Characterizing the Interaction between Trace Metal and Dissolved Organic Matter from the Florida Coastal Everglades

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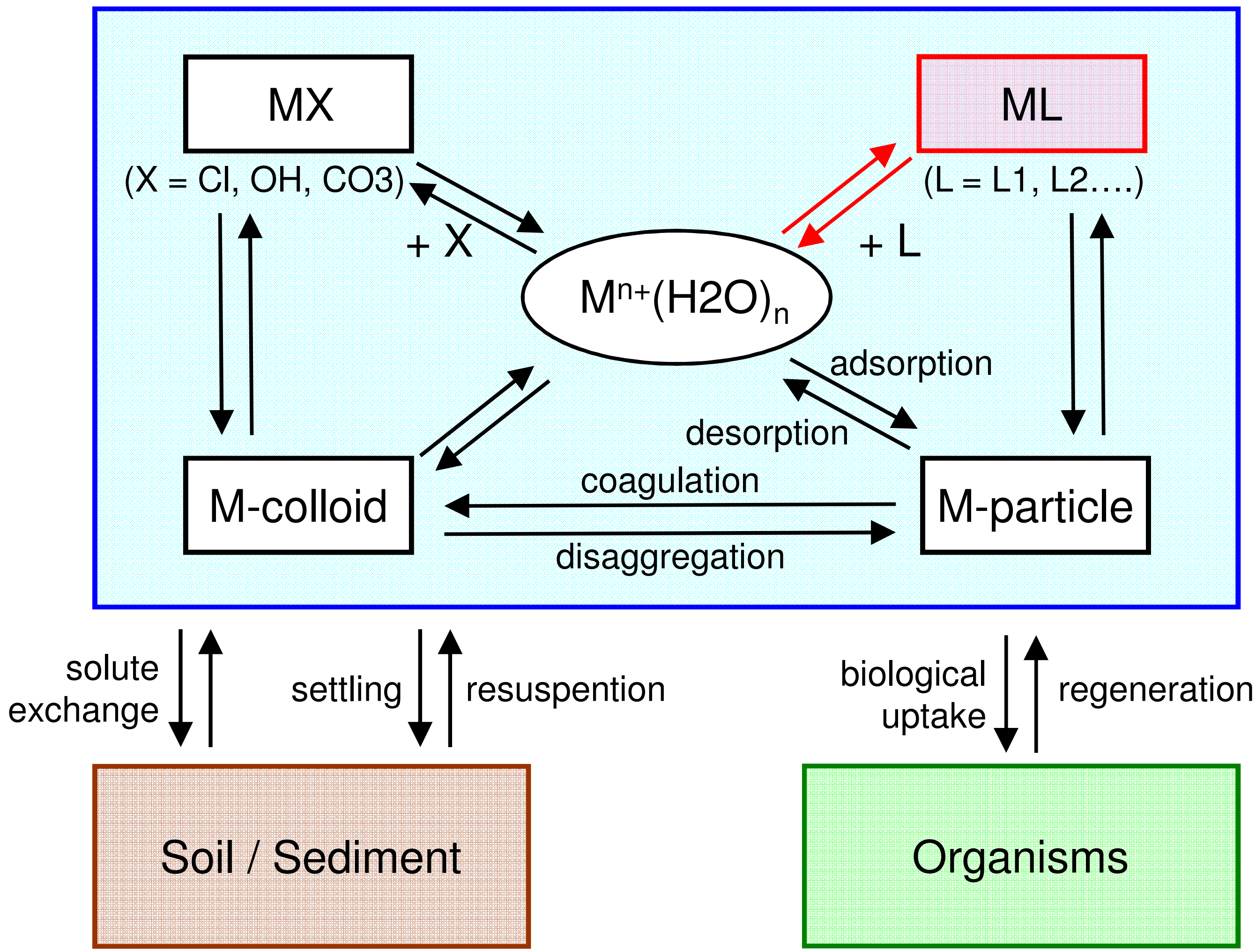
Dissolved organic matter (DOM) affects the trace metal speciation



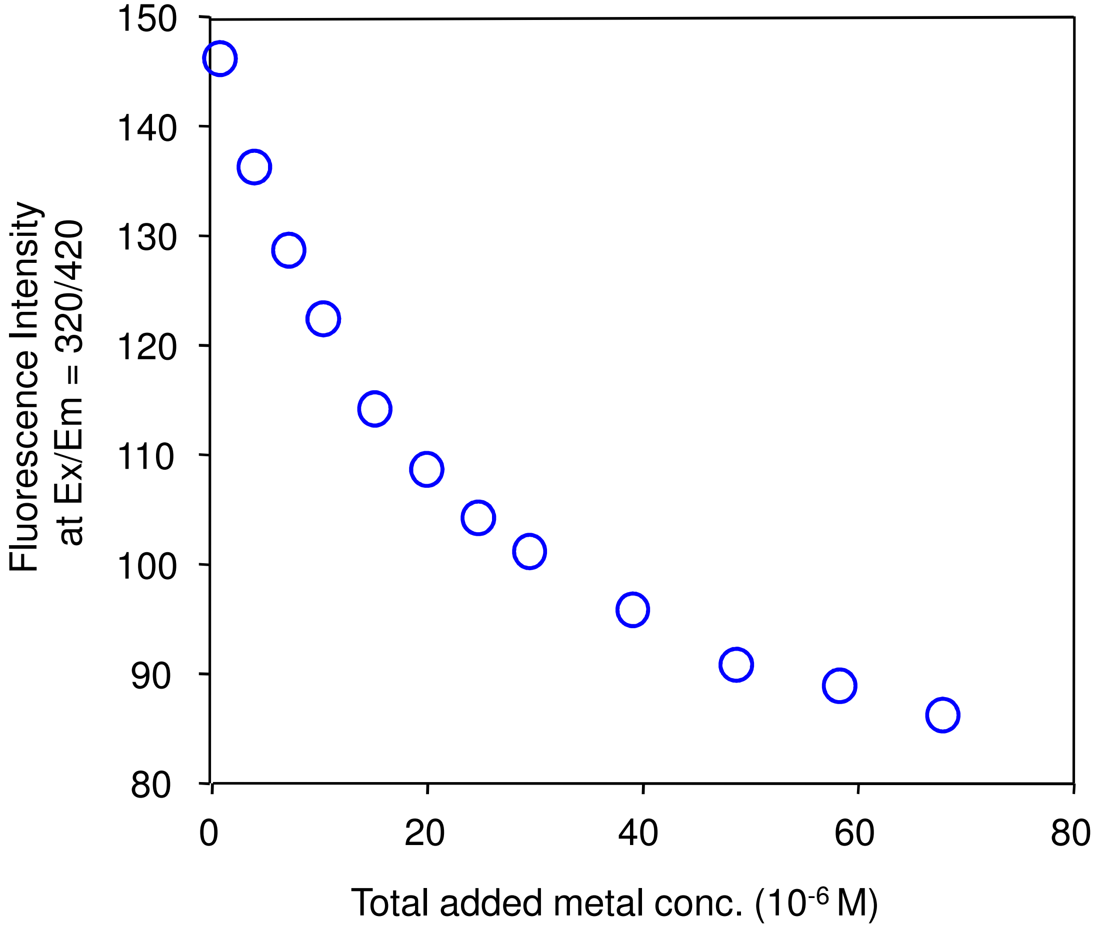
modified from Santschi et al., 1997

Chemical characterization of metal ion binding properties of DOM

- Evaluation of ***functional groups*** of organic ligands
  - ✓Nuclear magnetic resonance (NMR)
  - ✓Extended X-ray absorption fine structure (EXAFS)
  - etc
- Evaluation of ***complexing capacities*** of organic ligands
  - ✓Electrochemical titration
  - ✓Fluorescence quenching titration
  - ✓Ion exchange
  - ✓Competitive ligand exchange with solid-phase extraction
  - etc

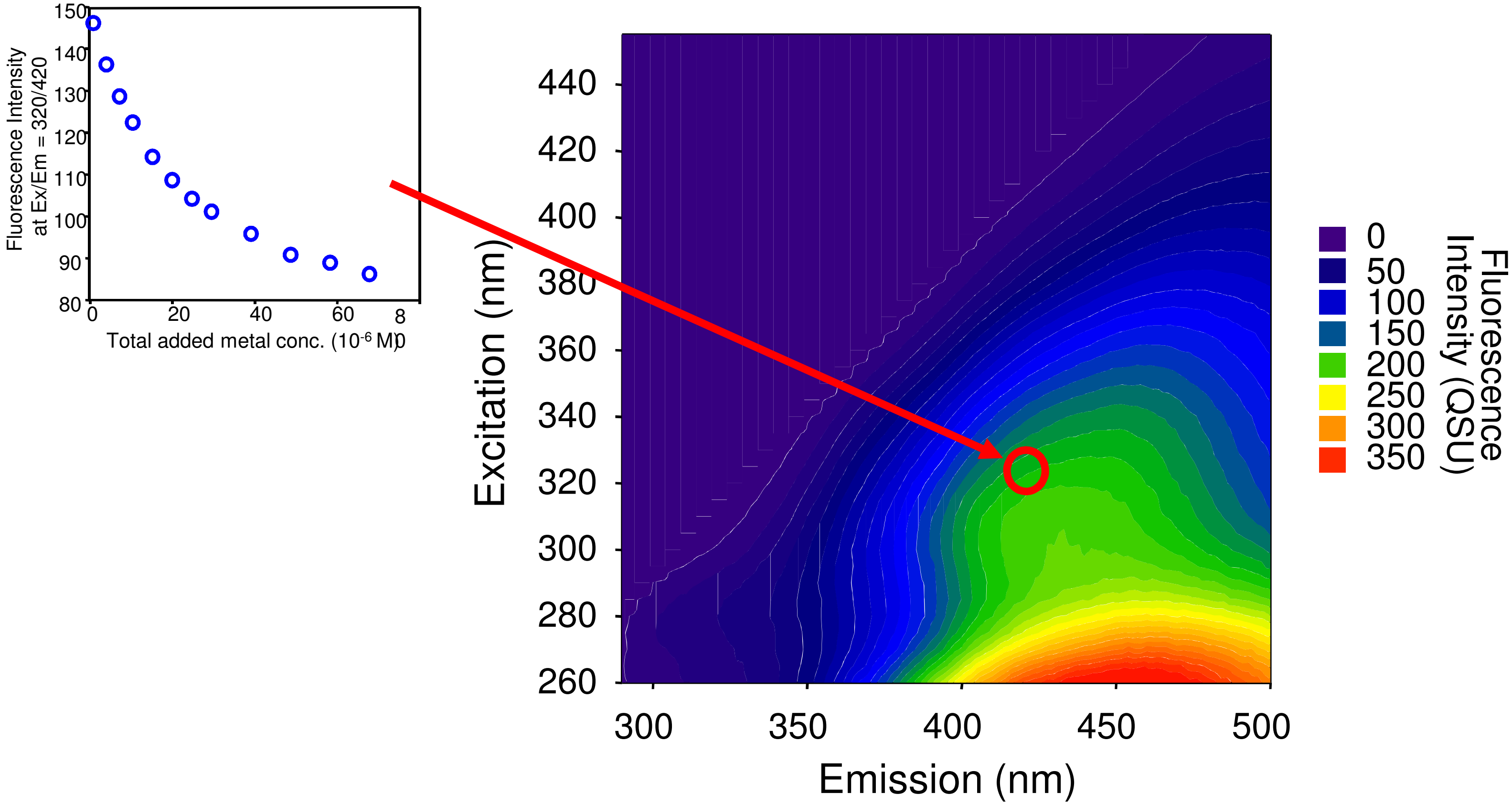
However, these methods can determine ***"average"*** metal ion binding properties of DOM.

Fluorescence quenching titration



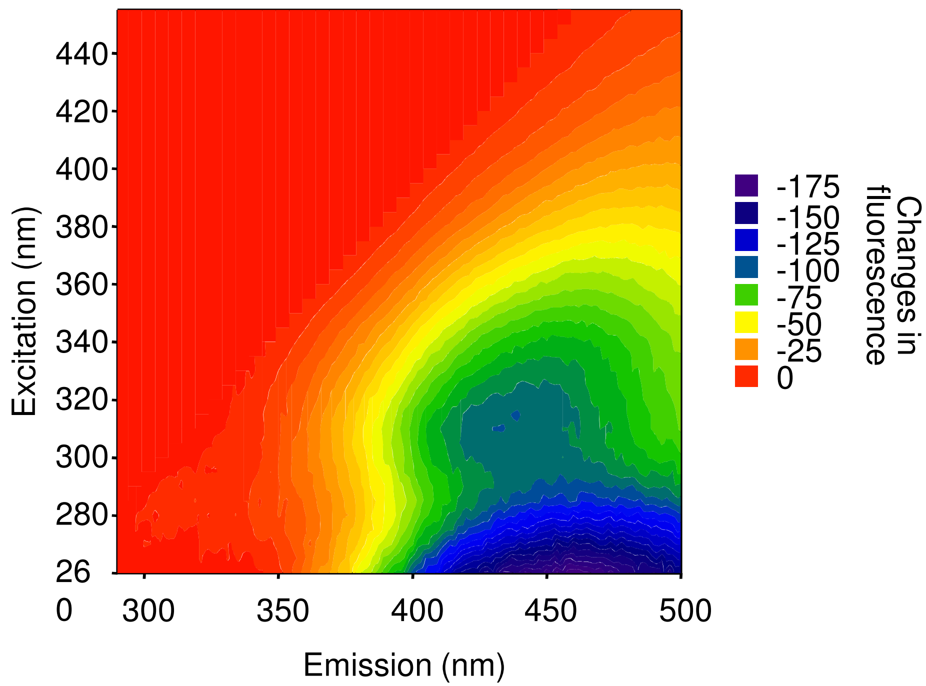
Excitation-Emission Matrix (EEM)

of surface water at SRS2



Changes in EEM of SRS2 water

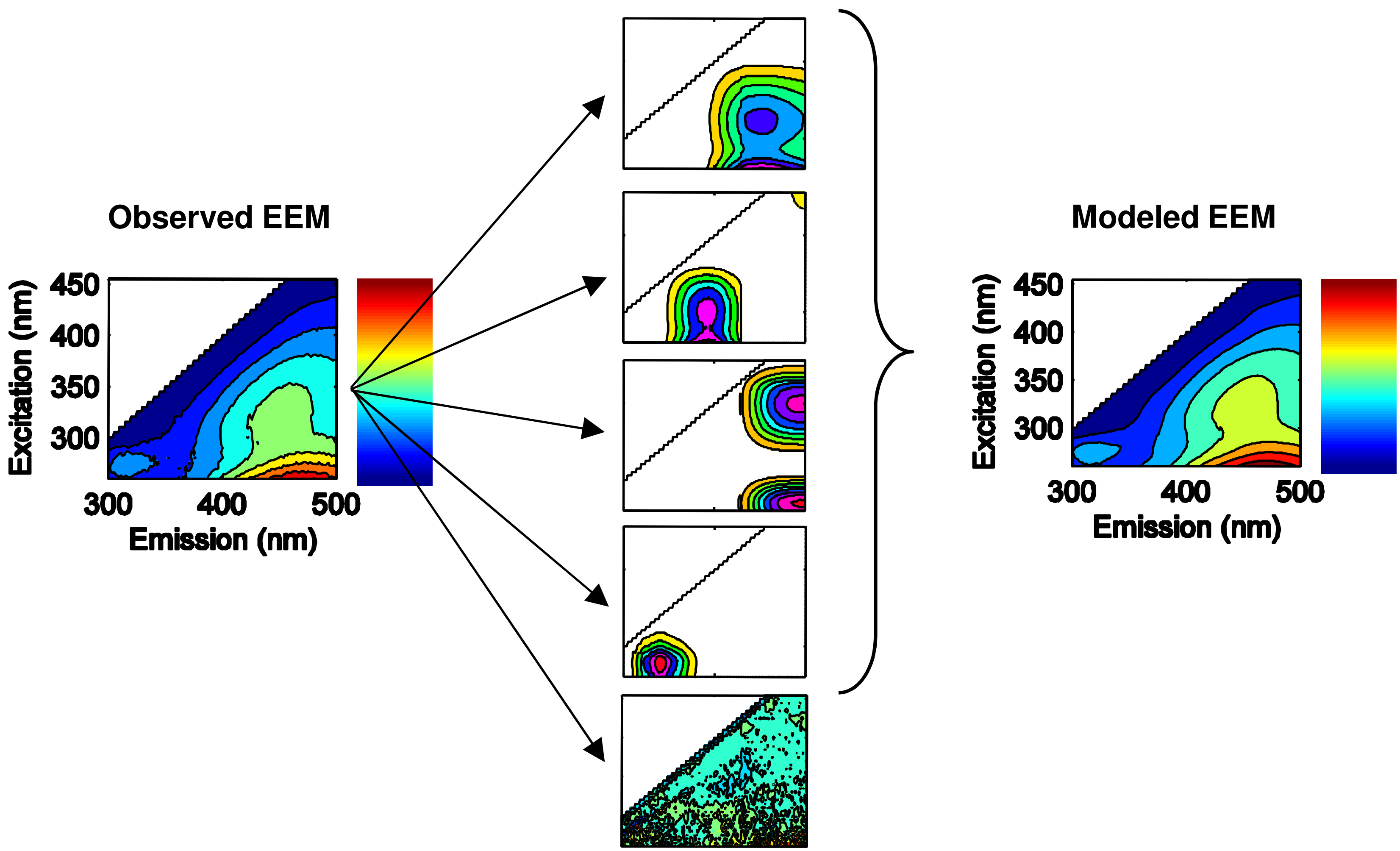
with 70µM Cu(II)



EEM is useful for determining the *binding capacities of each type of the fluorescence components* with trace metals. **However, peak picking technique is problematic for quantitative estimation.**

Parallel factor analysis (PARAFAC)

PARAFAC statistically decompose EEMs into independent fluorescent group



Purposes of the present study

To test the availability and sensitivity of combination technique of fluorescence quenching titration and EEM-PARAFAC

- **Reproducibility**

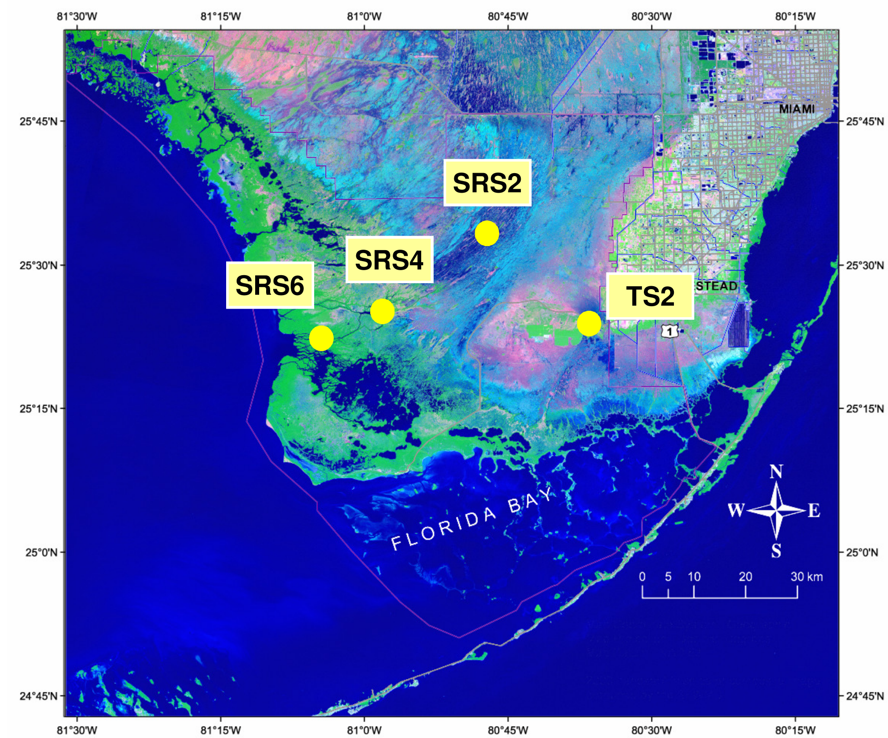
- **Differences in binding capacities among different fluorescent components / DOM in different sites / different trace metals**

Materials and Methods

✓ Surface water samples

4 FCE-LTER sites

- SRS2
- SRS4
- SRS6
- TS2

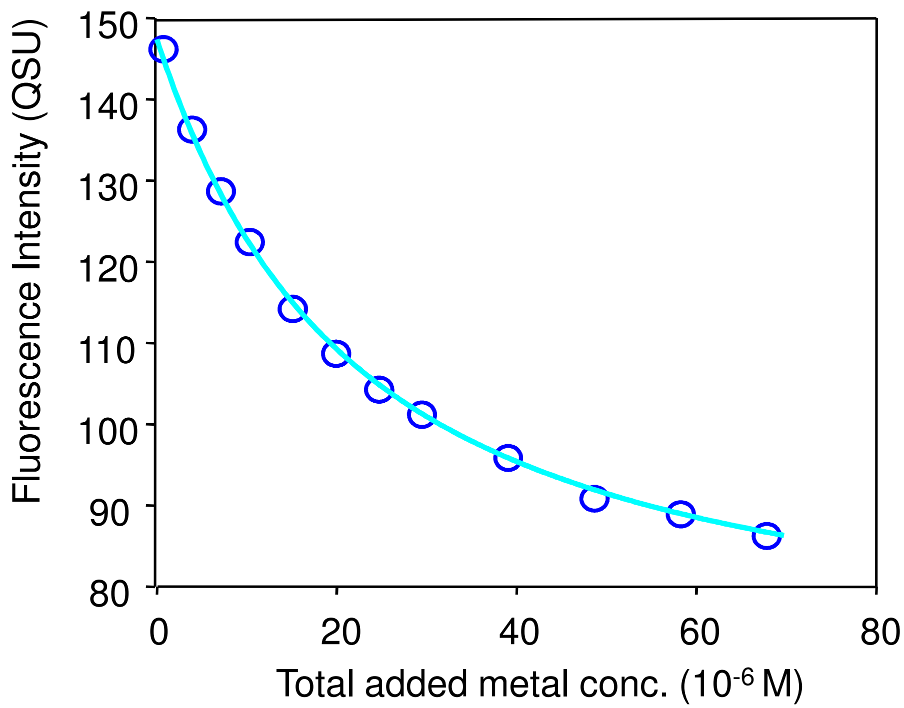


✓ Trace metals

- Cu(II): semi-hard metal
- Hg(II): soft metal

Materials and Methods

Modeling of fluorescence quenching curves



Ryan and Weber Model

$$I = I_0 + (I_{ML} - I_0)\left(\frac{1}{2K_M C_L}\right)\left(1 + K_M C_L + K_M C_M - \sqrt{(1 + K_M C_L + K_M C_M)^2 - 4K_M{}^2 C_L C_M}\right)$$

I: fluorescence intensity at the metal conc. $\boldsymbol{C_M}$

$\boldsymbol{I_0}$: fluorescence intensity without metal

$\boldsymbol{I_{ML}}$: fluorescence intensity which dose not change due to the addition of metal

$\boldsymbol{K_M}$: conditional stability constant

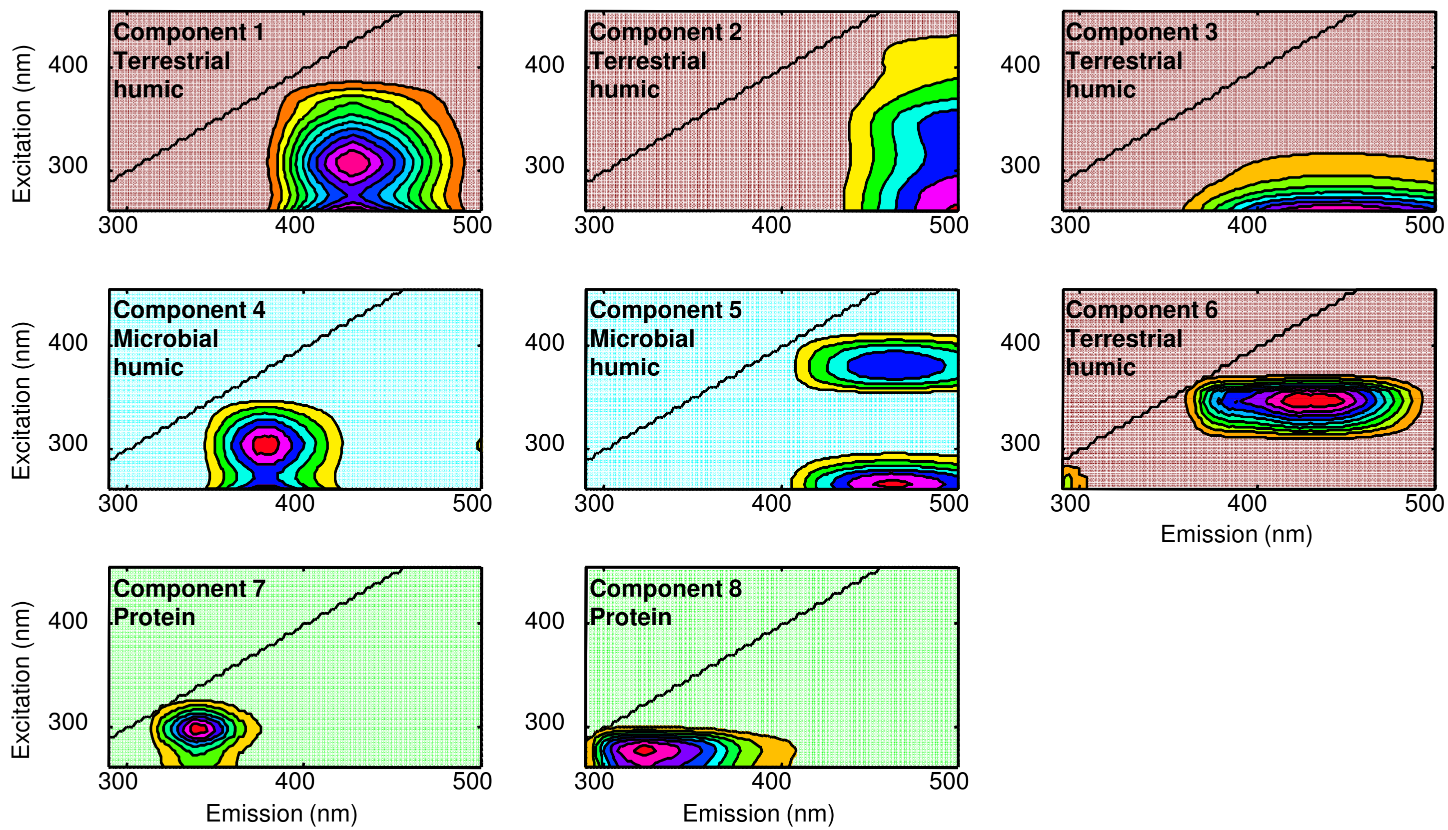
$\boldsymbol{C_L}$: total ligand concentration

$$f = \frac{(I_0 - I_{ML})}{I_0} \times 100$$

f: fraction of the initial fluorescence that corresponds to the binding fluorophores

Materials and Methods

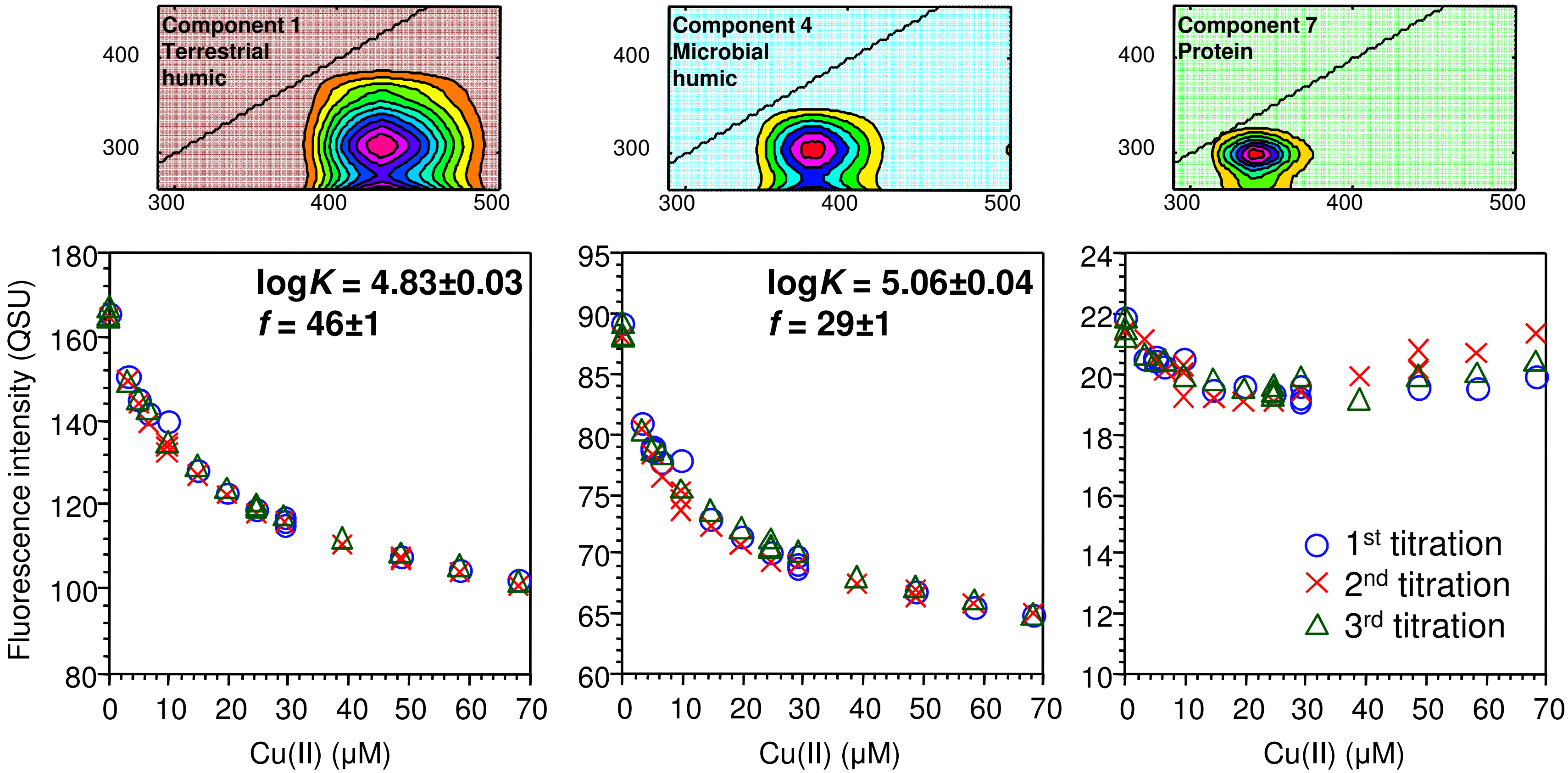
PARAFACE modeling



- **1108 surface water samples from Florida Coastal Everglades were used for FCE-PARAFAC model.**
- **Source characterization was carried out by comparison to previous PARAFAC studies (*Cory and Mcknight, 2005; Stedmon and Markager, 2005; Yamashita et al., 2008*).**

Reproducibility

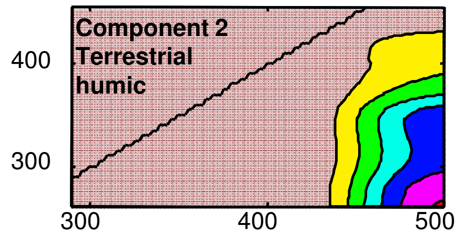
Triplicate titration experiments with Cu(II) for SRS2 water

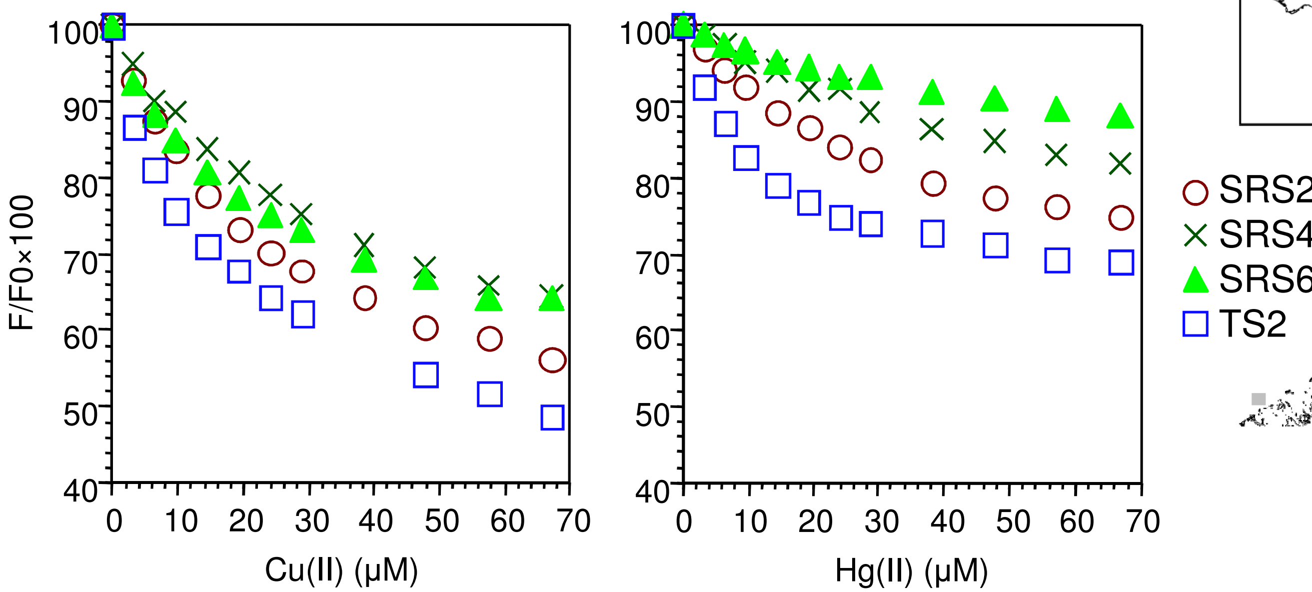


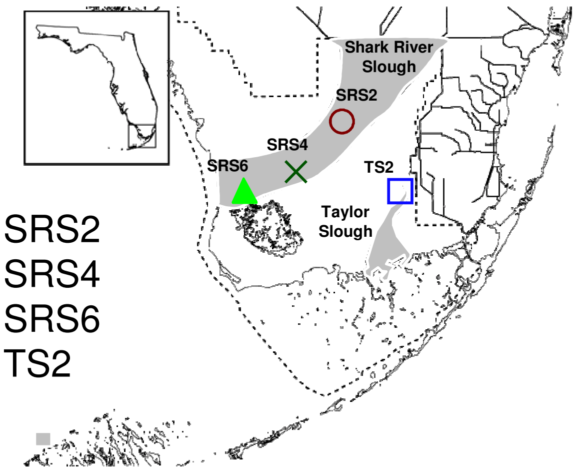
The combination of fluorescence quenching titration and EEM-PARAFAC is enough to reproducibly determine the binding capacity of individual humic-like components with trace metals.

Differences in quenching among DOM/trace metals

Titration experiments with Cu(II) or Hg(II) for 4 different samples

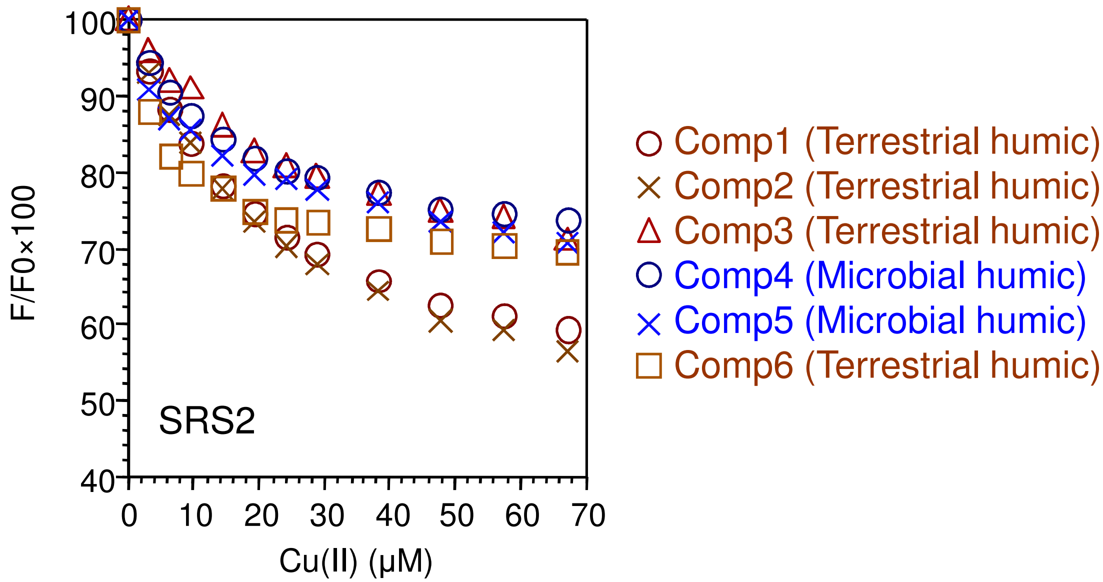






Differences in quenching among fluorescent components

Titration experiments with Cu(II) for SRS2 water

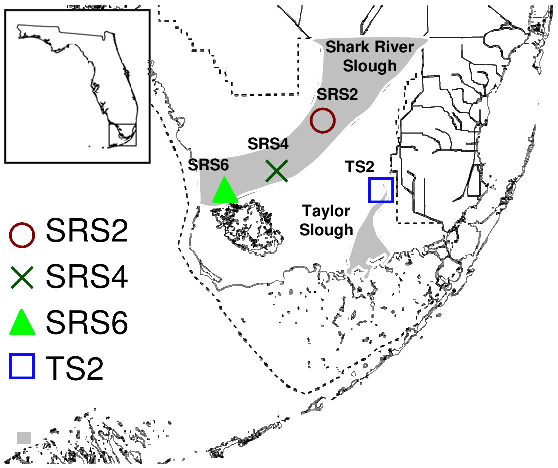


Fluorescence quenching titration with EEM-PARAFAC is a sensitive method to determine the differences in binding capacity of individual fluorescent components with trace metals.

The log*K* and *f* values of 6 humic-like components

The log*K* and *f* values for terrestrial and microbial humic-like components with Cu(II) and Hg(II) determined by Ryan and Weber Model

Component	Site	Cu(II)			Hg(II)		
		log*K*	*f* (%)	R^2	log*K*	*f* (%)	R^2
Component 1	SRS2	4.74	52	1.00	4.93	30	1.00
	SRS4	4.49	47	1.00	5.24	18	0.99
	SRS6	4.72	41	1.00	4.17	16	0.97
	TSPH2	4.91	54	0.99	4.84	38	1.00
Component 2	SRS2	4.62	59	1.00	4.67	34	1.00
	SRS4	4.48	53	1.00	4.75	26	0.99
	SRS6	4.68	47	1.00	4.31	20	0.99
	TSPH2	4.81	61	0.99	5.01	35	1.00
Component 3	SRS2	4.68	37	1.00	4.26	33	0.99
	SRS4	5.75	14	0.98		not modeled	
	SRS6	6.32	13	0.89		not modeled	
	TSPH2	4.67	42	0.98	4.69	22	0.99
Component 4	SRS2	4.83	32	1.00	4.90	27	1.00
	SRS4	5.04	25	0.98	6.76	11	1.00
	SRS6	5.54	22	0.94	4.20	16	0.99
	TSPH2	5.08	38	0.99	4.90	38	1.00
Component 5	SRS2	4.96	32	0.98	4.76	40	1.00
	SRS4	4.71	38	0.99	5.11	27	1.00
	SRS6	4.91	35	0.99	4.09	32	0.99
	TSPH2	5.10	36	0.89	5.17	42	1.00
Component 6	SRS2	5.25	32	1.00	4.71	48	1.00
	SRS4	5.13	30	0.99	4.53	42	1.00
	SRS6	5.37	31	0.99	3.92	49	0.99
	TSPH2	5.45	30	0.99	4.97	49	1.00



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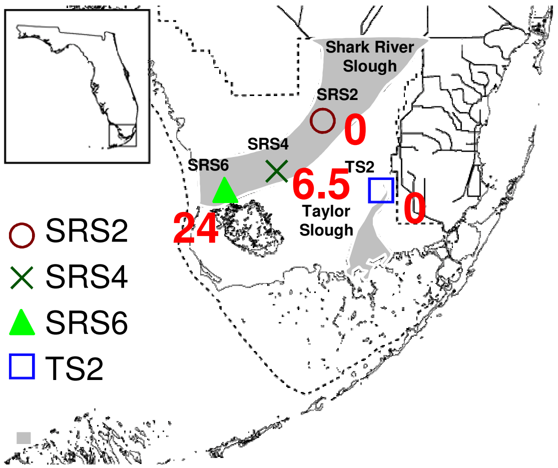

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	TSPH2	5.10	36	0.89	5.17	42	1.00
Component 6	SRS2	5.25	32	1.00	4.71	48	1.00
	SRS4	5.13	30	0.99	4.53	42	1.00
	SRS6	5.37	31	0.99	3.92	49	0.99
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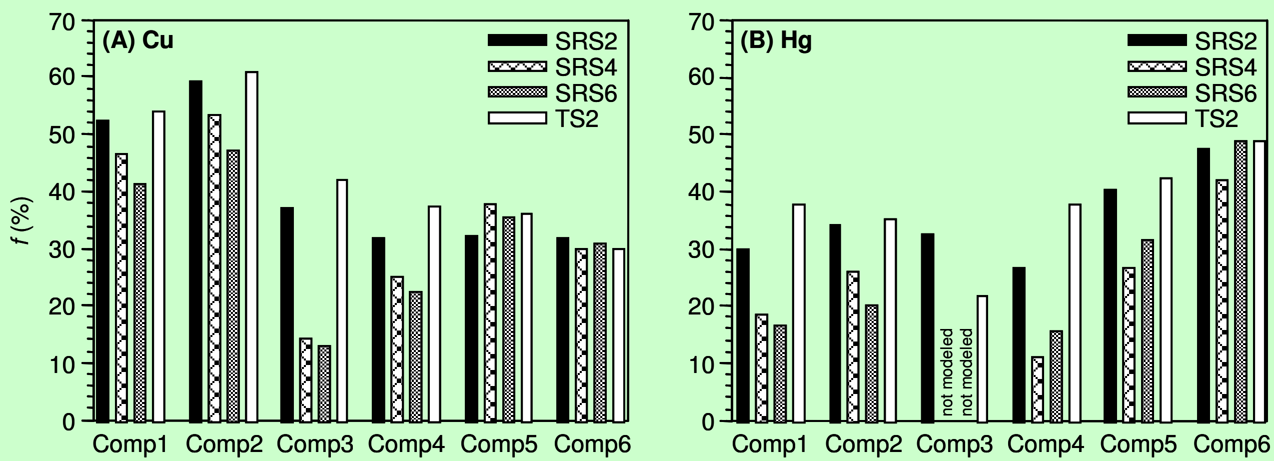

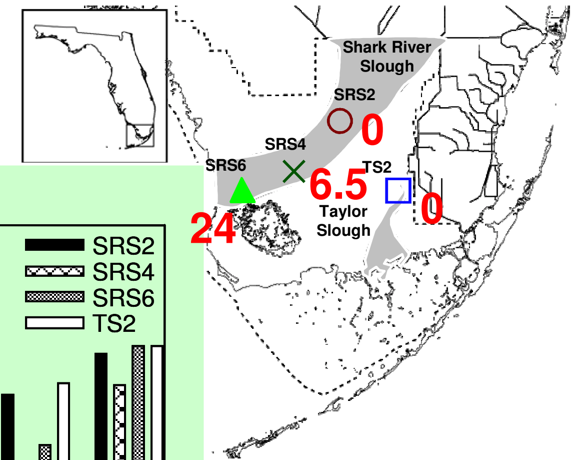

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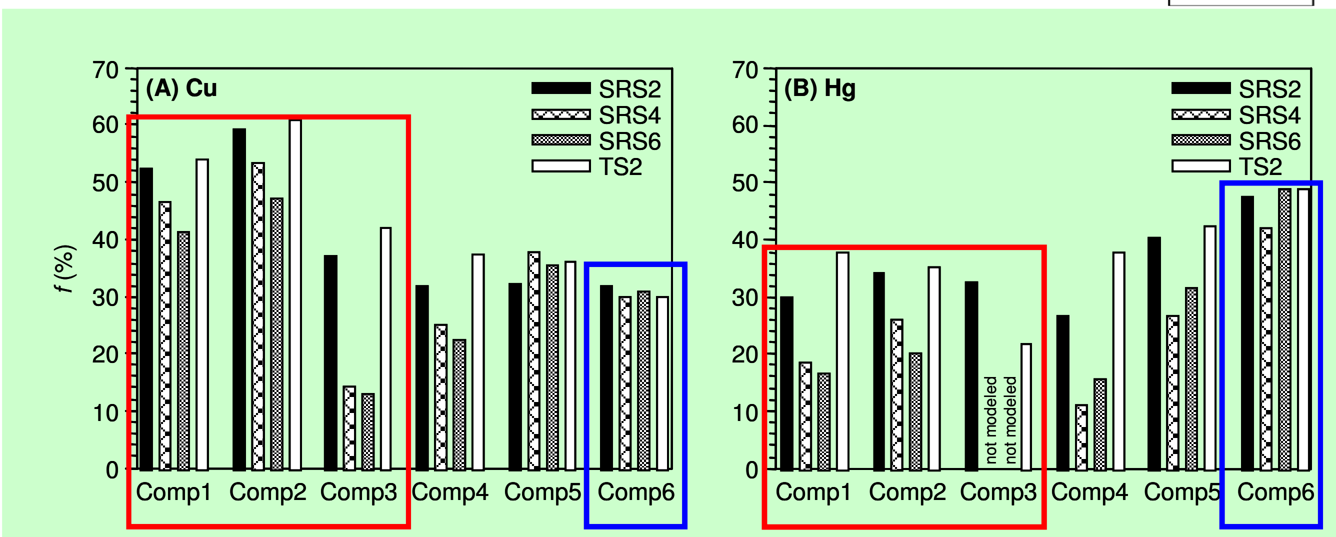

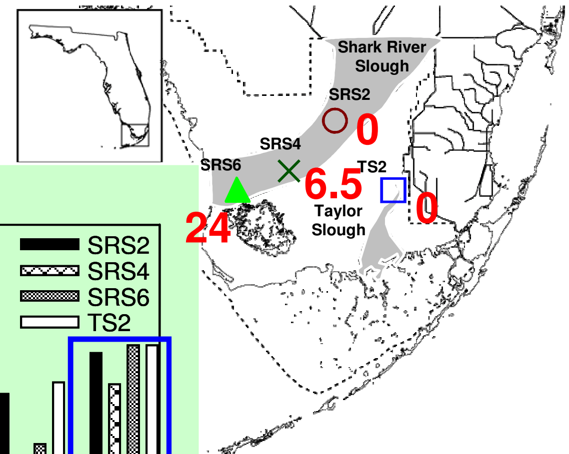

Component	Site	Cu(II) logK	Cu(II) f (%)	Cu(II) R^2	Hg(II) logK	Hg(II) f (%)	Hg(II) R^2
	TSPH2	5.08	38	0.99	4.90	38	1.00
Component 5	SRS2	4.96	32	0.98	4.76	40	1.00
	SRS4	4.71	38	0.99	5.11	27	1.00
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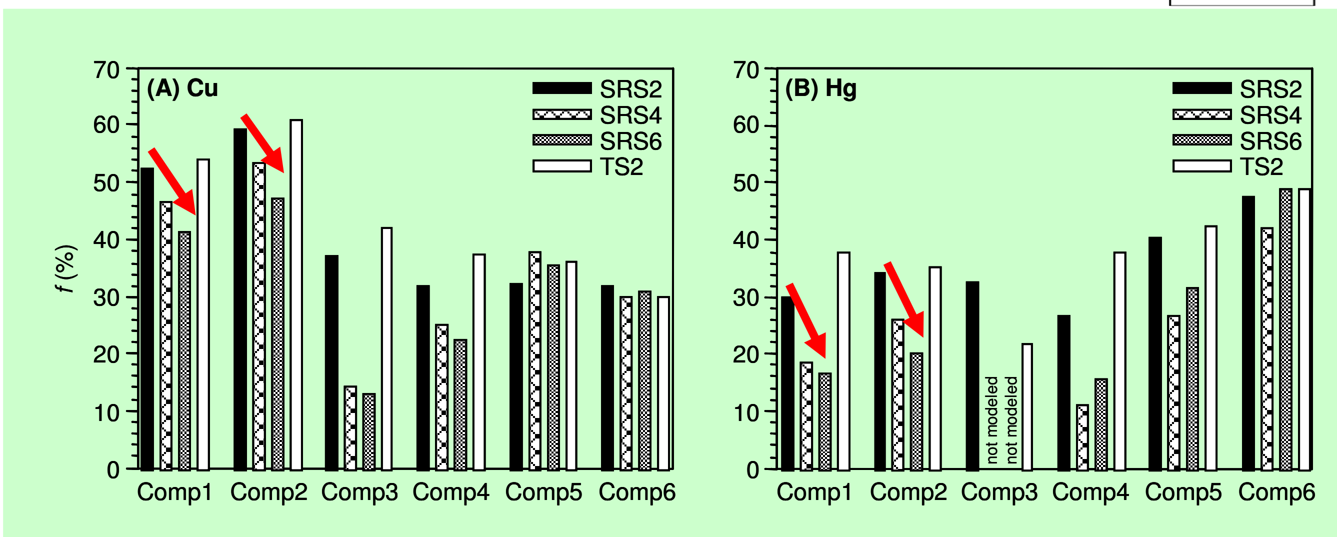

Component	Site	Cu(II) log*K*	Cu(II) *f* (%)	Cu(II) R^2	Hg(II) log*K*	Hg(II) *f* (%)	Hg(II) R^2
	TSPH2	5.08	38	0.99	4.90	38	1.00
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	SRS4	4.71	38	0.99	5.11	27	1.00
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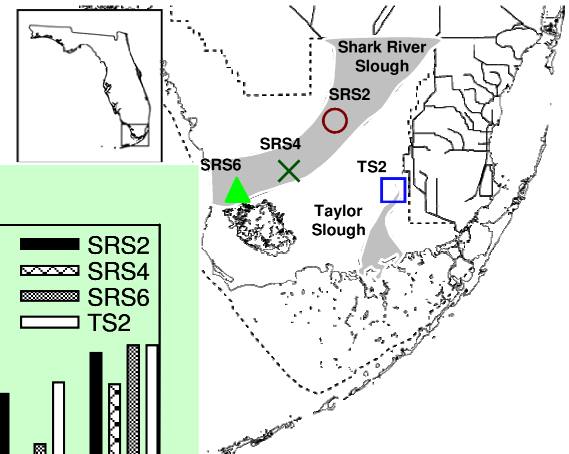
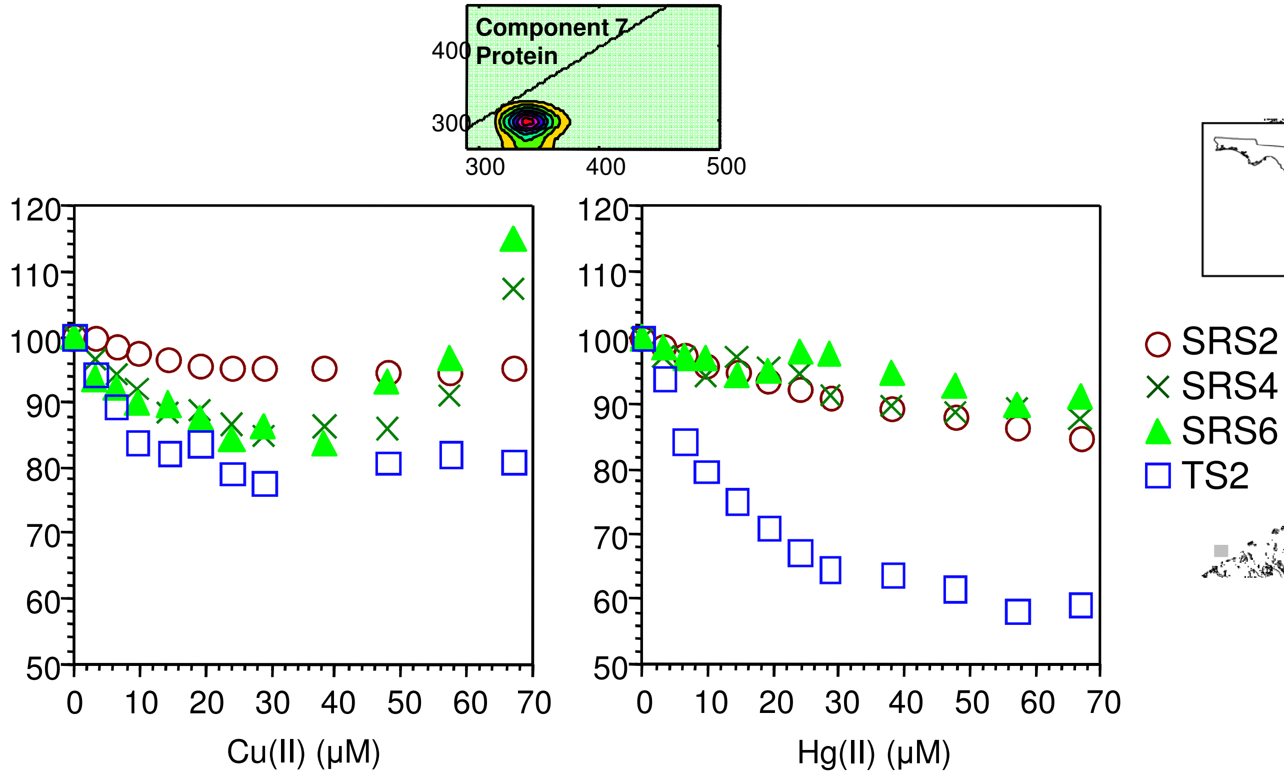
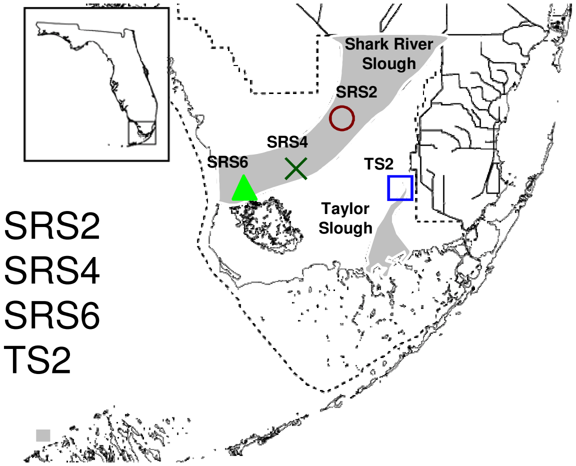


Changes in fluorescence of protein-like components

Titration experiments with Cu(II) or Hg(II) for 4 different samples





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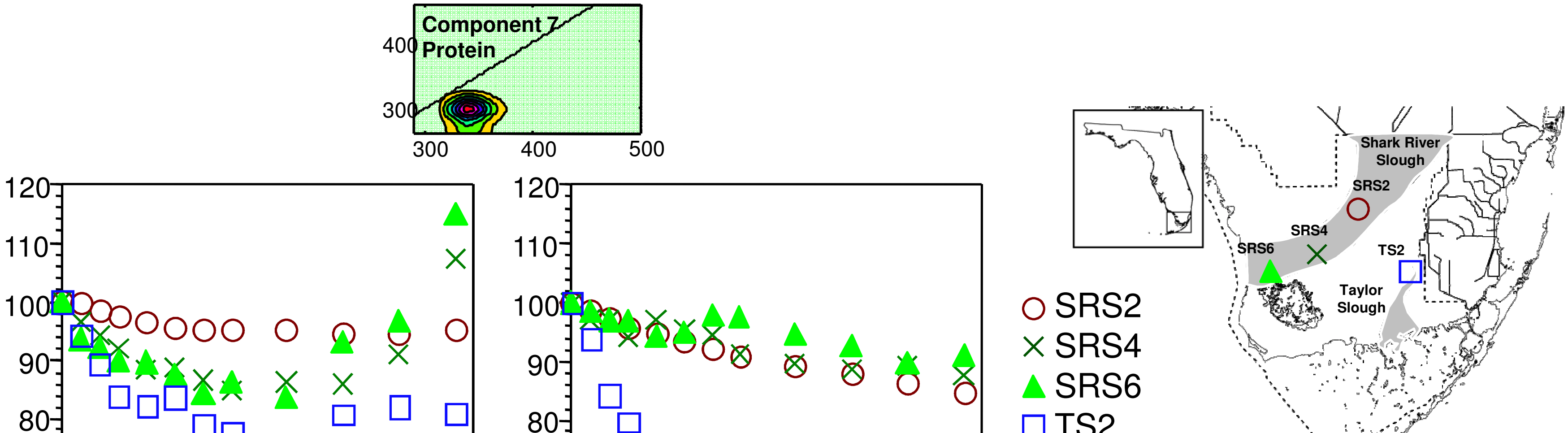

Increases in fluorescence intensity at the later stage of the Cu(II) addition experiment might be the result of:

- Changes in quantum yields by changes in 3D-structure of protein-molecules due to high concentrations of Cu(II).
- Changes in quantum yields of protein molecules from a shift of protein-inorganic complexes to protein-Cu(II) complexes.
- Release of protein molecules due to replacement from DOM-protein interaction to DOM-Cu(II) interactions.

Summary

- **The combination of fluorescence quenching titration and EEM-PARAFAC provides adequate reproducibility and sensitivity for the determination of the binding capacity of individual humic-like components with trace metals.**

- **The trace metal binding capacity and behavior was different among humic-like components determined by PARAFAC.**

- **The changes in protein-like fluorescence intensity with Cu(II) additions indicate that EEM-PARAFAC is also effective in evaluating the changes in molecular environments of DOM, like as DOM-DOM interactions.**

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- **Geochemistry Group at SERC for support to Lab work**