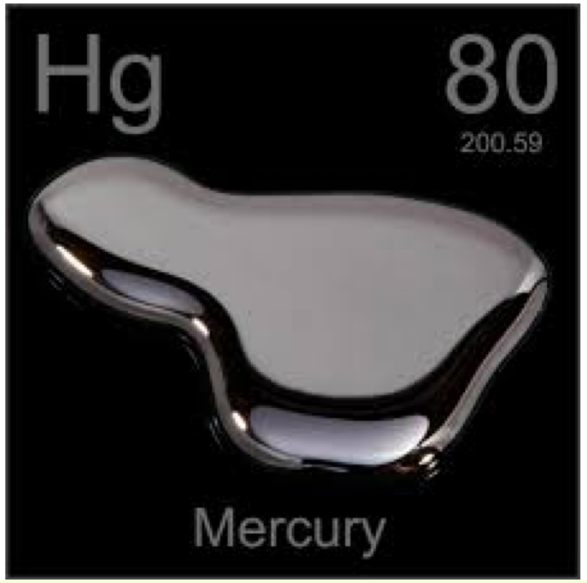
Hg(II)-Dissolved Organic Matter (DOM) Interactions in Freshwater and their Removal in Conventional Water Treatment

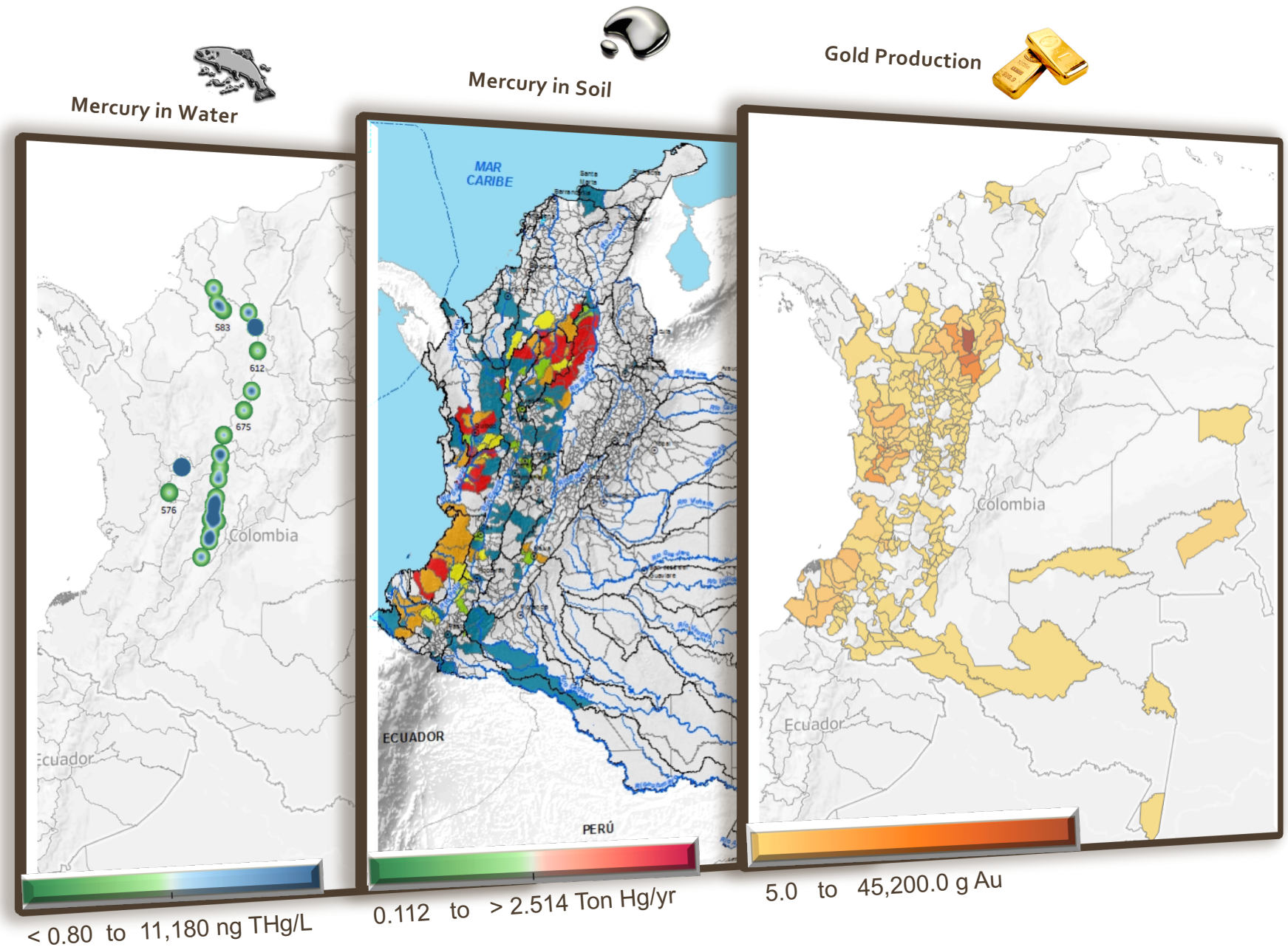
Farith Diaz, Ph.D.

Advisors: Desmond Lawler and Lynn Katz

Department of Civil, Architectural and Environmental Engineering

The University of Texas at Austin

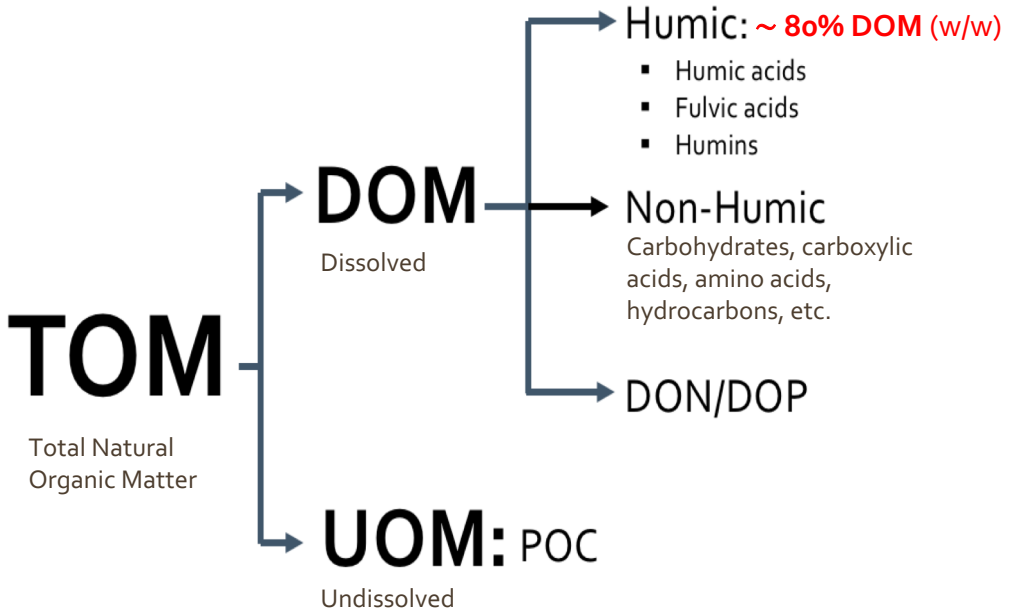




More than 200 rivers, out of the 1,150 rivers of the country, cross heavily mercury polluted ecosystems.

Gold production: source: UPME (map version Sep-2018)
Mercury in soil: source IDEAM (map version: 1.0, 03-Feb-2018)
Mercury in water: Data source: Grupo Laboratorio de Calidad Ambiental (IDEAM) (personal communication, September 28, 2017

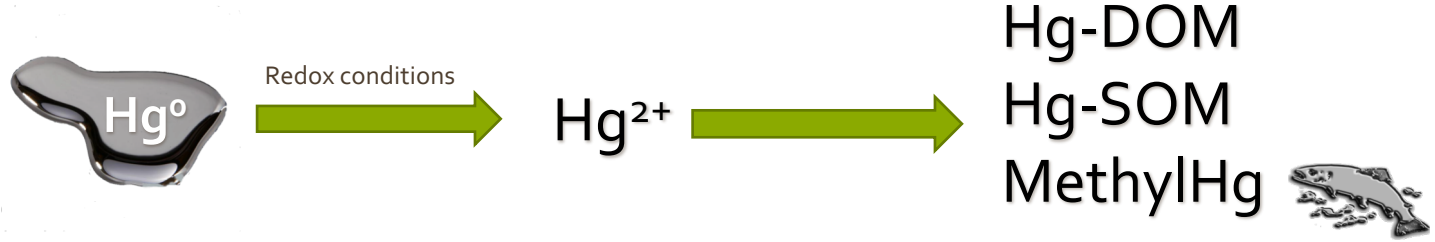
Hg-DOM complexation in aquatic environments



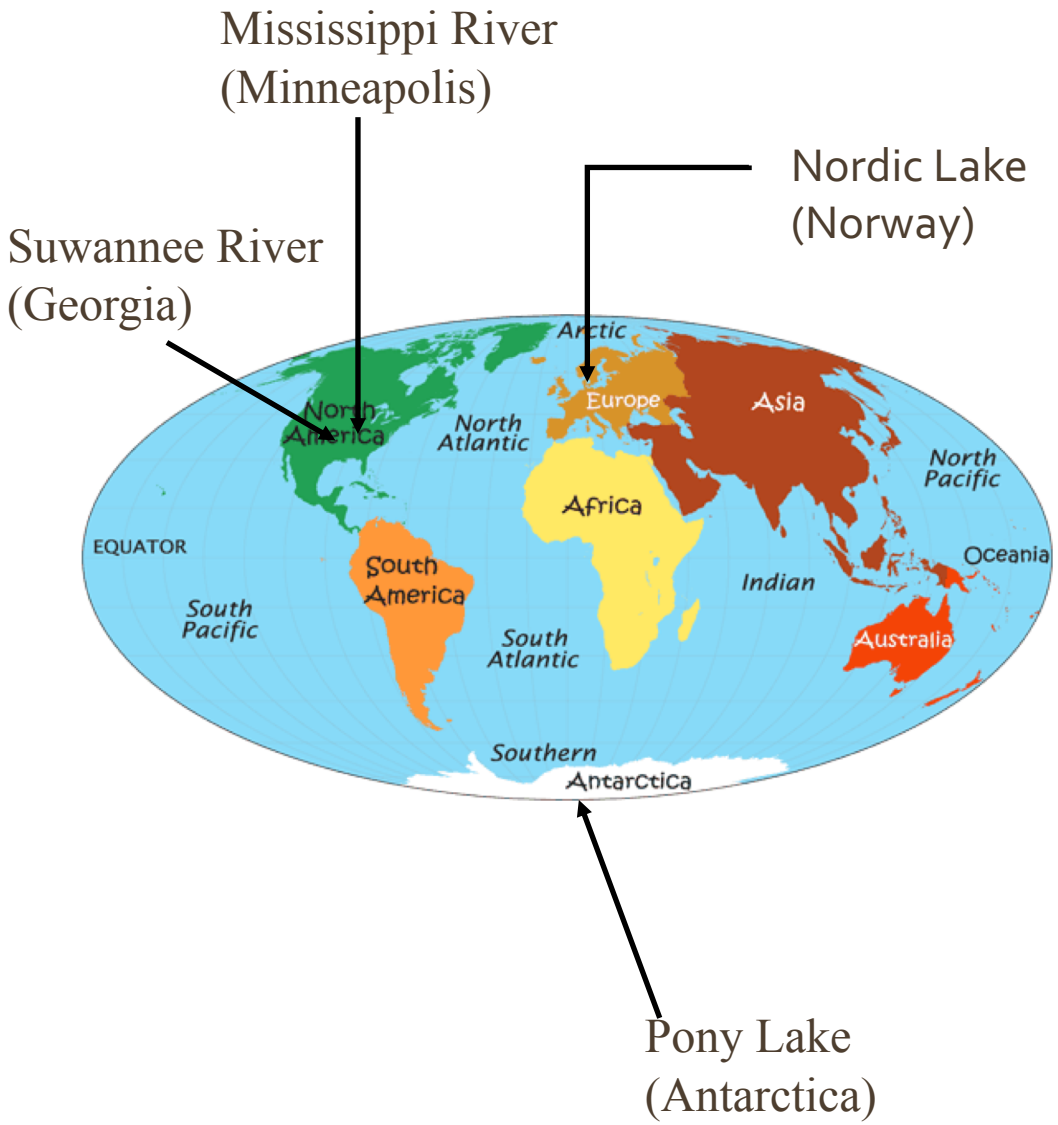
Adapted from Ravichandran (2004) and Pagano, Bida, and Kenny (2014)

Humic substances: Mixture of hydrophobic and hydrophilic compounds with different functional groups available for metal complexation.

Main functional groups: carboxylic acids, phenols, ammonium ions, alcohols, and thiols.



Selection of Natural Organic Matter (NOM)



Bought from the International Humic Substances Society (IHSS)

[a]Catalog Number	NOM Description	% C	% Aromatic 165-110 ppm	% Aliphatic 60-0 ppm	Acidic functional groups (meq/g C)		
					[b]Sred	[a]Phenolic	[a]Carboxyl
1R109F	Pony Lake Fulvic Acid	52.47	12	61	2.46	1.75	7.09
2S101F	Suwannee River Fulvic Acid	52.34	22	35	0.294	2.84	11.17
2S101H	Suwannee River Humic Acid	52.63	31	29	0.410	3.72	9.13
1R105H	Nordic Aquatic Humic Acid	53.33	38	15	0.488	3.23	9.06
2R101N	Suwannee River NOM	50.70	23[c]	27[c]	N.A.	2.47	11.21
1R110N	Upper Mississippi River NOM	49.98	19	37	N.A.	0.830	12.43

[a]IHSS (http://humic-substances.org/), [b]Manceau and Nagy (2012), [c]IHSS for NOM reference 1R101N

Preparation and characterization of DOM stock solutions

Solid NOM
(IHSS)

Millipore water
pH adjustment

Sonicator and
magnetic mixer

Filtration
0.45-µm Cellulose Nitrate
Membrane Filter

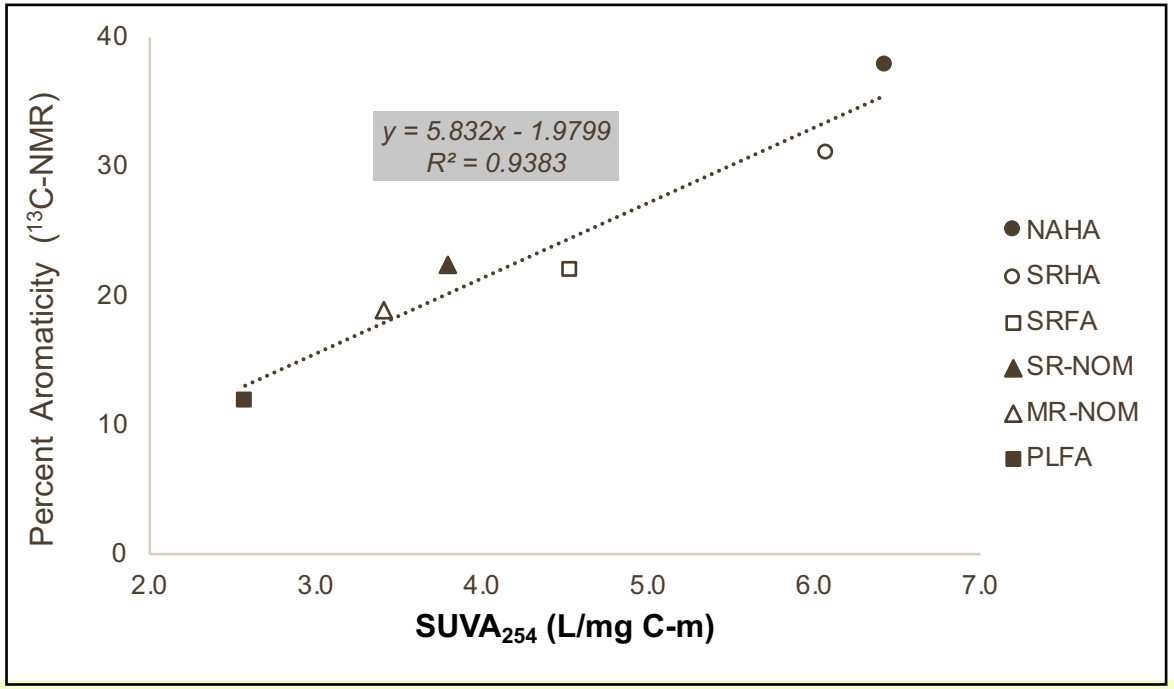
DOM Solution
4°C

Characterization of DOM solutions

Specific ultraviolet absorbance (SUVA)
(proxy for aromatic content)

$$SUVA = \frac{(UV_{254} \text{ in } cm^{-1})100 \ \frac{m^{-1}}{cm^{-1}}}{(DOC \text{ in } mg/L)}$$

NOM	NOTATION	% Aromatic 165-110 ppm[a]	SUVA (L/mg C-m)
Pony Lake Fulvic Acid	PLFA	12	2.57±0.13
Suwannee River Fulvic Acid	SRFA	22	4.53±0.20
Suwannee River Humic Acid	SRHA	31	6.08±0.13
Nordic Aquatic Humic Acid	NAHA	38	6.42±0.03
Suwannee River NOM	SR-NOM	23	3.80±0.03
Upper Mississippi River NOM	MR-NOM	19	3.35±0.03



NOM selection

	NOM	% C	% Aromatic 165-110 ppm	Acidic functional groups (meq/g C)		
				Sred	Phenolic	Carboxyl
Pony Lake	PLFA	52.47	12	2.46	1.75	7.09
Suwanee River	SRFA	52.34	22	0.294	2.84	11.17
Suwanee River	SRHA	52.63	31	0.410	3.72	9.13
Nordic Aquatic	NAHA	53.33	38	0.488	3.23	9.06

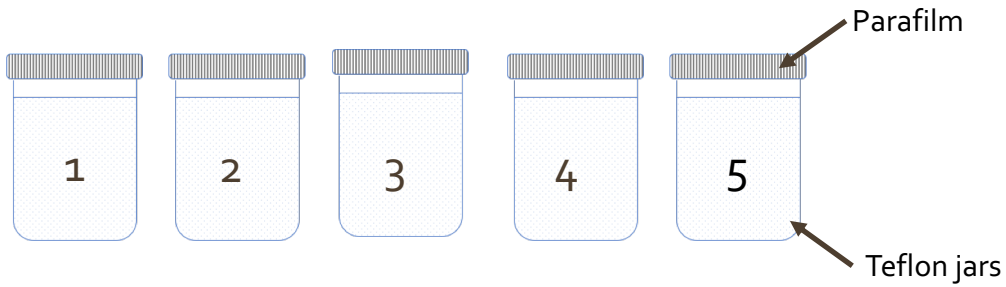
Low and high Hg(II) doses

NOM	DOC (mg/L)	Hg (µg/L)	Hg/DOM ratio (µg/mg)	Alum Dose (mg/L)	pH
Each NOM	5.0	0.5 10.0	0.05 1.00	30 (2.6 mg/L as Al^{3+})	6.7

Jar Test

DOM stock solution

Millipore water
0.01 M $NaNO_3$



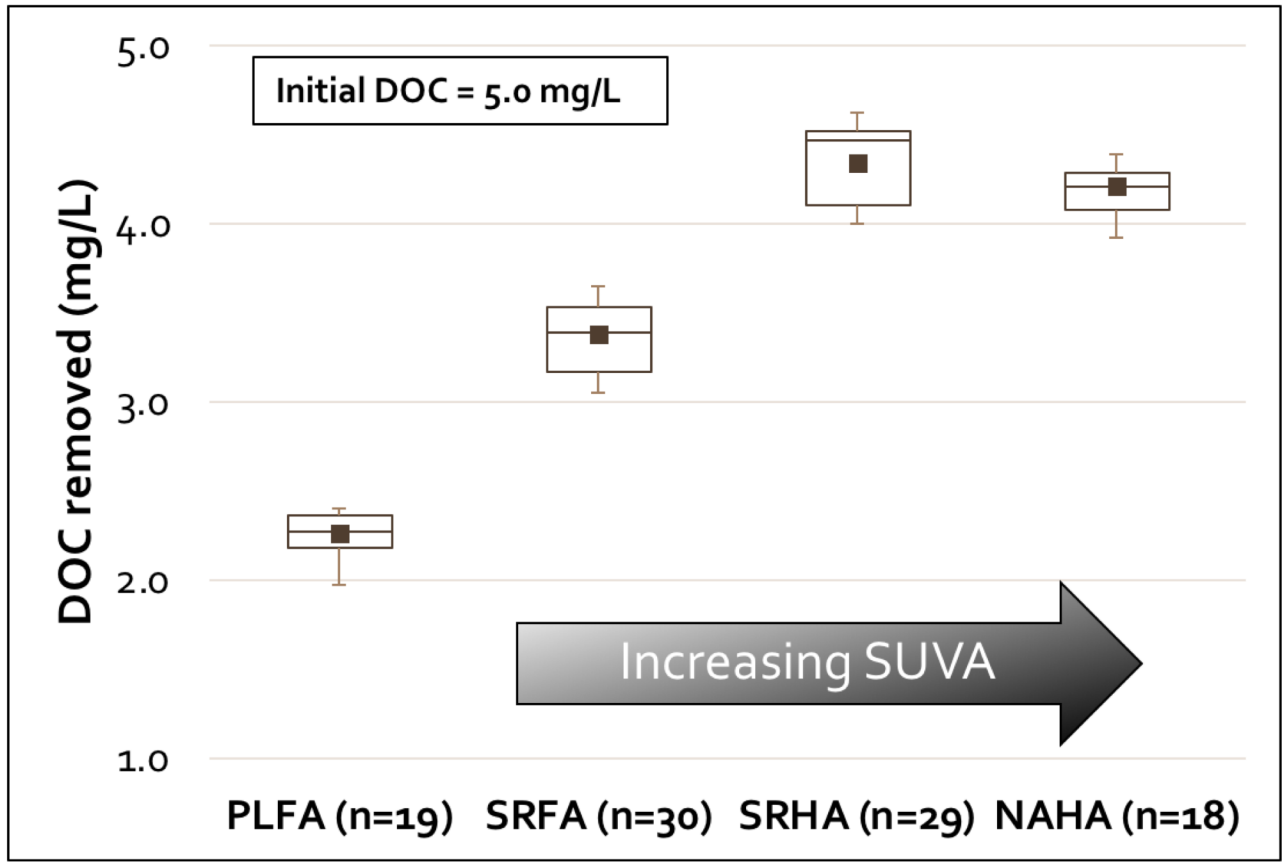
~ 200-mL DOM solution

Initial DOC = 5.0 mg/L
pH = 6.7
Alum dose = 30 mg/L
I.S.=0.01 M $NaNO_3$

1) pH adjustment (HNO_3 or NaOH)
2) Rapid mix for 2 minutes to add coagulant
   pH adjustment NaOH, HNO_3
3) Slow mixing for 20 min
4) Settling for 20 min
5) Centrifugation for 20 min @ 665xg

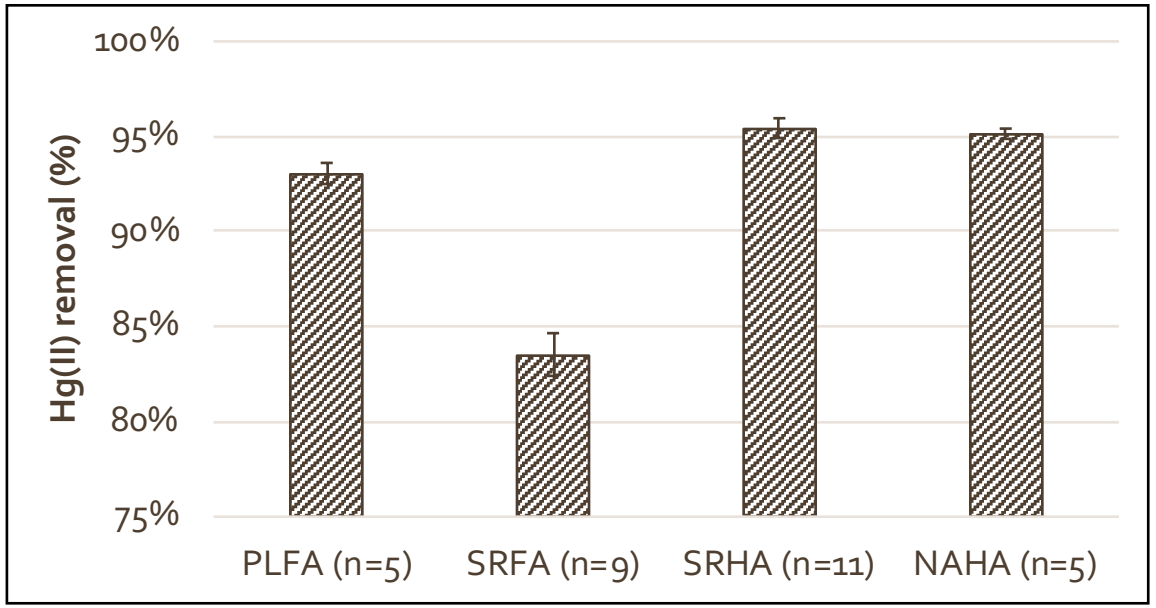
Results

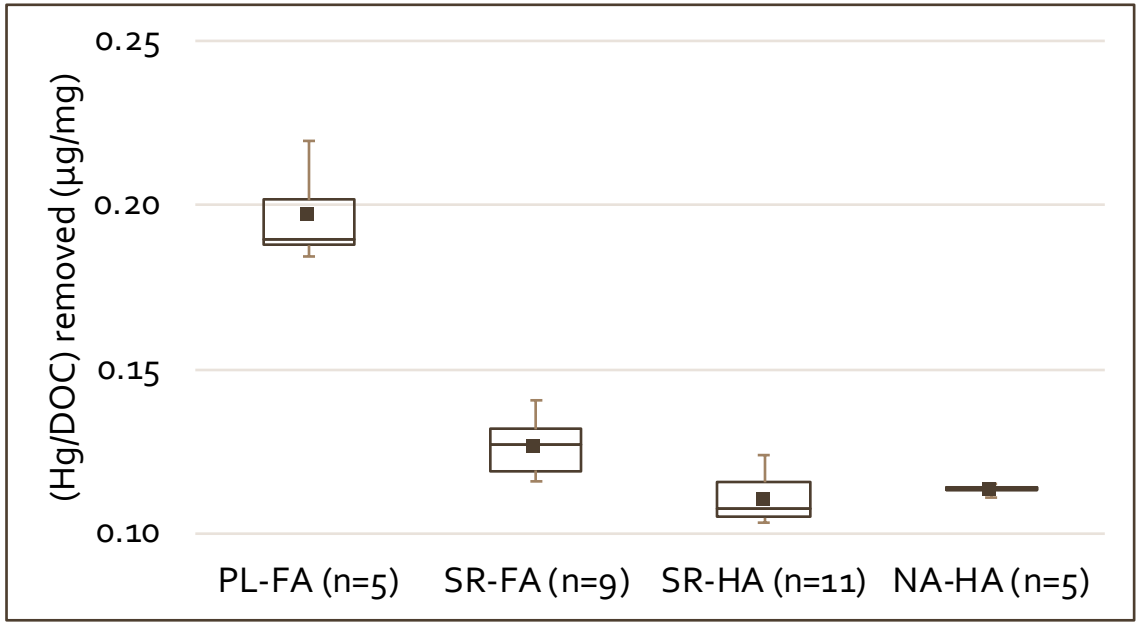
Carbon removal



NOM	SUVA (L/mg C-m)	DOC removal (%)
PLFA	2.57±0.09	46.8±1.2
SRFA	4.53±0.30	64.5±3.9
SRHA	6.08±0.16	83.4±2.3
NAHA	6.42±0.07	85.2±1.2

Results at low Hg/DOM ratio

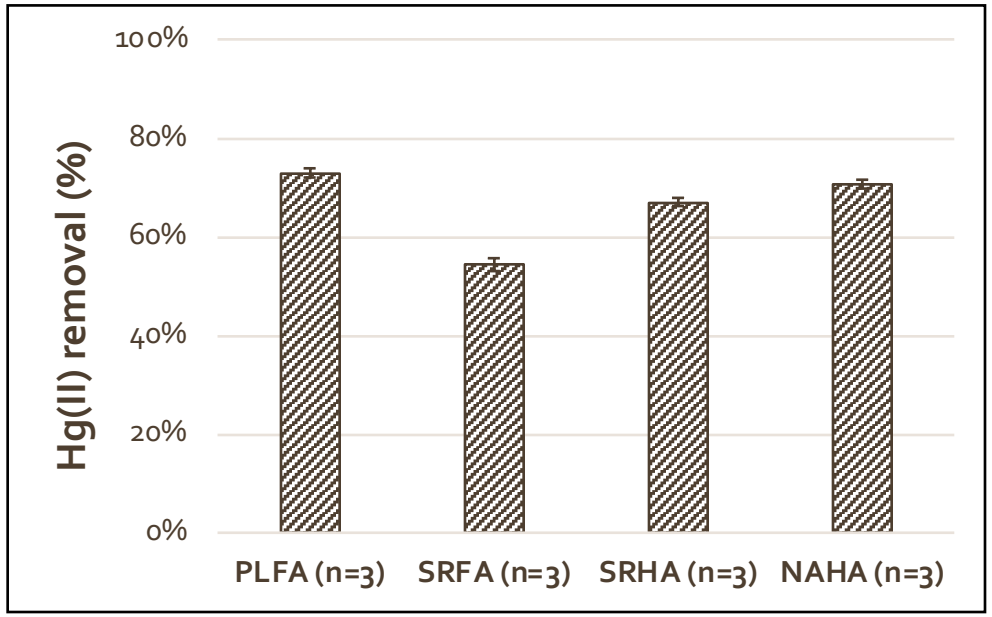


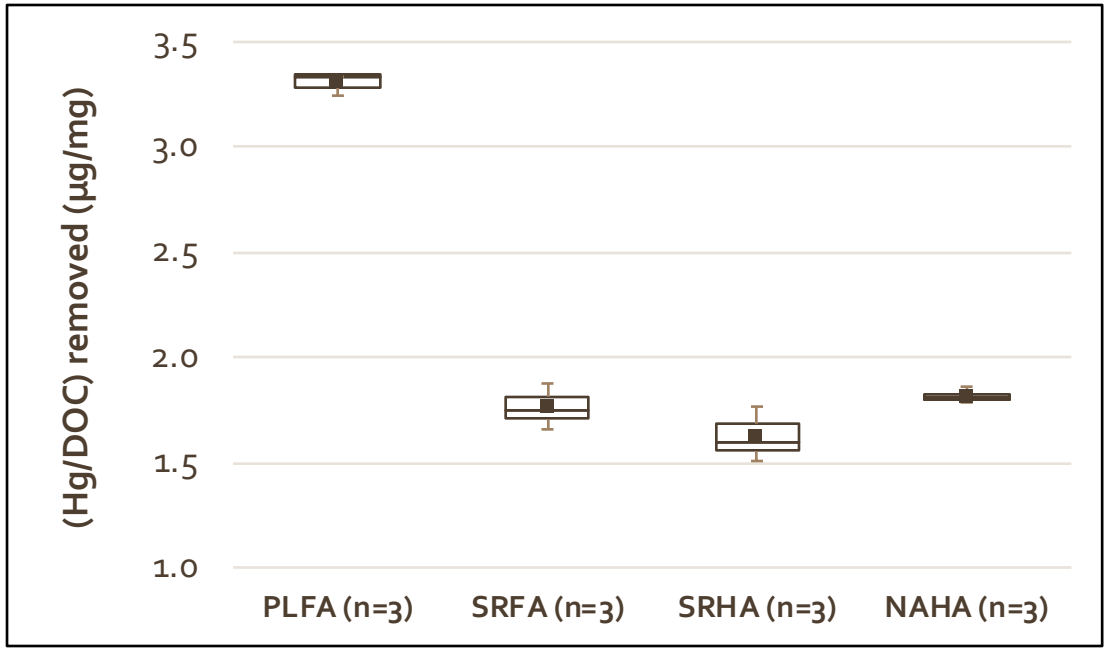


DOM	Carbon removed (%)	Hg(II) removed (%)
PLFA	47	93
SRFA	64	84
SRHA	83	95
NAHA	85	95

NOM	SUVA (L/mgC-m)	% Aromatic 165-110 ppm	Acidic functional groups (meq/g C)		
			Sred	Phenolic	Carboxyl
PLFA	2.53±0.13	12	2.46	1.75	7.09
SRFA	4.51±0.20	22	0.294	2.84	11.17
SRHA	5.94±0.13	31	0.410	3.72	9.13
NAHA	6.49±0.03	38	0.488	3.23	9.06

Results at high Hg/DOM ratio





DOM	Carbon removed (%)	Hg(II) removed (%)
PLFA	47	73
SRFA	64	54
SRHA	83	67
NAHA	85	71

NOM	SUVA (L/mgC-m)	% Aromatic 165-110 ppm	Acidic functional groups (meq/g C)		
			Sred	Phenolic	Carboxyl
PLFA	2.53±0.13	12	2.46	1.75	7.09
SRFA	4.51±0.20	22	0.294	2.84	11.17
SRHA	5.94±0.13	31	0.410	3.72	9.13
NAHA	6.49±0.03	38	0.488	3.23	9.06

Conclusions

- While Hg(II) binding ligands in DOM play an important role in the distribution of mercury in aquatic environments, their role in removing Hg(II) from solution is dependent on the ability of the fraction of DOM containing these ligands to adsorb to the aluminum hydroxide flocs.

- Sred controls Hg(II) removal in water treatment only when the Sred/Hg(II) >> 1 regardless the aromaticity:

- When Sred/Hg(II) is < 1, Hg(II) will be distributed along the structure of the DOM and the removal of Hg(II) depends of the extent of the DOM removal (DOM removal is controlled by the aromaticity (hydrophobicity) in alum coagulation).

- In summary, not only does the character of DOM determine the extent of the removal of carbon, it also determines the minimum removal of Hg. Higher Hg(II) removal depends on the presence of Sred in the hydrophobic portion.