Environ. Sci. Technol. **2000**, *34,* 2196−2200

Mercury Speciation in the Presence of Polysulfides

JENNY AYLA JAY,*,† FRANÇOIS M. M. MOREL,‡ AND HAROLD F. HEMOND†

The Ralph M. Parsons Laboratory, Department of Civil and Environmental Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, and Guyot Hall, Department of Geology, Princeton University, Princeton, New Jersey 08544

Environmental mercury methylation appears modulated by sulfide concentrations, possibly via changes in mercury availability to sulfate reducing bacteria, the major agents of this process in aquatic systems. Consequently, there has been much recent interest in quantifying the chemical speciation and lipid solubility of mercury in the presence of sulfide and of polysulfides, which form by reaction of sulfide with elemental sulfur or as intermediates in sulfur cycling. We quantify a large increase in the solubility of cinnabar ($HgS_{(s)}$) in the presence of elemental sulfur, particularly at high pH. Based on our data and those of Paquette and Helz, we propose that the complex, $Hg(S_x)_2^{2-}$, dominates the speciation of Hg(II) in such waters. At lower sulfide concentrations and at high pH, the data are best fitted by considering also the formation of the species HgS_xOH^-. Octanol−water distribution (D_{ow}) experiments confirm the charged nature of the dominant mercury−polysulfide complexes and imply the presence of a minor lipophilic polysulfide complex, such as HgS_5. The recently reported decrease in D_{ow} with increasing sulfide concentration also occurs in the presence of polysulfides.

Introduction

The methylation of mercury is known to occur chiefly in anoxic waters and is thought be generally mediated by sulfate-reducing bacteria (*1*−*9*). Understanding the factors that may control mercury methylation thus requires that we understand the bioavailability of mercury in such systems and the solubility and chemical speciation of mercury in sulfidic waters. It has been suggested that lipid soluble species such as $HgCl_2$ (*10*−*13*) or $HgS^0_{(aq)}$ (*2, 3*) may diffuse passively through biological membranes and thus be available for methylation.

The solubility of cinnabar ($HgS_{(s)}$) and the formation of mercury-sulfide species ($Hg(SH)_2$, HgS_2H^-, HgS_2^{2-}) as a function of pH and sulfide concentration (here defined as the sum of H_2S, HS^-, and S^{2-}) have been extensively studied starting with the early work of Schwarzenbach and Widmer in 1963 (*14*). Table 1 gives the equilibrium constants, as rounded to the nearest 0.5 log units, as compiled by Benoit et al. (*1*) for the mercury−sulfide species. (Ionic strength differences between the Benoit et al. model and our conditions are not significant.) The existence of another species, $HgS^0_{(aq)}$, which would not have been detected in the work of Schwarzenbach and Widmer because of relatively high concentrations of other mercury−sulfide species, has been proposed; its concentration has been estimated by two different methods, both of which involve relating the binding affinities of mercury to those of other metals (*15*−*18*). In our model, we use $10^{-9.3}$, the average of the two literature estimates for the equilibrium constant of $HgS^0_{(aq)}$. On the basis of octanol−water partitioning experiments, Benoit et al. (*2*) proposed that $HgS^0_{(aq)}$ may be the mercury species most available for methylation.

TABLE 1. Constants Used in This Study for Mercury−Sulfide Interactions[a]

formation reactions for mercury−sulfide species	log *K*	ref
$HgS_{(cinn)} + HS^- = HgS_2^{2-} + H^+$	−13.0	Benoit et al. (*1*)
$HgS_{(cinn)} + HS^- = HgS_2H^-$	−4.5	Benoit et al. (*1*)
$HgS_{(cinn)} + HS^- + H^+ = Hg(SH)_2$	+1.0	Benoit et al. (*1*)
$HgS_{(cinn)} + H^+ = HgSH^+$	−16.81	Dyrssen (*18*)
$HgS_{(cinn)} = Hg^{2+} + S^{2-}$	−53.5	Benoit et al. (*1*)
$HgS_{(cinn)} = HgS(aqueous)$	−9.3	Dyrssen (*17, 18*)

[a] Constants from the Benoit et al. model (*1*) are averages of literature values, rounded to the nearest 0.5 log unit. The ionic strength of the model runs (approximately 0.5 M) is similar to that in our experiments (I = 0.3 M) so ionic strength corrections are not significant.

Only one study so far has addressed the possible formation of complexes between mercury and polysulfides (S_x^{2-} where x = 3−6) and their influences on mercury solubility (*4*). Polysulfides can form readily in sulfidic waters either by reaction of sulfide with elemental sulfur or directly as intermediates in the biological oxidation or reduction of sulfur. Concentrations of total S(0) present in the form of polysulfides up to 0.1 mM have been measured in the Lower Mystic Lake, MA (*19*). Although there is some uncertainty in the literature regarding the existence of S_6^{2-} as well as the equilibrium constants for particular polysulfide species, the total concentrations of polysulfides predicted by the various models are similar. (We have used the equilibrium constants reported by Boulègue and Michard (*20*)). In this article, $S(-II)_T$ represents the total concentration of H_2S, HS^-, S^{2-}, S_3^{2-}, S_4^{2-}, S_5^{2-}, S_6^{2-}, HS_4^-, and HS_5^-, since each polysulfide chain can be envisioned as possessing one sulfur atom of oxidation state (−II).

In this study we extend the study of Paquette and Helz by studying the effect of polysulfides on cinnabar solubility at lower $S(-II)_T$. Our results combined with those of Paquette and Helz lead us to propose a new chemical speciation scheme for mercury in the presence of polysulfides. We also extend the results of Benoit et al. (*2*) by measuring the octanol−water partitioning of mercury in the presence of polysulfides.

Experimental Methods

Solubility Experiments. The solubility of cinnabar in the presence of sulfide and elemental sulfur was measured in duplicate bottles at conditions ranging from pH 6 to 10 and $S(-II)_T$ concentrations from 2 μM to 5 mM (measured by iodometry). $S(-II)_T$ (by iodometry) and total mercury measurements were taken after equilibration in triplicate in most cases and duplicate as a minimum. Aliquots from several bottles were withdrawn and remeasured on different days to

* Correspondence author phone: (617)225-0810; fax (617)225-0813; email: jay@cambridgeenvironmental.com. Current address: Cambridge Environmental Inc., 58 Charles Street, Cambridge, MA 02141.

† Massachusetts Institute of Technology.

‡ Princeton University.

10.1021/es9911115 CCC: $19.00
Published on Web 04/21/2000

confirm that sulfide and total dissolved mercury concentrations were stable.

While serum bottles containing 0.1 g of cinnabar (Johnson Matthey) and 0.1 g of orthorhombic elemental sulfur (Mallinckrodt) were purged with deoxygenated (passed through a heated column of copper filings) high-purity nitrogen through a 30 cm long Teflon needle, 50 mL of deoxygenated buffer (pH 7 and 8 Hydrion buffers contained sodium phosphate and potassium phosphate, and pH 9 and 10 Hydrion buffers contained sodium carbonate and sodium bicarbonate, Aldrich) was transferred to each bottle. Ionic strength was approximately 0.3 M, and resazurin was added as a redox indicator. Each bottle was capped with a Teflon-faced butyl rubber septum (or a butyl rubber septum when contamination was not an issue due to high sulfide, and repeated sampling was necessary), crimped, and purged with deoxygenated nitrogen as above. Ti-Nitrotriacetic acid (NTA, as Ti(III), 0.1 mM) was added to the bottles as a reductant; significant complexation is not predicted under the conditions of the experiments (*21*). Aliquots of a stock solution of hydrogen sulfide (standardized by iodometry), prepared using washed crystals of $Na_2S{\cdot}9H_2O$ (Mallinckrodt) and deoxygenated water, were also added by syringe. Foil-wrapped bottles were equilibrated, unstirred, in a nitrogen-filled glovebox.

Aliquots containing approximately 1−2 ng of mercury were withdrawn through the septa using an acid-cleaned glass syringe and a Teflon or stainless steel needle preflushed with deoxygenated nitrogen. Blanks of both of these procedures gave unmeasurable signals, and duplicate experiments comparing the methods gave the same results.

Total Mercury Analysis. The contents of each syringe were filtered through 0.02 μm Anotop syringe filters into a Teflon tube. Pretested bromine monochloride (BrCl) was added in sufficient quantities so that the sample retained the color of the bromine monochloride. Mercury-free hydroxylamine (0.5 mL) was added to neutralize the excess BrCl, and the mixture was poured into a 300 mL of bubbler flask, with 1% stannous chloride reductant. Mercury was trapped on a gold column and quantified by dual amalgamation, cold vapor atomic fluorescence spectrometry (*22, 23*). Reagent blanks were between 0.05 and 0.2 ng of mercury and were consistent throughout a given day using the same batch of reagents. The detection limit was a function of the volume of sample added (e.g., for a 1 mL aliquot, the detection limit was 3 nM).

Octanol−Water Partitioning Experiments. Octanol−water partitioning was measured at pH 8 in the presence and absence of polysulfides and at $S(-II)_T$ concentrations ranging from 5×10^{-5} M to 5×10^{-3} M. Aliquots from the solubility experiment bottles were filtered through 0.02 μm Anotop filters (to remove solid mercuric sulfide) into a three-way stopcock. After flushing the stopcock with sample, a second glass syringe containing mercury-clean nitrogen-purged octanol was attached, octanol (Sigma) was rinsed through the stopcock, and the sample was transferred to the octanol-containing syringe. The ratio of octanol to aqueous sample was between 1 and 5. This syringe (with stopcock closed) was floated in a closed container of water with gentle shaking for 1.5 h (shown to be adequate to reach a plateau of extracted mercury). The aqueous phase was analyzed for mercury as previously described, and mercury partitioning into octanol was determined by difference.

Determination of Constants. Modeled Paquette and Helz data (*4, 5*) consisted of 17 different conditions, from pH 6.3 to 9.4 (data at lower pH were excluded, as polysulfide formation is important at neutral and higher pH) and from 2 to 23 mM $S(-II)_T$. Data from this study consisted of 19 conditions, from pH 7 to 10, from 2 μM to 5 mM $S(-II)_T$.

Formation constants for the proposed mercury−polysulfide species were estimated using FITEQL (*24*), an iterative, gradient-directed nonlinear least squares optimization program. The program optimized mercury−polysulfide formation constants by minimizing the difference between expected and measured total dissolved mercury concentrations under all tested pH and $S(-II)_T$. FITEQL reported the optimal formation constant for a particular species as well as the lowest WSOS/DF or weighted sum of squares of the difference between the measured and predicted total soluble mercury concentrations divided by the degrees of freedom. Standard deviations for individual data points were not known for both data sets; therefore, default values were used in the model.

Given equilibrium among polysulfide species (all expected to be soft-sphere ligands), it is likely that the increased cinnabar solubility observed when polysulfides are present is a result of many different complexes. We inferred the identity of possible complexes by assuming analogous behavior with the mercury−sulfide system.

Results

Cinnabar Solubility in the Presence and Absence of Polysulfides. Measurements of dissolved mercury after 3, 10, and approximately 30 days in the presence of cinnabar at pH 8 showed no significant variations with time (data not shown); thus, equilibrium between the dissolved and solid phases appears to be achieved within a few days. As will be discussed later, our dissolved mercury measurements in the absence of S(0) agree with previous data and published thermodynamic constants.

At high $S(-II)_T$, ($\geq$1 mM) in the presence of S(0) (and consequently, the presence of polysulfides), our data generally agreed with those of Paquette and Helz. At low pH, the dissolved mercury concentration in the presence of S(0) was approximately 3-fold higher than in the absence of S(0). At high pH, this increase went up to about 200-fold (Figure 1a). The dissolved mercury concentration decreased along with $S(-II)_T$ (Figure 1b,c); the trend of increasing solubility with pH became more pronounced at the lower $S(-II)_T$. (Note that in Figure 1 some scatter in the points results from lumping the data for a range of $S(-II)_T$ in each graph.)

As can be seen in Figure 1, the data obtained at high pH differed significantly from the model proposed by Paquette and Helz; the measured solubility was up to 100 times larger than predicted by their model. To improve the speciation model, we considered the formation of several possible mercury−polysulfide complexes besides HgS_xH^-, which was proposed by Paquette and Helz. We chose the species by analogy with the complexes that have been proposed for the reaction between mercury and sulfide (Table 1). As seen in Table 2, the species that gave the best fit of the data (smallest WSOS/DF; see Experimental Methods) was $Hg(S_x)_2^{2-}$. Note that the model calculations are unable to distinguish between complexes of the various polysulfides ($x = 3, 4, 5, 6$). The species $Hg(S_x)_2^{2-}$ gave the best fit for the Paquette and Helz data set as well as for that set combined with ours.

Including the previously proposed species, HgS_xH^-, along with $Hg(S_x)_2^{2-}$ did not improve the model fit. This was true for the other species as well, except for HgS_xOH^-, which gave a small improvement in the fit. The role of this species in accounting for the high solubility of cinnabar at low $S(-II)_T$ and high pH can clearly be seen in Figure 1b,c. Including the species HgS_xH^- (along with $Hg(S_x)_2^{2-}$ and HgS_xOH^- at their optimal formation constants) resulted in no improvement of the model; the fit degraded above a $K_{formation}$ for HgS_xH^- of −4.0.

As a general measure of the quality of the fit obtained with our speciation model ($Hg(S_x)_2^{2-}$ and HgS_xOH^-) and that of Paquette and Helz (HgS_xH^-), we plotted for all available

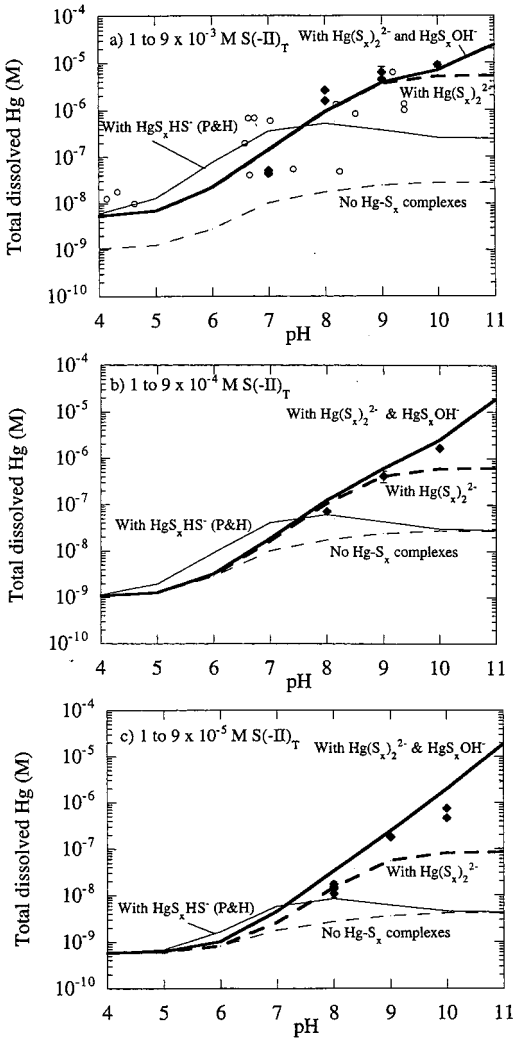

FIGURE 1. (a–c) Predicted and observed total soluble mercury as a function of pH in the presence of cinnabar and elemental sulfur: (a) 1 to 9 × 10^{-3} M (average = 4.35 × 10^{-3} M) S(−II)$_T$, (b) 1 to 9 × 10^{-4} M (average = 5.13 × 10^{-4} M) S(−II)$_T$, and (c) 1 to 9 × 10^{-5} M (average = 6.86 × 10^{-5} M) S(−II)$_T$. *I* = 0.3 M for all data points. Solid symbols are data from this study; open symbols are from Paquette and Helz. Lines represent the total dissolved mercury in equilibrium with cinnabar at the average sulfide concentration of the experiments plotted on the graph, as predicted under four scenarios. The plain dashed line is the calculated solubility in the absence of mercury–polysulfide complexes. The plain solid line is the calculated solubility according to the Paquette and Helz model, which includes HgS_xH^-. The bold dashed line depicts the calculated solubility considering $Hg(S_x)_2^{2-}$ as the only mercury–polysulfide complex, while the bold solid line includes $Hg(S_x)_2^{2-}$ and HgS_xOH^- (both of the proposed new species).

data points the log(predicted Hg_T/observed Hg_T), where Hg_T represents the total concentration of dissolved mercury. As seen in Figure 2, the predicted and measured values are within a factor of 10 for our model, while they diverge by a factor of up to 100 for the previous model. (Note that a log(predicted Hg_T/observed Hg_T) of 0.3 corresponds to a difference of a factor of 2, while the experimental error was less than 15%.) How well the estimated values for the constants $Hg(S_x)_2^{2-}$ and HgS_xOH^- are constrained by the data is shown by the calculation of the WSOS/DF (Figure 3a,b). In the case of $Hg(S_x)_2^{2-}$, the WSOS/DF has a clear minimum, and thus the value of the constant is well-constrained. In the case of HgS_xOH^-, the minimum is much shallower (note the change in scale in Figure 3b); accordingly, the constant is less well-constrained.

Octanol–Water Partitioning. The octanol–water distribution coefficient (D_{ow} = Hg_T in octanol/Hg_T in water) was determined at pH 8 for various S(−II)$_T$ in the absence of S(0). Our results were in good agreement with the model of Benoit et al. (Figure 4), showing a large decrease in D_{ow} with increasing sulfide concentration. The model calculates D_{ow} by summing up expected contributions to D_{ow} from uncharged species, $HgS^0_{(aq)}$ and $Hg(SH)_2$, according to the equation

$$D_{ow} = \sum_i K_{ow,i} \cdot \chi_i \qquad (1)$$

where χ_i represents the mole fraction of species i at equilibrium in the aqueous phase, and K_{ow} equals 25 for both $HgS^0_{(aq)}$ and $Hg(SH)_2$ (*2*).

The presence of S(0) in the system resulted in insignificant changes in the octanol solubility of mercury; both the magnitude of D_{ow} and its decrease with S(−II)$_T$ were the same with and without S(0) (compare Figure 4a,b). This result is surprising since the concentration of $HgS^0_{(aq)}$, the species which is presumably responsible for most of the octanol solubility (*2, 3*), should not be affected by the presence of polysulfides and its contribution to the total dissolved mercury (which increases with the addition of polysulfides) should decrease along with the ratio $HgS^0_{(aq)}/Hg_T$. (see Figure 4b). Indeed, calculations based on Benoit et al.'s model predict much smaller D_{ow}'s than observed. Thus it appears that, at least in the presence of polysulfides, some species other than $HgS^0_{(aq)}$ and $Hg(SH)_2$ may partition significantly into the octanol.

The simplest way to account for our result is to consider that some uncharged mercury–polysulfide species present at a minor concentration may have a significant octanol water partitioning. We assumed the presence of HgS_5, for S_5^{2-} is predicted to be the dominant polysulfide. Based on Hansch and Leo's additive method, and starting with $HgS^0_{(aq)}$ and $Hg(SH)_2$ as starting points (to estimate a range), assuming alternating single and double bonding between sulfur atoms (*25, 26*), the resulting value for K_{ow,HgS_5} is between 900 and 11 × 10^3. To account for the observed data, the species HgS_5 must thus be present at approximately 10–100 pM in equilibrium with cinnabar and elemental sulfur (see Supporting Information for further discussion). Importantly, the concentration of this species does not change with S(−II)$_T$, and it can account for the increase in D_{ow} at all three S(−II)$_T$ (Figure 4).

Discussion

It is clear that polysulfides increase the solubility of cinnabar, especially at high pH. Based on our results and those of Paquette and Helz, we propose a new mercury–polysulfide speciation model that includes the species $Hg(S_x)_2^{2-}$ and HgS_xOH^-, with the equilibrium constants, $10^{-11.7}$ and $10^{-15.7}$, respectively. To exemplify the importance of these species to mercury speciation, we have compared the solubility of mercury and its speciation in the presence of cinnabar at pH 8 as a function of sulfide in both the presence and absence of S(0) (Figure 5). Shown in the figure are our measurements of total dissolved mercury under both conditions, which agree well with the model. In the presence of S(0), the polysulfide complexes account for most of the dissolved mercury and substantially increase its solubility.

The calculated solubility and speciation of mercury as a function of pH in the presence of cinnabar and S(0) at 1 mM S(−II)$_T$ is shown in Figure 6, along with some of our measured data. In the speciation model presented in Figures 5 and 6, we have included not only the dominant mercury–polysulfide species $Hg(S_x)_2^{2-}$ and HgS_xOH^-, but also the proposed minor uncharged species, HgS_5. Insofar as our octanol–water partitioning results in the absence of elemental sulfur confirm

TABLE 2. Formation Constants and Weighted Sum of Squares over Degrees of Freedom (WSOS/DF) for Various Likely Mercury−Polysulfide Complexes[a]

formation reactions for new Hg−S_x species	P&H data		P&H and Jay et al. data	
	log *K*	WSOS/DF	log *K*	WSOS/DF
$HgS_{(cinn)} + HS^- + (x-1)S(0)_{(orth)} = \mathbf{HgS_xHS^-}$	−3.9	12.7	−3.8	9.3
$HgS_{(cinn)} + (x-1)S(0)_{(orth)} = \mathbf{HgS_x^0}$	−5.9	11.1	−5.9	7.8
$HgS_{(cinn)} + HS^- + (x-1)S(0)_{(orth)} = \mathbf{HgS_xS^{2-}} + H^+$	−11.7	4.28	−11.7	3.8
$HgS_{(cinn)} + (x-1)S(0)_{(orth)} + H_2O = \mathbf{HgS_xOH^-} + H^+$	−14.7	6.4	−15.4	7.8
$HgS_{(cinn)} + HS^- + 2(x-1)S(0)_{(orth)} = \mathbf{Hg(S_x)_2^{2-}} + H^+$	−11.8	3.2	−11.7	3.1
$HgS_{(cinn)} + HS^- + 2(x-1)S(0)_{(orth)} = \mathbf{Hg(S_x)_2^{2-}} + H^+$	did not converge		−11.7	2.6
$HgS_{(cinn)} + (x-1)S(0)_{(orth)} + H_2O = \mathbf{HgS_xOH^-} + H^+$			−15.7	

[a] Species bolded in formation reaction. The model proposed here is shown in the last two rows (WSOS/DF from a simultaneous optimization). Reported for $I = 0.3$ M.

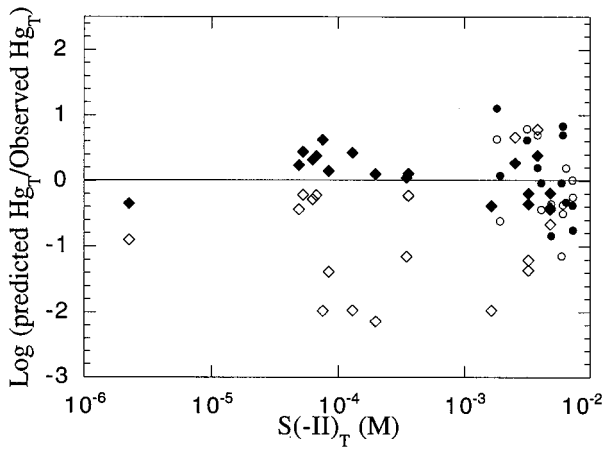

FIGURE 2. Log of the ratio (predicted Hg_T/observed Hg_T) where Hg_T is the total soluble mercury in equilibrium with cinnabar, for all data points in the both data sets under two modeling scenarios. Circles depict this parameter using the Paquette and Helz data set, while diamonds represent data from this study. Open symbols represent results from modeling calculation using the previous mercury−polysulfide model, allowing HgS_xHS^- as the only mercury−polysulfide complex, and closed symbols depict calculation using the model proposed in this study ($Hg(S_x)_2^{2-}$ and HgS_xOH^-).

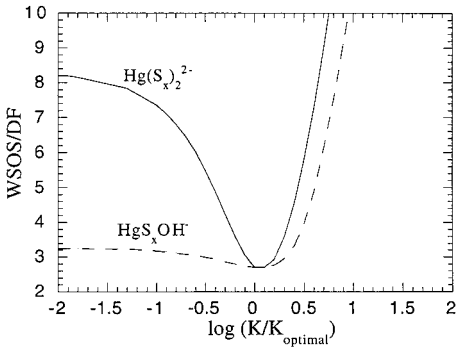

FIGURE 3. Residual error calculated by FITEQL as the formation constants for $Hg(S_x)_2^{2-}$ and HgS_xOH^- are varied, keeping all other values constant. Both Paquette and Helz data and those from this study were used in this analysis.

those of Benoit et al., they support the presence of a hydrophobic mercury−sulfide species such as $HgS^0_{(aq)}$ dominant at lower sulfide concentrations (we are unable to make a stronger statement regarding the existence of this species as it would not be dominant under the conditions we tested.)

Although we have no direct evidence for the species $Hg(S_x)_2^{2-}$ and HgS_xOH^-, the indirect evidence provided by the variations in cinnabar solubility with pH and $S(-II)_T$ is fairly strong. The evidence for HgS_5 is more indirect since it

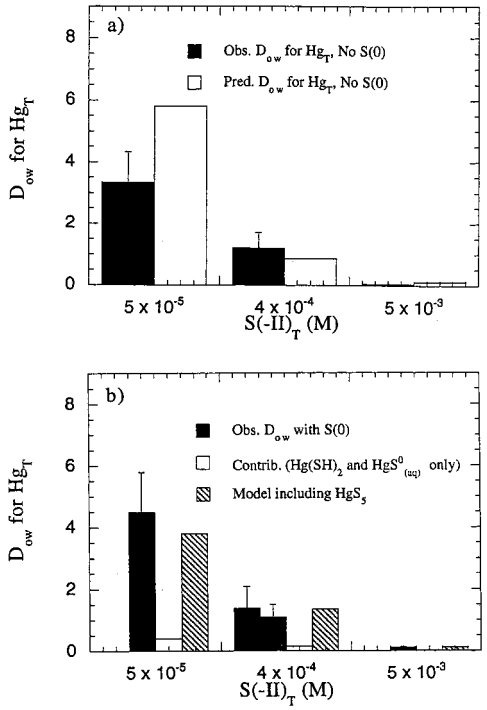

FIGURE 4. Experimentally determined octanol−water distribution coefficients (D_{ow}) (dark bars) for dissolved mercury species at pH 8 in equilibrium with cinnabar in the absence (a) and presence (b) of S(0). For comparison, the predicted contribution to D_{ow} from $HgS^0_{(aq)}$ and $Hg(SH)_2$ is shown by the white column (using the measured values of $K_{ow} = 25$ for both (*2*)). Error bars represent one standard deviation, propagated error. In the presence of S(0), shaded bars depict the D_{ow} predicted including the above species, as well as 10 pM HgS_5 (estimated K_{ow} of 11 000). Duplicate experiments were performed at 4×10^{-4} M $S(-II)_T$.

is based on octanol−water partition data. Further, the equilibrium constant for this species is also dependent on the value estimated for its K_{ow}. Since we used a fragment approach, whether the sulfur atoms are singly or doubly bonded to each other would result in a difference of a factor of 10 in the estimated K_{ow} and, hence, a factor of 10 in its equilibrium constant. (Note that the prediction of K_{ow} for $Hg(SH)_2$ by the fragment method does not agree particularly well with the data of Benoit et al.)

From the point of view of the toxicology of mercury, the most important process is its methylation, which, presumably, depends on the concentrations of mercury species and their permeability through biological membranes. Under conditions where mercury is at equilibrium with cinnabar (the case shown in Figures 5 and 6) the presence of polysulfides could serve to increase mercury bioavailability

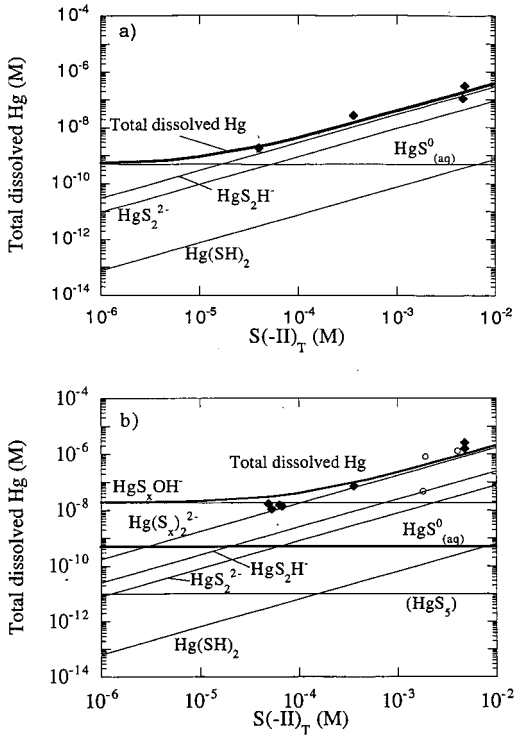

FIGURE 5. The equilibrium composition of dissolved mercury species in equilibrium with cinnabar at pH 8 as a function of $S(-II)_T$ (a) in the absence and (b) in the presence of elemental sulfur. Lines in (b) are based on the new species and equilibrium constants proposed in this work. Data points at pH 7.8−8.5 are shown on the graph (circles represent Paquette and Helz data, and diamonds depict data from this study).

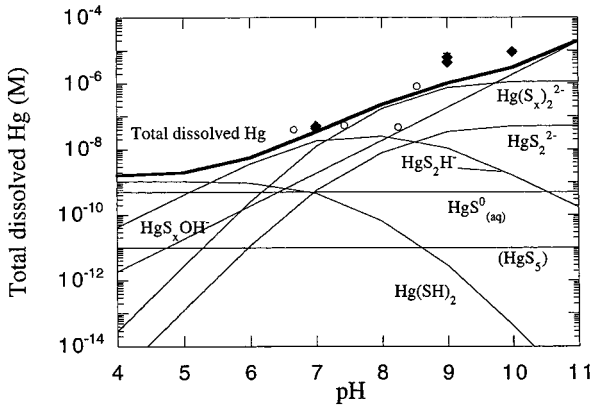

FIGURE 6. Speciation of dissolved mercury in equilibrium with cinnabar and elemental sulfur at 1 mM $S(-II)_T$ as a function of pH, according to the model proposed in this study. Data points at $S(-II)_T$ from 1.6 to 3.8 mM are shown on the graph (circles represent Paquette and Helz data, and diamonds depict data from this study).

if the membrane permeability of the species were simply dependent on the octanol−water partitioning. It is not certain, however, that uncharged mercury−sulfide and mercury−polysulfide species would diffuse equally well through membranes, due to their differences in size.

When total mercury is fixed, complexation with polysulfides may have two competing effects on mercury bioavailability: the possible formation of low concentrations of uncharged mercury−polysulfide species with presumably a high K_{ow} and the decrease in concentration of $HgS^0_{(aq)}$ due to the formation of dominant charged mercury−polysulfides species. At sulfide concentrations below 10 μM, the presence of polysulfides results in an overall decrease (approximately 3-fold) in the predicted D_{ow} of mercury. At higher sulfide, a slight (up to 2-fold) increase in overall D_{ow} is predicted.

While speculations of the effects of polysulfides on methylation are certainly reasonable, their validity will ultimately need to be tested by direct measurements of methylation rates in the presence and absence of S(0).

Acknowledgments

The authors wish to thank Lynn Roberts and Rob Mason for their initial inspirations at the conception of this study, their technical guidance through rigorous laboratory methods, and their continuing advice. Also, we greatly appreciate the invaluable comments of Cindy Gilmour and Janina Benoit and the meticulous laboratory assistance of Karen Murray. We are grateful to Dan Brabander, Miriam Chirico, Samantha Roberts, Dianne Newman, Nicole Keon, David Senn, and three anonymous reviewers for their helpful comments on the manuscript,. This work was supported by the NIEHS Superfund Basic Research Fund (Grant P42-ESO4675-08) and a GE Graduate Fellowship to Jenny Ayla Jay.

Supporting Information Available

The full data set and FITEQL tables, further information concerning K_{ow} calculations for HgS_5, and a sensitivity analysis of the model to HgS_xH^-. This material is available free of charge via the Internet at http://pubs.acs.org.

Literature Cited

(1) Benoit, J.; Gilmour, C.; Mason, R.; Heyes, A. *Environ. Sci. Technol.* **1999**, *33*, 951−957.
(2) Benoit, J. M.; Mason, R.; Gilmour, C. *Environ. Toxicol. Chem.* **1999**, *18*, 2138−2141.
(3) Benoit, J. M.; Gilmour, C. C.; Mason, R. P.; Riedel, G. S.; Riedel, G. F. *Biogeochem.* **1998**, *40*, 249−265.
(4) Paquette, K. E.; Helz, G. R. *Environ. Sci. Technol.* **1997**, *31*, 2148−2153.
(5) Paquette, K. Ph.D. Dissertation, University of Maryland, College Park, MD, 1994.
(6) Gilmour, C.; Henry, E. *Environ. Pollut.* **1991**, *71*, 131−169.
(7) Gilmour, C.; Henry, E.; Mitchell, R. *Environ. Sci. Technol.* **1992**, *26*, 2281−2287.
(8) Watras, C.; Bloom, N.; Claas, S.; Morrison, K.; Gilmour, C.; Craig, S. *Water, Air, Soil Pollut.* **1995**, *80*, 735−745.
(9) Matilainen, T.; Verta, M. *Can. J. Fish. Aquat. Sci.* **1995**, *52*, 1597−1608.
(10) Gutknekt, J. *J. Membr. Biol.* **1981**, *61*, 61−66.
(11) Mason, R.; Reinfelder, J.; Morel, F. *Water, Air, Soil Pollut.* **1995**, *80*, 915−921.
(12) Mason, R.; Reinfelder, J.; Morel, F. *Environ. Sci. Technol.* **1996**, *30*, 1835−1845.
(13) Barkay, T.; Gillman, M.; Turner, R. *Appl. Environ. Microbiol.* **1997**, *63*, 4267−4271.
(14) Schwarzenbach, G.; Widmer, M. *Helv. Chim. Acta* **1963**, *46*, 2613−2628.
(15) Dyrssen, D. *Mar. Chem.* **1985**, *15*, 285−293.
(16) Dyrssen, D. *Mar. Chem.* **1988**, *24*, 143−153.
(17) Dyrssen, D. *Mar. Chem.* **1989**, *28*, 241−249.
(18) Dyrssen, D.; Wedborg, M. *Water, Air, Soil Pollut.* **1991**, *56*, 507−519.
(19) Jay, J. A. Ph.D. Dissertation, Massachusetts Institute of Technology, Cambridge, MA, 1999.
(20) Boulègue, J.; Michard, G. *J. Franc. d'Hydrol.* **1978**, *9*, 27−34.
(21) Morel, F.; Hering, J. *Principles and applications of aquatic chemistry;* John Wiley & Sons: 1993.
(22) Gill, G.; Fitzgerald, W. *Mar. Chem.* **1987**, *20*, 227−243.
(23) Bloom, N.; Fitzgerald, W. *Anal. Chim. Acta* **1988**, *208*, 151−161.
(24) Herbelin, A.; Westall, J. Department of Chemistry, Oregon State University, Corvalis, OR, 1996.
(25) Giggenbach, W. *Inorg. Chem.* **1972**, *11*, 1201−1207.
(26) Clarke, E. T.; Solouki, T.; Russell, D.; Martell, A.; McManus, D. *Anal. Chim. Acta* **1994**, *299*, 97−111.

Received for review September 28, 1999. Revised manuscript received March 6, 2000. Accepted March 13, 2000.

ES9911115