Determination of Mercury Complexation with Dissolved Organic Matter in a Contaminated Aquatic Environment

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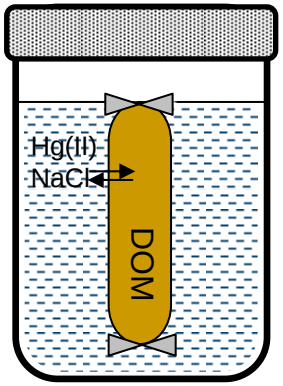
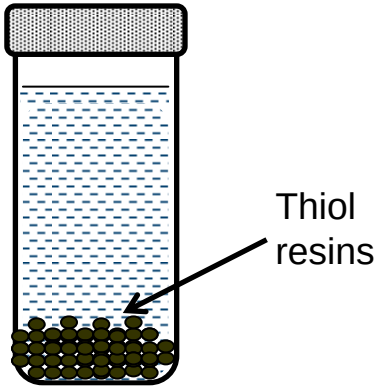
Background

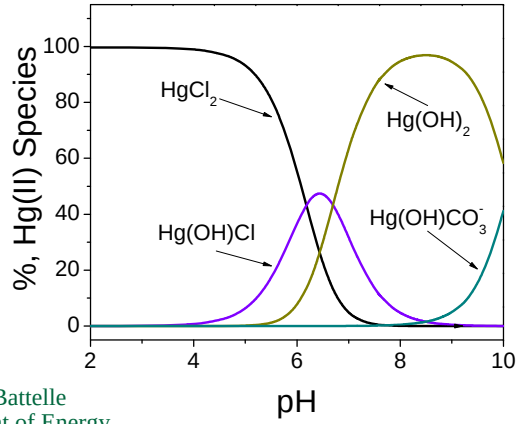
- The East Fork Poplar Creek (EFPC) in Oak Ridge, Tennessee heavily contaminated by past mercury release (>200,000 kg)
- The role of DOM in mercury speciation is unknown in EFPC ([DOC] = 1.3 – 1.8 ppm, pH = 7.5 – 8.2)
- Reported binding constants of Hg(II)-DOM(thiols) show a wide variation (log K = 20 – 40)

Objectives

- Determine the strong binding sites (thiols-like) in EFPC DOM using an equilibrium dialysis ligand exchange (EDLE) technique (Haitzer et al., ES&T, 2002).
- Determine the stability constants of Hg(II)-DOM(thiols) complexes using a modified ion exchange method
- Calculate Hg(II) speciation in EFPC water using an equilibrium approach.







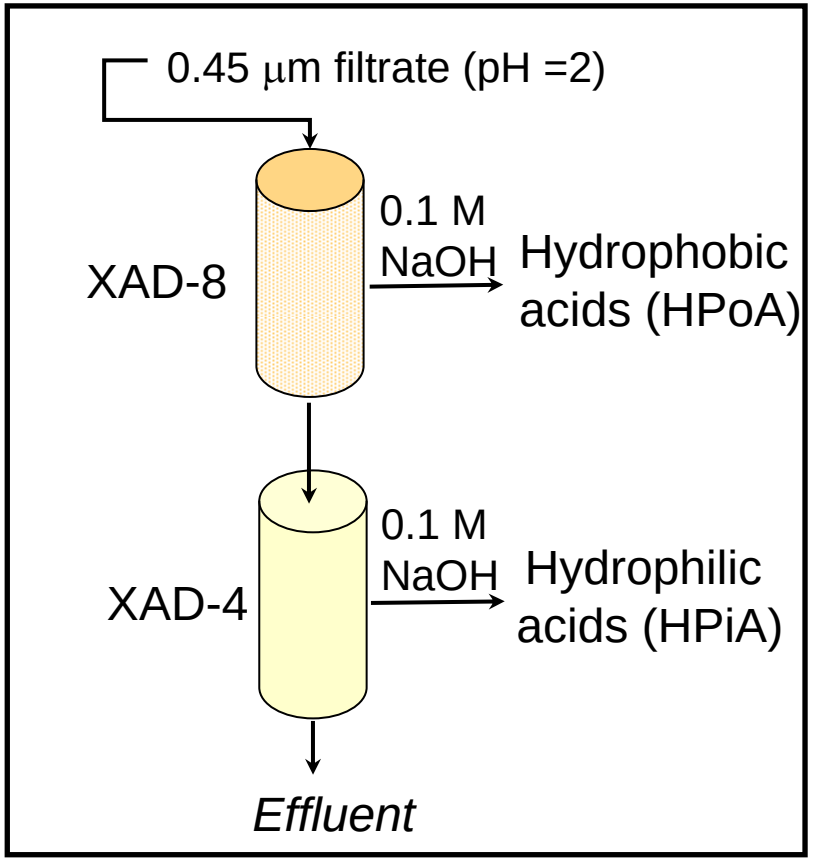
DOM → Hg(II) Species?

Experimental Materials and Methods

1. Isolation of Hydrophobic and Hydrophilic Acids

- **EFPC water sampling:** collected September, 2008 (pH = 7.8, DOC = 1.7 ppm)
- **Extraction procedures*:** See scheme shown on right. After collecting HPoA and HPiA fractions, samples were immediately passed through a H^+-saturated cation-exchange resin column and freeze-dried

*Aiken et al., 1992, *Org. Geochem.* **18**(4), 567-573.

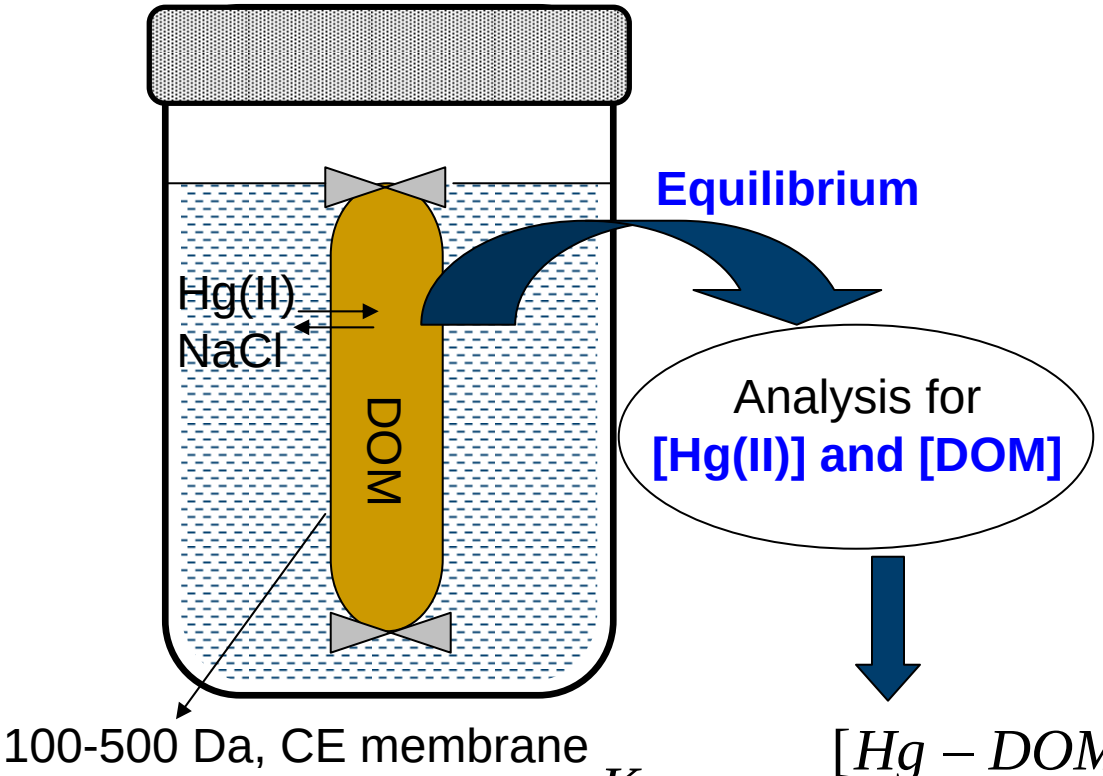


Schematic of XAD-8/XAD-4 Isolation

Experimental Materials and Methods

2. Determination of Strong Binding Sites in DOM

- Equilibrium Dialysis Ligand Exchange (EDLE) Method



Experimental conditions:

Inside bag (10 mL):

—10 ppm DOM

— 0.1 M NaCl

— pH = 8.0±0.1

Outside bag (90 mL):

— Varying total [Hg(II)] = 0.1–750 ug/L

— 0.1 M NaCl

— pH = 8.0±0.1

Equilibrated in 5 days

$$K_{DOM'} = \frac{[Hg-DOM]}{[Hg^{2+}](DOM)}$$

(defined by Haitzer et al., 2002)

$$[Hg-DOM] = [Hg(II)]_{inside} - [Hg(II)]_{outside}; \qquad [Hg^{2+}] = \frac{[Hg(II)]_{outside}}{A}$$

Experimental Materials and Methods

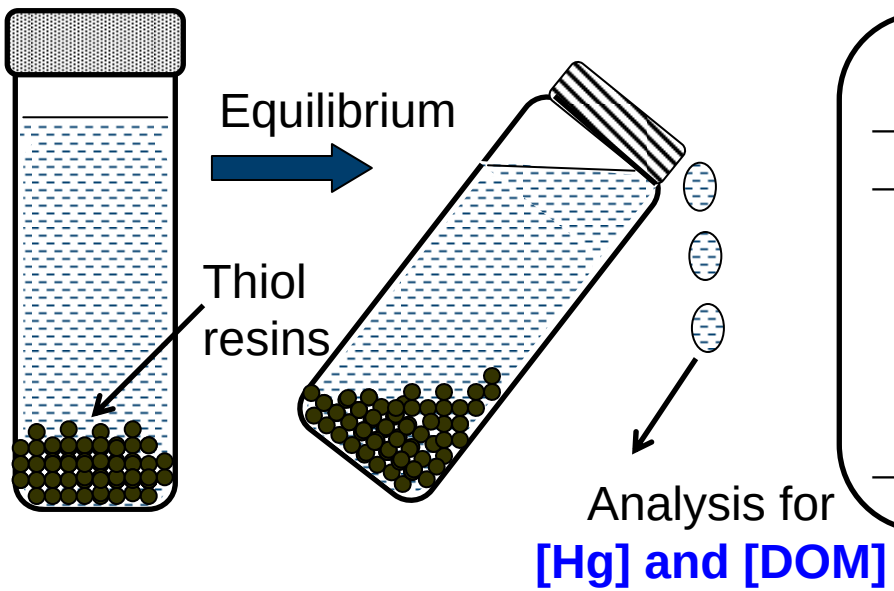
3. Determination of Stability Constants of Hg(II)-DOM(thiols):

- Modified Ion Exchange Method

Theoretical Consideration:

$$\left(\frac{D_0}{D_L}-1\right)\cdot A=\sum_i K_{HgL_i}[L^-]_{aq}^i$$

$$Hg^{2+}+iL^-=HgL_i\,,\quad K_{HgL_i}=\frac{[HgL_i]}{[Hg^{2+}][L^-]^i},\qquad i=1,2,\cdots$$



Experimental Conditions:

— 30 mg **thiol resin** (Ambersep GT74)

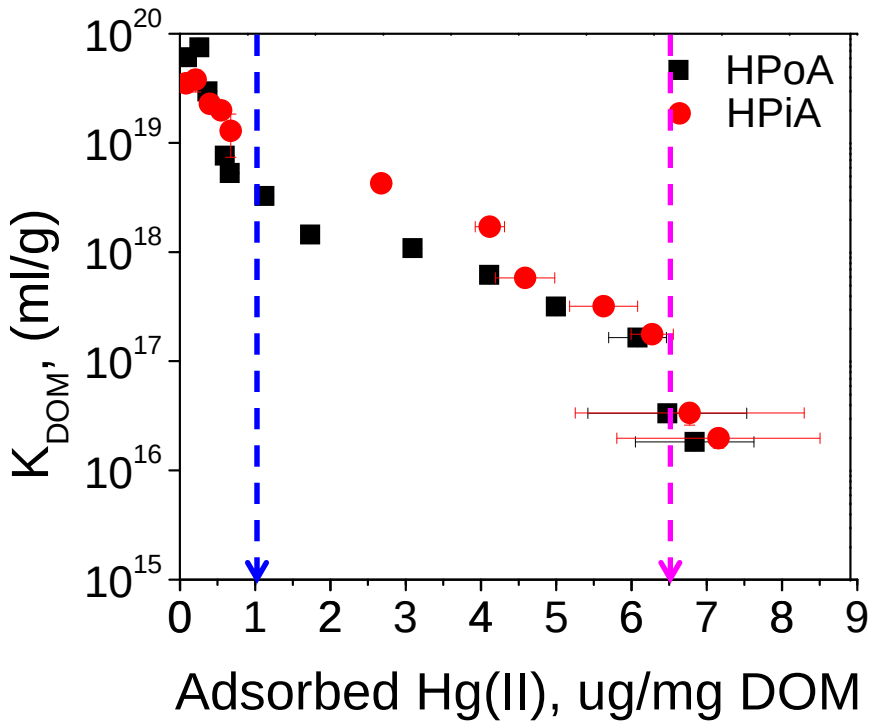
— 30 mL solution containing:

- 0.1 M NaCl
- pH = 8.0±0.1 (1 mM $NaHCO_3$)
- varying [DOM] (25–25 ppm)
- spiked with Hg(II) at 1.2 ppb(6 nM)

— Equilibrated in 5 days

Results

1. Strong Binding Sites in DOM — EDLE Results



$$K_{DOM'} = \frac{[Hg - DOM]}{[Hg^{2+}](DOM)}$$

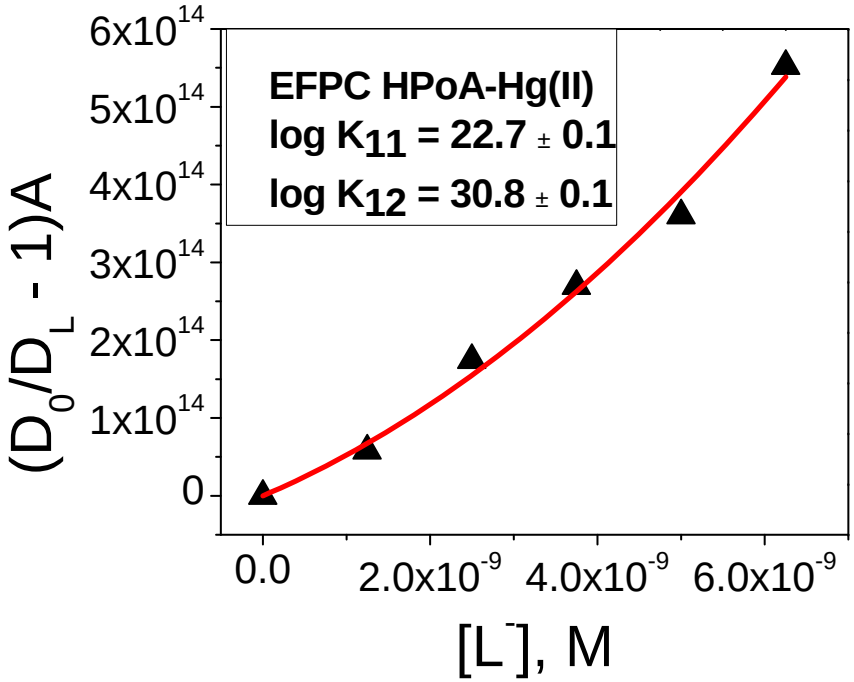
(i) The binding strength of thiols in DOM exhibits a **continuous distribution**.

(ii) The maximum binding sites ≈ 30 nmol/mg DOM in 0.1 M NaCl medium.

(iii) The **strongest sites (thiols-like) ≈ 5 nmol/mg DOM** (consistent with Haitzer et al., 2002).

Results

2. Stability Constants of Hg(II)-DOM — Ion Exchange Results



$$\left(\frac{D_0}{D_L}-1\right)\cdot A = K_{11}[L^-]+K_{12}[L^-]^2$$

DOM	Log K_{11}	Log K_{12}
EFPC HPoA	22.7 ±0.1	30.8 ±0.1
EFPC HPiA	21.9 ±0.1	30.1 ±0.1
FRC HA	23.6±0.1	31.6 ± 0.2
FRC FA	22.5 ±0.1	30.7 ±0.1

i) 1:1 and 1:2 complexes are simultaneously formed.

ii) Binding strength: FRC HA > EFPC HPoA ≈ FRC FA > EFPC HPiA

Results: Comparison of Binding Constants

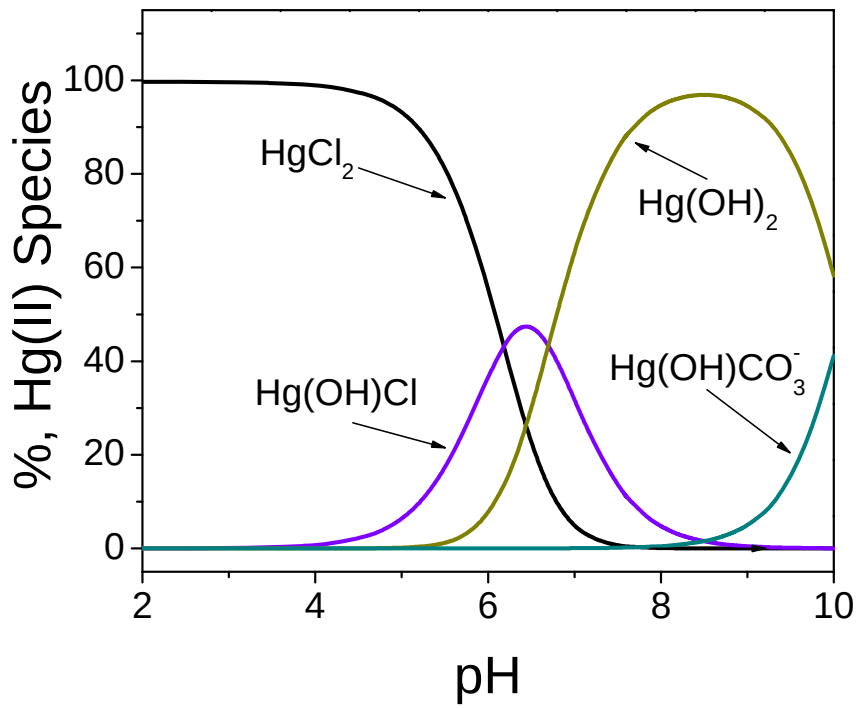
DOM	Log K_{11}	Log K_{12}	pH	I (M)	Method	Ref.
EFPC HPoA	22.7 ±0.1	30.8 ±0.1	8.0 ±0.1	0.1	Ion exchange	This work
EFPC HPiA	21.9 ±0.1	30.1 ±0.1	8.0 ±0.1	0.1	Ion exchange	This work
FRC HA	23.6±0.1	31.6 ± 0.2	8.0 ±0.1	0.1	Ion exchange	This work
FRC FA	22.5 ±0.1	30.7 ±0.1	8.0 ±0.1	0.1	Ion exchange	This work
DOM	21 - 24		7.5	na	Reducible Hg	Lamborg et al., 2003
HPoA HPiA	21.4–23.8 20.6–22.4		4 – 6	0.06	CLE-SSE	Benoit et al., 2001
HPoA	28.5	28.7	7.0	0.1	EDLE	Haitzer et al., 2002/2003
DOM	29.9–33.5		7.4–7.8	na	CLE-SPE	Black et al., 2007
DOM	26.1–26.9		7.0–7.5	0.6	CLE-SSE	Han and Gill, 2005

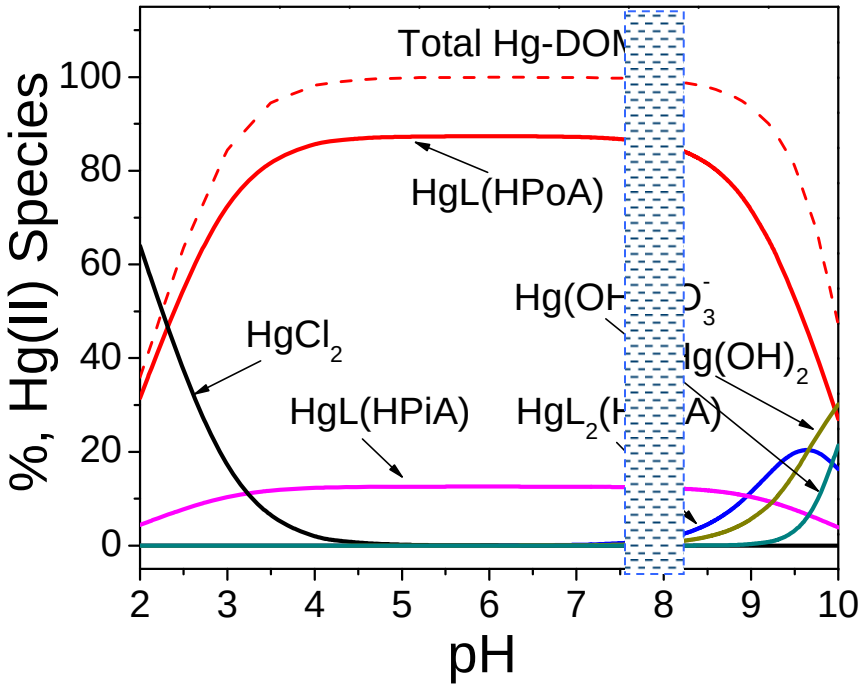
Results

3. Aqueous Species Modeling in EFPC

-- PHREEQC Code (Parkhurst and Appelo, 2004)

DOM





Hg-DOM(thiols) complexes dominate in EFPC

Conclusions

- DOM from EFPC and FRC can form strong complexes with Hg(II) through thiols-like functional groups: log K_{11} = 21.9 – 23.6 and log K_{12} = 30.1 – 31.6
- Observed binding strength in the order: FRC HA > EFPC HPoA ≈ FRC FA > EFPC HPiA
- Hg(II)-DOM(thiols) complexes are predicted to dominate in EFPC water, and are expected to play important role in Hg(II) biogeochemical processes
- Modified ion exchange method is found to be useful for determining Hg(II) complexation constants with strong binding sites (thiols) in DOM

Acknowledgments

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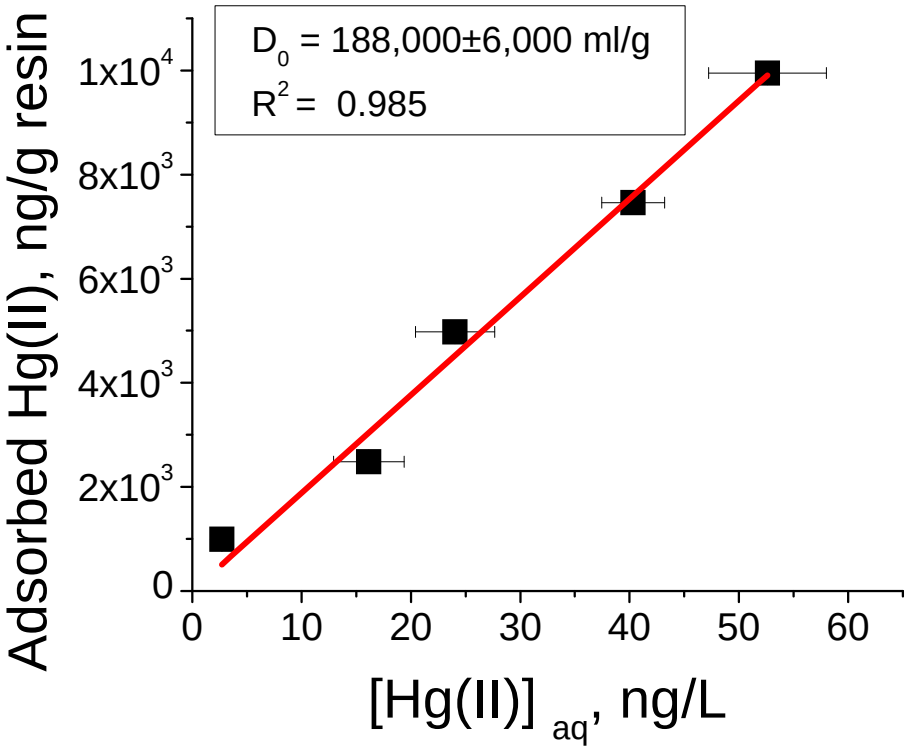
- ORNL is managed by UT-Battelle LLC for US DOE under contract DE-AC05-00OR22725.

The following slides are for questions

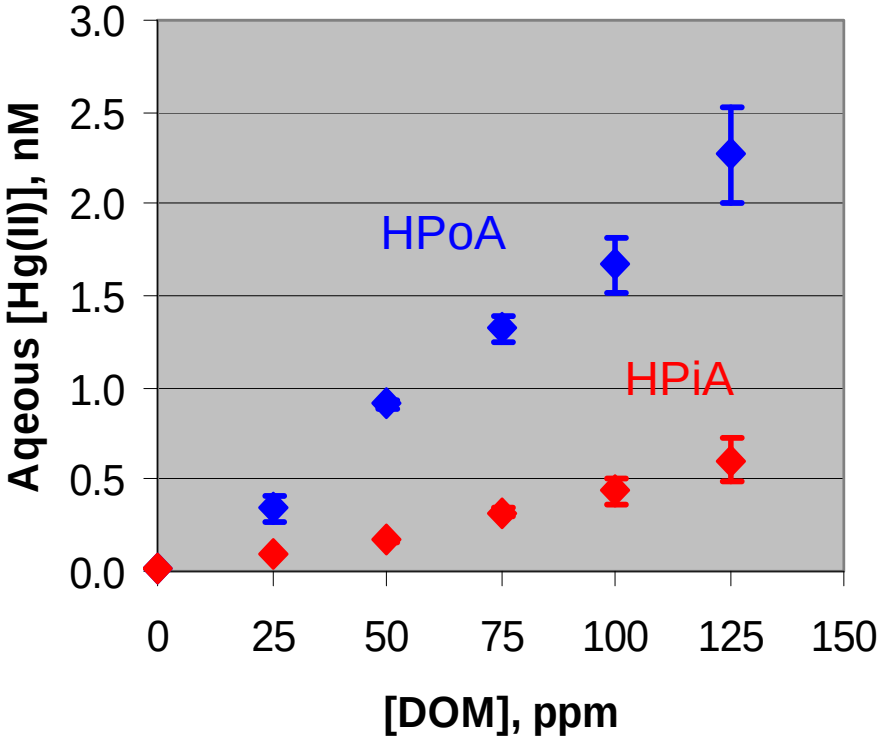
Hg(II) distribution coefficient between thiol resin and aqueous solution in the absence of DOM



Experimental Conditions:

- 30 mg **thiol resin** + 30 mL soln.
- 0.1 M NaCl
- pH = 8.0±0.1 (1 mM $NaHCO_3$)
- varying [Hg(II)] = 1 - 10 μg/L
- W/o DOM
- Equilibrium 5 days

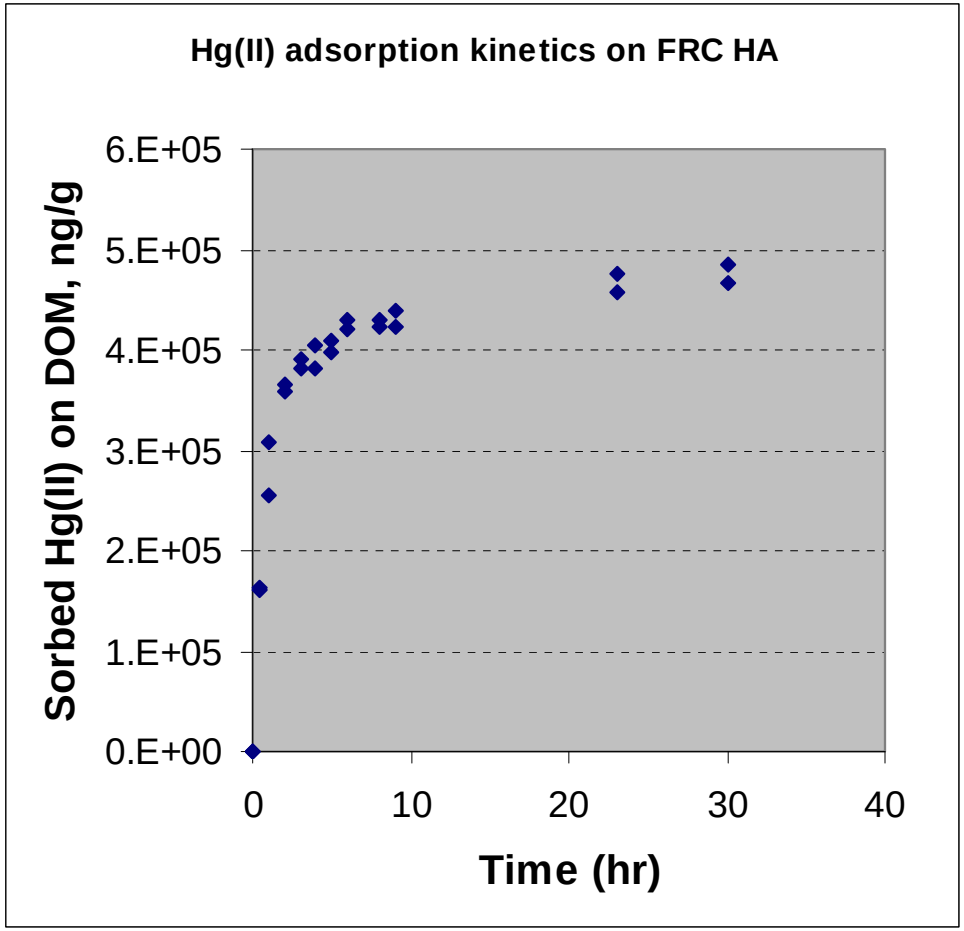
Aqueous Hg(II) concentrations increased with increasing DOM suggesting the formation of strong Hg(II)-DOM complexes



Experimental Conditions:

- 30 mg **thiol resin** + 30 mL soln.
- 0.1 M NaCl
- pH = 8.0±0.1 (1 mM $NaHCO_3$)
- Varying [DOM] = 0 – 125 ppm
- Spiked [hg(II)] = 1.2 ppb (6 nM)
- Equilibrium 5 days

Hg(II) adsorption kinetics on DOM through dialysis membrane



Experimental conditions:

Inside bag (10 mL):

—100 ppm DOM

— 0.1 M NaCl

— pH = 8.0±0.1

Outside bag (90 mL):

— total [Hg(II)] =5 ug/L

— 0.1 M NaCl

— pH = 8.0±0.1

Theoretical Consideration – Ion Exchange method

If DOM is not sorbed onto thiols resin

$$\left(\frac{D_0}{D_L}-1\right)\cdot A = K_{11}[L^-]+K_{12}[L^-]^2$$

If certain amount of DOM is sorbed onto resin, a correction for D_L is required.

$$D_L = \frac{[Hg(II)]_R^L - Q_{Hg-DOM}/m}{[Hg(II)]_{aq}^L + Q_{Hg-DOM}/V}$$

Where $Q_{Hg\text{-}DOM}$ is amount (mol) of Hg associated with sorbed DOM and can be calculated by assuming the sorbed and dissolved DOM have the same affinity toward Hg(II):

$$\frac{[Hg(II)-DOM]_R}{[DOM]_R} = \frac{[Hg(II)-DOM]_{aq}}{[DOM]_{aq}}$$

$$Q_{Hg-DOM} = [Hg(II)-DOM]_R \times V$$