Molecular- and Atomic-Level Approaches to Characterize Dissolved Organic Matter: Insights for Mercury Bioavailability in the Florida Everglades

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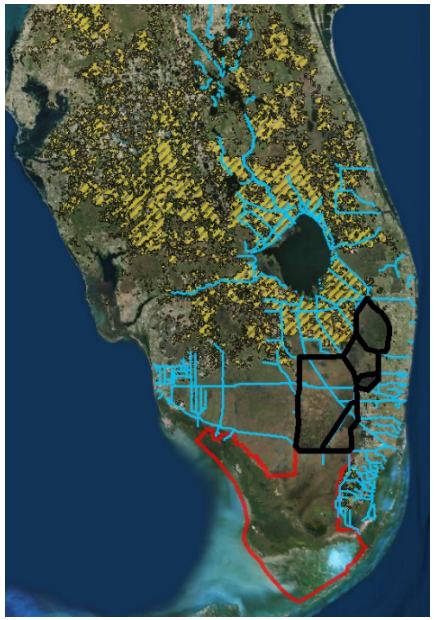
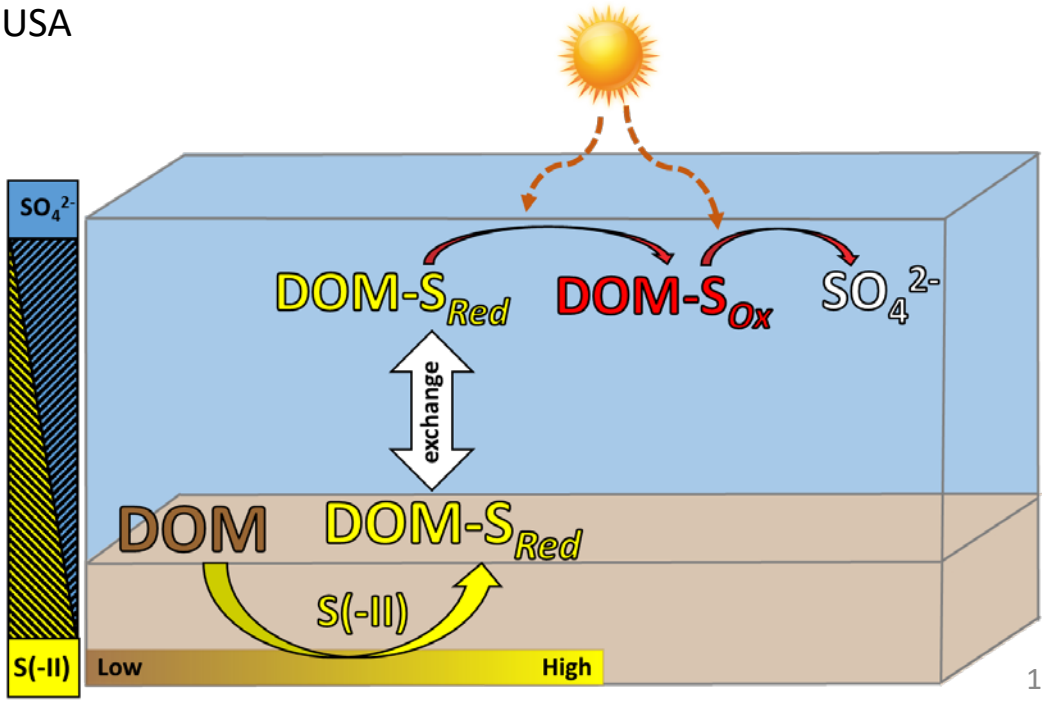
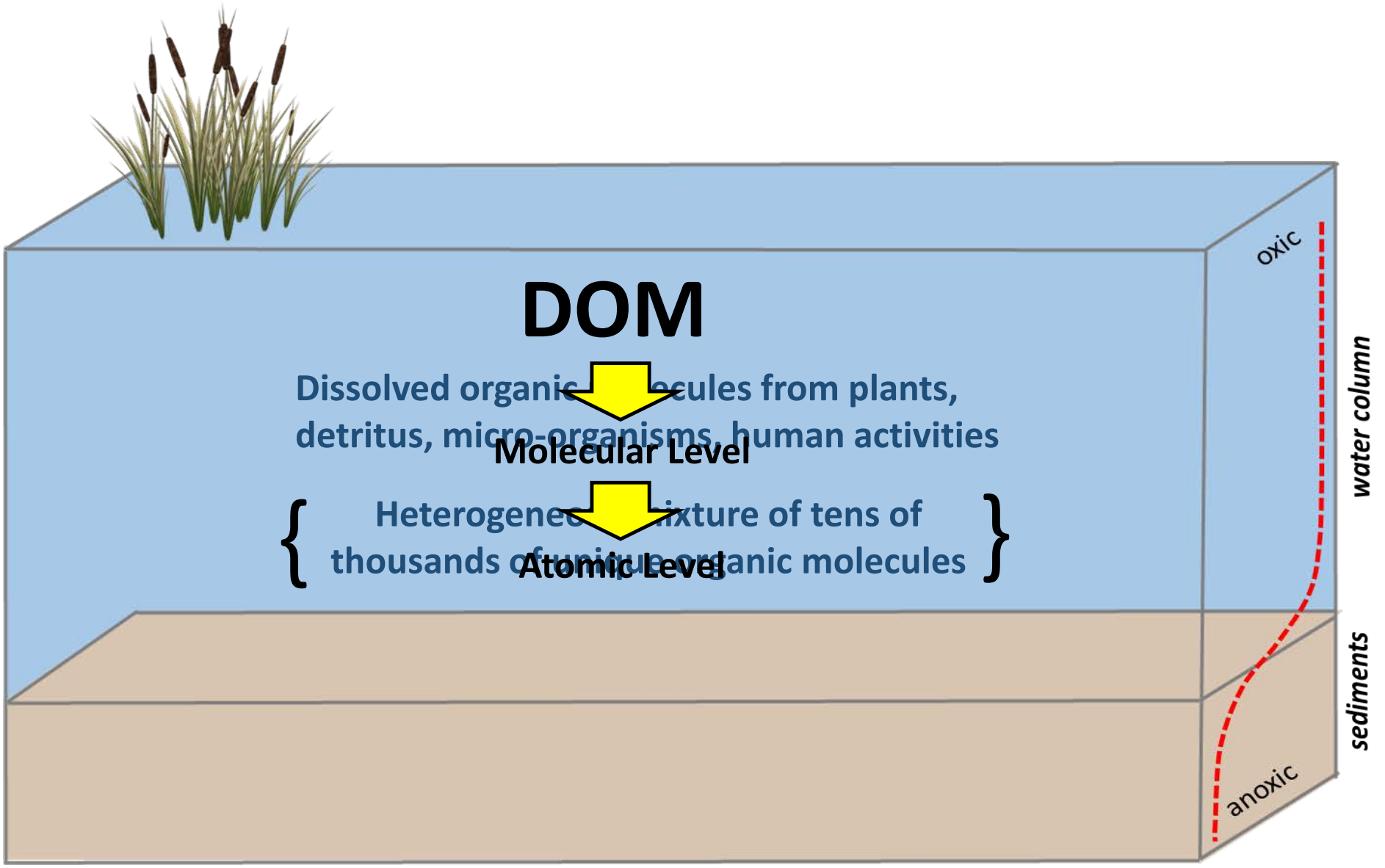
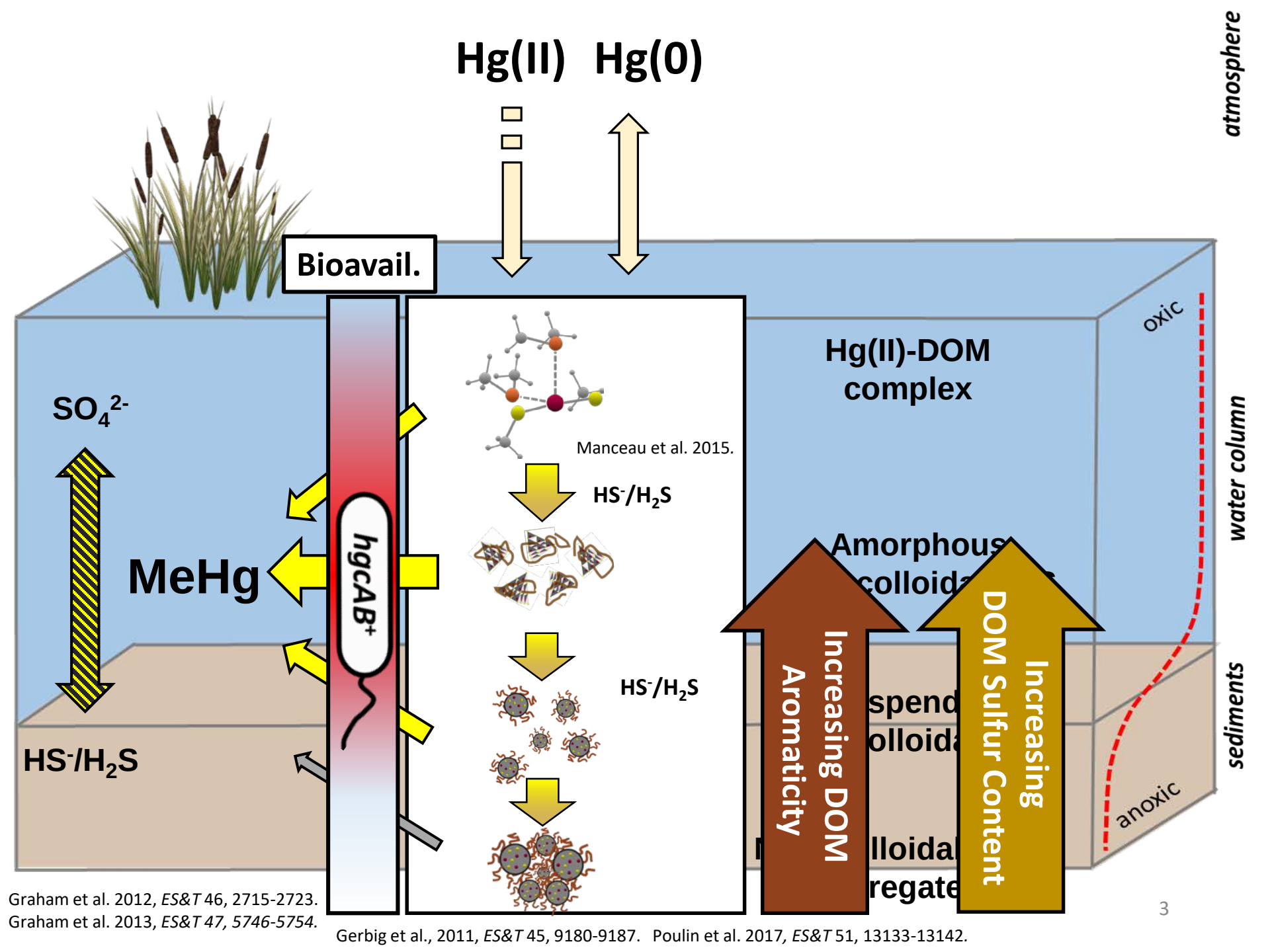




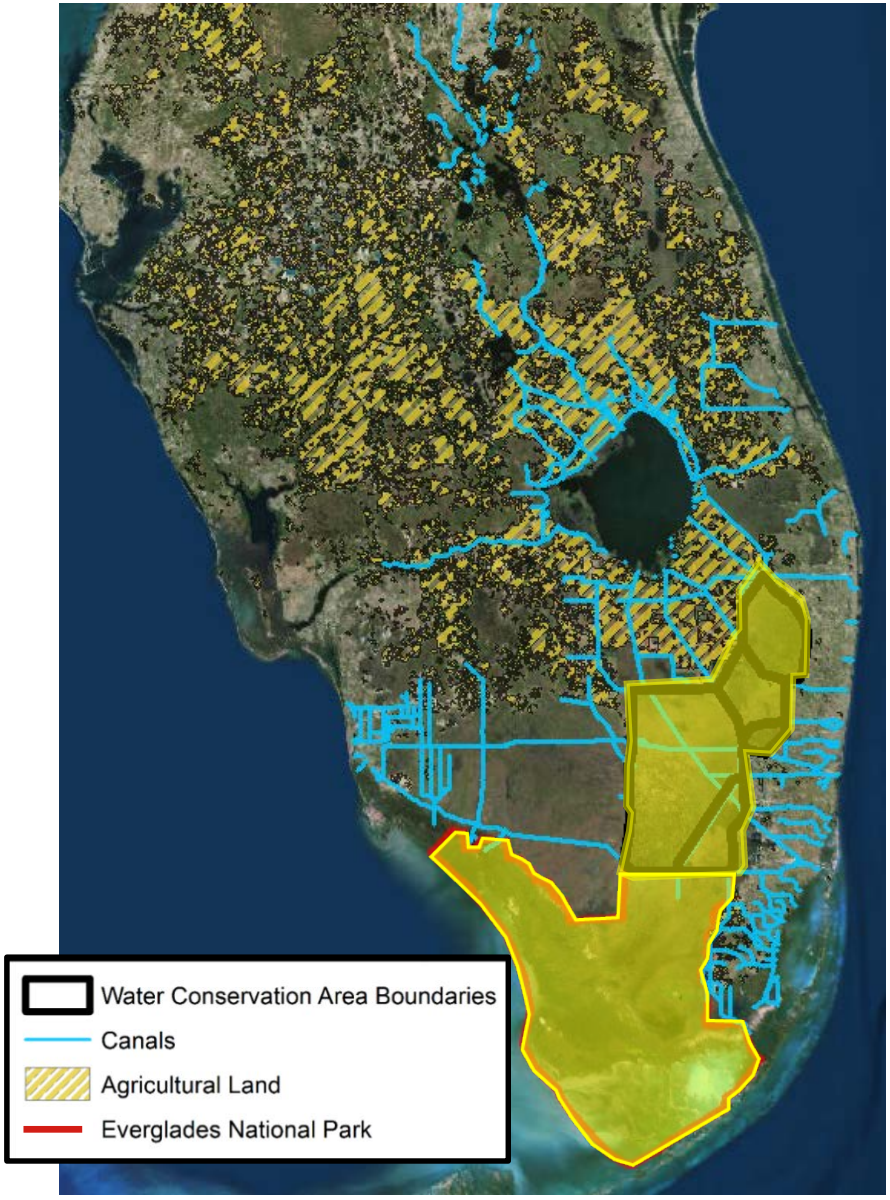

DOM
Dissolved organic molecules from plants, detritus, micro-organisms, human activities
Molecular Level
Heterogeneous mixture of tens of thousands of unique organic molecules
Atomic Level
oxic
anoxic
water column
sediments



Graham et al. 2012, *ES&T* 46, 2715-2723.
Graham et al. 2013, *ES&T 47, 5746-5754.*

Gerbig et al., 2011, *ES&T* 45, 9180-9187. Poulin et al. 2017, *ES&T* 51, 13133-13142.

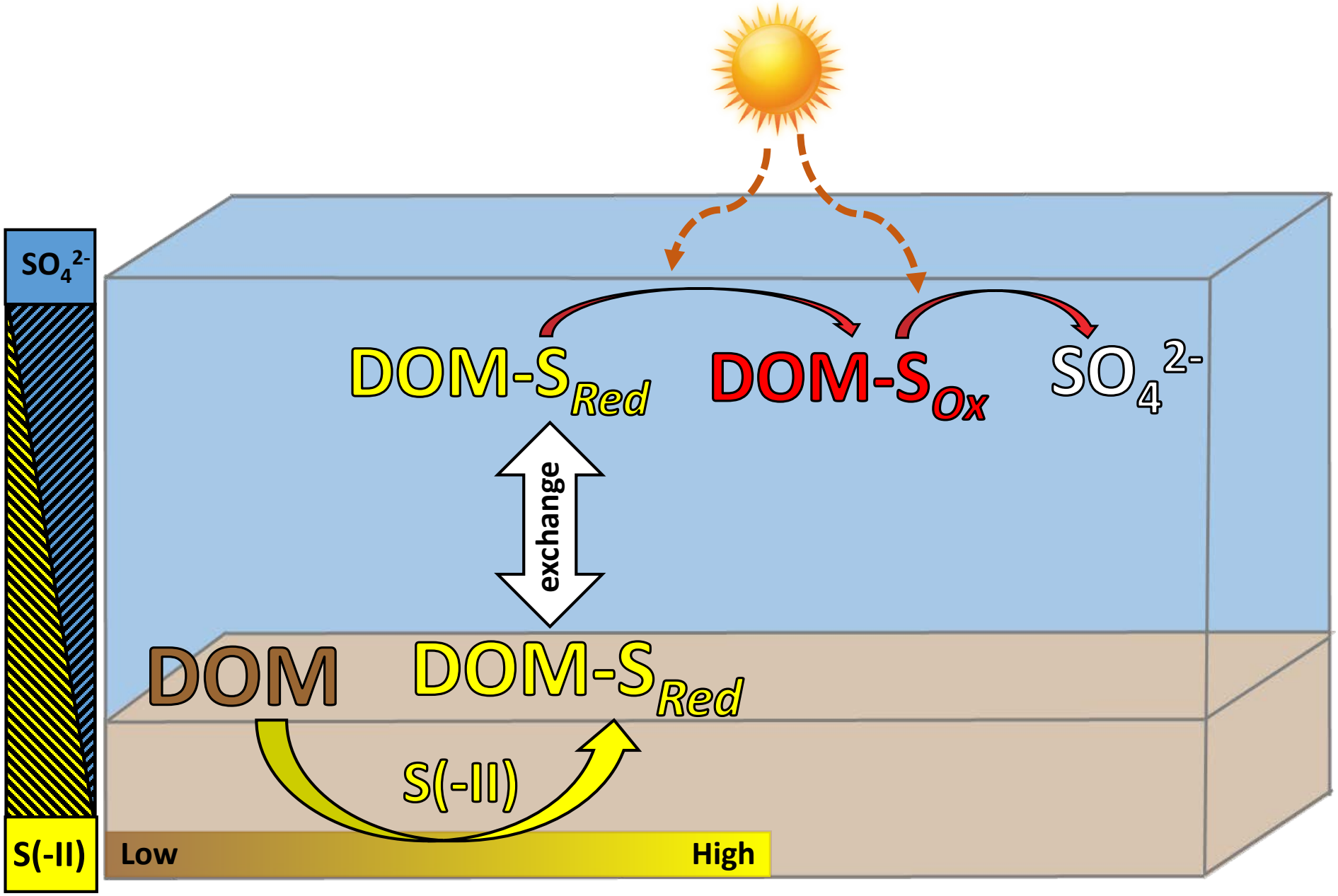
Greater Everglades Ecosystem



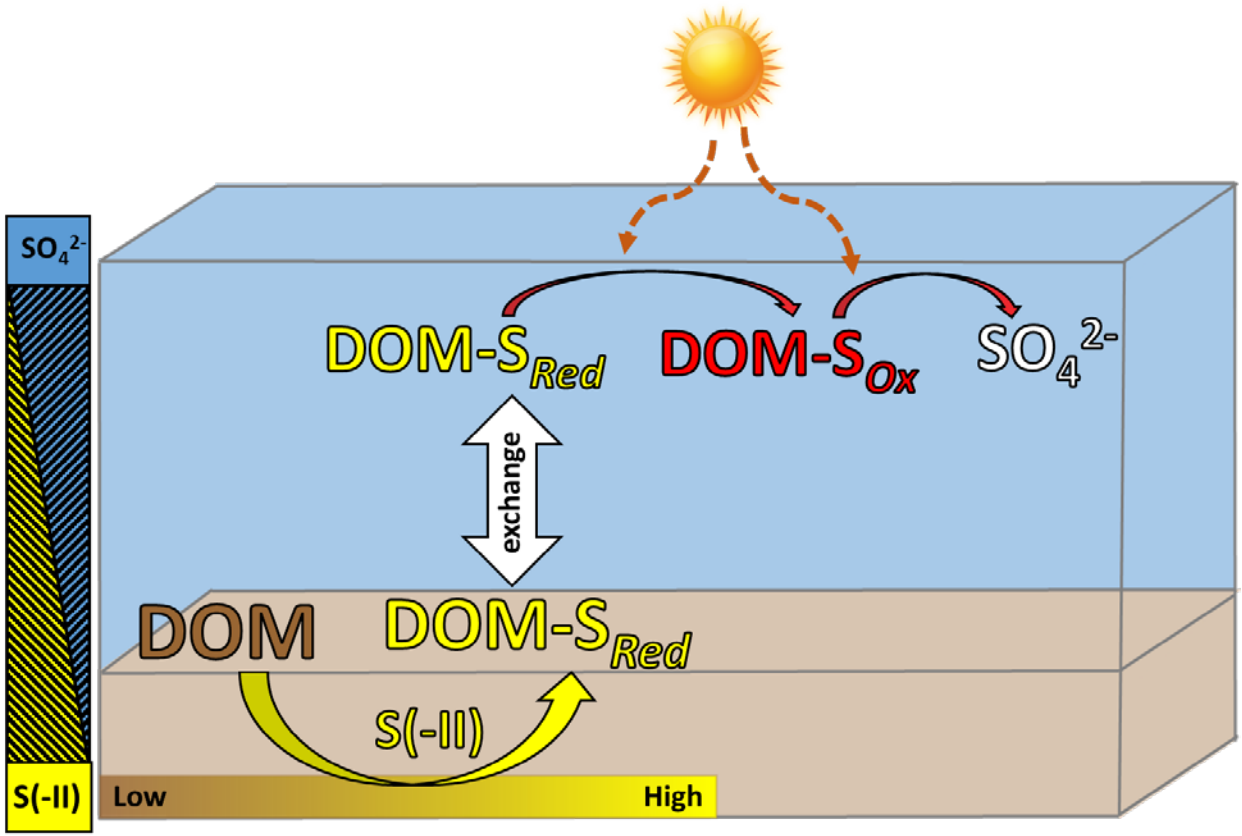
Research Goal: Provide a process-level understanding of the biogeochemical controls on mercury methylation (synergistic and antagonistic) from interactions of mercury, sulfur, and DOM.

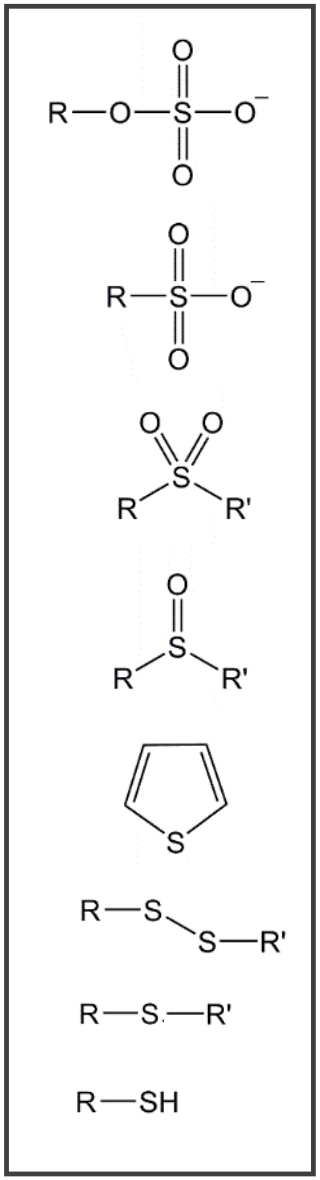
- **[DOC]**
- **DOM aromaticity (i.e., SUVA)**
- **DOM reduced sulfur content**
  - **Molecular-level and atomic-level approaches**

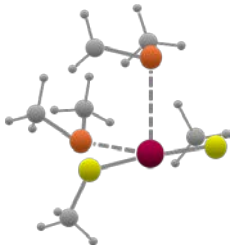
Inform restoration management


SO_4^{2-}
DOM-S_{Red}
DOM-S_{Ox}
SO_4^{2-}
exchange
DOM
DOM-S_{Red}
S(-II)
S(-II)
Low
High

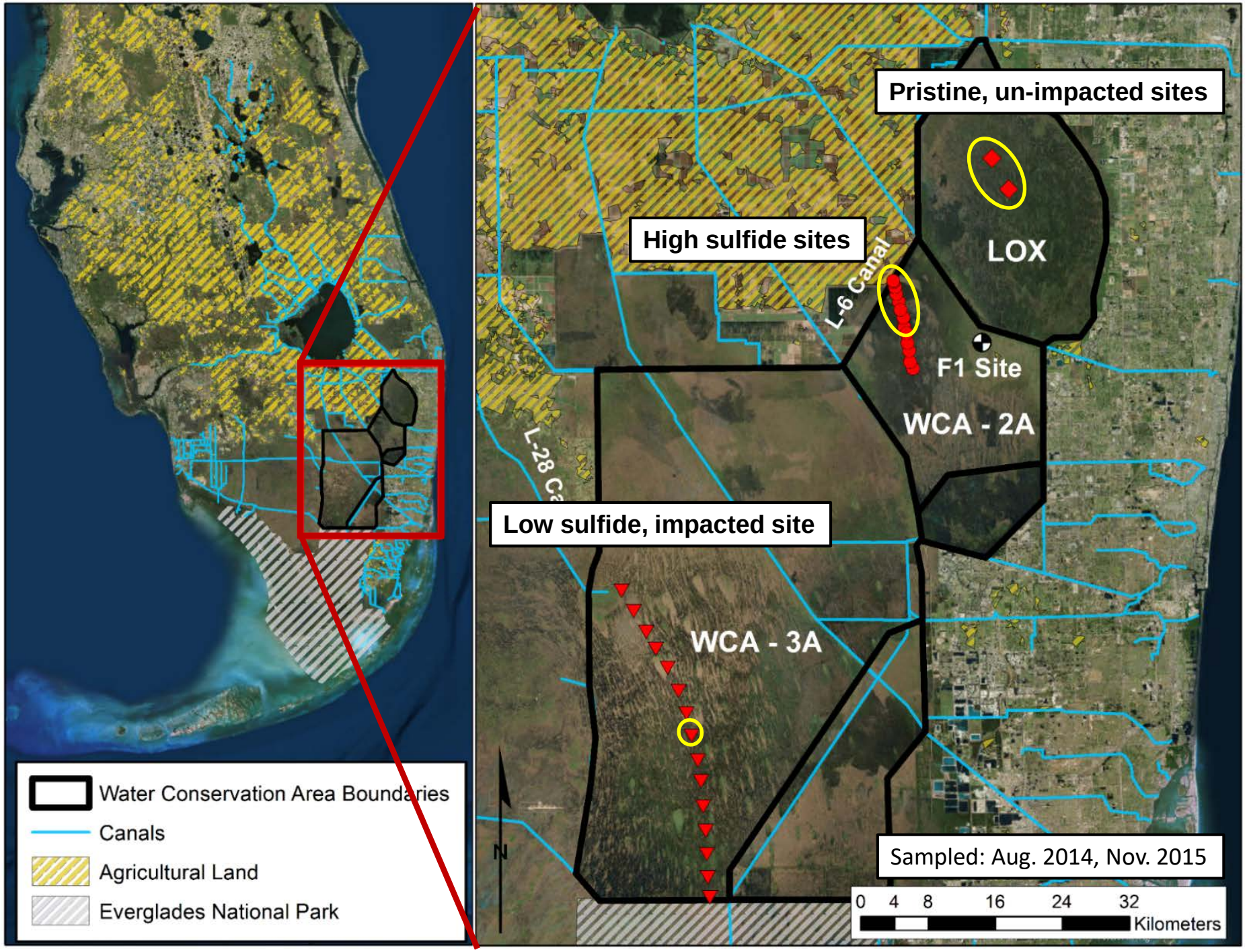
Conceptual Model







Hg(II)-DOM Complex


Pristine, un-impacted sites
High sulfide sites
LOX
L-6 Canal
F1 Site
WCA - 2A
L-28 Ca
Low sulfide, impacted site
WCA - 3A
N
Sampled: Aug. 2014, Nov. 2015
0 4 8 16 24 32
Kilometers
Water Conservation Area Boundaries
Canals
Agricultural Land
Everglades National Park

Methods

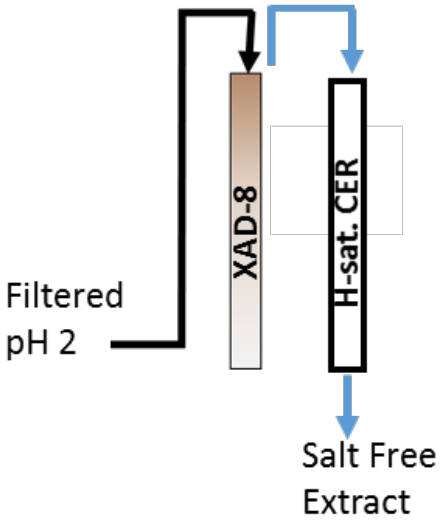
Filtered Whole Water

- 0.45 µm filtered
- Surface water (air/water interface)
- Pore water (10 cm below sediment/water interface)

All Sites: Aqueous Characterization

- Sulfide (ISE)
- Anions (SO_4^{2-}, NO_3^-, Cl^-)
- Cation (Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+})
- [DOC] and DOM $SUVA_{254}$

Select Sites: DOM Isolation

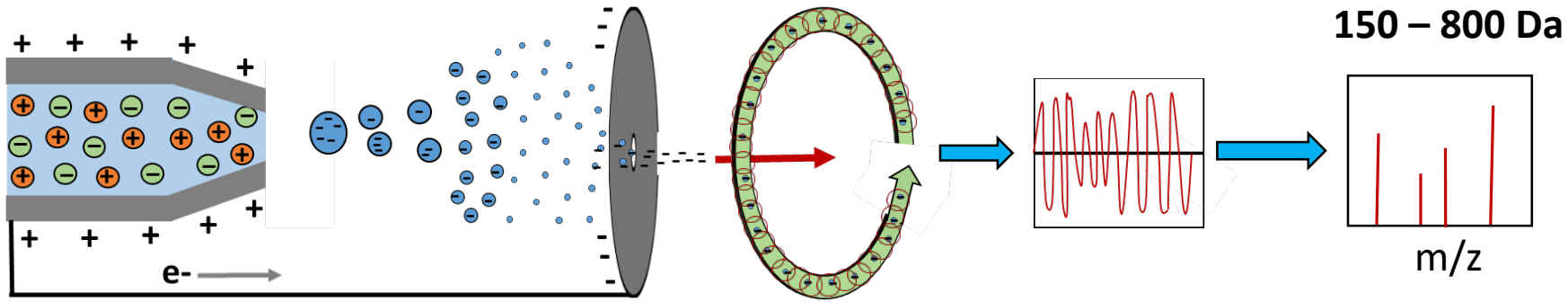


- Sulfide removed by purging (pH 5)
- Isolation of HPOA fraction with anoxic solutions
  - ~50% of the DOC
- Salt-free extract analyzed for
  - elemental composition
  - FT-ICR-MS
  - S XANES
  - Stable S isotope signature

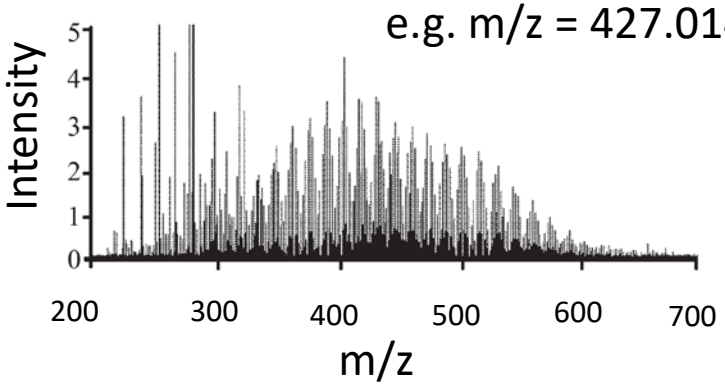
Method by Aiken et al., 1992

Molecular-Level Measurement

Electrospray Ionization **Ion Cyclotron Resonance** **Fourier Transform**



Ultrahigh resolution
e.g. m/z = 427.014638



Stubbins et al., 2010

~3000 – 5000
formulas / sample

Elemental Stoichiometries

$C_XH_XO_XN_XS_X$

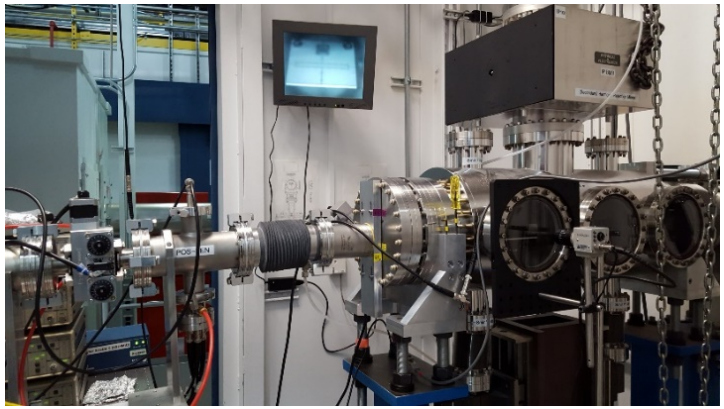
Compound Classification

Presence / Absence of molecules between samples

Atomic Level Measurements

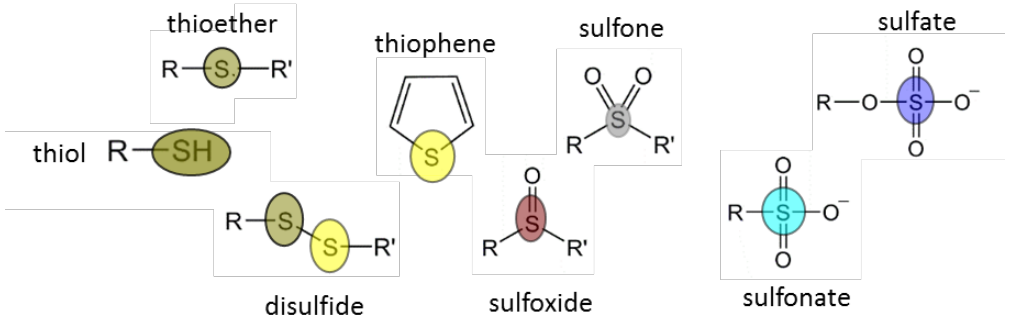
- **Sulfur K-Edge XANES spectroscopy**
  (Advanced Photon Source; 9-BM-B)

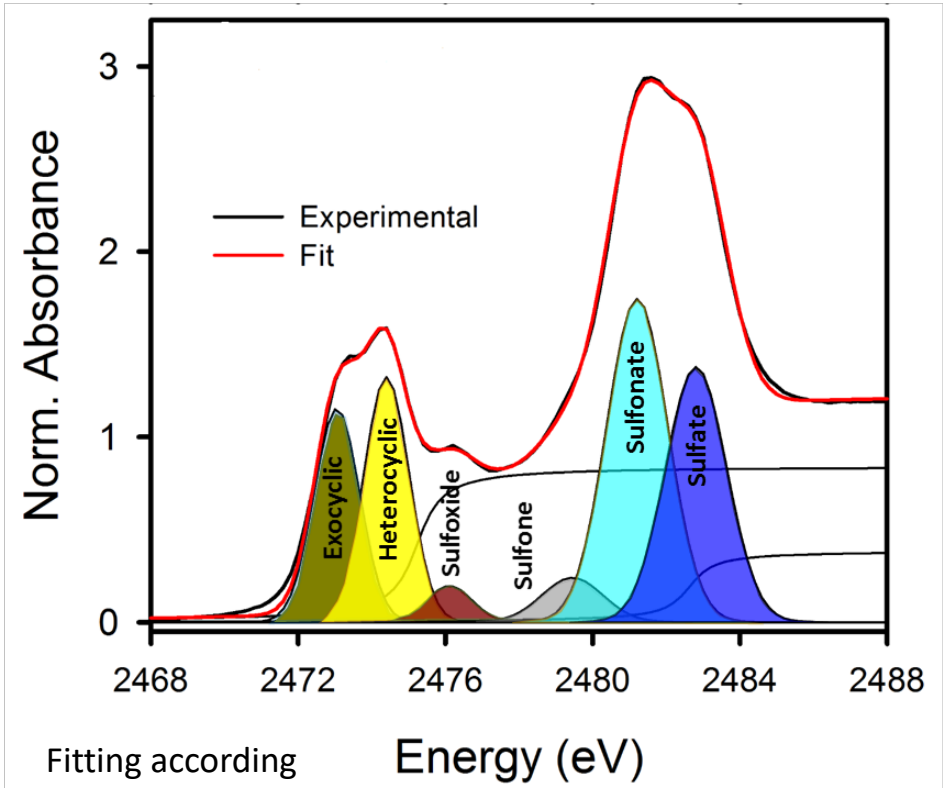
  Distribution of sulfur speciation



- **Stable Sulfur Isotope Measurement**

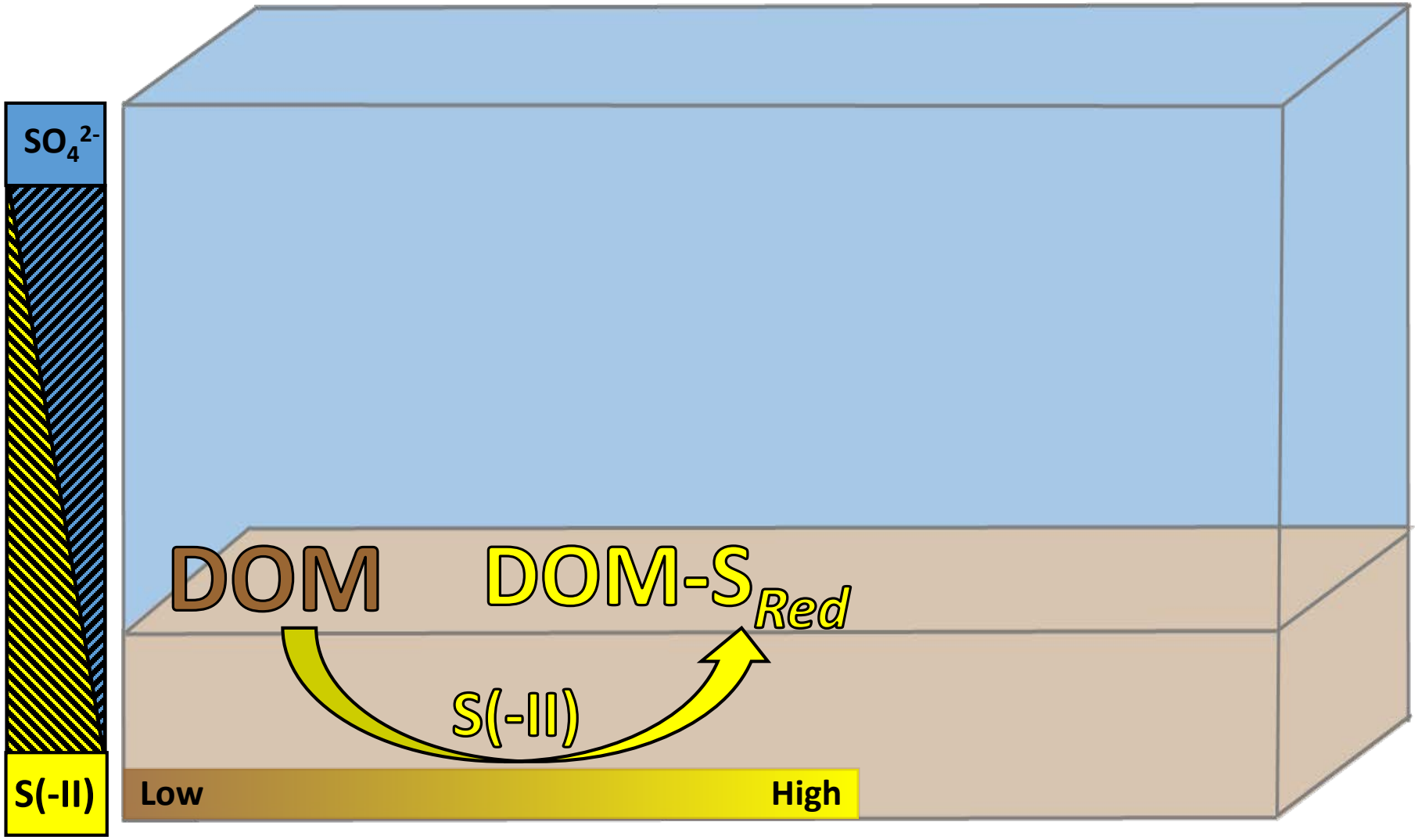
  USGS Reston Stable Isotope Laboratory



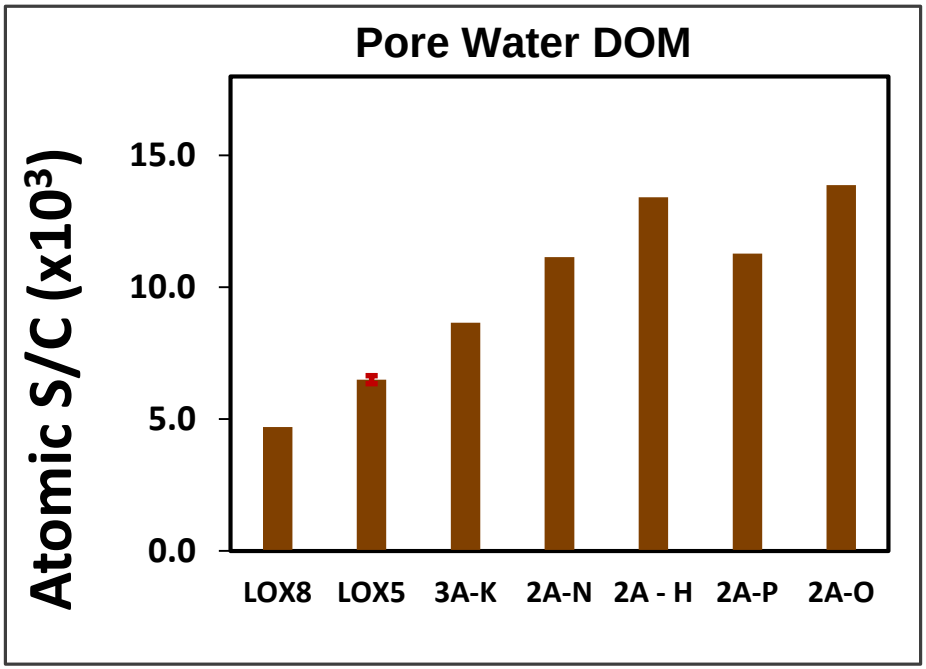


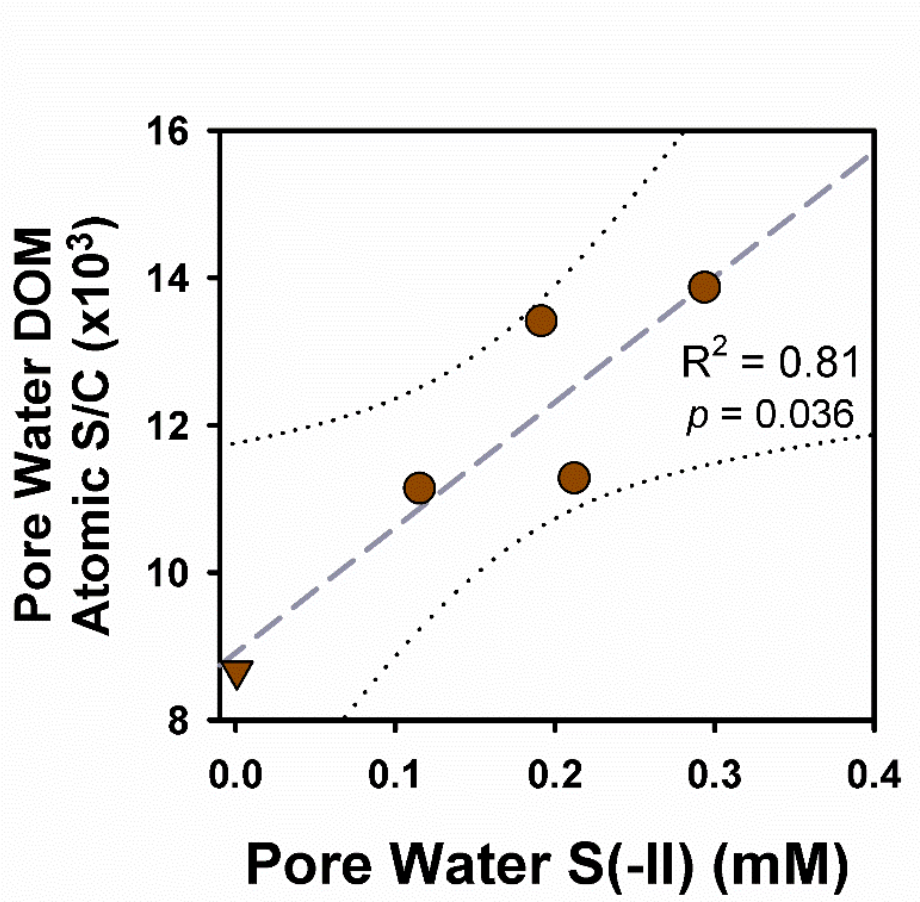
Fitting according to Manceau & Nagy, 2012

Conceptual Model



Total Sulfur Content

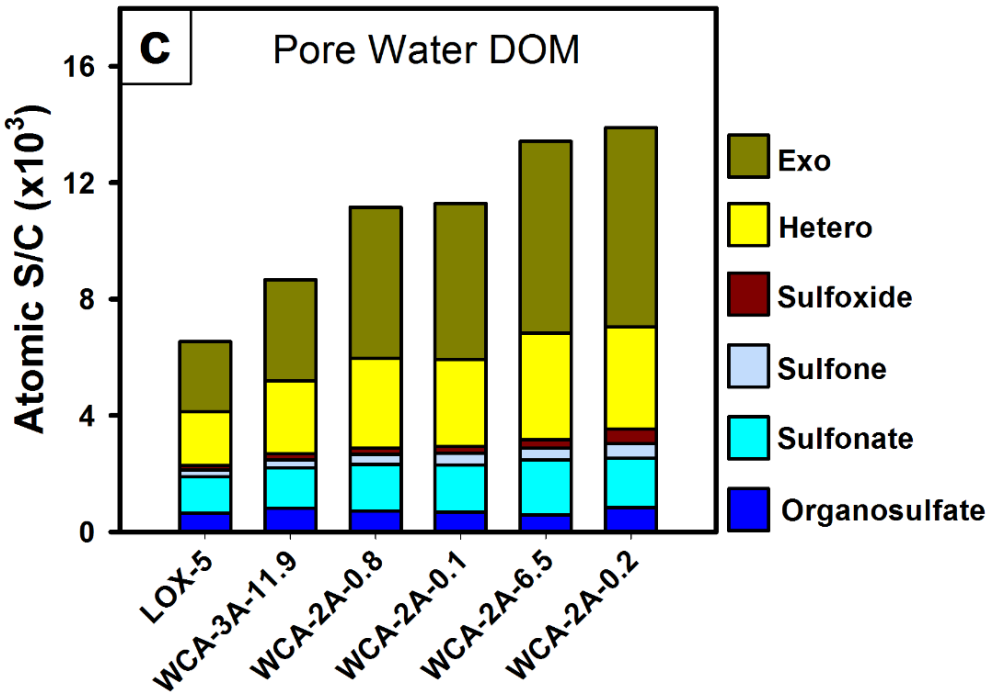


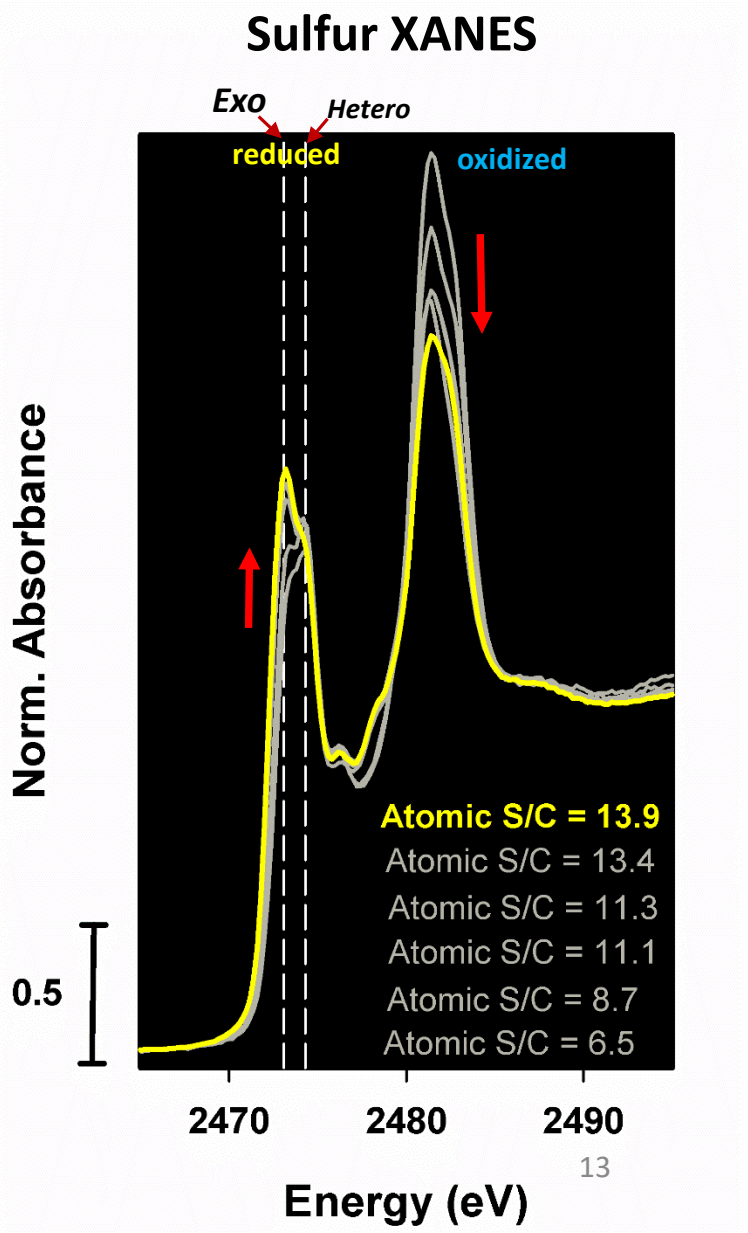


Poulin et al., 2017 *Environ. Sci. Technol*. **51**, 3630-3639.

Sulfur XANES Analysis

In sulfidic pore waters
~85% of enriched sulfur was S_{Red}





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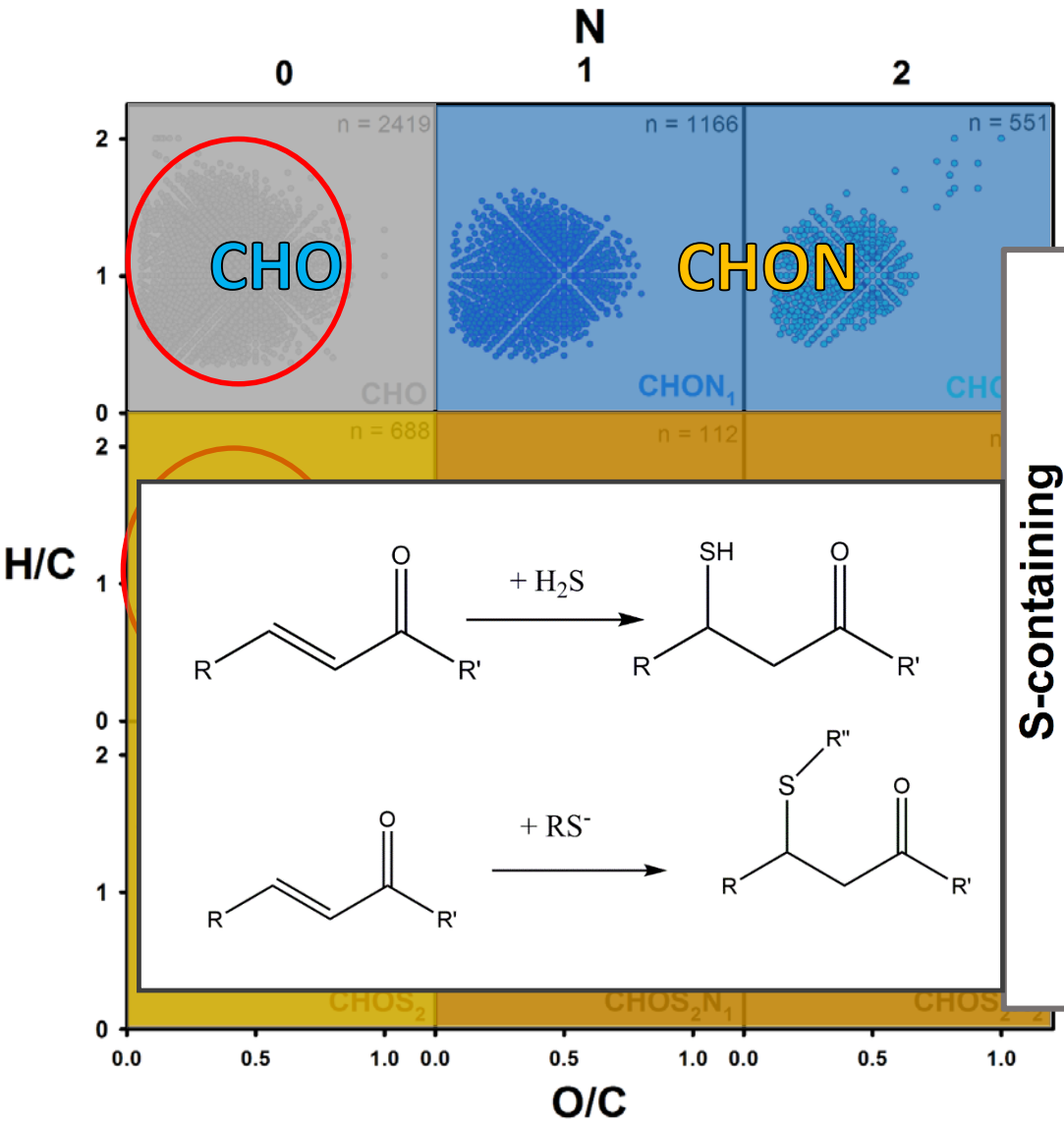
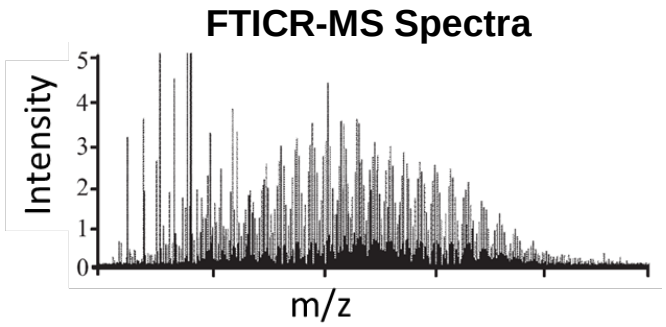
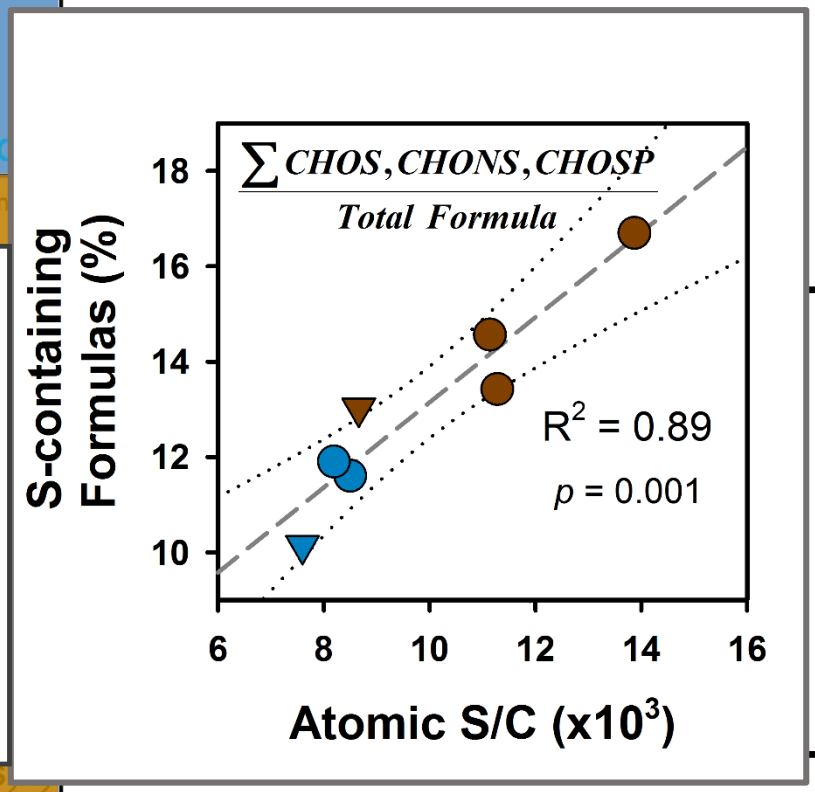
FT-ICR-MS

Pore Water DOM: Atomic S/C = 13.9 (x10^3)



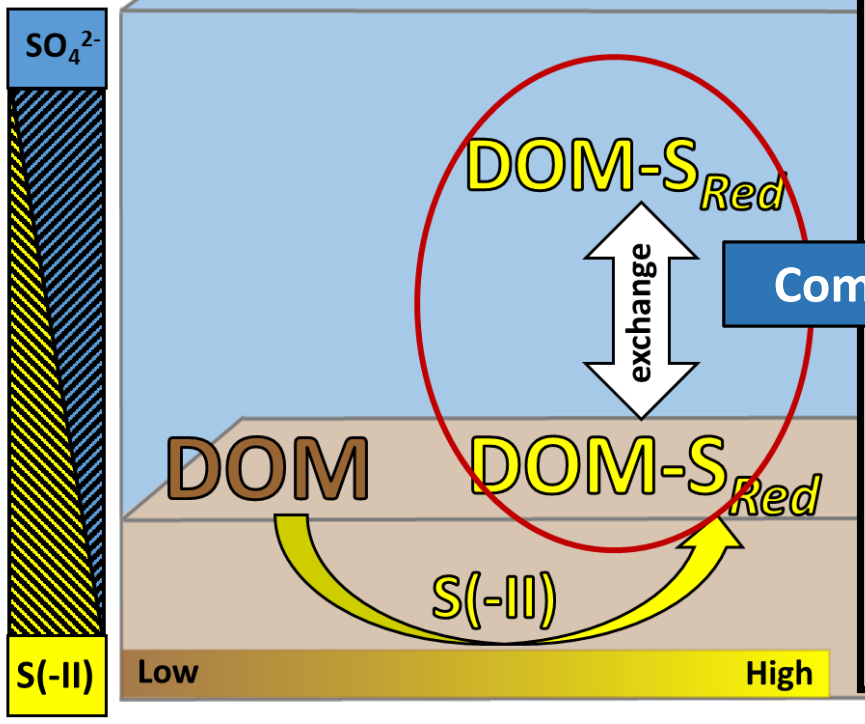




Poulin et al., 2017 *Environ. Sci. Technol*. **51**, 3630-3639.

Pore Water – Surface Water Exchange

- Total Sulfur Content
- CHOS formula assignments
- Sulfur Speciation

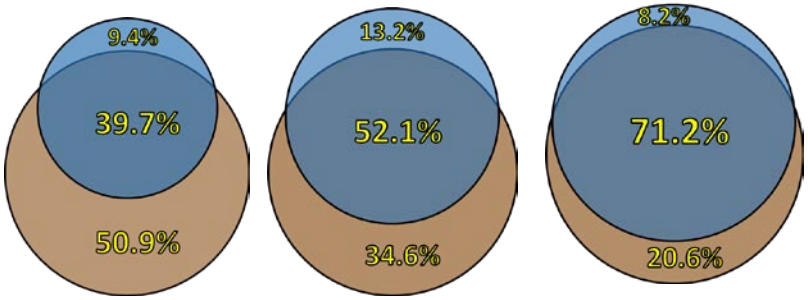


Vertical Distribution of CHOS Assignments

Unique to SW

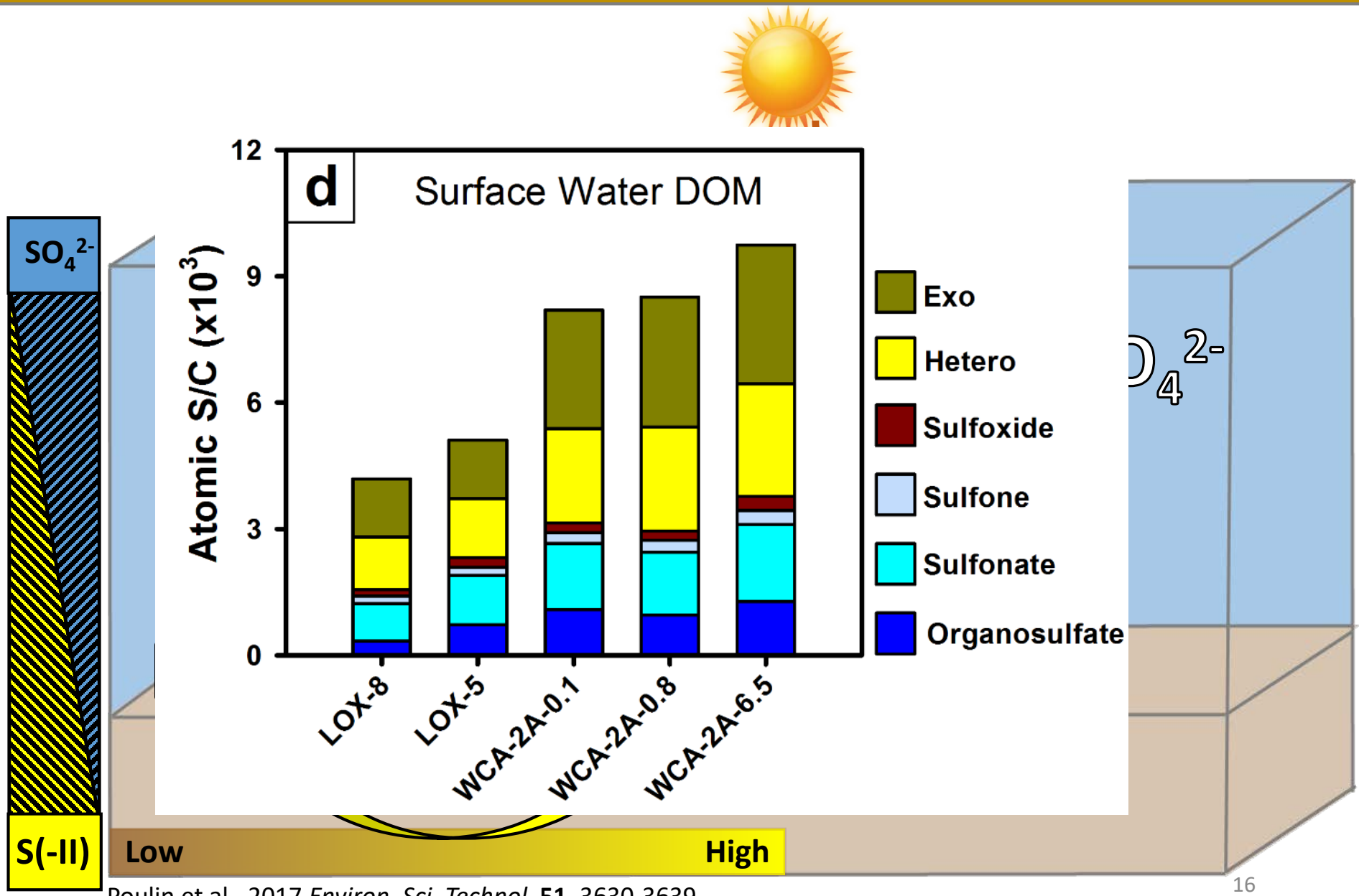
Common

Unique to PW



Increasing S(-II)

Organic S Oxidation – Field Evidence



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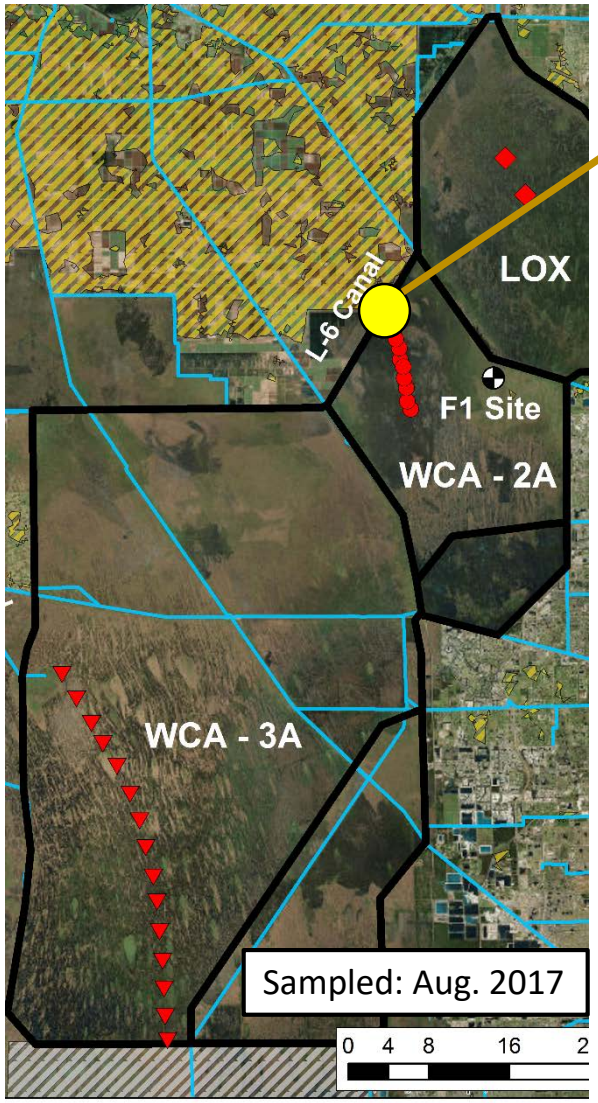
Organic S Oxidation – Lab Evidence



Extract the HPOA Fraction

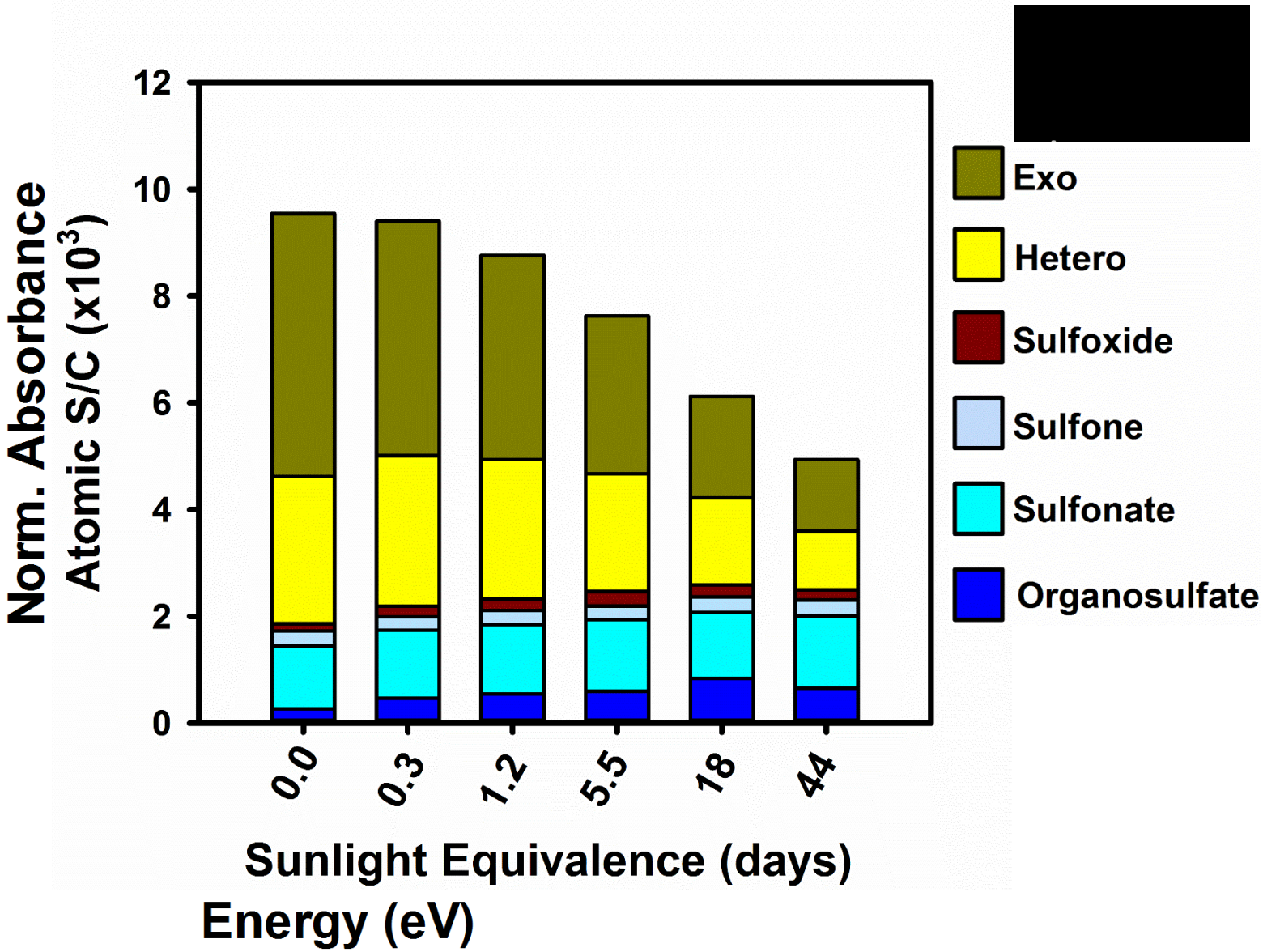
Laboratory Oxidation Experiments

- pH 7
- T = 30° C
- Irradiance equivalent to 8 hr – 44 days of solar exposure in South FL.
- Dark O_2 Purge
- Dark Anoxic Control

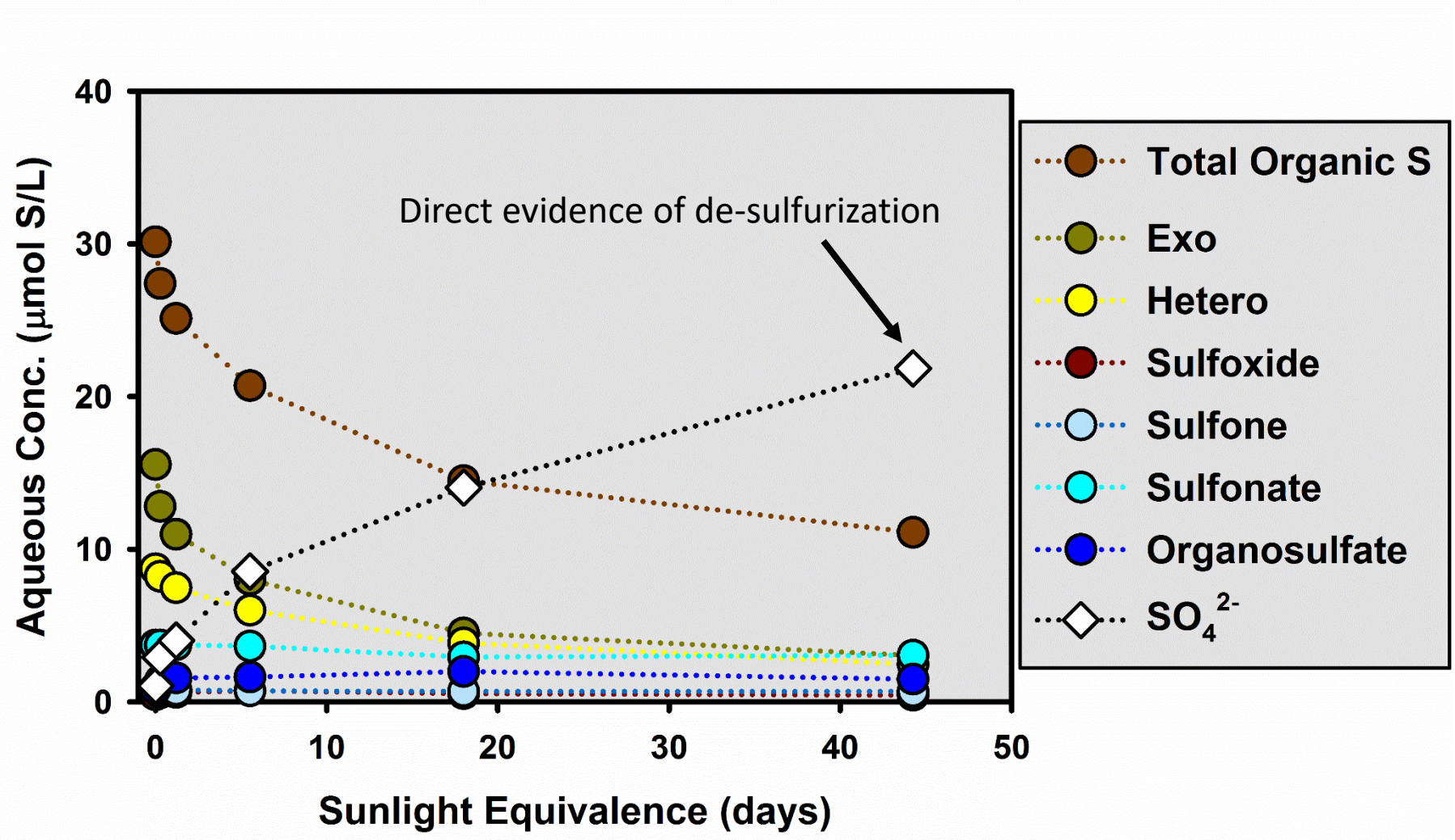
Measure Inorganic Byproducts $S_2O_3^{2-}$ SO_4^{2-}

Re-isolate HPOA for S XANES Analysis

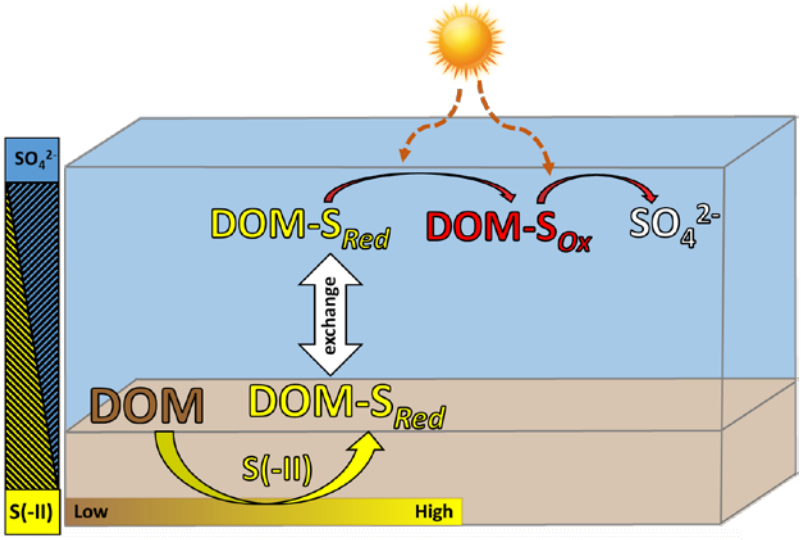
Organic S Oxidation – Lab Evidence

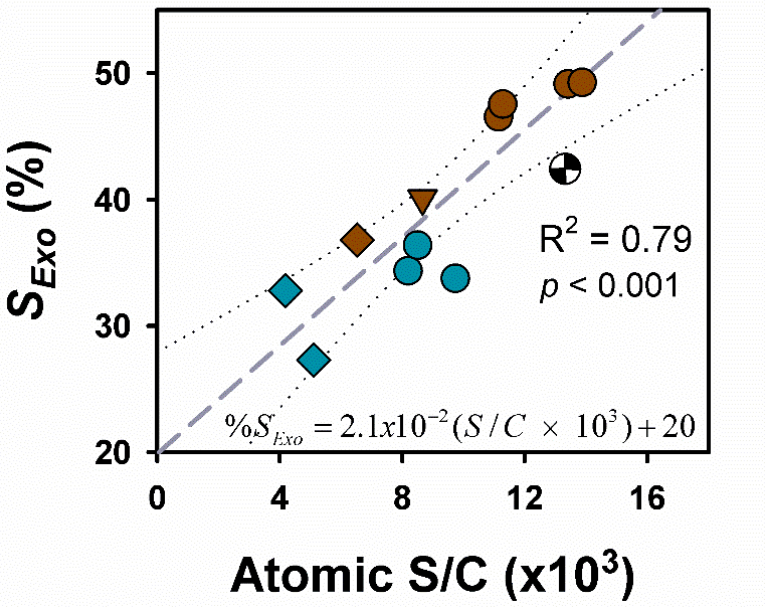


Organic S Oxidation – Lab Evidence



Conclusions and Implications





- Complementary use of molecular and atomic-level measurements to provide a process-level understanding of controls on DOM sulfur chemistry in the Everglades
- Sulfurization of DOM is anticipated to enhance the bioavailability of mercury in Everglades wetlands.
  - S-enriched DOM is delivered south towards Everglades National Park
- Reduced organic sulfur groups are labile to photochemical oxidation.
- Established predictive relationships to estimate DOM S speciation based on sulfur content.

Acknowledgements

Colleagues

George Aiken (USGS WMA)

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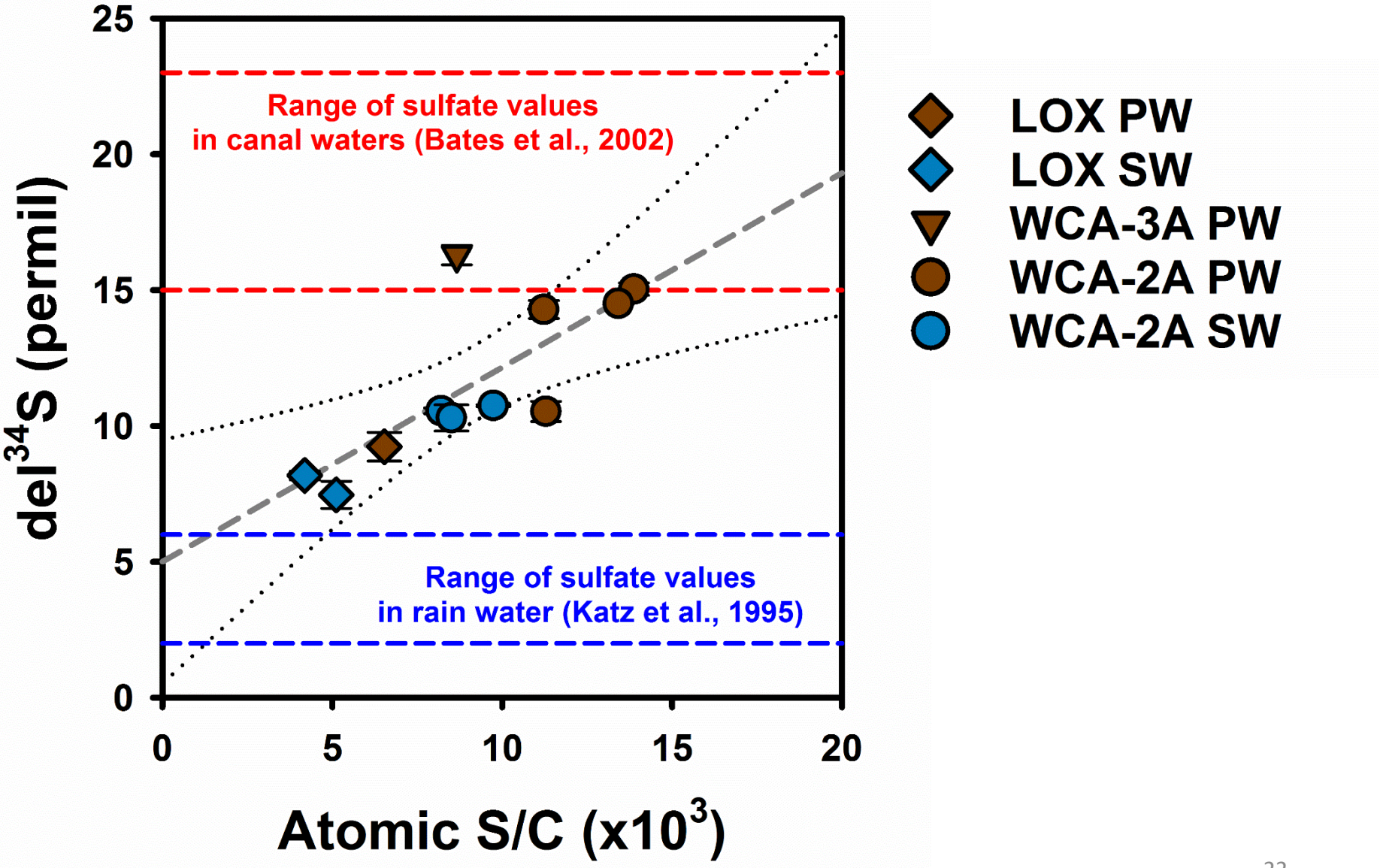
USGS science for a changing world

- Priority Ecosystems Sciences Program
- Water Mission Area
- Environmental Health Toxics and Contaminants Programs

NSF **National Science Foundation** (EAR-1629698, EAR-1628956)

Argonne NATIONAL LABORATORY

Stable Sulfur Isotope Measurements



Preliminary Results