mercury concentration, which is usually less than 25 pM (8); therefore, the strong site binding constants in the $10^{25.8}$ to $10^{27.2}$ M⁻¹ range will apply to mercury(II) speciation.

At the total mercury concentrations in the Everglades peats, the strong binding sites will control mercury(II) binding. The estimated strong binding capacity of the F1 peat exceeds that of the 2BS peat by only 33%, while the 2BS methylmercury concentration exceeds that of F1 by an order of magnitude. The difference in mercury(II) binding by the two peat samples from the Everglades does not seem to be sufficient to explain the higher methylmercury concentrations at the 2BS site. In addition to the peat, mercury(II) methylation will be slowed at the F1 site by higher concentrations of dissolved organic matter and sulfide. Perhaps the binding of mercury(II) by peat, dissolved organic matter, and sulfide combines to result in the relatively low methylation rate observed by Gilmour et al. (2) at the F1 site.

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