DISTRIBUTION OF MERCURY SPECIES IN THE EVERGLADES: A GEOCHEMICAL PERSPECTIVE AND IMPLICATIONS ON MERCURY BIOACCUMULATION

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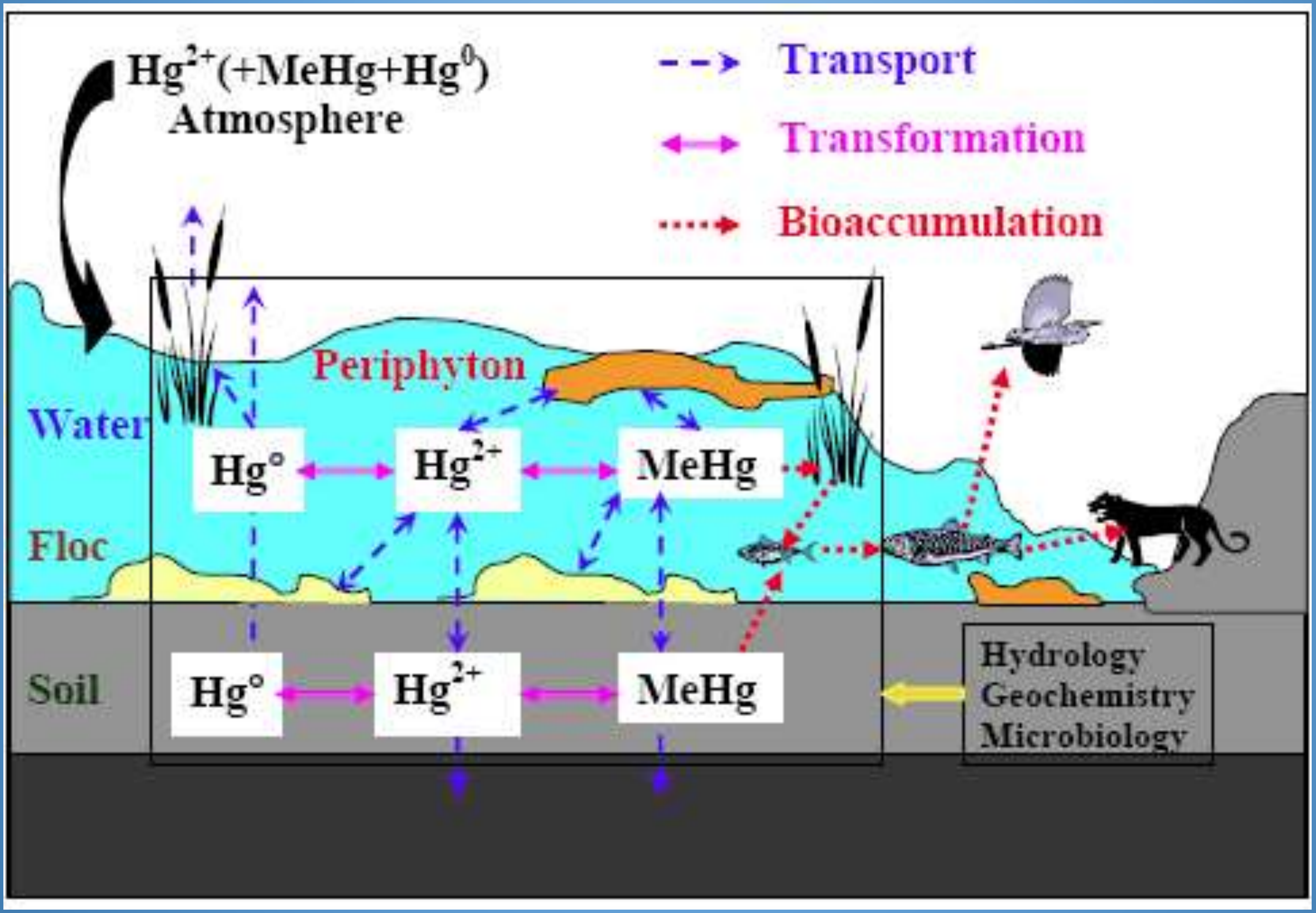
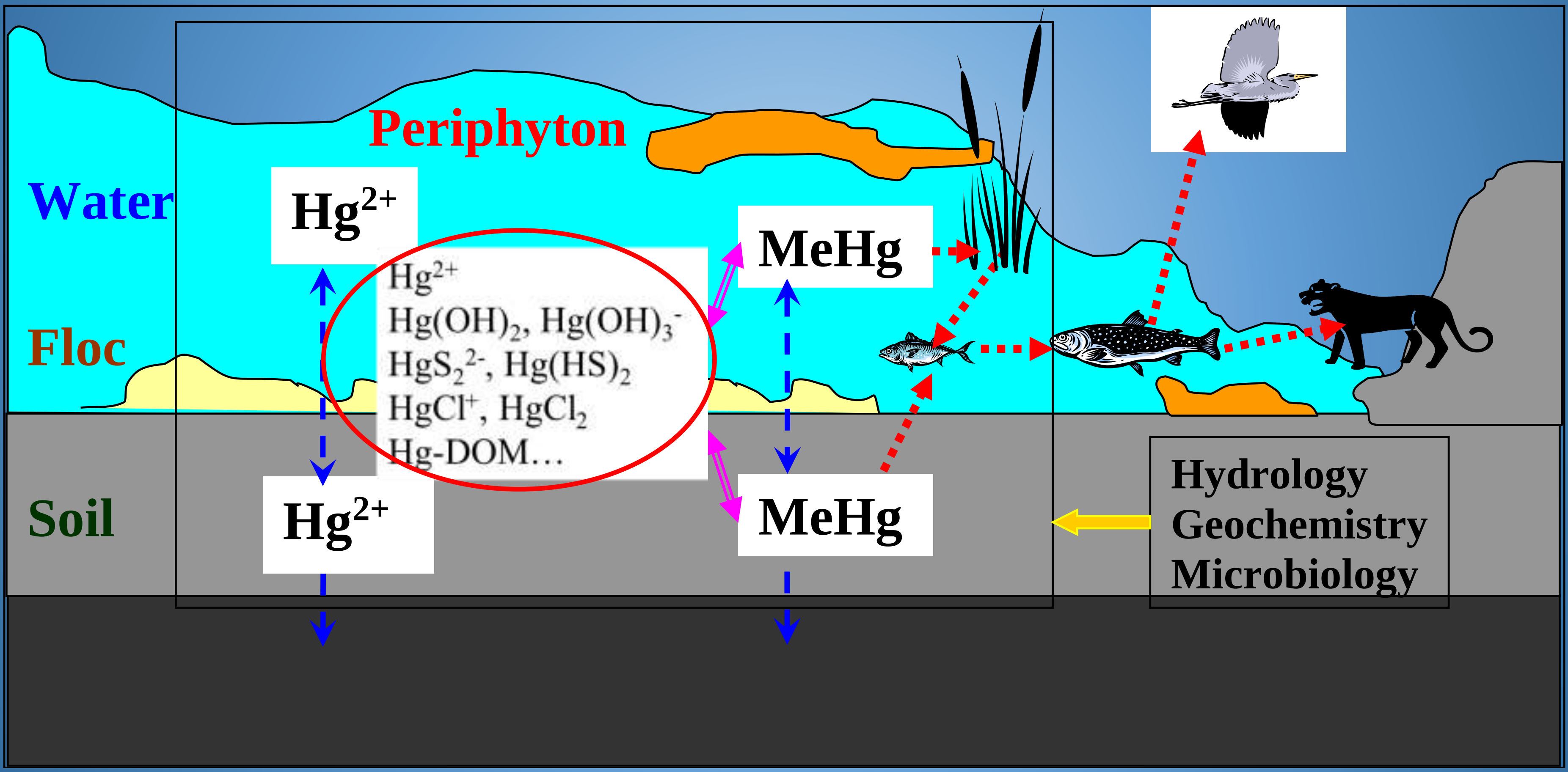
Mercury Cycling in the Everglades



(Liu et al, 2009)

Inorganic Mercury (iHg) Speciation and Hg Cycling



Objective

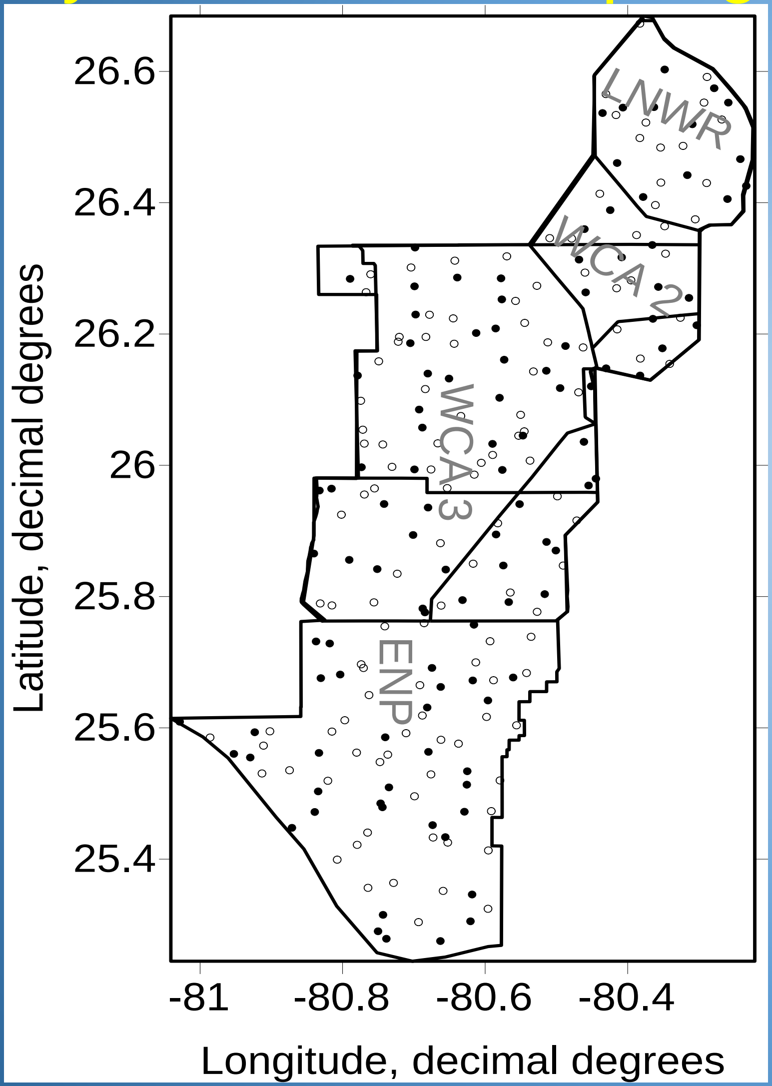
Understand how geochemical factors regulate speciation of inorganic Hg and subsequently influence Hg cycling in the Everglades.

Geochemical Modeling of Hg Speciation

- Geochemical Model
  - PHREEQC **(Parkhurst and Appelo, 2013)**
- Data Sources
  - Everglades Regional Environmental Monitoring and Assessment Program (R-EMAP)
  - USGS ACME
  - SFWMD DBHYDRO

R-EMAP

System-wide sampling

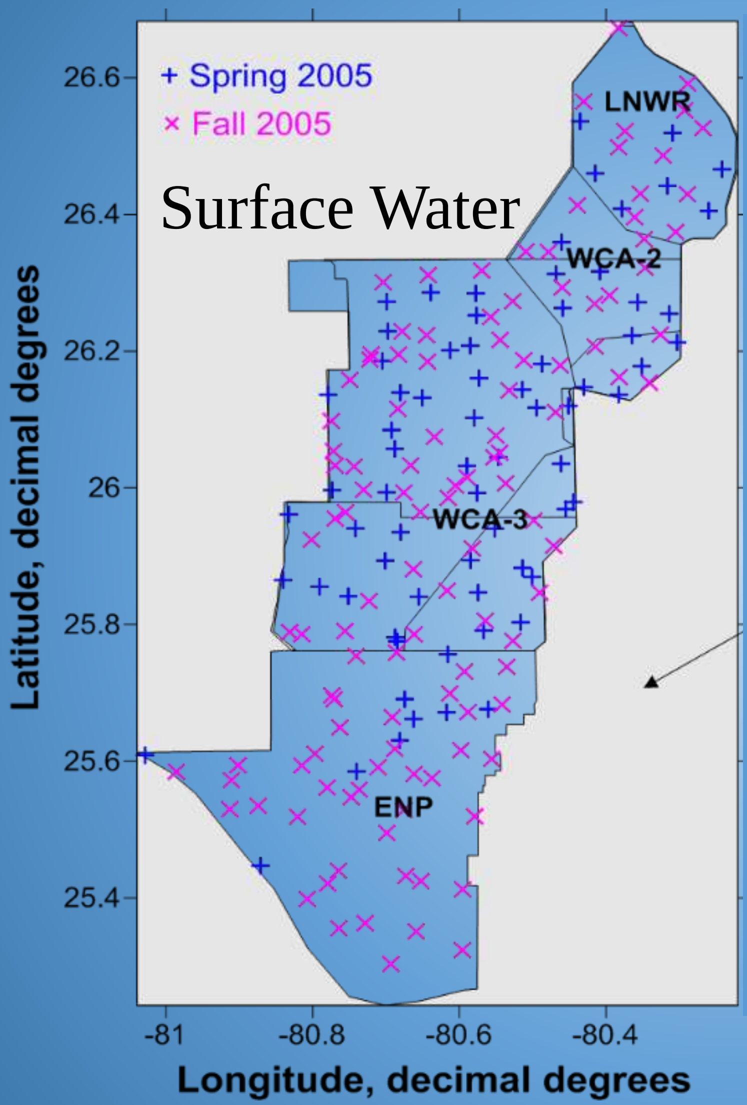


A long list of parameters

Surface Water	DO, Cond., pH, Temp., Secchi Depth, TP, TKN, NH_3, NO_{2+3}, SO_4, Cl, Turbidity, TOC, Eh, depth, S^{2-}, APA. Dissolved: SO_4, NH_4, NO_{2-3}, PO_4 THg, MeHg
Porewater	TP, TN, SO_4, S^{2-}, Anions (Cl, NO_{2-3}, SRP)
Soil	Bulk Density, TP, AFDW, Type, Thickness, SO_4, Mineral Content, APA. THg, MeHg
Floc	Bulk Density, TP, AFDW, Type, Thickness, SO_4, Mineral Content, APA. THg, MeHg
Periphyton	THg, MeHg
Mosquitofish	THg, length, weight, sex, food habits

(Scheidt and Kalla, 2007)

Data Sources



2005 R-EMAP

Dataset:
THg, MeHg, Biogeochemical parameters

Sampling stations:
109 in dry season
119 in wet season

[S^{2-}] > 0.02 mg/L
18 in dry season
21 in wet season

USGS ACME
SFWMD DBHYDRO

Model Input

- Physicochemical Parameters
  - pH
  - Redox Potential
  - Hg Binding Ligands
    - Cl^-, Br^-, SO_4^{2-}…
- Hg-DOM Complexation
- Hg-Sulfide Complexation

Hg-DOM Complexation

- Binding Sites
  - Thiol Groups (RS^-)
  - Oxygen Functional Groups (RO^-)

- $Hg(OH)_2 + RSH^{n-} + H^+ = RSHg^{(n-1)-} + 2H_2O$

  Log K = 20.8 **(Skyllberg, 2008)**

- Determination of RS^- Concentrations

  $[RS^-] = 0.00017[DOC]$

  (Benoit et al., 2001)

Everglades DOM Isolates	Molecular Weight	Carbon Content (%)	Reduced S Fraction (mol/mol DOM)
Hydrophobic	1031	52.2	0.12
Hydrophilic	862	49.3	0.05

Hg-Sulfide Complexation

- Database:

$Hg(OH)_2 + 2HS^- = HgS_2^{2-} + 2H_2O$ Log K=31.24

$Hg(OH)_2 + 2HS^- + 2H^+ = Hg(HS)_2 + 2H_2O$ Log K=43.82

(Skyllberg, 2008)

- Complementary:

$Hg(OH)_2 + H^+ + 2HS^- = HgHS_2^- + 2H_2O$ Log K=38.10

$Hg(OH)_2 + H^+ + HS^- = HgHSOH + H_2O$ Log K=22.70

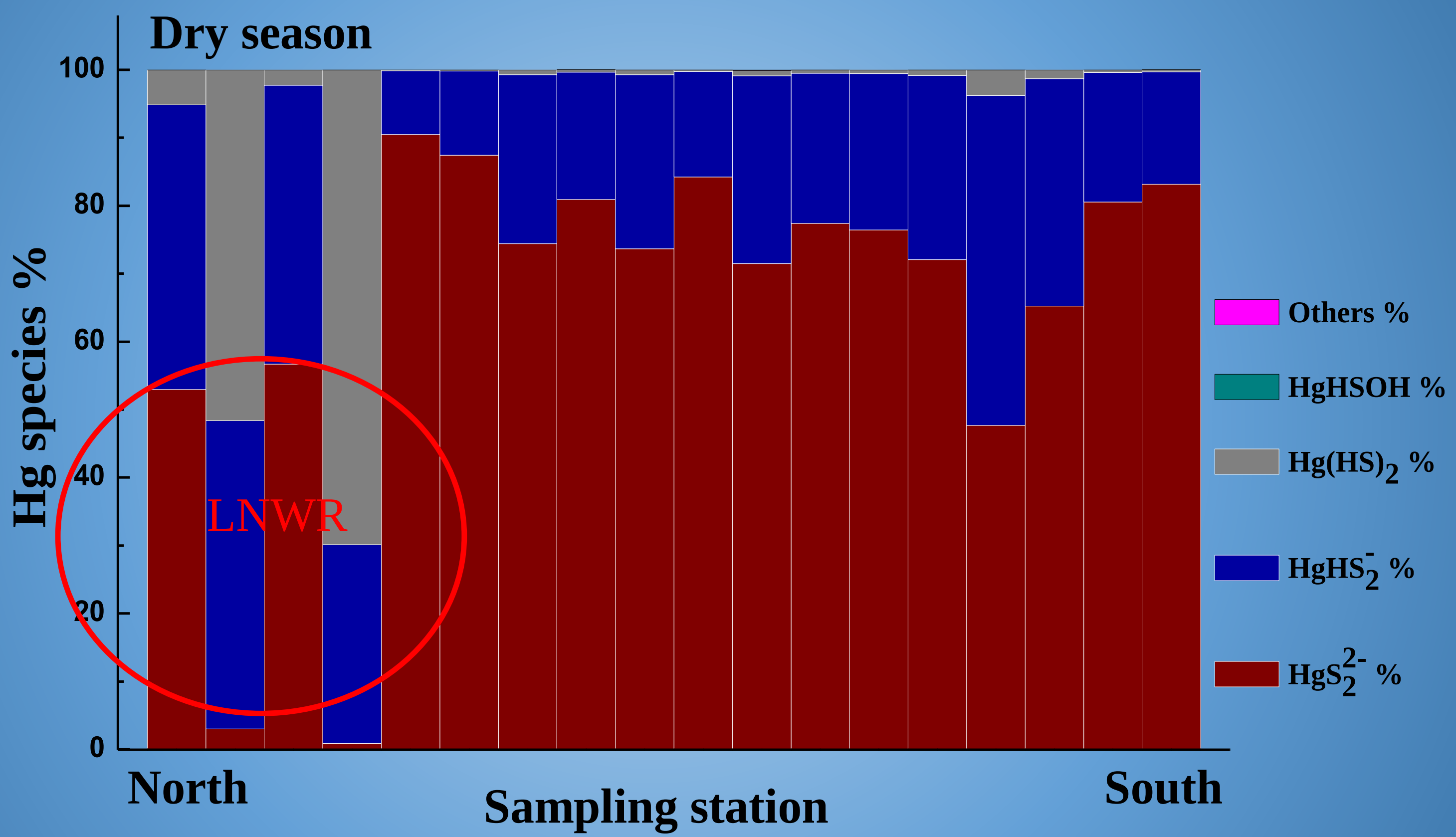
- Sulfide Concentrations
  - ≥0.02 mg/L
  - <0.02 mg/L
    - 0.00000032 mg/L (0.00001 µM)
    - 0 mg/L

Hg species in Everglades Surface Water
($[S^{2-}]$ > 0.02 mg/L)

Station	Hg mol/L	HgS_2^{2-} mol/L	$HgHS_2^-$ mol/L	$Hg(HS)_2$ mol/L	HgHSOH mol/L	$RSHg^{(n-1)-}$ mol/L	$HgCl_2$ mol/L
12	1.45E-11	1.20E-11	2.39E-12	4.43E-14	1.70E-21	1.94E-22	3.44E-29
35	9.97E-12	8.04E-12	1.90E-12	3.48E-14	2.81E-22	5.42E-24	4.19E-33
40	1.70E-11	1.11E-11	5.67E-12	2.23E-13	2.30E-21	1.15E-22	9.01E-32
64	8.97E-12	4.28E-12	4.36E-12	3.36E-13	1.18E-21	4.49E-23	3.43E-32
72	6.48E-12	4.67E-12	1.76E-12	5.10E-14	1.22E-21	1.16E-22	1.29E-31
74	5.98E-12	4.57E-12	1.38E-12	3.23E-14	7.99E-22	5.28E-23	4.48E-32
76	1.15E-11	8.88E-12	2.53E-12	5.48E-14	1.73E-21	1.17E-22	5.20E-32
86	1.15E-11	8.20E-12	3.17E-12	9.42E-14	2.83E-21	2.53E-22	2.88E-31
96	1.10E-11	9.24E-12	1.70E-12	2.49E-14	1.39E-21	2.16E-22	2.56E-31
97	3.09E-11	2.28E-11	7.91E-12	2.14E-13	3.71E-21	2.59E-22	2.43E-31
100	1.30E-11	1.05E-11	2.43E-12	4.48E-14	1.31E-21	1.34E-22	1.66E-31
102	1.40E-11	1.04E-11	3.48E-12	9.55E-14	2.72E-21	6.59E-22	1.90E-30
110	3.49E-11	3.16E-11	3.28E-12	2.78E-14	2.31E-22	5.12E-24	6.31E-33
117	2.54E-11	2.34E-13	7.43E-12	1.78E-11	1.67E-19	7.16E-19	7.12E-27
118	1.65E-11	9.33E-12	6.75E-12	3.74E-13	7.93E-21	1.10E-21	1.39E-30
120	3.29E-11	9.97E-13	1.49E-11	1.70E-11	1.43E-19	2.65E-19	3.03E-27
121	7.98E-12	3.34E-12	4.23E-12	4.08E-13	2.68E-21	2.49E-22	3.67E-31
350	2.24E-11	1.96E-11	2.78E-12	3.20E-14	3.38E-22	1.10E-23	2.40E-32

Sample model output

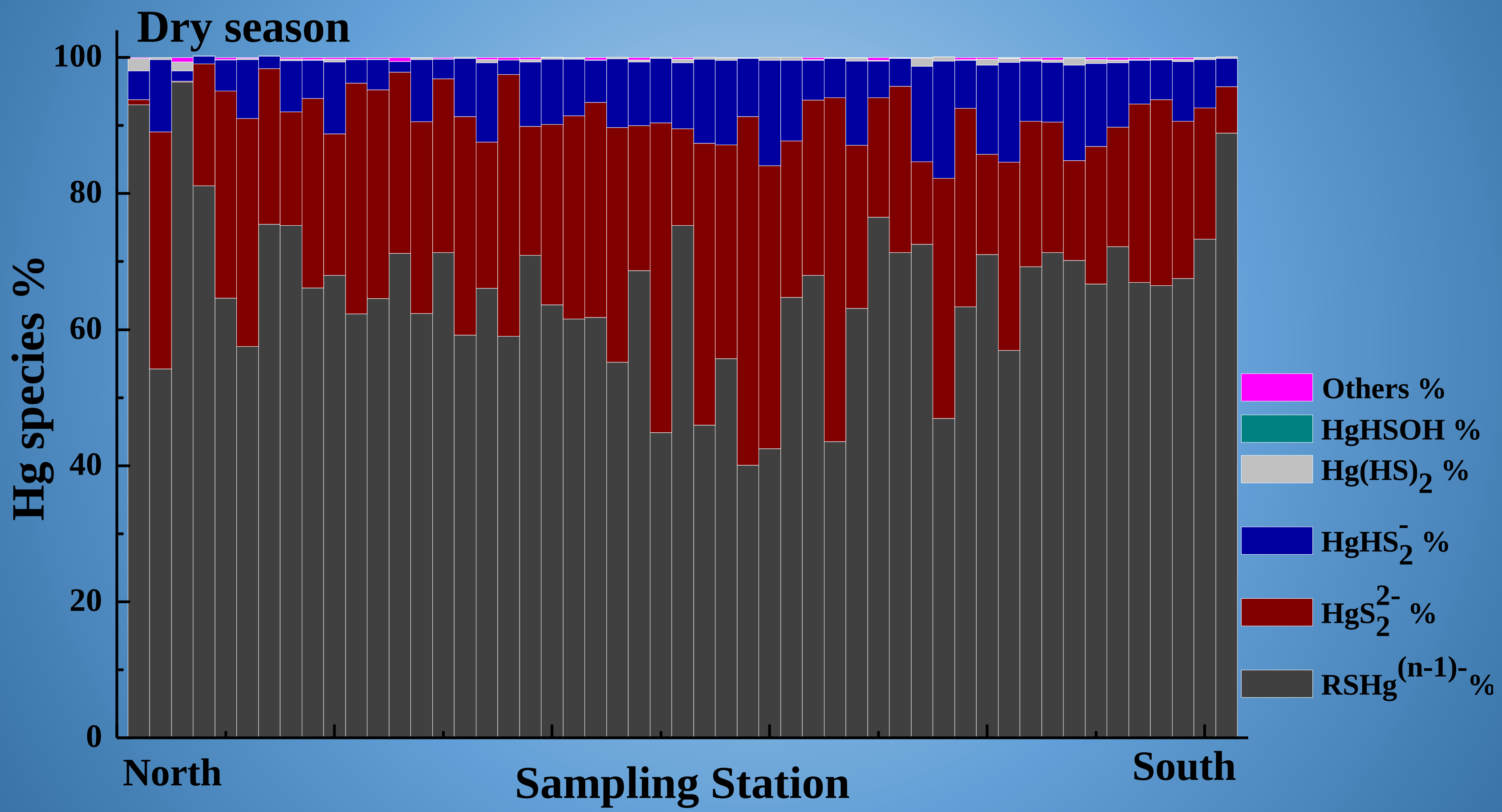
Relative Distribution of iHg Species
($[S^{2-}] > 0.02$ mg/L)



HgS_2^{2-}, $HgHS_2^-$, and $Hg(HS)_2$ are major species.

Relative Distribution of iHg Species

(Assuming $[S^{2-}] = 0.00000032$ mg/L)



$RSHg^{(n-1)-}$ and Hg-sulfide complexes are major species.

Relation of iHg Species with MeHg

($[S^{2-}] > 0.02$ mg/L)

MeHg	Surface water iHg species					
	HgS_2^{2-}		$HgHS_2^-$		$Hg(HS)_2$	
	Dry	Wet	Dry	Wet	Dry	Wet
Surface water	0.88** (18)	0.39 (21)	0.08 (18)	0.53** (21)	-0.37 (18)	0.42 (21)
Epiphytic periphyton	0.9* (5)	0.11 (11)	0.9* (5)	0.32 (11)	-0.3 (5)	0.28 (11)
Floc	0.50* (16)	-0.10 (17)	0.18 (16)	0.42 (17)	0.01 (16)	0.45 (17)
Soil	-0.22 (18)	0.13 (21)	0.67** (18)	0.20 (21)	0.72 (18)	0.21 (21)

** Significant correlations at $p < 0.001$ level;
* Significant correlations at $p < 0.05$ level

Relation of iHg Species with MeHg

(Assuming $[S^{2-}]$ = 0.00000032 mg/L)

MeHg	Surface water iHg species							
	HgS_2^{2-}		$HgHS_2^-$		$Hg(HS)_2$		$RSHg^{(n-1)-}$	
	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet
Surface water	0.27 (51)	-0.12 (92)	-0.12 (51)	0.21* (92)	-0.18 (51)	0.20 (92)	0.41** (51)	0.48** (92)
Floating mat periphyton	0.09 (6)	-0.10 (16)	-0.26 (6)	0.21 (16)	-0.26 (6)	0.15 (16)	0.09 (6)	0.48 (16)
Epiphytic periphyton	0.34 (17)	-0.12 (64)	-0.34 (17)	0.24 (64)	-0.35 (17)	0.22 (64)	0.34 (17)	0.40** (64)
Floc	0.26 (50)	-0.25 (71)	-0.27 (50)	0.15 (71)	-0.23 (50)	0.27* (71)	0.19 (50)	0.26* (71)
Soil	0.07 (51)	0.30** (91)	-0.20 (51)	0.24* (91)	-0.01 (51)	0.36** (91)	0.31* (51)	0.30** (91)

** Significant correlations at $p < 0.001$ level;

* Significant correlations at $p < 0.05$ level

Relation of iHg Species with MeHg

(Assuming $[S^{2-}] = 0$ mg/L)

MeHg	iHg species in surface water	
	$RSHg^{(n-1)-}$	
	Dry	Wet
Surface water	0.45** (51)	0.46** (92)
Floating mat periphyton	-0.14 (6)	0.51* (16)
Epiphytic periphyton	0.34 (17)	0.37** (64)
Floc	0.23 (50)	0.23 (71)
Soil	0.31* (51)	0.26* (91)

** Significant correlations at $p < 0.001$ level;

* Significant correlations at $p < 0.05$ level

Hg speciation and mosquitofish Hg

Sulfide concentrations	Hg species in surface water	Hg in mosquitofish	
		Dry season	Wet season
[S] > 0.02 mg/L	HgS_2^{2-}	0.47 (16)	0.11 (20)
	$HgHS_2^-$	-0.16 (16)	-0.14 (20)
	$Hg(HS)_2$	-0.29 (16)	-0.21 (20)
[S] = 0.00000032 mg/L	$RSHg^{(n-1)-}$	0.06 (39)	0.15 (85)
	HgS_2^{2-}	0.02 (39)	-0.02 (85)
	$HgHS_2^-$	0.18 (39)	0.14 (85)
	$Hg(HS)_2$	0.06 (39)	0.06 (85)
[S] = 0 mg/L	$RSHg^{(n-1)-}$	0.08 (39)	0.17 (85)

Summary

- Sulfide and DOM dominate iHg speciation in Everglades surface water.
- Distribution of iHg species have implications on Hg methylation and bioaccumulation, but more studies are needed.

Next Step…

- Porewater and bottom water

- DOM quality variations

- More accurate sulfide concentration

- MeHg speciation

Acknowledgements

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