Kinetic Controls on the Formation of Complexes Between Mercury and Dissolved Organic Matter

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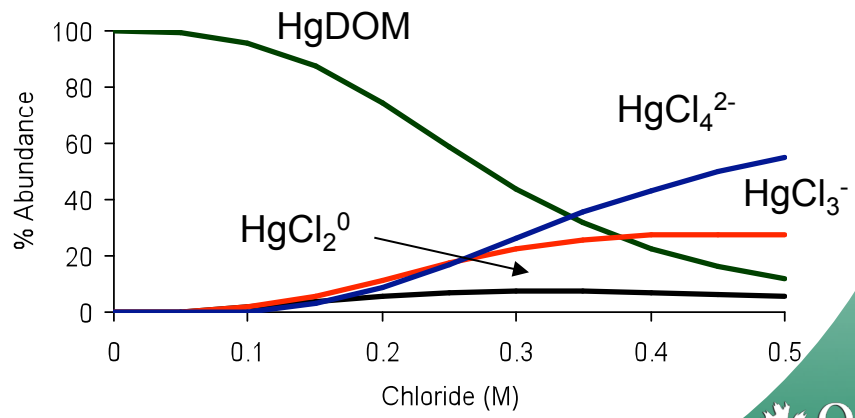
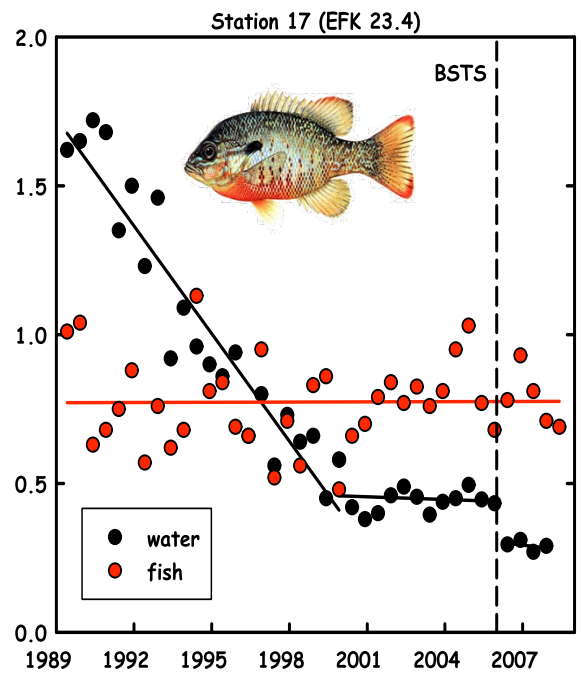
Mercury complexation

- Why do we care about complexation?
  - Important in Hg methylation/demethylation processes
  - Important in Hg reduction reactions
- What complexes are important under equilibrium conditions?
  - Equilibrium models predict Hg-DOM complexes dominate under oxic conditions in most aquatic environments
- Are kinetics important?



What role does kinetics play in Hg complexation in EFPC?

- 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



What role does kinetics play in Hg complexation in EFPC?

- UEFPC originates at Outfall 200
  - HgT: 1300 ng/L
    - 93% dissolved
    - 95% reactive Hg
  - DOC: 15 mg C/L*
- Melton Hill Lake water is added to the creek to control flow
  - HgT: 3 ng/L
    - < 10% reactive Hg
  - DOC: 17 mg C/L
- 4:1 mixing ratio of lake to outfall water
- Equilibrium models predict Hg-DOM complexes dominate

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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

Solid Phase Extractions (SPE)

- C_{18} cartridges: extracts hydrophobic complexes
  - Inorganic complexes: 5%
  - Small organic complexes: 12%
  - NOM isolates: 35-75%
  - UEFPC: 74%

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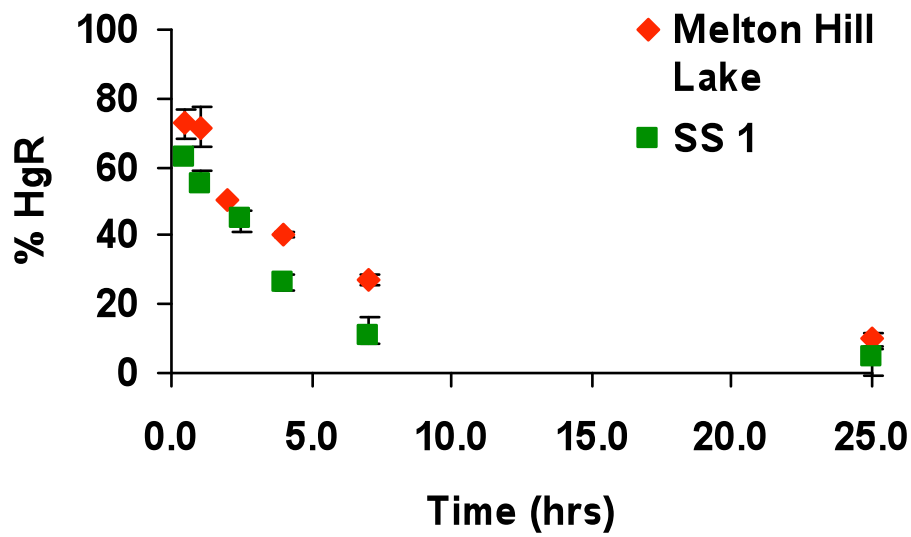
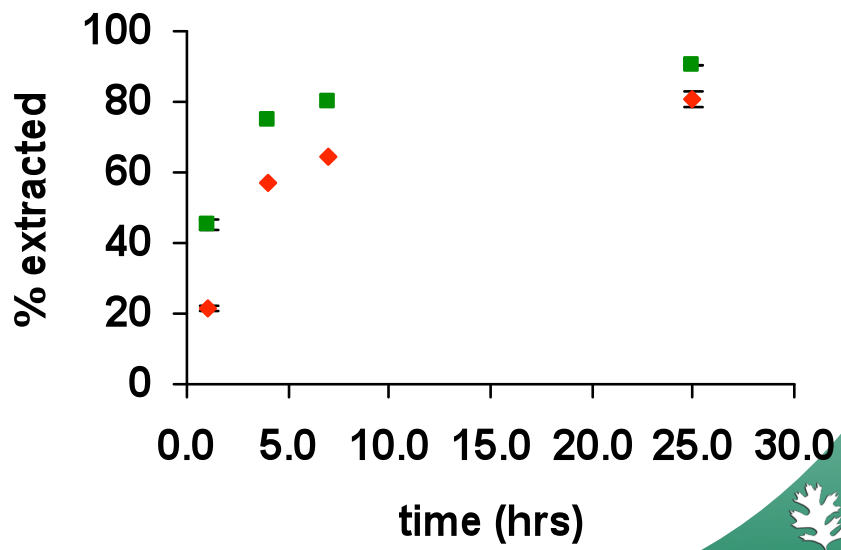
Formation Rate of Hg-DOM complexes: UEFPC

Reactive Hg



- **Experimental conditions**
  - **Filtered creek water**
  - **100 ng/L Hg spike**
  - **pH 7.8**

Solid Phase Extractable Hg



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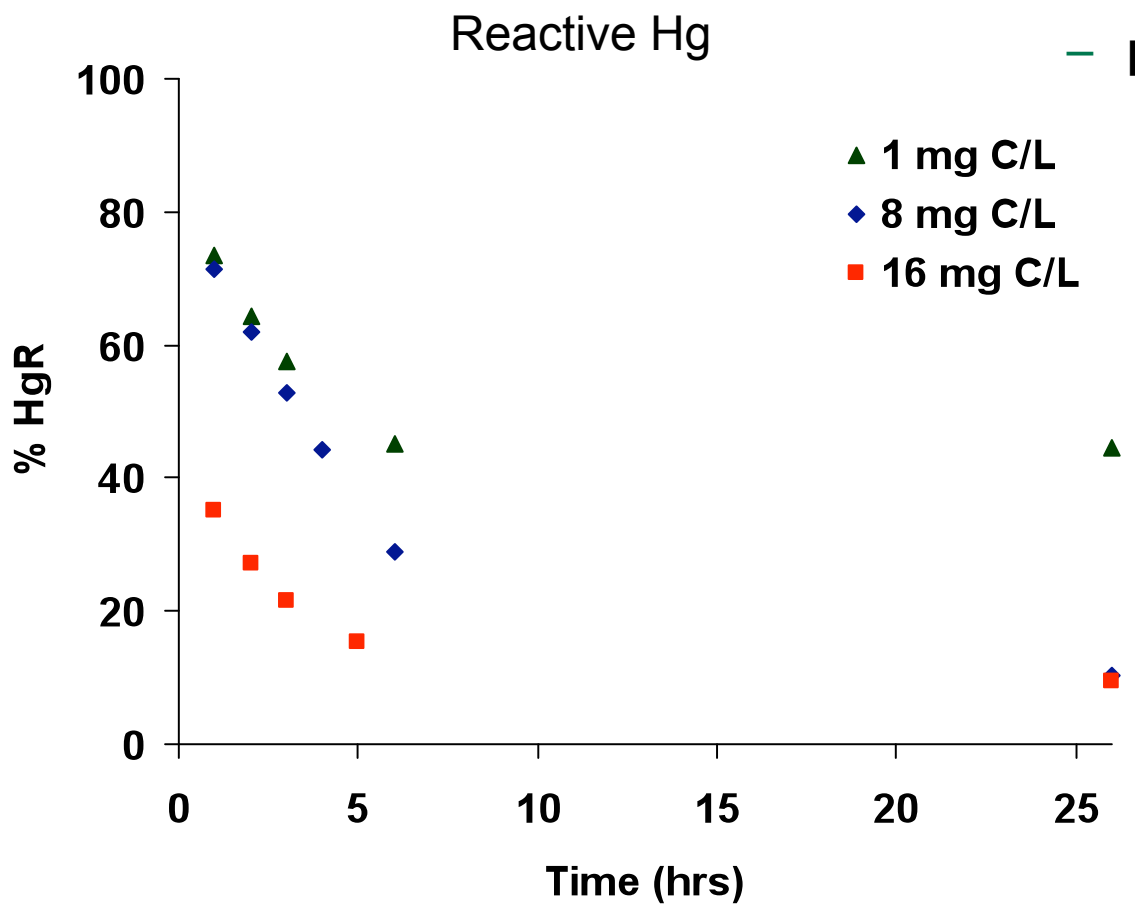
Formation Rate of Hg-DOM complexes: NOM Isolate

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



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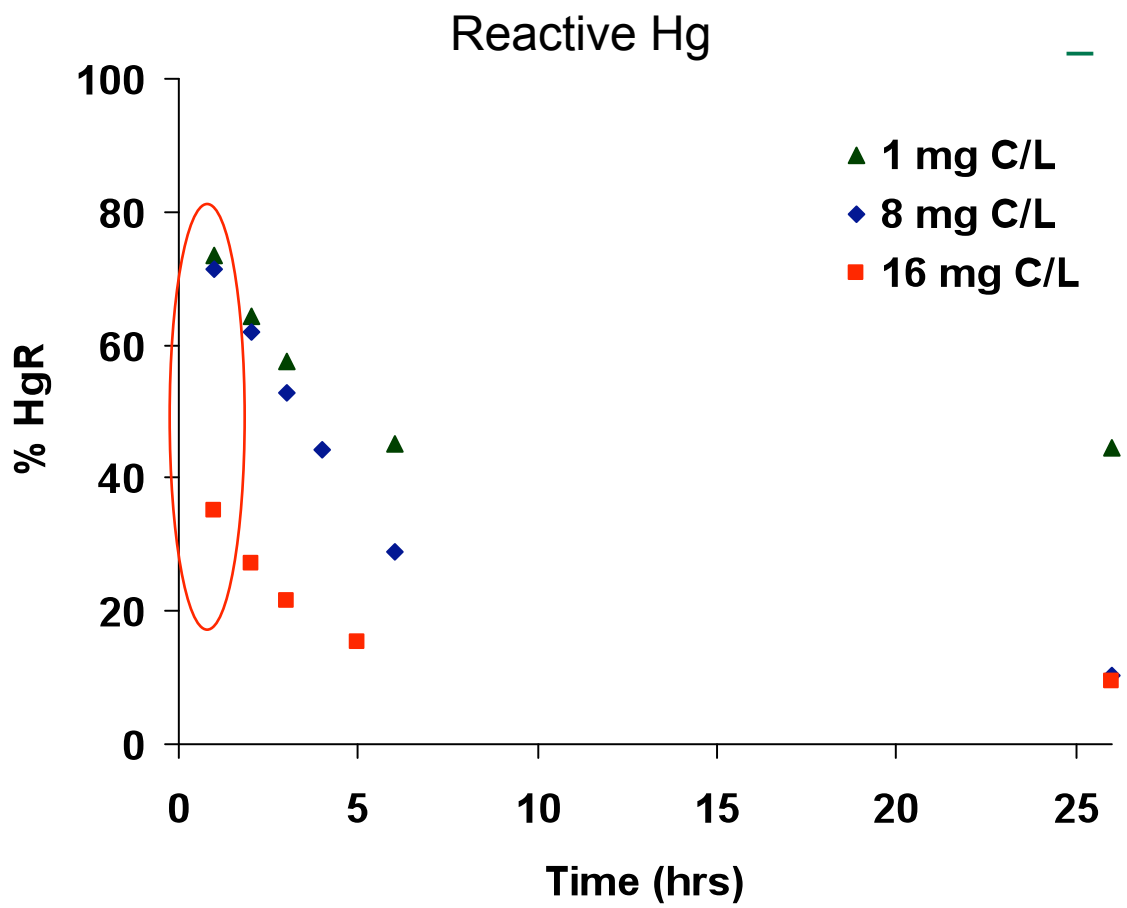

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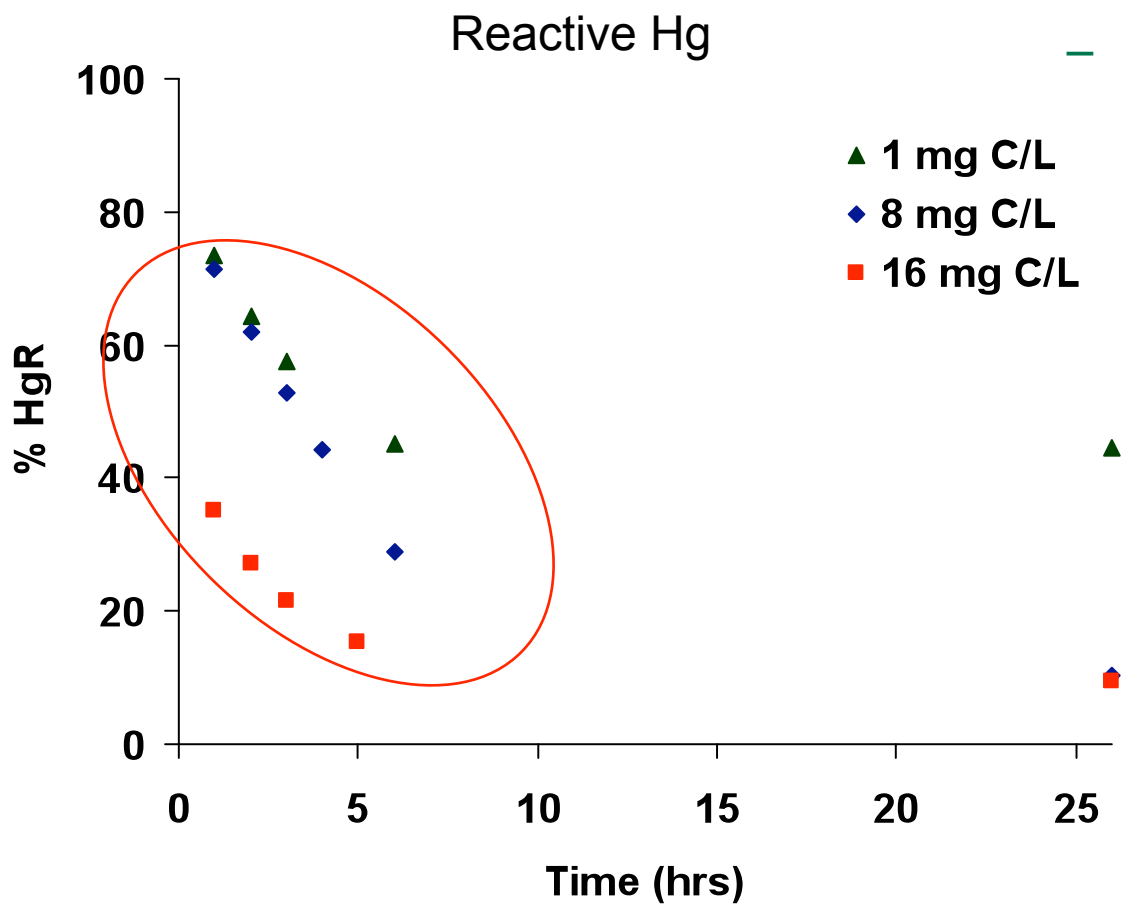

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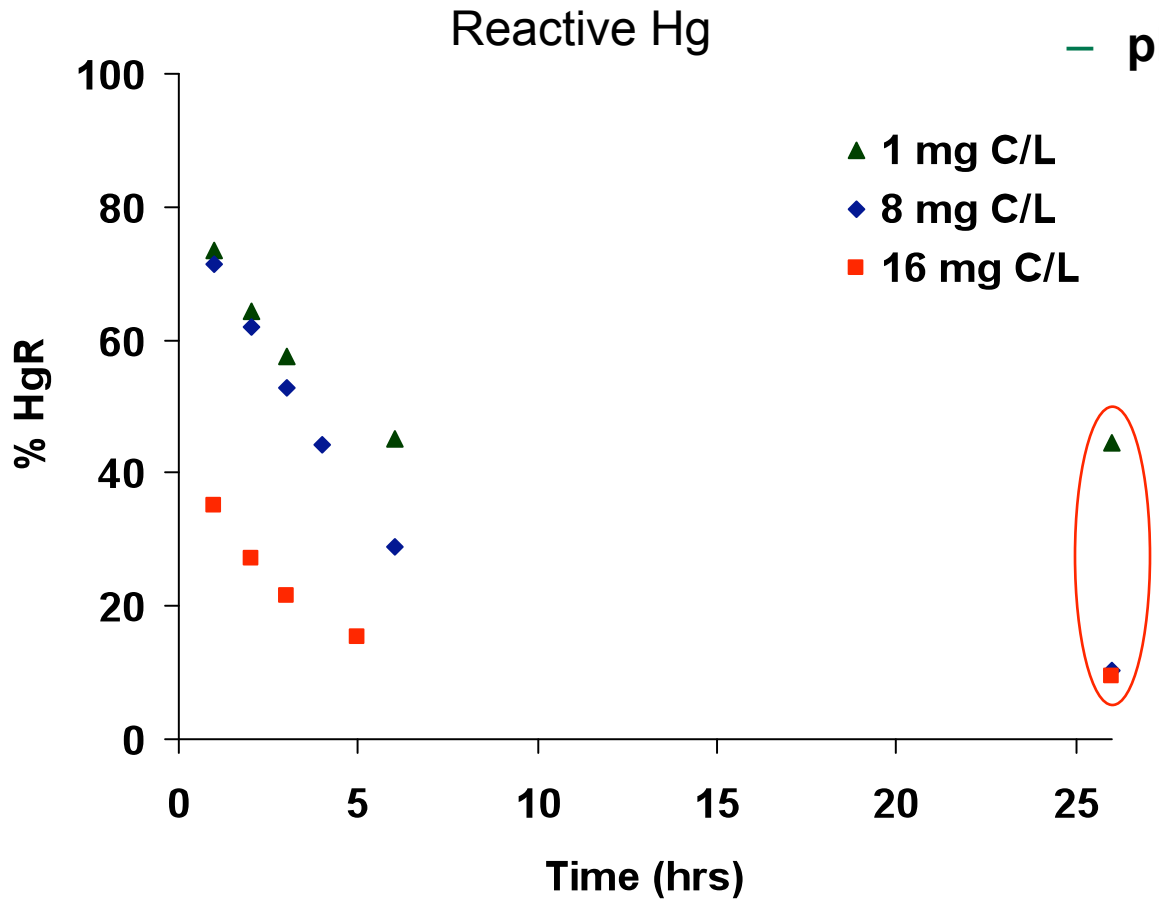

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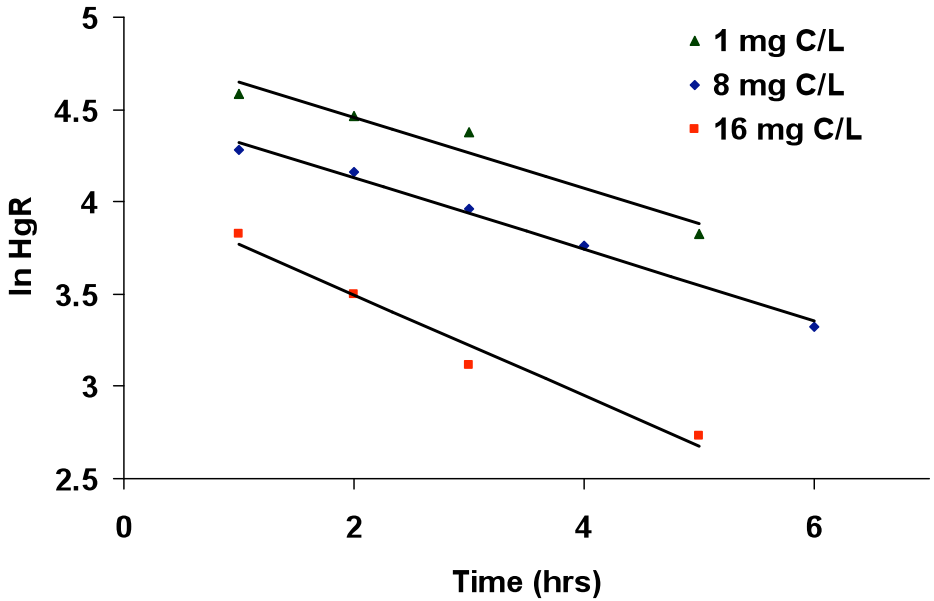

DOC (mg/L)	% HgR T= 1hr	% HgR T= 26hr	k (hr^{-1})	$t_{1/2}$ (hr)
1	73	44	0.16 ± 0.02	4.3
8	72	15	0.18 ± 0.02	3.8
16	35	9	0.25 ± 0.04	2.8
Melton Hill Lake	71	4	0.17 ± 0.02	4.1
SS1	55	10	0.29 ± 0.02	2.4

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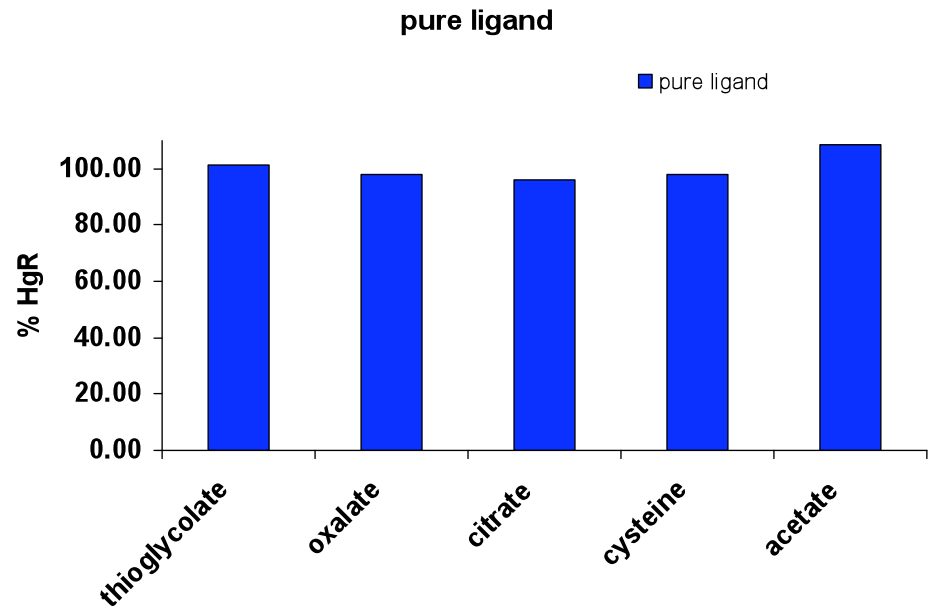
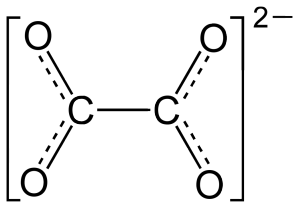
Formation Rate of Hg-DOM complexes: NOM and small organic ligands

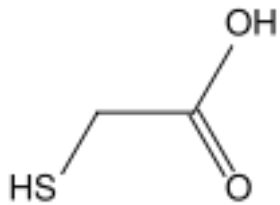
- **UEFPC contains both large NOM and small organic ligands (acetate and citrate)**
- **Pure ligand solutions**
  - **20 μM ligand + Hg**

HgR after 16 hrs equilibration

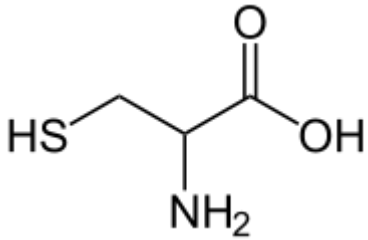




oxalate



thioglycolate



cysteine

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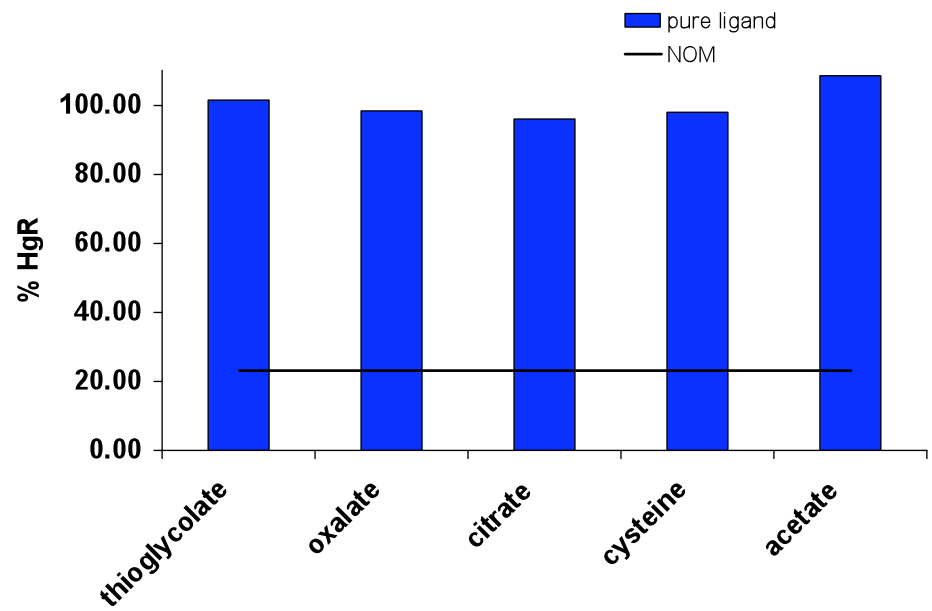
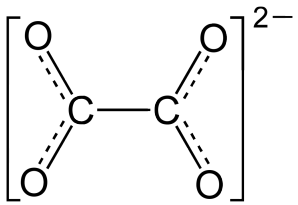
Formation Rate of Hg-DOM complexes: NOM and small organic ligands

- **UEFPC contains both large NOM and small organic ligands (acetate and citrate)**
- **Pure ligand solutions**
  - **20 µM ligand + Hg**
  - **8 mg C/L NOM + Hg**

HgR after 16 hrs equilibration





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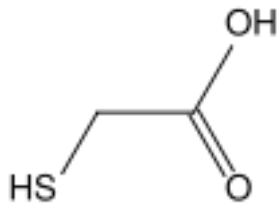

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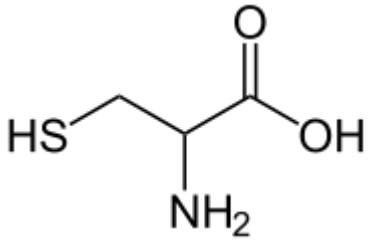

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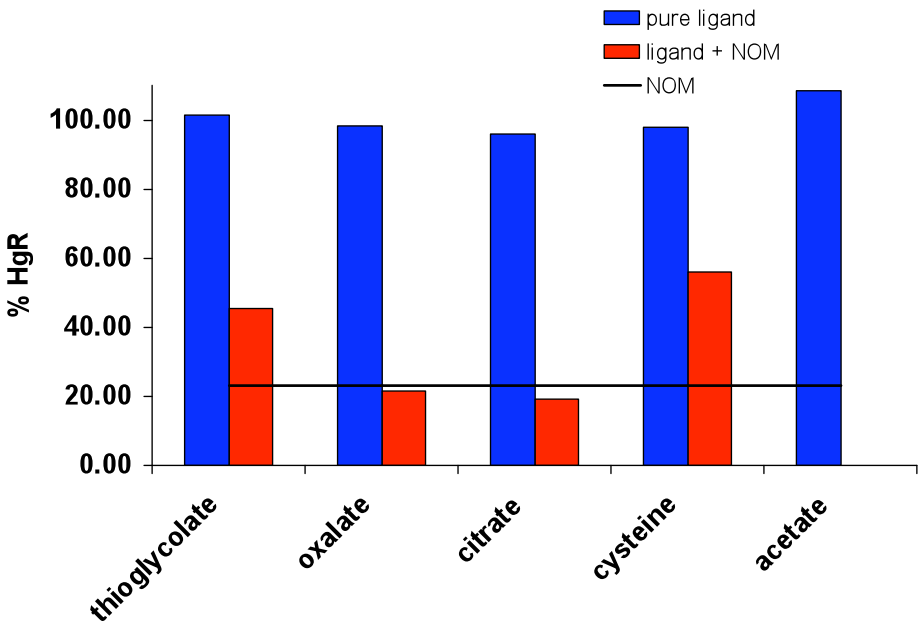
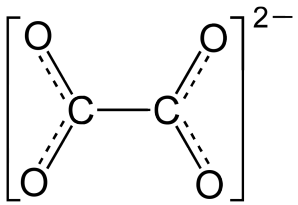
- **Pure ligand solutions**
  - **20 µM ligand + Hg**
  - **8 mg C/L NOM + Hg**
- **Ligand/NOM solutions**
  - **8 mg C/L NOM + 20 µM ligand + Hg**
  - **Functional group on ligand in excess of reduced sulfur on NOM**

HgR after 16 hrs equilibration





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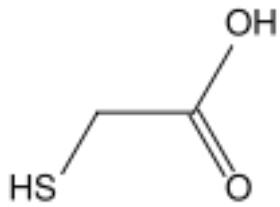

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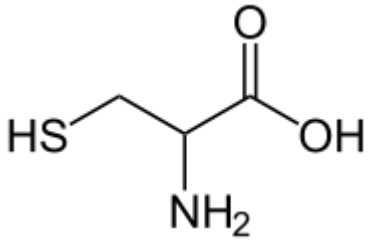

cysteine

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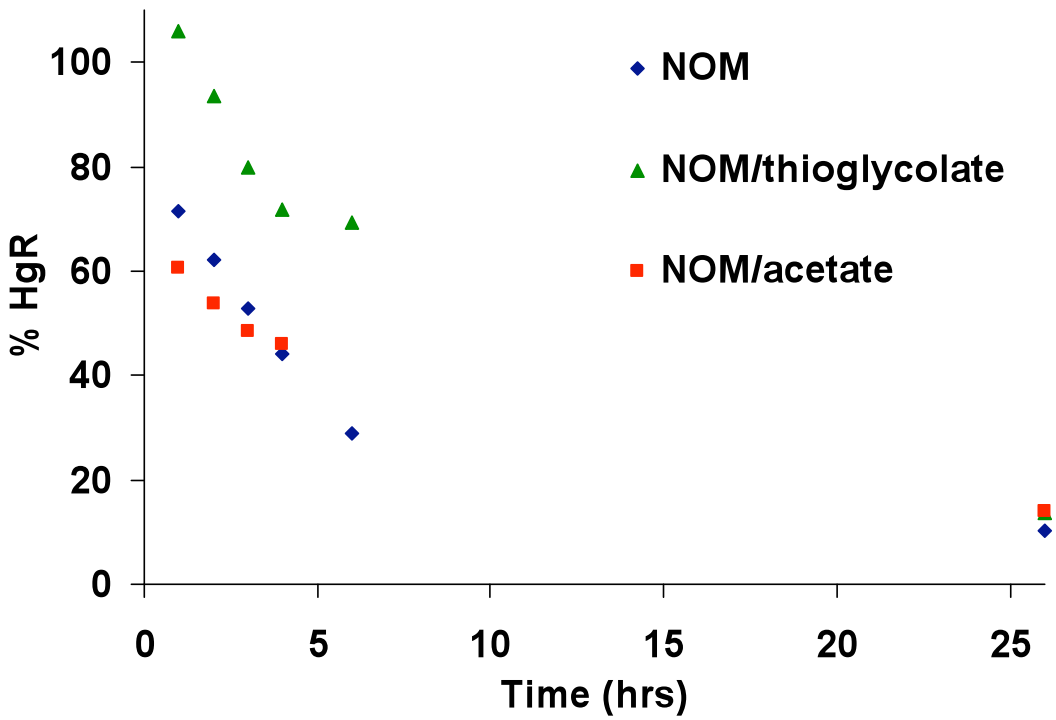
Formation Rate of Hg-DOM complexes: NOM and small organic ligands

ligand	% HgR T= 1hr	% HgR T= 26hr	k (hr^{-1})	$t_{1/2}$ (hr)
No ligand	71	12	0.18 ± 0.02	3.8
acetate	60	14	0.15 ± 0.03	4.6
thioglycolate	106	14	0.09 ± 0.02	7.7



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What Does this mean for Hg complexation in UEFPC?

- Constant source of reactive mercury mixing with natural organic matter
- Hg-DOM complexes take several hours to form ($t_{1/2}$ 2.4-7.7 hrs)
- Pool of reactive Hg likely always present in the UEFPC
- What does this mean for the cycling of Hg in the UEFPC?
  - Equilibrium conditions can not be assumed
- 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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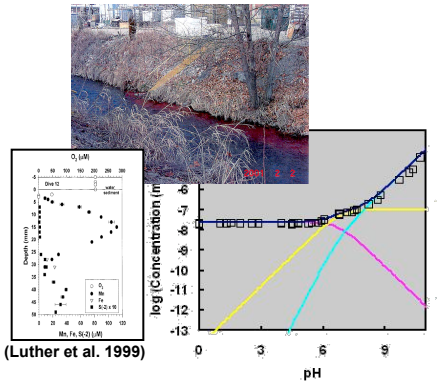
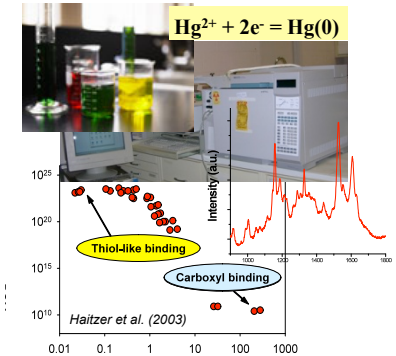
Strategy for understanding contaminant transformation and environmental behavior

Field biogeochemistry

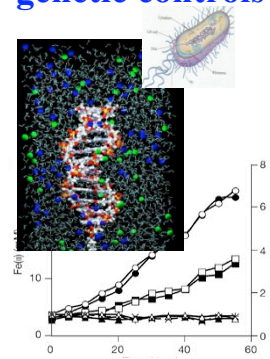


(Luther et al. 1999)

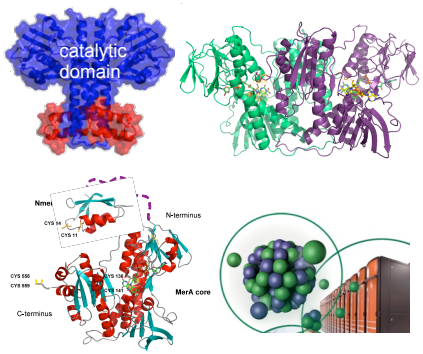
Fundamental rates and mechanisms



Microbial and genetic controls



Molecular structure and simulations



Transformation in field | **Speciation & mechanisms** | **Molecular dynamics**

Sediment-water interface
Species/ abundance
Microbial communities

Coupled microbial and geochemical reactions

Molecular level understanding of contaminant association and reaction

Reaction mechanisms and kinetics of mercury methylation and demethylation

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With collaborators from:
Argonne National Laboratory
Pacific Northwest National Laboratory
Smithsonian Institutions
Tennessee Technological University
University of California, San Francisco
University of Georgia
University of Missouri
University of Tennessee

Additional posters including:

1. Brooks et al., Comparison of Two Mercury Contaminated Surface Water Bodies,
2. Johs et al, Biomolecular Aspects of Mercury Transformations,
3. Palumbo et al, An Evaluation of Microbial Community Structure and Function in Mercury Contaminated Stream Sediments
4. Guo et al, Product Dissociation Pathways in MerB Catalysis: A Molecular Dynamics Study
5. Dong et al, Roles of Dissolved Organic Matter in Aqueous Speciation of Hg(II) and CH_3Hg^+ in East Fork Poplar Creek, Oak Ridge, Tennessee

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