Kinetic controls on the interaction of mercury with dissolved organic matter

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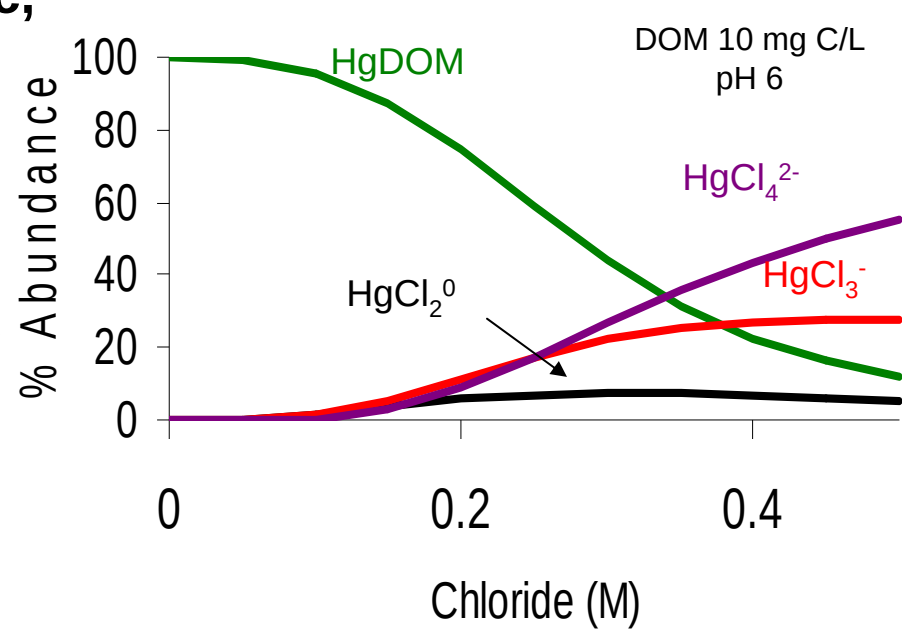
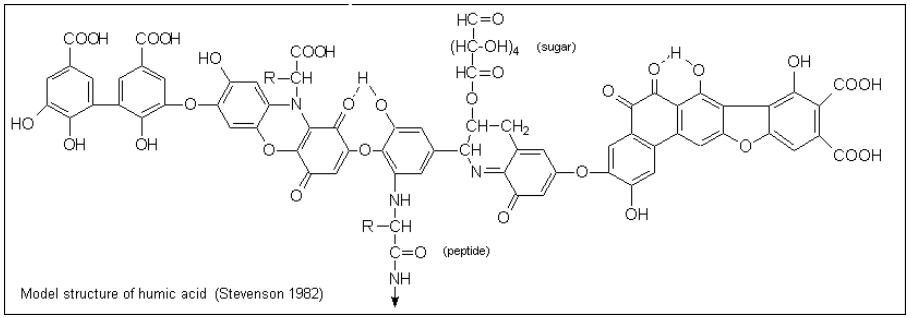
Mercury complexation

- **Under equilibrium conditions Hg-DOM complexes dominated in oxic, freshwater systems**
  - **Result of strong interaction with reduced thiol functional groups**
- **Formation constants for Hg-DOM complexes range (log k 22.4-47.7)**
  - **Different DOM composition**
  - **Different analytical methods**
  - **Binding modes (mono vs bidentate)**
- **Mechanism controlling Hg complexation not understood**
- **Most studies assume that equilibrium complexation is established**



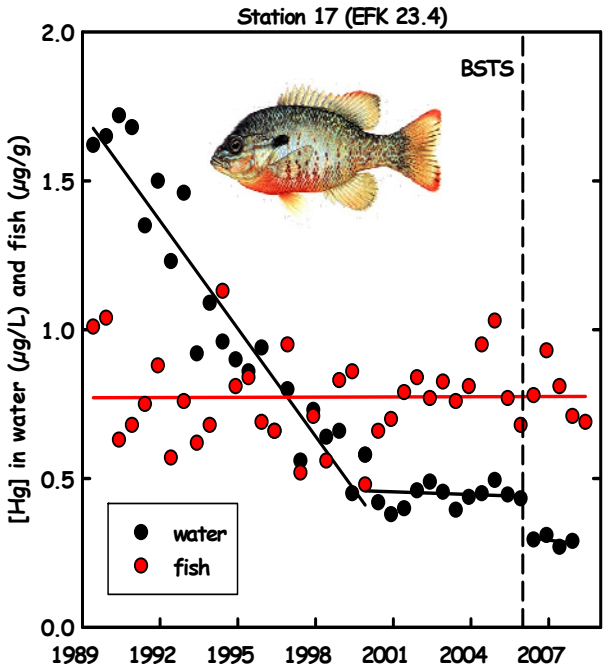


Questions:

- **Are kinetics important in the complexation of Hg with DOM?**
  - **Laboratory experiments examining the rate of Hg-DOM complexation**
    - **DOM isolate**
    - **Creek water**
- **Does kinetics influence the complexation of Hg in the environment?**
  - **Does the rate of Hg-DOM complexation influence the complexation in natural systems**
    - **Upper East Fork Poplar Creek (UEFPC)**

Background

- **East Fork Poplar Creek**
  - **Headwaters in Y-12 National Security Complex in Oak Ridge, TN**
  - **1950-1963 industrial processes at Y-12 required >10 million kg Hg**
  - **~127,000 kg (9.4 m^3) released to EFPC**
- **Decrease in HgT concentration in water has not resulted in decrease Hg in fish**



Background

- **UEFPC originates inside Y-12 (Outfall 200)**
  - **HgT: 1300 ng/L**
    - **>90% dissolved**
    - **Process water**
- **Melton Hill Lake water is added to the creek to control flow**
  - **HgT: 3 ng/L**
  - **DOC: 1.4 mg C/L**
- **4:1 mixing ratio of lake to outfall water**
- **Equilibrium models predict Hg-DOM complexes dominate**

Experiments

- **Techniques used to differentiate Hg complexes**
- **Laboratory experiments examining Hg interactions with DOM isolates and UEFPC water**
- **Hg complexation in EFPC**

Techniques to Differentiate Hg complexes

Stannous Chloride Reactive Hg (HgR)

Hg^{2+}-ligand + Sn^{2+} ⟶ Hg^{0} + Sn^{4+}

Ligand	% HgR
Cl	98
citrate	95
cysteine	97
oxalate	98
thioglycolate	101
SR NOM	11
GT NOM	6
Outfall 200	95
Melton Hill	<10
UEFPC (S17)	10

Solid Phase Extractions (SPE)

- **C_{18} cartridges: extracts hydrophobic complexes**
  - **Inorganic complexes: 5%**
  - **Small organic complexes: 12%**
  - **UEFPC: 74%**

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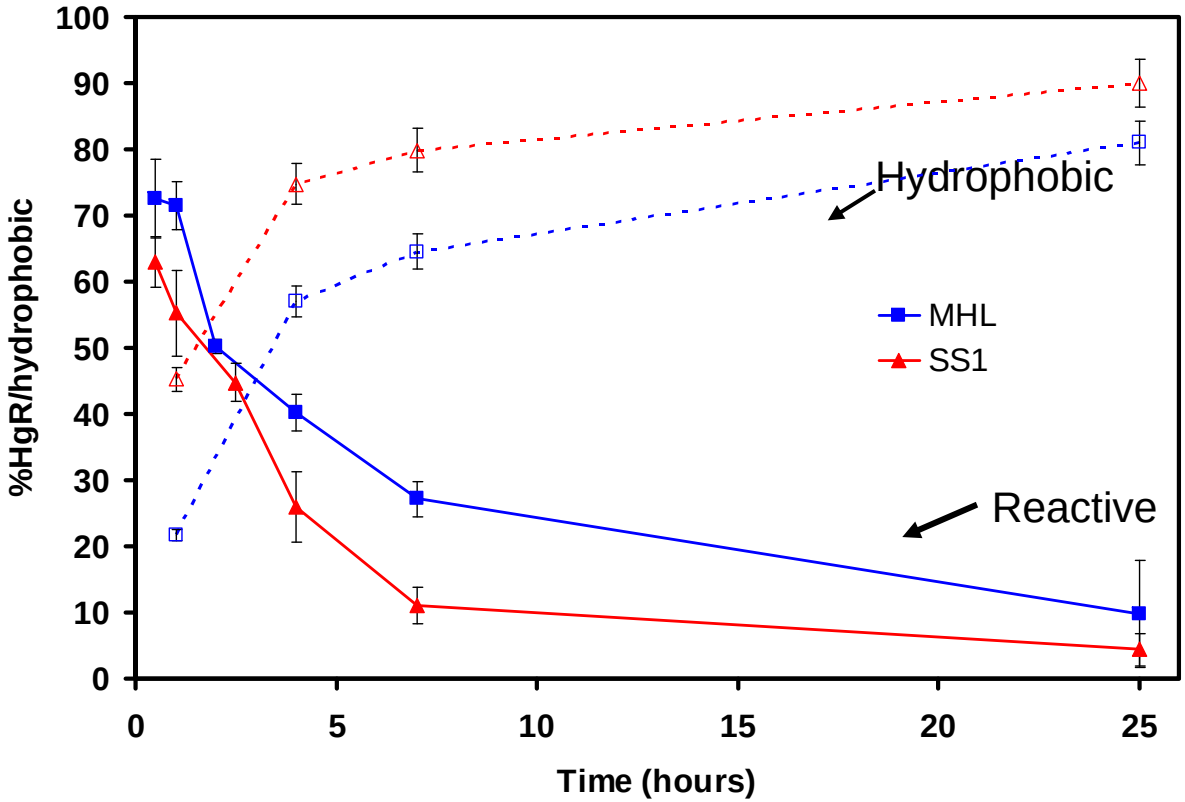
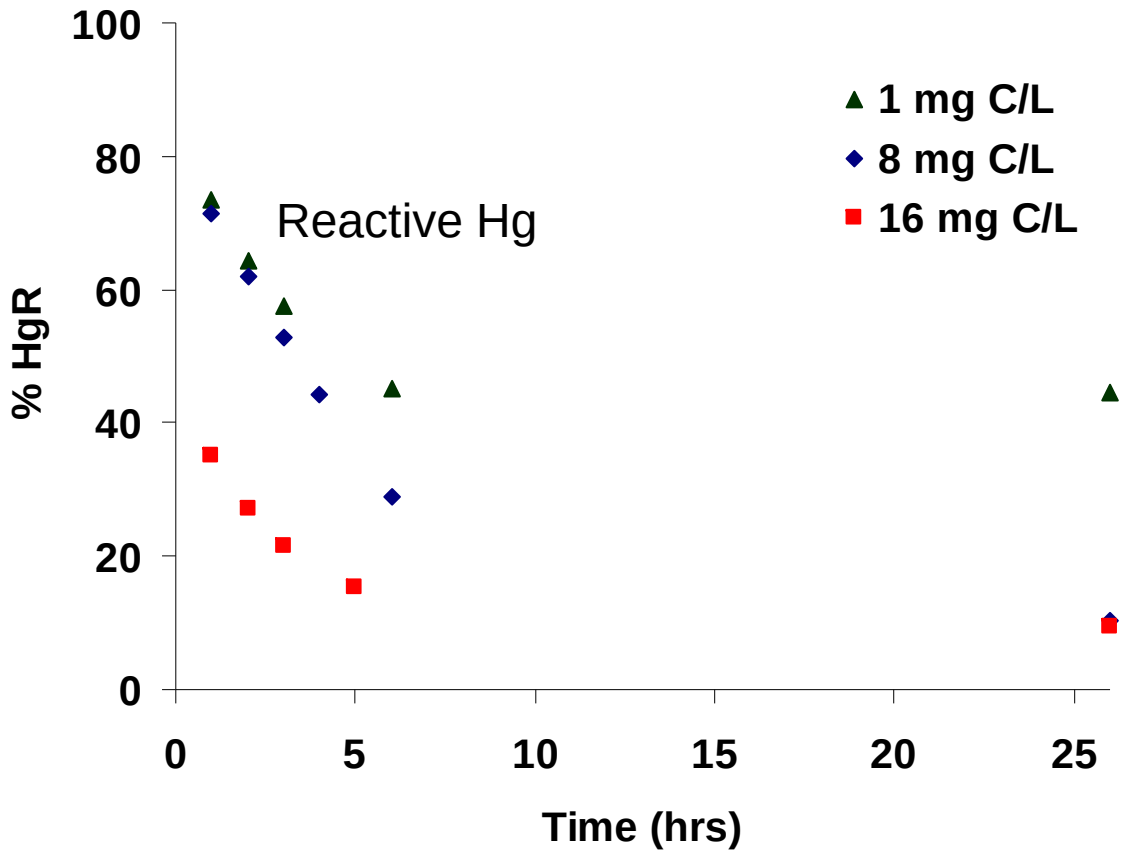
Formation Rate of Hg-DOM complexes: UEFPC



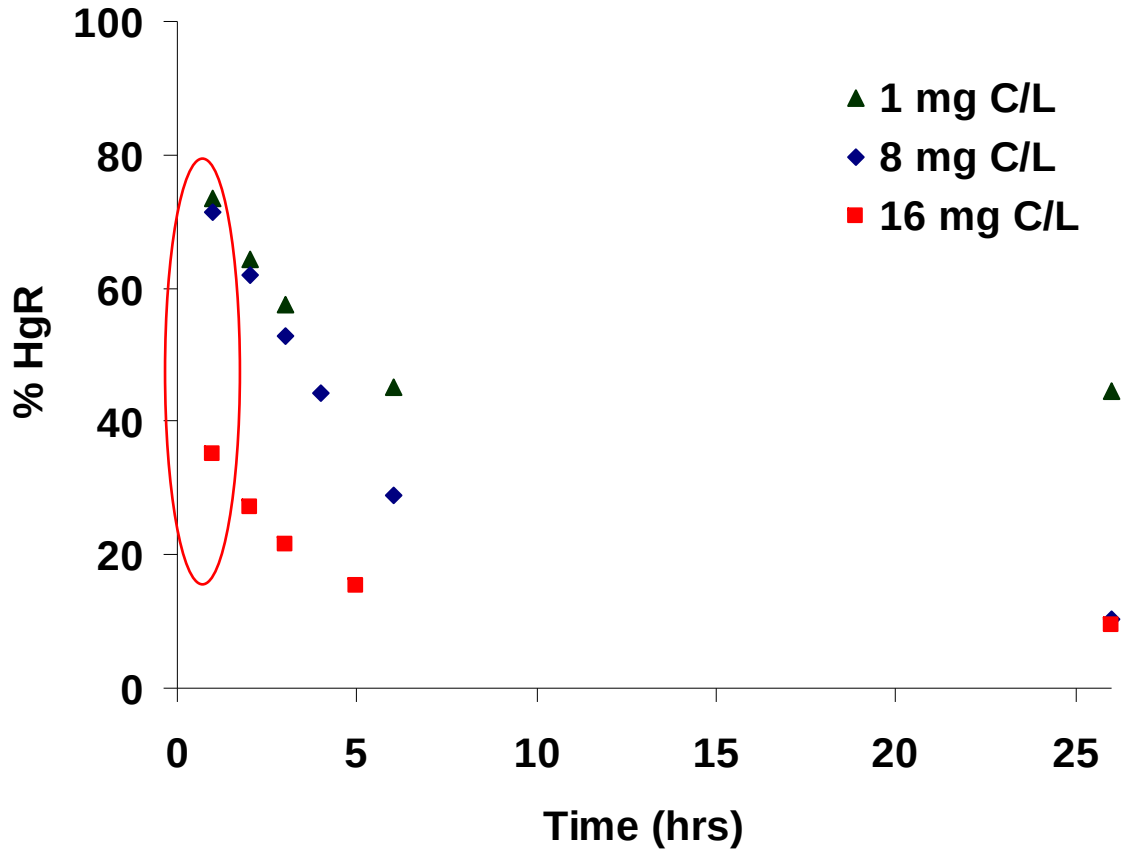
- **Experimental conditions**
  - **Filtered creek water (MHL and SS1-0.2 km)**
  - **100 ng/L Hg spike**
  - **pH 7.8**

Formation Rate of Hg-DOM complexes: NOM Isolate



- **Experimental Conditions**
  - **NOM isolate: Unfractionated Suwannee River NOM**
  - **100 ng/L Hg spike**
  - **pH 7.5, I 0.1 M**

Formation Rate of Hg-DOM complexes: NOM Isolate



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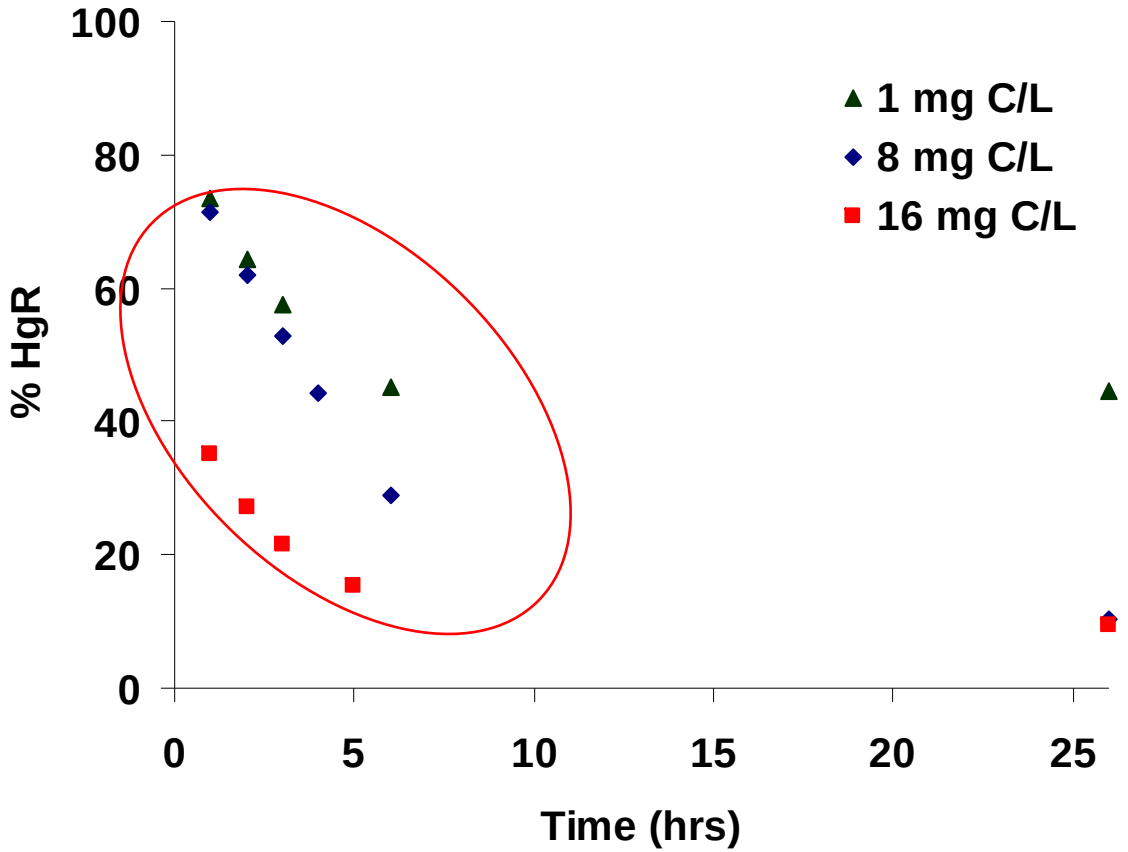

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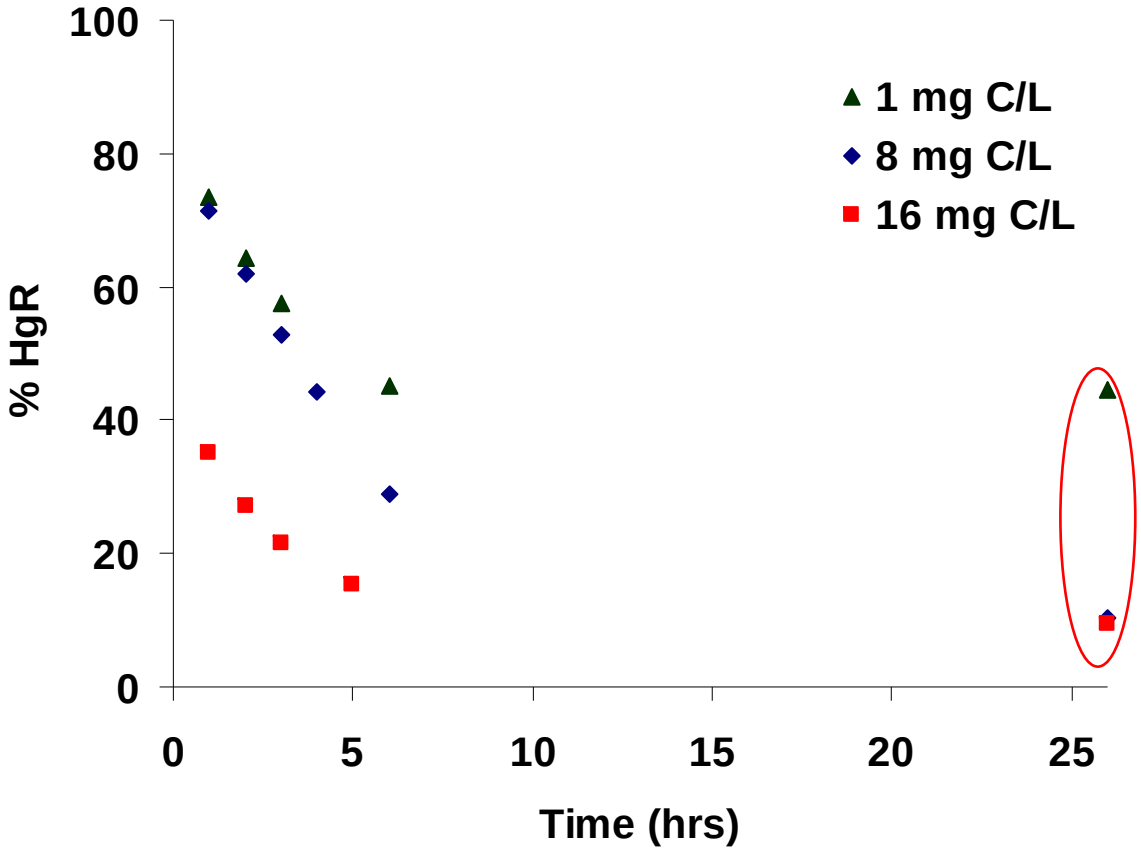

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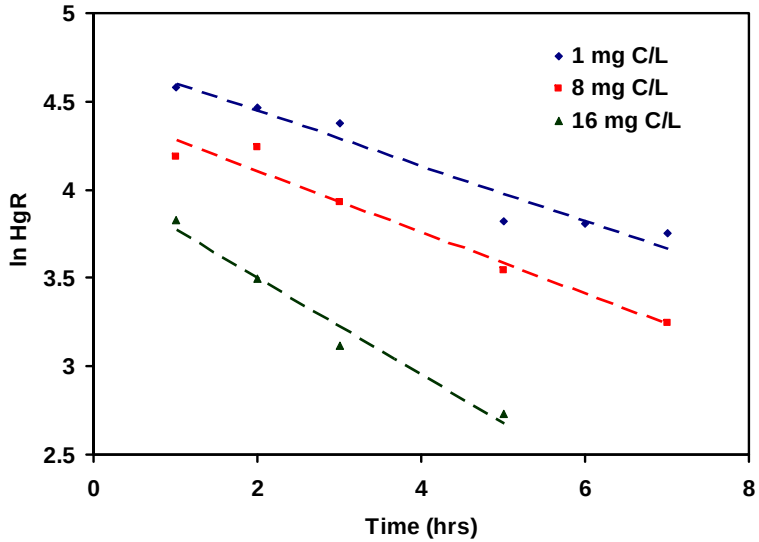
Formation Rate of Hg-DOM complexes: NOM Isolate

Solution	HgT (ng/L)	DOC (mg C/L)	k (hr^{-1})
Station 0.2	100	1.5	0.24
MHL	50	1.4	0.19
MHL	100	1.4	0.16
MHL	200	1.4	0.08
SR NOM	100	1.0	0.09
SR NOM	100	8.0	0.15
SR NOM	100	16.0	0.21

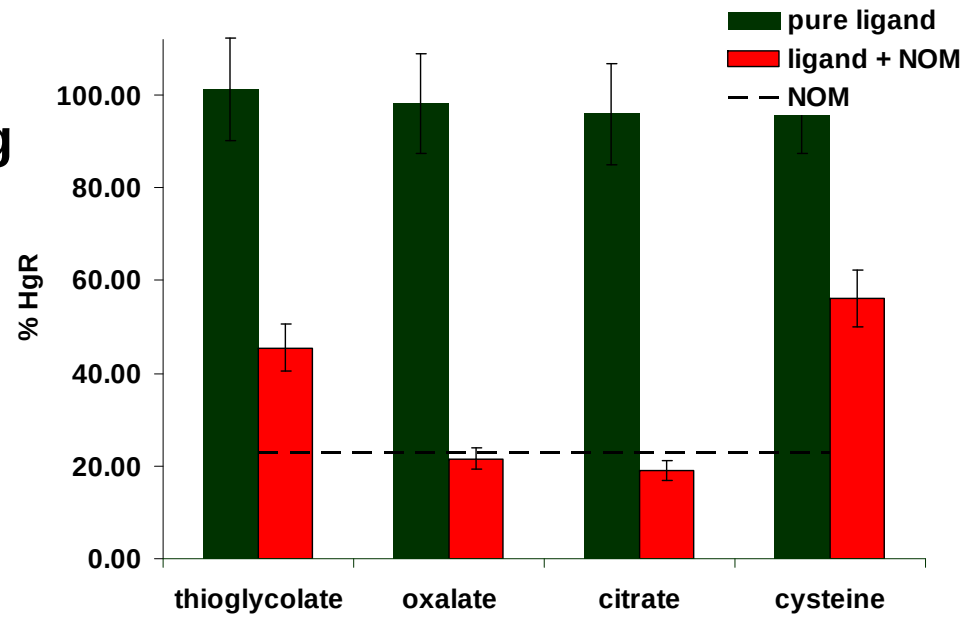


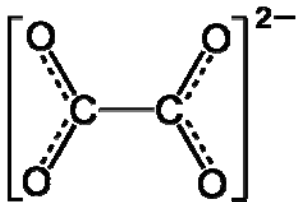
- **Rate constants range 0.07-0.24 hr^{-1}**
  - **Higher DOM concentration, larger rate**
  - **Higher Hg concentration, lower rate**

Competitive interactions between NOM and LMW ligands

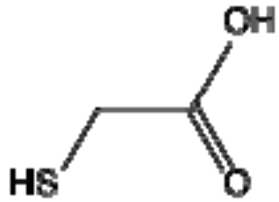
- **Non-thiol containing ligands do not change the interaction of Hg with NOM**
- **Thiol containing ligands decrease the association of Hg with NOM after 16 hours**
  - **Complexation constants for Hg bound to thiol containing LMW ligands in the same range as Hg-NOM constants**
- **Longer equilibration (>24hours) results in Hg-NOM complexes dominating**

HgR after 16 hrs equilibration

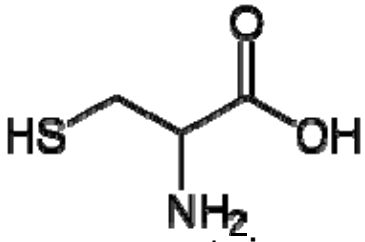




oxalate



thioglycolate

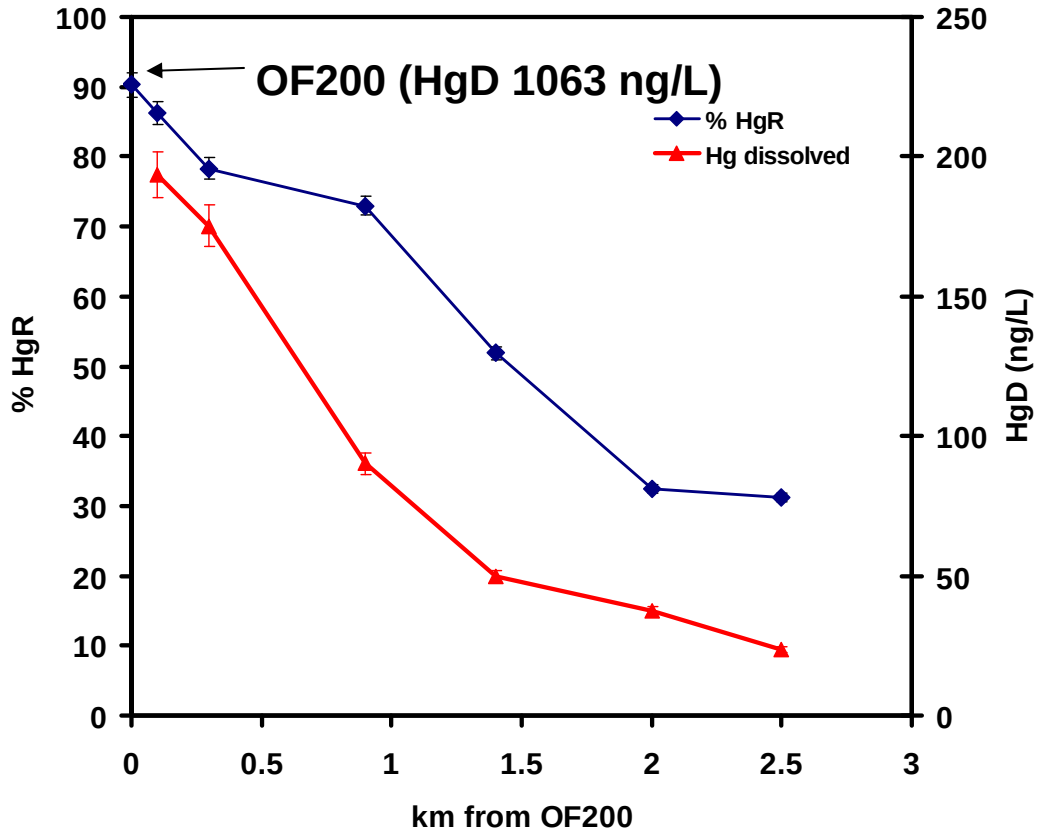


cysteine

Interaction of Hg with NOM

- **The interaction of Hg with NOM is more complex than the interaction with LMW thiols**
  - **Binding environment (hydrophilic/hydrophobic)**
  - **Mode of binding (mono, bi, tridentate)**
  - **Conformational changes during binding**

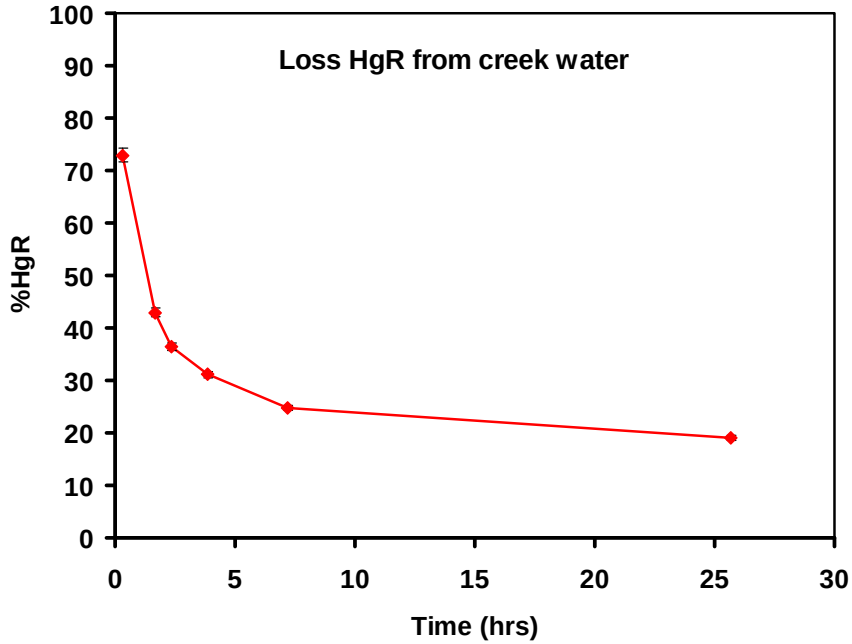
What role does kinetics play in Hg complexation in EFPC?



- **Reactive Hg measured in upper 2.5 km of EFPC**
- **At all sites in creek, Hg-DOM should dominate if equilibrium was established**
  - **HgR ~ 10%**
- **High % HgR throughout creek**
  - **Decreases downstream as Hg-Dom complexes form**
- **Dissolved Hg also decrease as Hg sorbs onto particles**

What role does kinetics play in Hg complexation in EFPC?

- **Sample collected 0.9km from Outfall 200**
  - **% HgR decreased over time**
  - **NOM involved in Hg-NOM complexation exists in water**
- **Hg-NOM complexation is not at equilibrium in EFPC**
- **Presence of reactive species could influence Hg cycling in this system**



What Does this mean for Hg complexation in EFPC?

- **Constant source of reactive mercury mixing with natural organic matter**
- **Pool of reactive Hg always present in the UEFPC**
- **Equilibrium conditions can not be assumed**
- **Presence of reactive species needs to be considered when Hg cycling in examined**
  - **Hg methylation**
  - **Particle reactivity**
  - **Reduction reactions**
- **How does this apply to other systems?**
  - **Similar reactions have been observed when rainwater is mixed with high DOC river water**

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