Coupling Mass Spectrometry with Optical Spectroscopy and Chemical Tests to Evaluate and Monitor Dissolved Organic Matter in Natural Waters

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August 7th

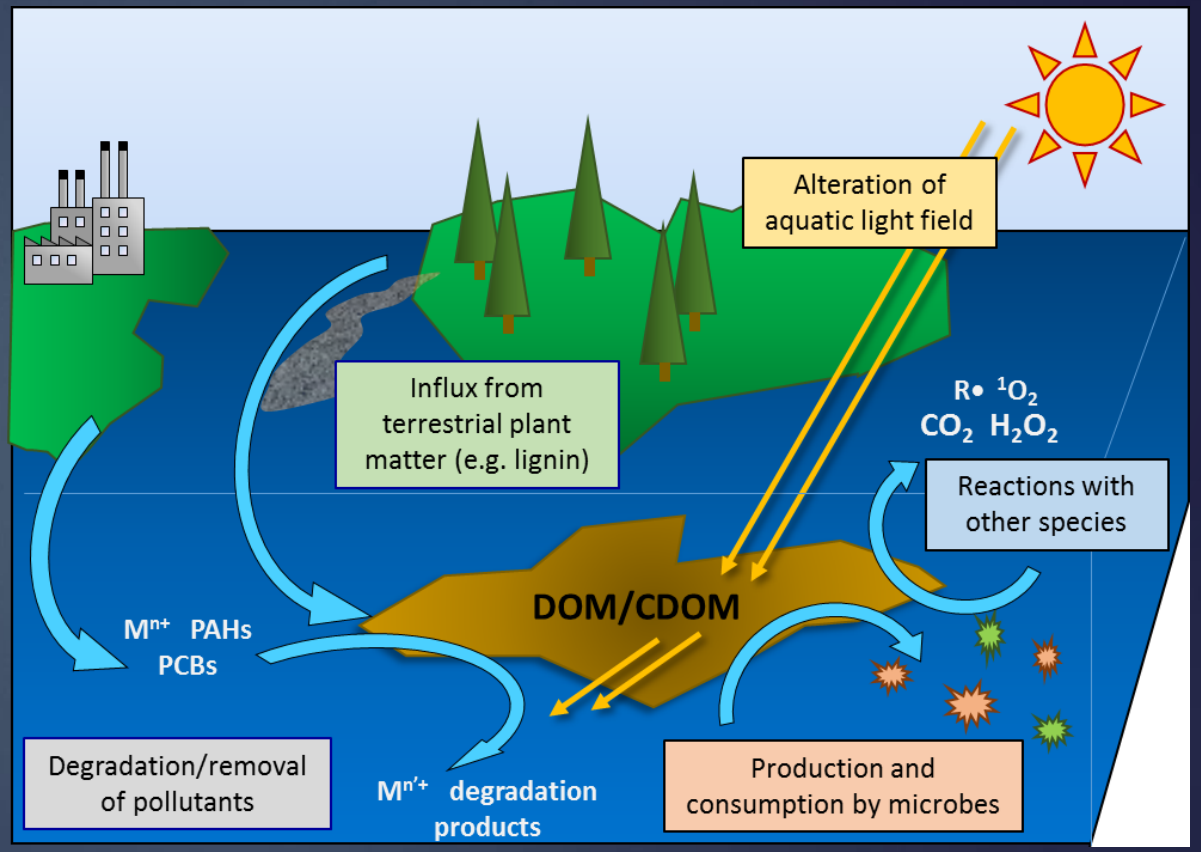
What is DOM/Chromophoric DOM?

- **DOM definition:** Complex, heterogeneous mixture of thousands of dissolved organic compounds
  - 20 – 70% is **chromophoric** (CDOM)
- **CDOM definition:** portion of DOM that absorbs light in both the visible and UV wavelengths
- Complexity of the material makes it very hard to study and define

Coble, P. G. *Chem. Rev.* **2007**, *107*, 402-418.

Why study DOM/CDOM?

- Marine DOM is one of Earth's largest carbon reservoirs
- Reactivity in the aquatic environment
- Possible impacts on the global carbon cycle



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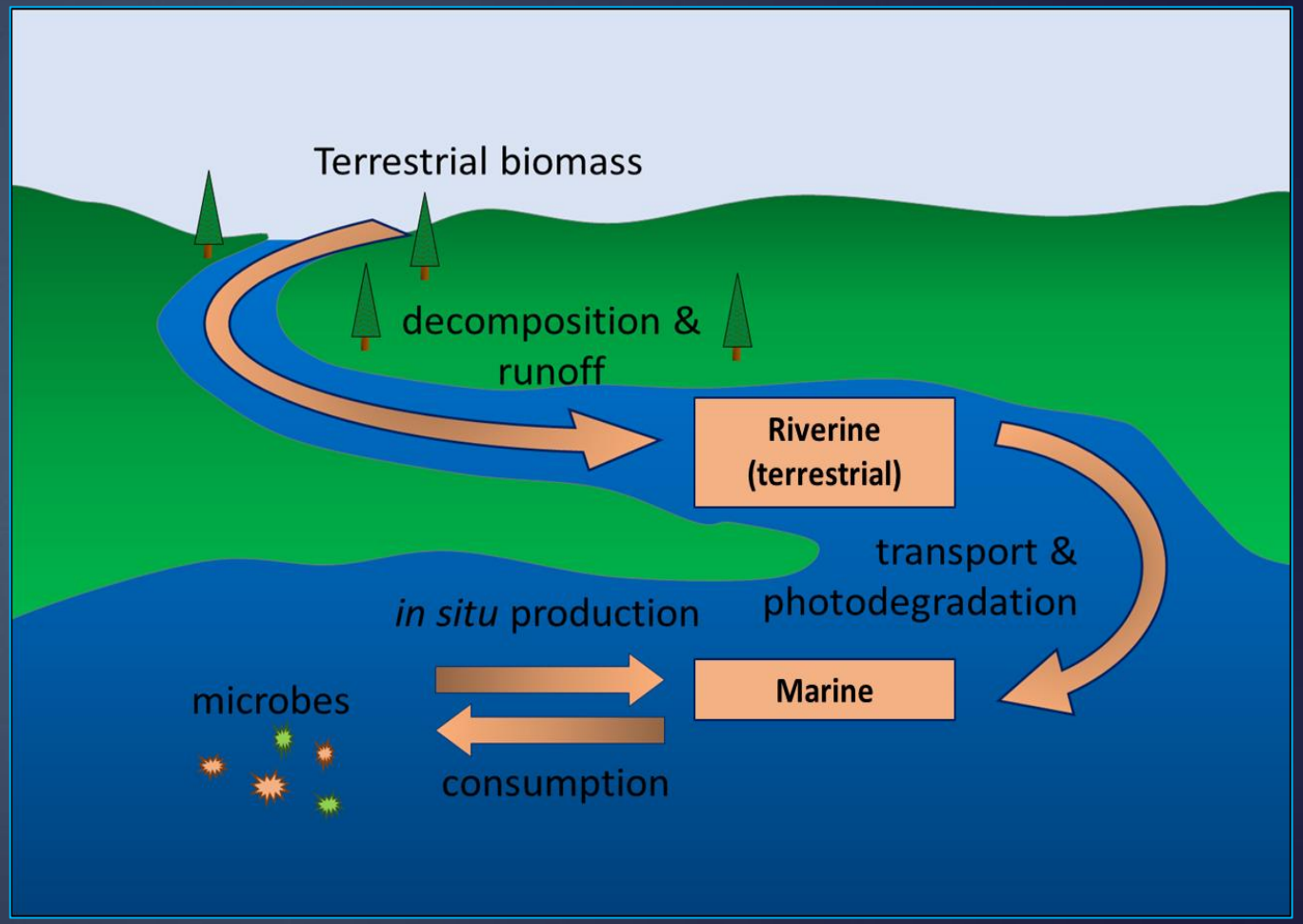
Hedges, J. I, In Biogeochemistry of Marine Dissolved Organic Matter, 2002.
Hedges, J. I. *Mar. Chem.* 1992, *39* (1-3), 67–93.
Zepp, R. G. *Photochem. Photobiol. Sci.* 2007, *6* (3), 286.
Golanoski, K. *Environ. Sci. Technol.* 2012, *46* (7), 3912–3920.
Coble, P. G. *Chem. Rev.* 2007, *107*, 402-418.

Why study DOM/CDOM?

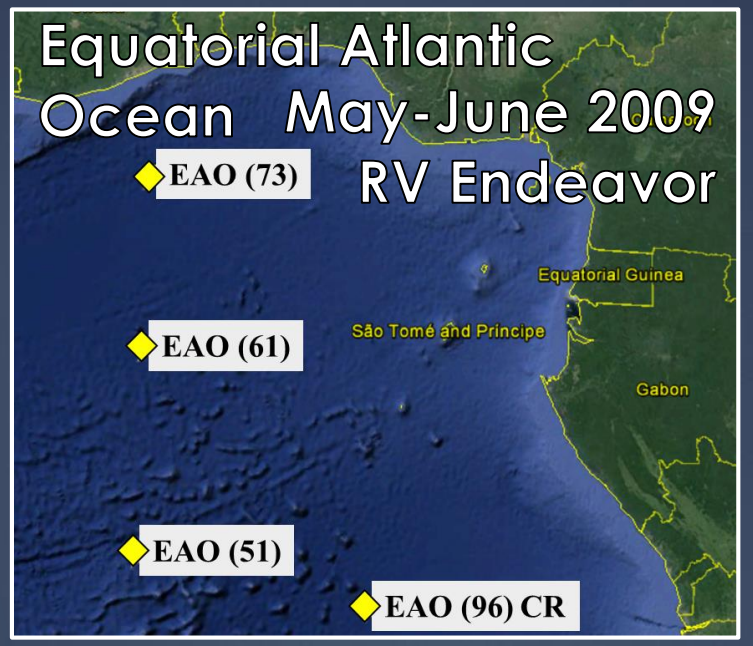
- Marine DOM/CDOM source and structure?
- Terrestrial? In-situ?
  - Use optical properties and MS



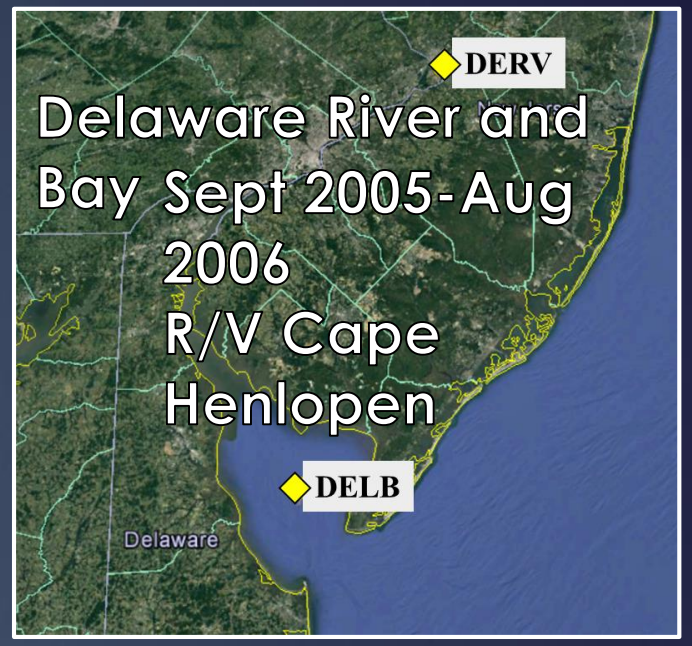
Repeta, Geochim. Cosmochim. Ac, 66, 955-962, 2002.
Andrew, A, Mar. Chem. 148, 33–43, 2013
Baluha, D. R. A Deuterium Labeling Method for the Characterization of (Chromophoric) Dissolved Organic Matter Using Ultrahigh Resolution Electrospray Ionization Mass Spectrometry, University of Maryland College Park, 2015.

Collection: Sample Locations

Station ALOHA:
Depth profile (11 samples)



4 Locations:
5m and 1000m (6 samples)



2 Locations:
River and Lower Bay (2 samples)

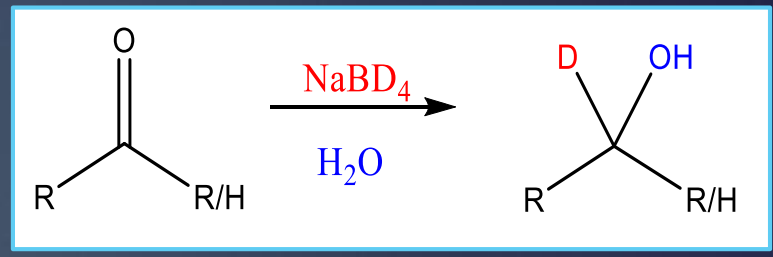
2 Reference Materials (from IHSS):

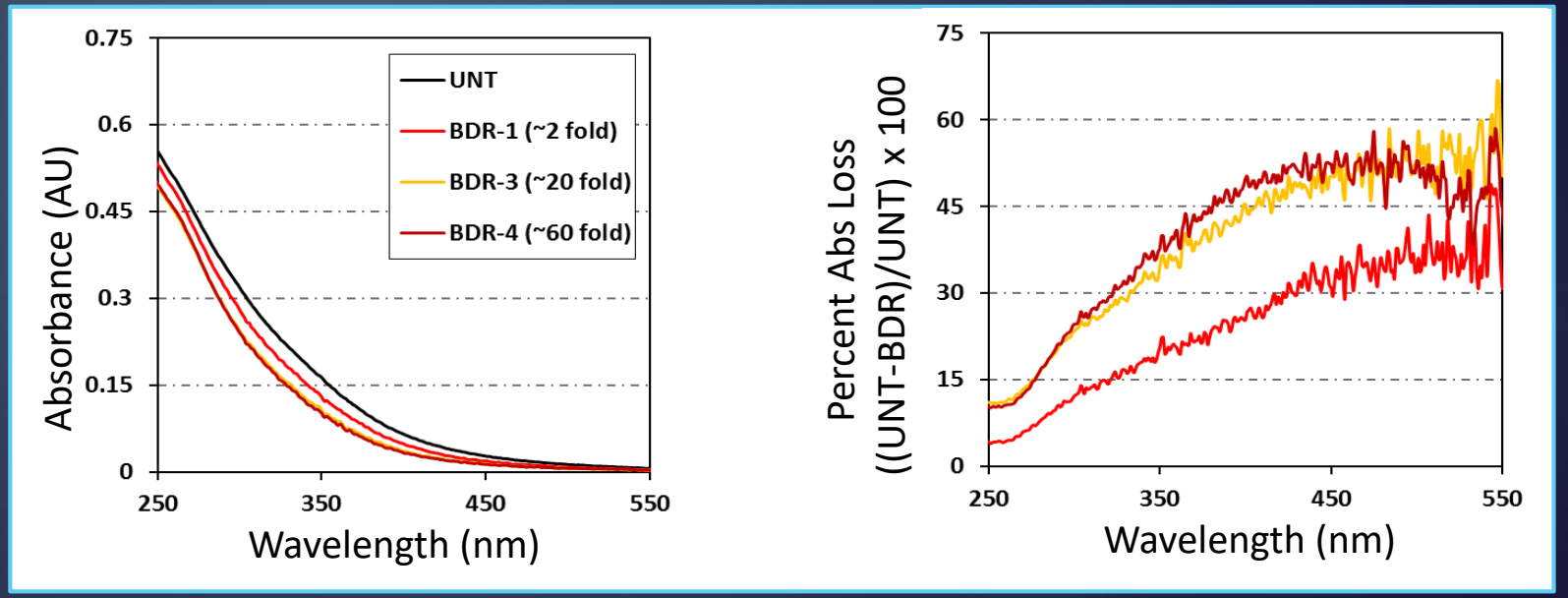
- Suwannee River Fulvic Acid (terrestrial)
- Pony Lake Fulvic Acid (microbial)

Optical Properties of CDOM

Reduction by Sodium Borodeuteride ($NaBD_4$)

- Reduces carbonyl containing species
  - Aromatic ketones and aldehydes and quinones
- Loss of absorbance

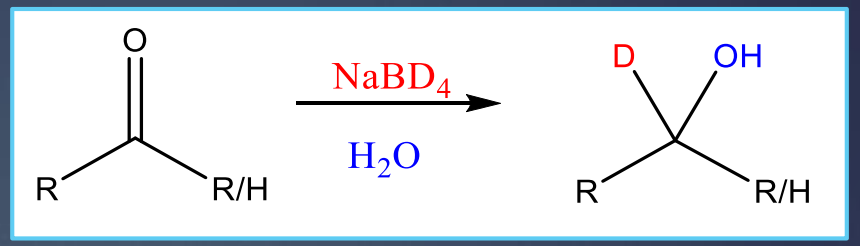


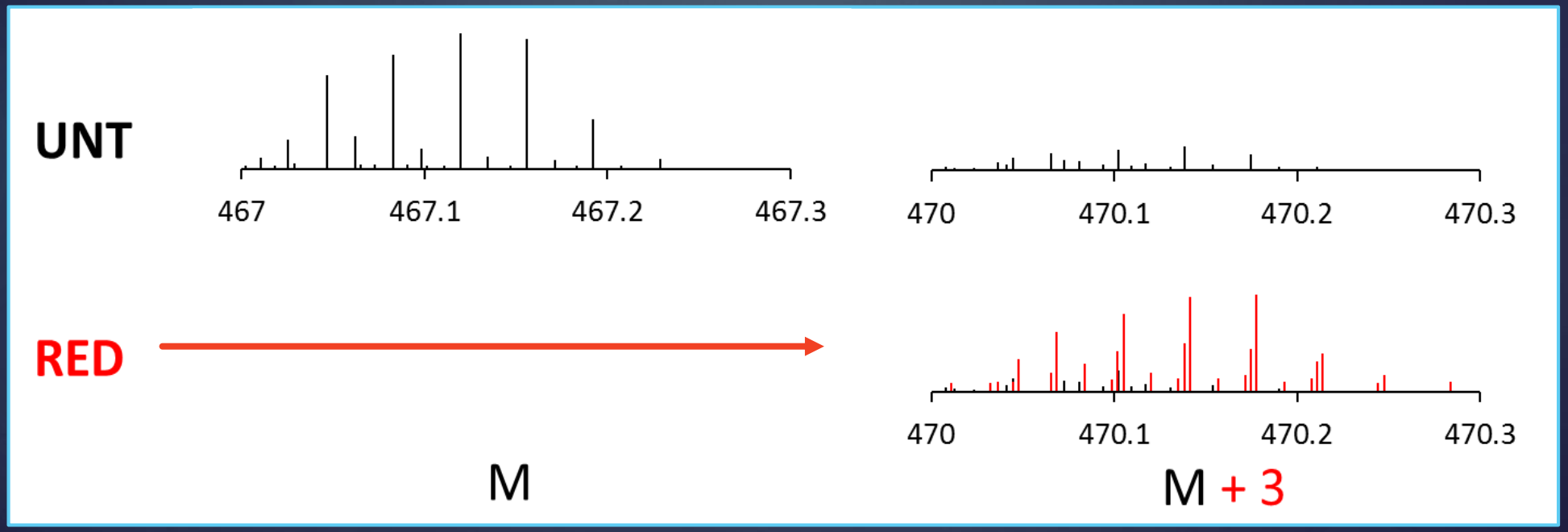


Del Vecchio, R.; Blough, N. V. *Environ. Sci. Technol.* **2004,** *38,* 3885 – 3891.
Baluha, D. R.; Blough, N. V.; Del Vecchio, R. *Environ. Sci. Technol.* **2013**, *47* (17), 9891–9897.

MS coupled with reduction by sodium borodeuteride ($NaBD_4$)

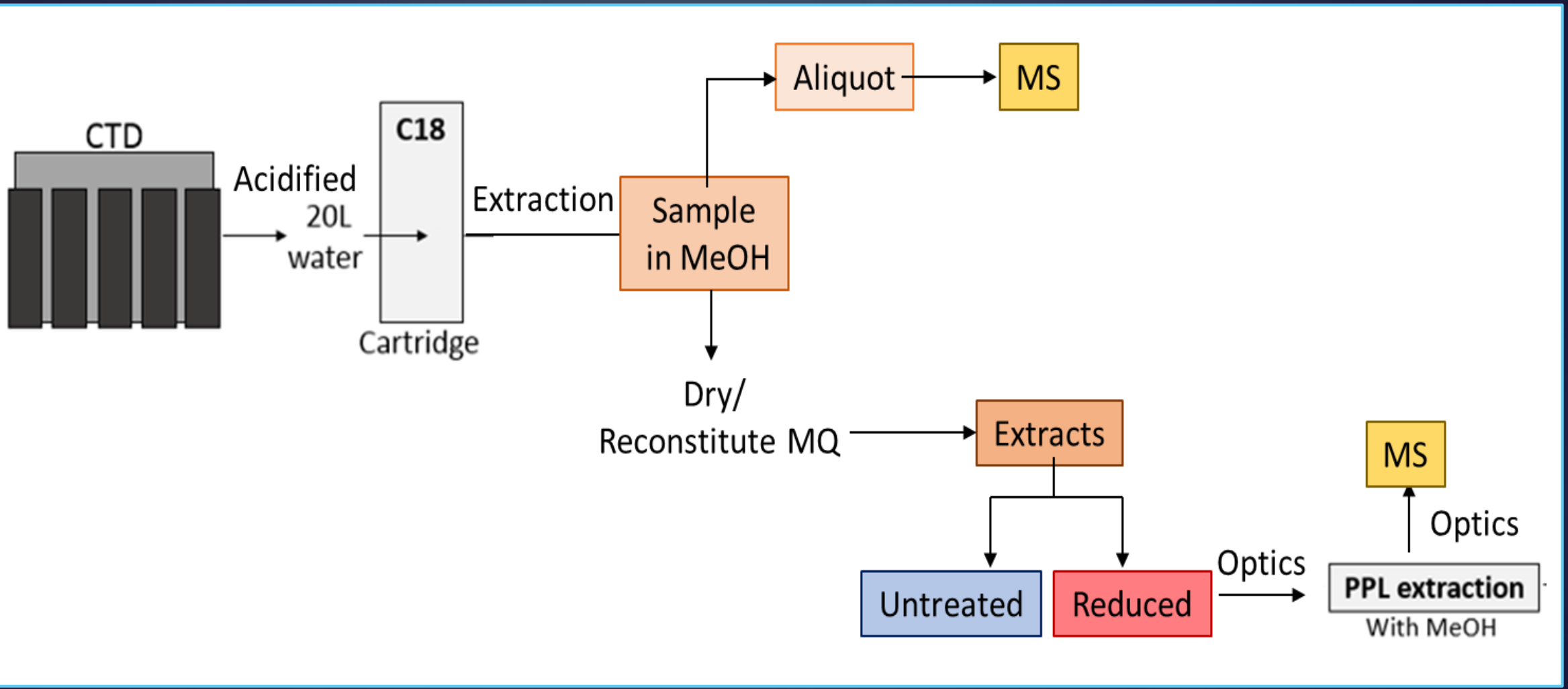
- FT-ICR-MS: Produces unique mass markers
  - M + 3.0219*n*





Baluha, D. R. *Environ. Sci. Technol.* **2013**, *47* (17), 9891–9897.

Collection: Method Preparation and Extraction



Collection: MS Data Acquisition

- 12T ESI-FT-ICR MS (negative ion mode)
- Averaged 500 scans
  - mass resolution at 400,000 (at mass 400 *m/z*)
- S/N ratio > 10 obtained
- Mass accuracy < 0.2 ppm

HELMHOLTZ CENTRE FOR ENVIRONMENTAL RESEARCH – UFZ

Baluha, D. R. *Environ. Sci. Technol.* **2013**, *47* (17), 9891–9897
Baluha, D. R. A Deuterium Labeling Method for the Characterization of (Chromophoric) Dissolved Organic Matter Using Ultrahigh Resolution Electrospray Ionization Mass Spectrometry, University of Maryland College Park, 2015.

Collection: MS Data Analysis

MATLAB algorithms

Pre-processing of raw peak list

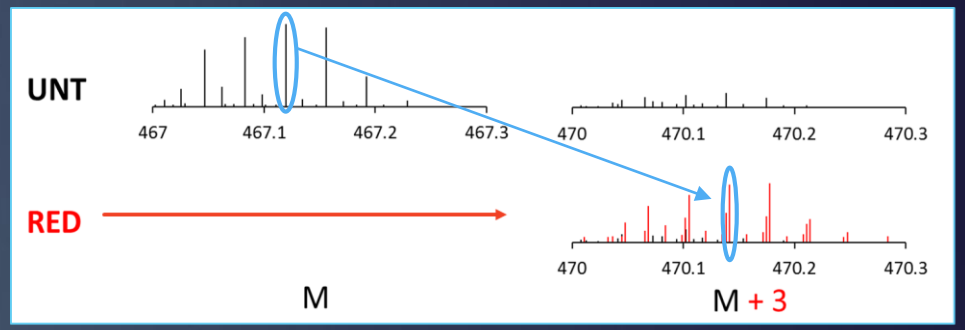
- Subtract blank
- Remove multiply charged peaks

Assigning Molecular Formulae

- Specify error tolerance
- Element inclusions
- Mass range

Finding Reduced Peaks

- Algorithm identifies species that contain $NaBD_4$ reducible groups.
- Searches the reduced sample for M + 3.0219*n* *m/z* off the untreated peak list.



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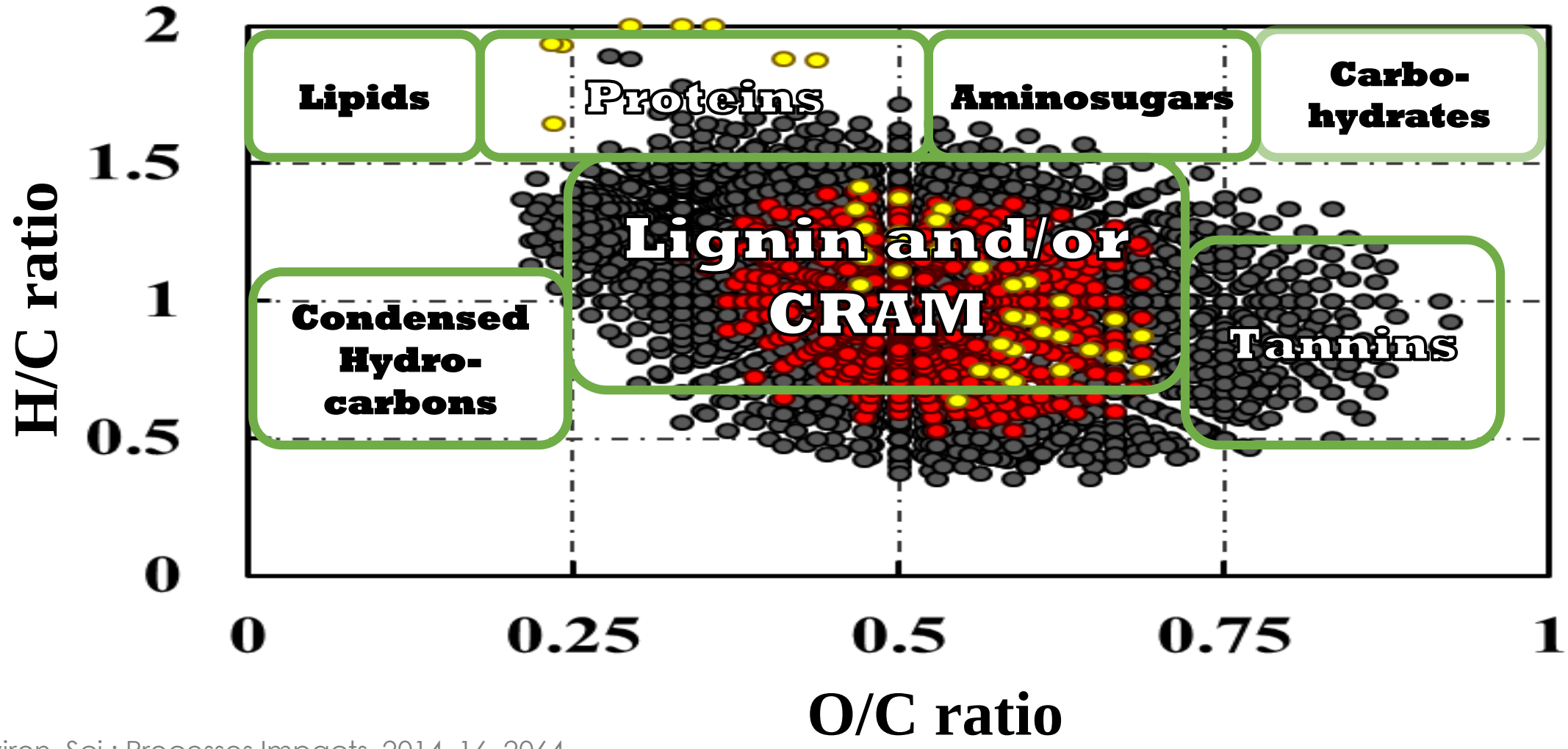
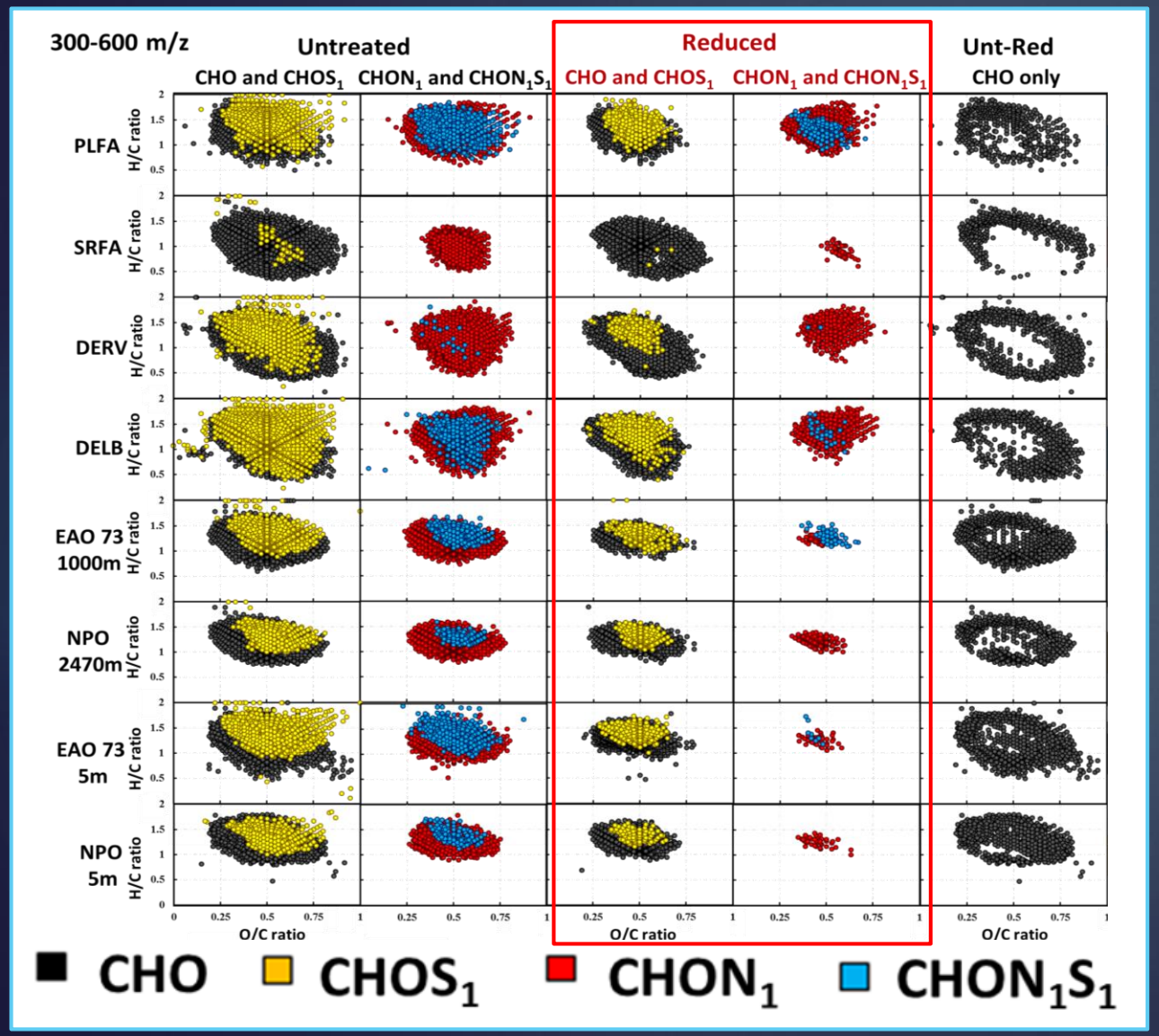
Baluha, D. R. A Deuterium Labeling Method for the Characterization of (Chromophoric) Dissolved Organic Matter Using Ultrahigh Resolution Electrospray Ionization Mass Spectrometry, University of Maryland College Park, 2015.

Results: Untreated

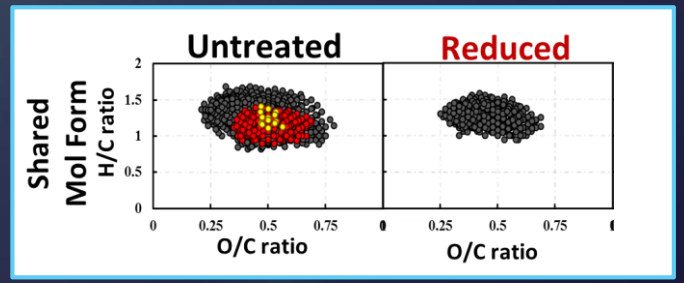


Environ. Sci.: Processes Impacts, 2014, 16, 2064

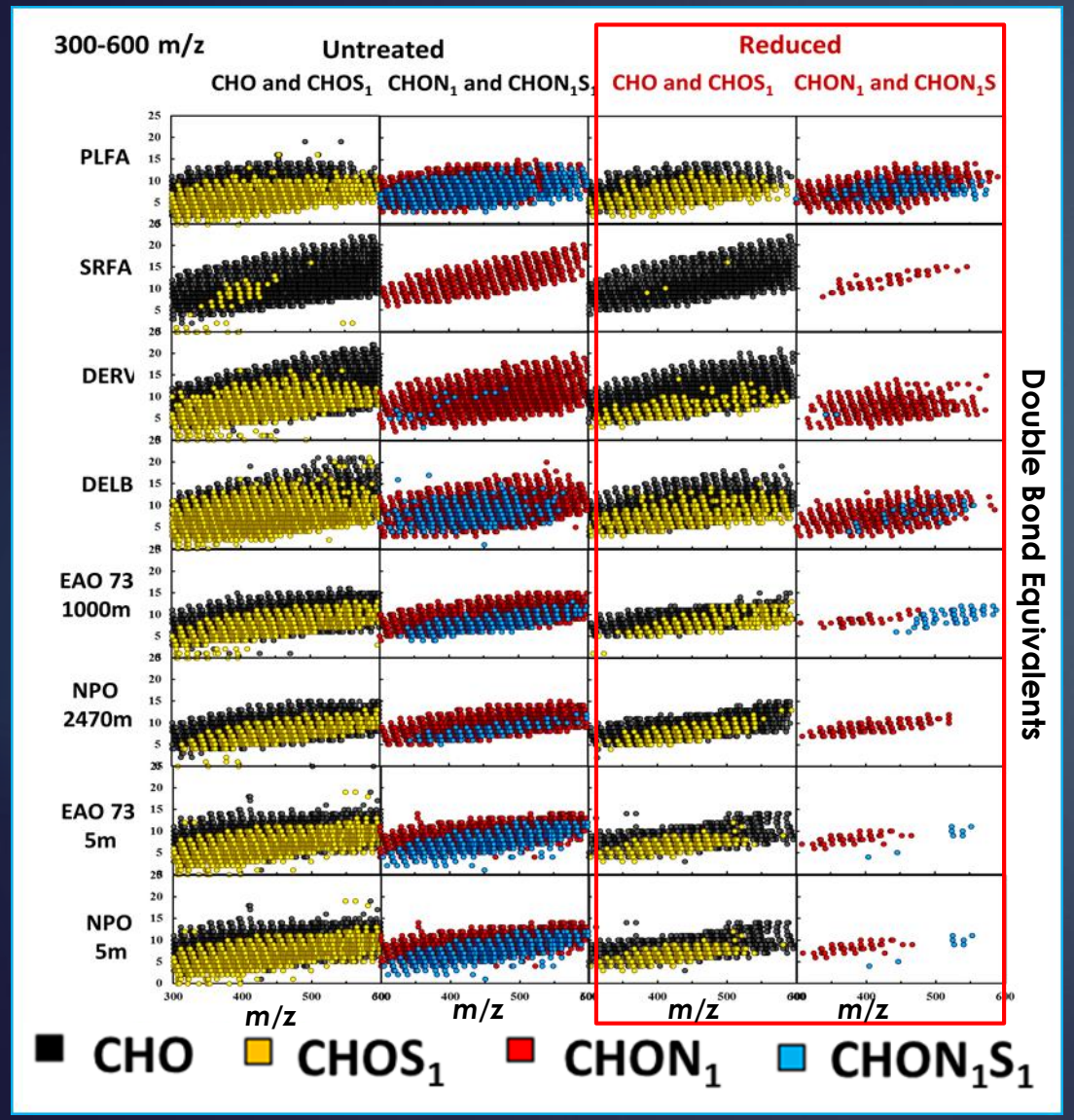
Results: Effects of Reduction



- O/C_{avg} ratios ~0.5
- SRFA,DERV, and DELB: H/C ratios < 1
- Open ocean samples (EAO and NPO) few assigned molecular formulae with H/C ratios < 1 and fewer < 0.5



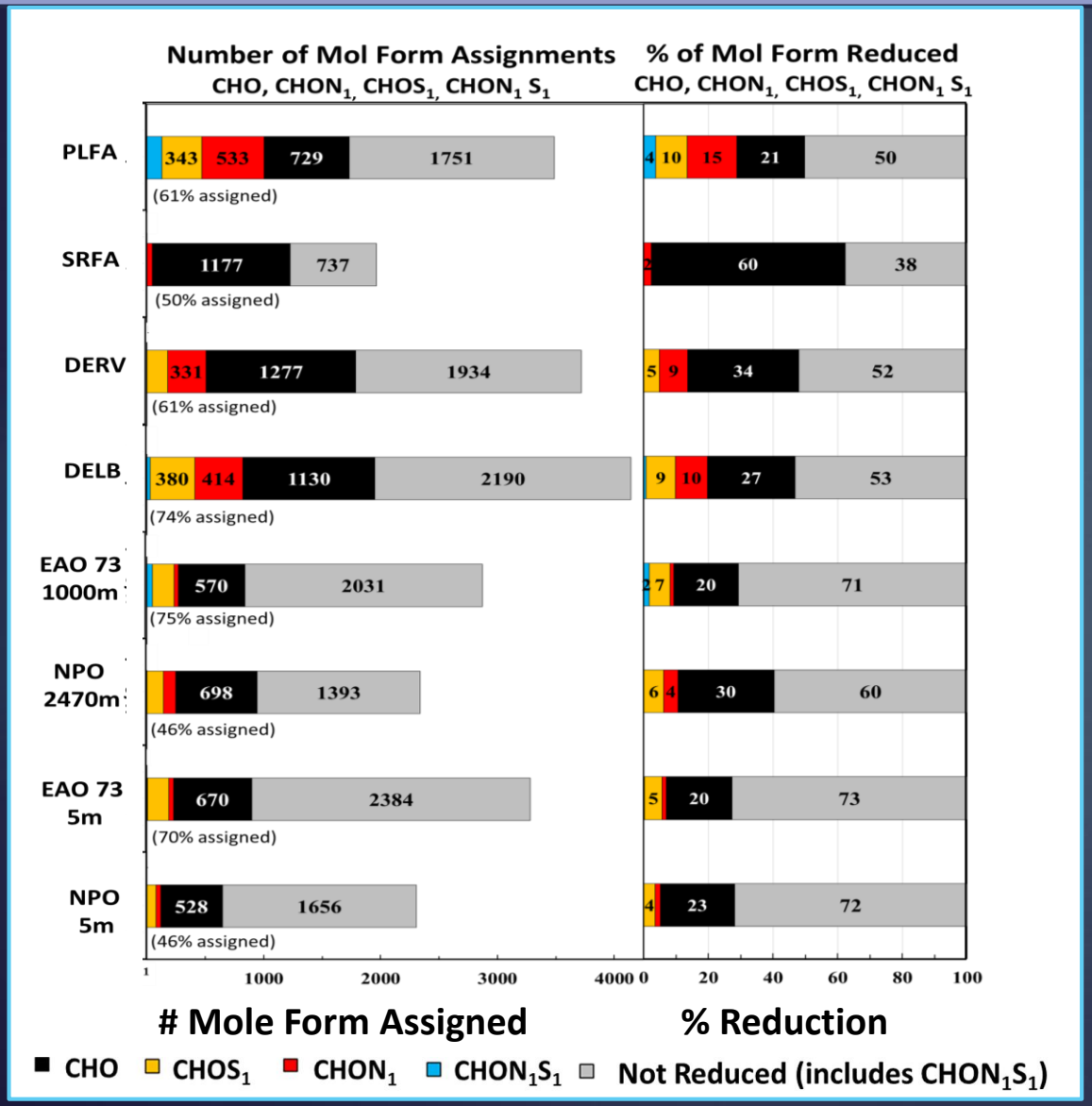
Results: Effects of Reduction



DBE= c +1 – *h*/2 + *n*/2

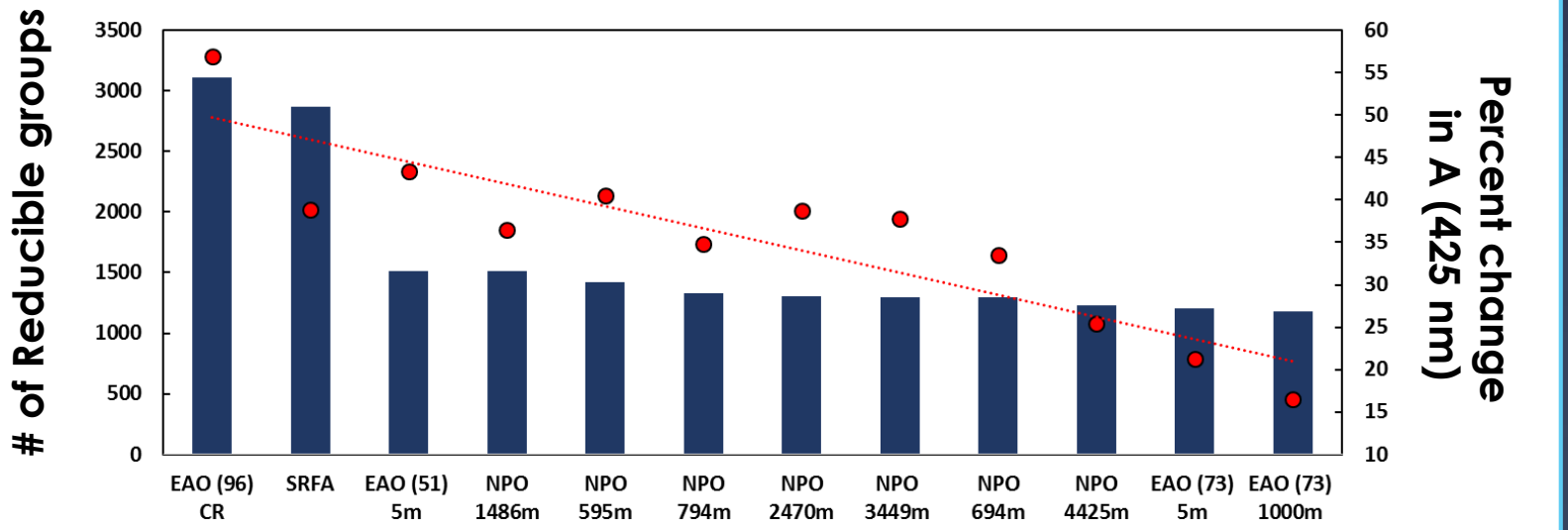
- Decreases with increasing distance from terrestrial sources
- Reduction occurring on higher DBE moieties

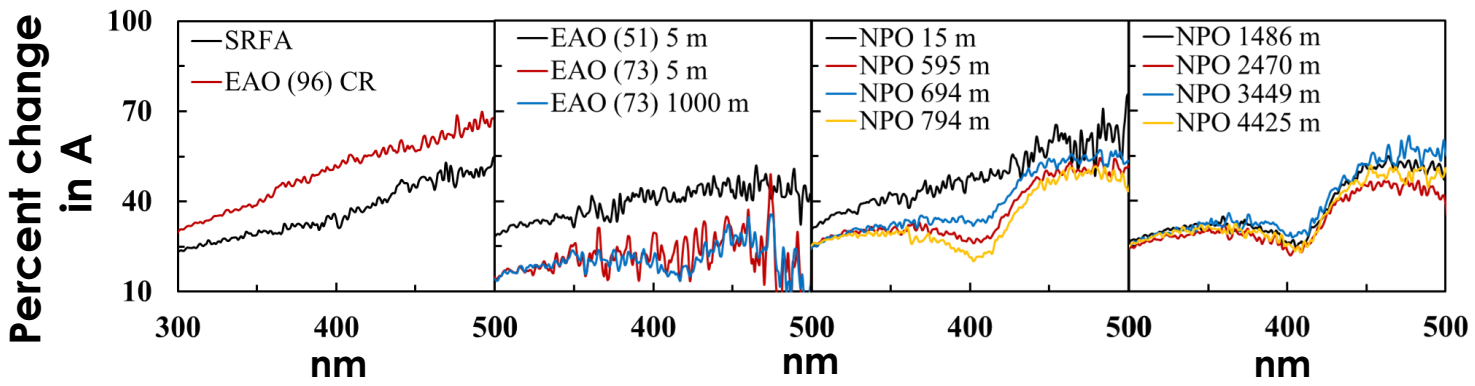
Results: Effects of Reduction



- Most reduction occurs on CHO only species
- The percent of reduced species decreases from terrestrial sources to off shore to ocean samples
- Open ocean surface samples show the least amount of reduction

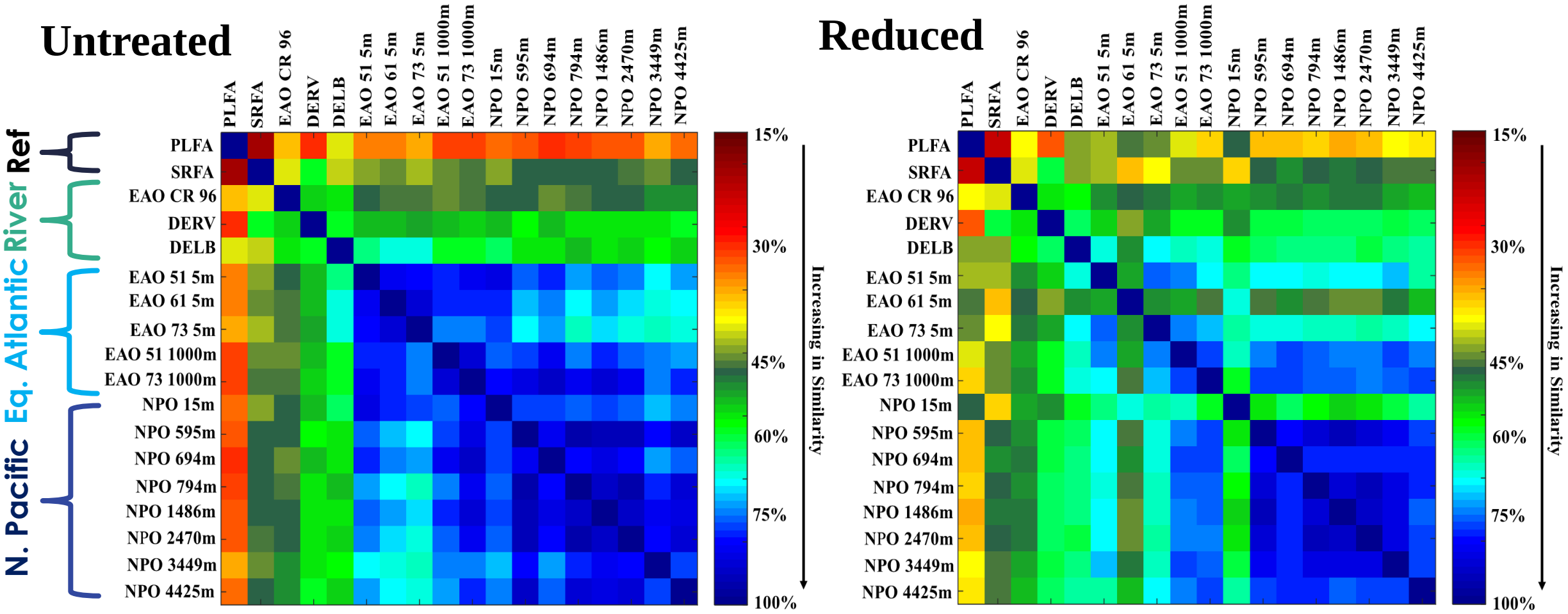
Results: Optics and Reduction





- EAO 96 Congo River out flow and SRFA: Highest number of reduced species
- EAO and NPO similar amounts of reduced peaks and absorption loss upon reduction (excluding surface samples, possibly due to photobleaching)

Results: 500 Highest Intensity Peaks Assigned Molecular Formulae ($CHON_{0-1}S_{0-1}$)



Summary:

- Combining all three techniques allows for a better understanding of the similarities/differences between CDOM/DOM samples
- All samples exhibit comparable absorption losses upon reduction, greatest over the visible range independent of location
- Terrestrial samples (untreated and reduced) show additional identified peaks at an H/C ratio <1 that are not observed in the open ocean
- Deep ocean waters from both EAO and NPO exhibit similar identified peaks (untreated and reduced)
- Open ocean and terrestrial samples, exhibit a common core of identified peaks at an H/C ratio >1

Acknowledgments

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Questions?