Understanding Anaerobic C Dynamics and Methane Production in Peatlands through Molecular Characterization of Porewater DOM Reactivity: Oxygen Shedding by DOM during Fermentation



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INTECOL 9
June 7, 2012

Peatlands

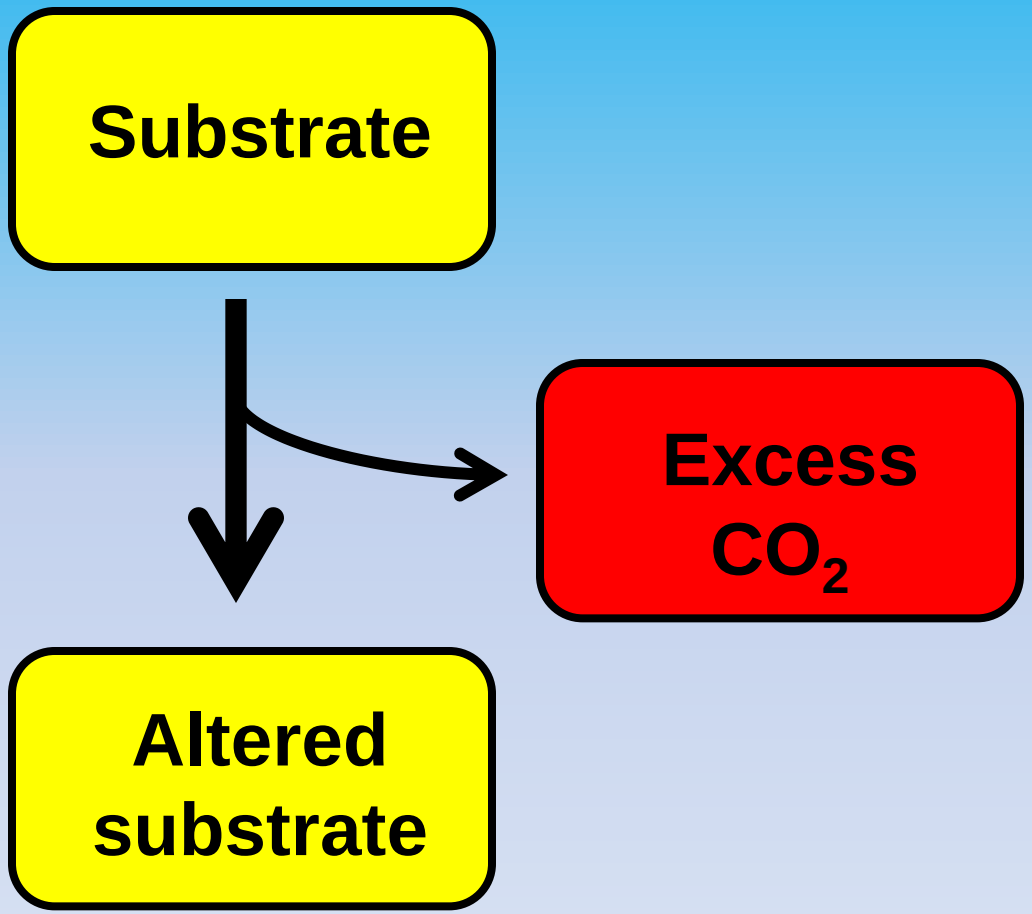
- Peat soils are estimated to store one-third of the world's soil carbon

- While the build-up of organic matter in peat is a store of carbon, this material is also decomposing, releasing CO_2 and CH_4 to the atmosphere

- Methanogenesis is the dominant pathway of decomposition

- CO_2 concentrations are often reported to be higher than CH_4 concentrations

Peatlands



Objective

- To identify the source of the excess anaerobic CO_2 production in peatlands relative to methane production

- To examine changes in DOM composition for evidence of CO_2 evolution

Sample collection

RL IV Bog

Depth (cm)	pH	DOC (mM)
10	4.2	4.71
50	4.3	5.64
100	4.4	7.17
150	4.5	7.95
200	4.8	9.38
250	5	11.43
290	5.2	10.32

RL IV Fen

Depth (cm)	pH	DOC (mM)
10	5.7	2.68
50	5.9	2.79
100	6.2	2.46
150	6.5	2.28
200	6.7	1.99
250	6.8	1.94
290	6.9	1.98

Approach

- **Ultrahigh resolution Fourier Transform Ion Cyclotron Resonance Mass Spectrometry (FT-ICR MS)**
  - **Distinguish individual elemental compositions of DOM molecules**
- **^{1}H-Nuclear Magnetic resonance (^{1}H-NMR)**
  - **Determine of the relative abundances of different functional groups contained in DOM**
- **PARAFAC Excitation/Emission Matrix (EEM) fluorescence spectroscopy**
  - **Investigate the optically active component of DOM**

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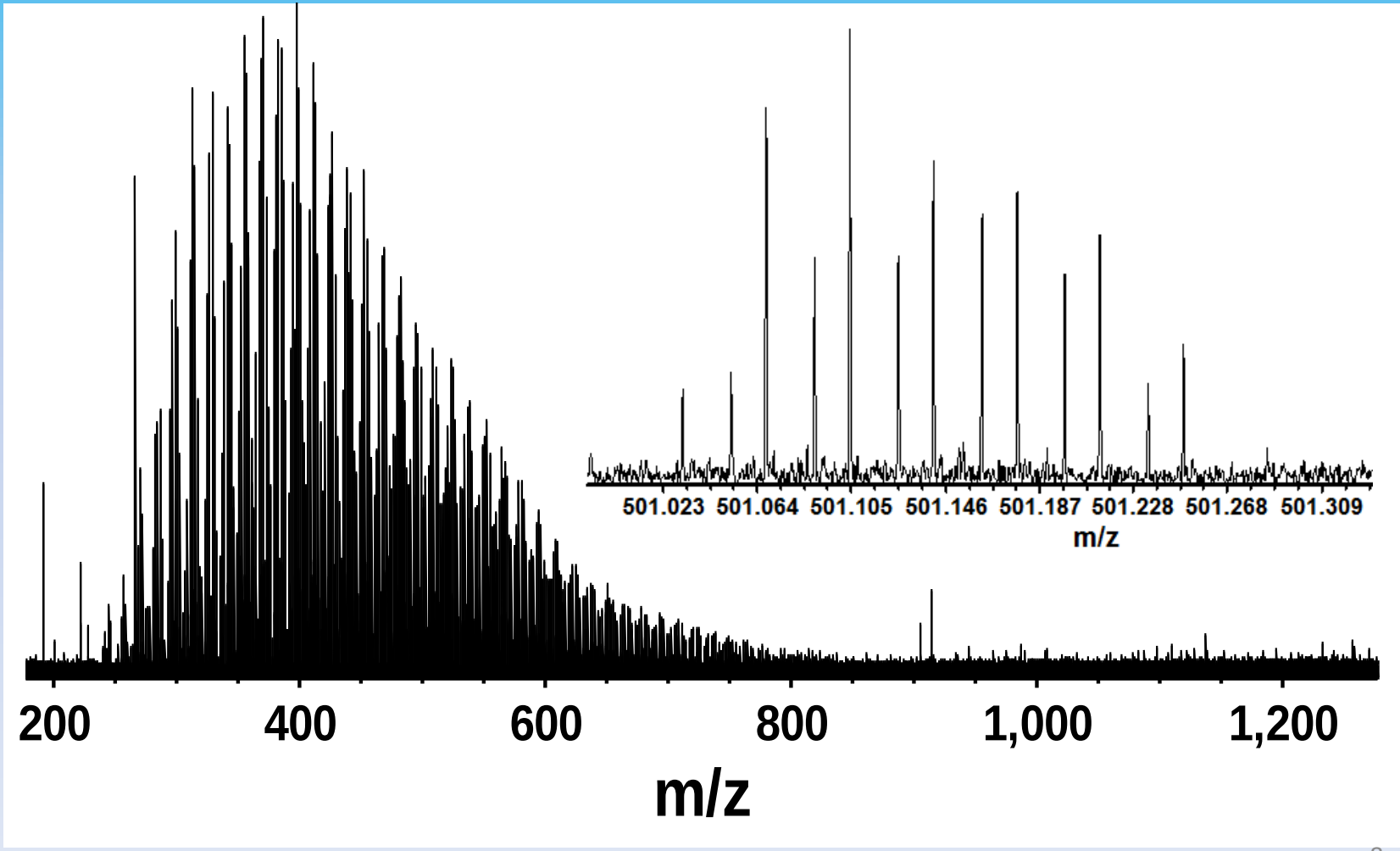
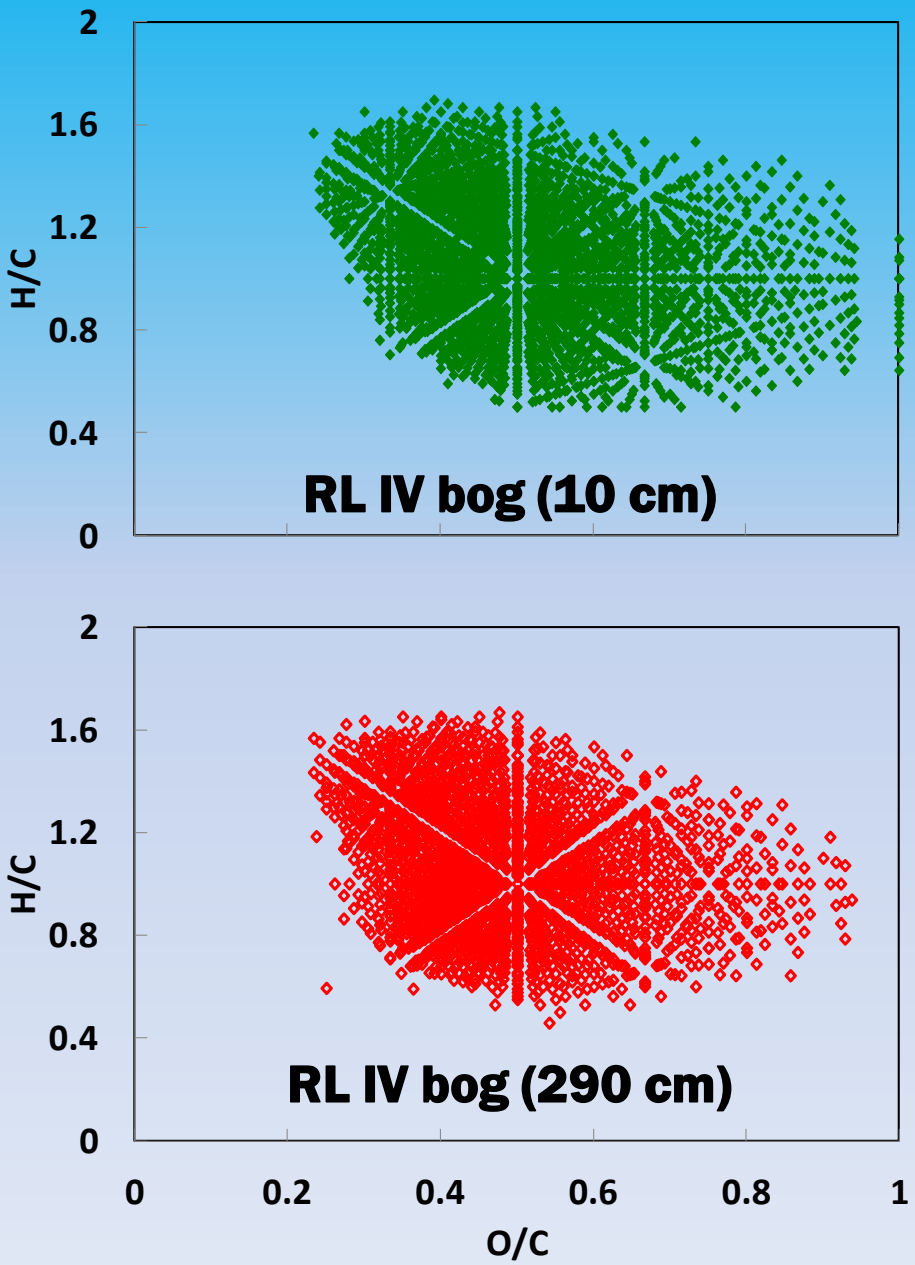
FT- ICR MS

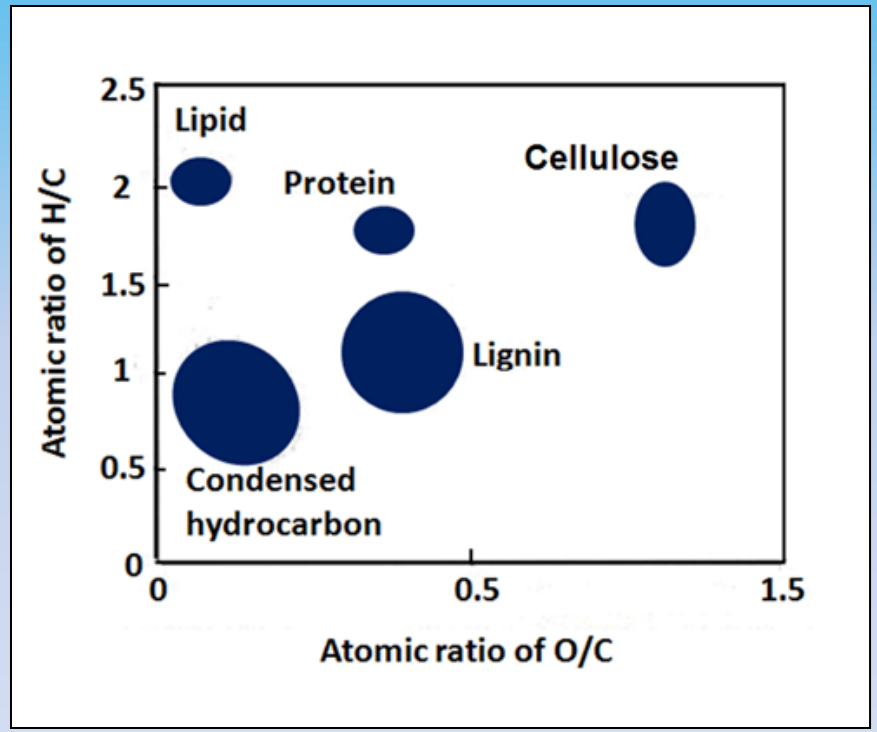
Negative-Ion Electrospray Ionization FT-ICR MS (9.4 Tesla)
4184 peaks > 6σ baseline noise (200 < m/z < 900)
$m/\Delta m_{50\%}$ = 680,000 at m/z 501
14 peaks at m/z 501



Bog vK diagrams

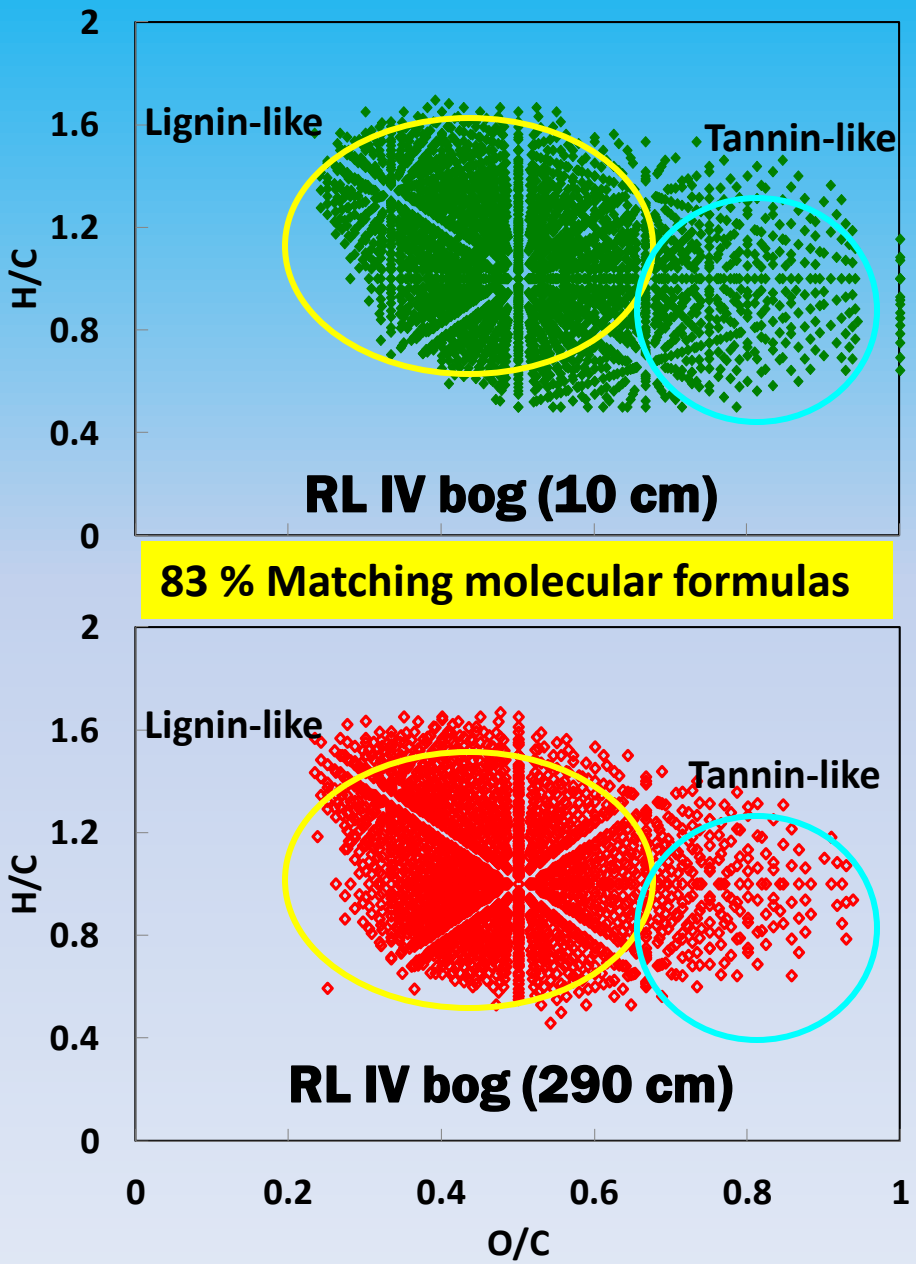


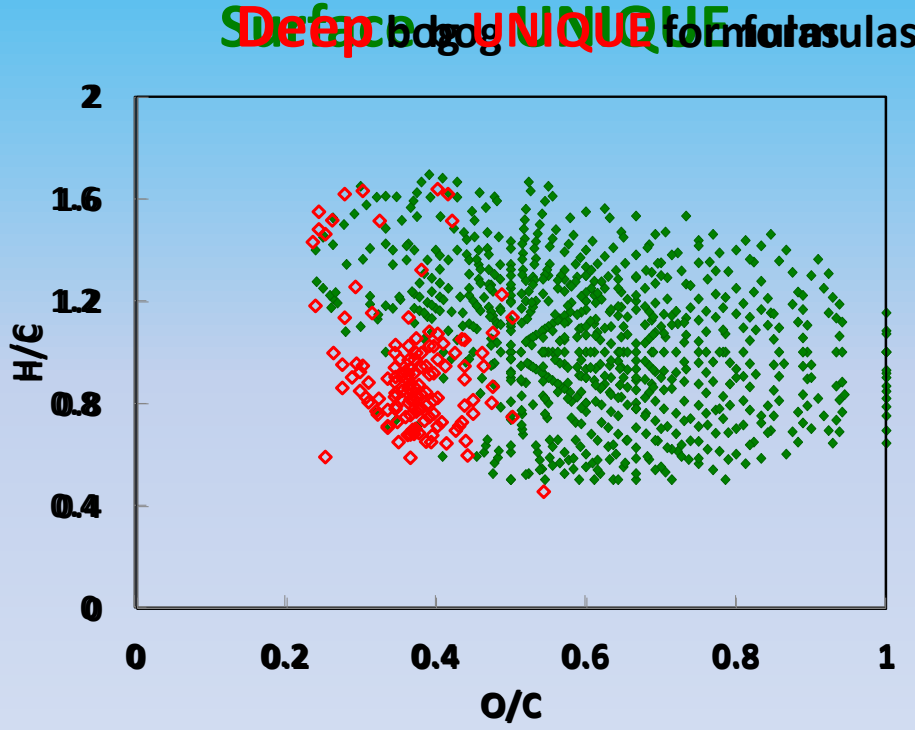
1- Identity different classes of compounds



2- Identify changes in DOM composition with depth

Bog vK diagrams

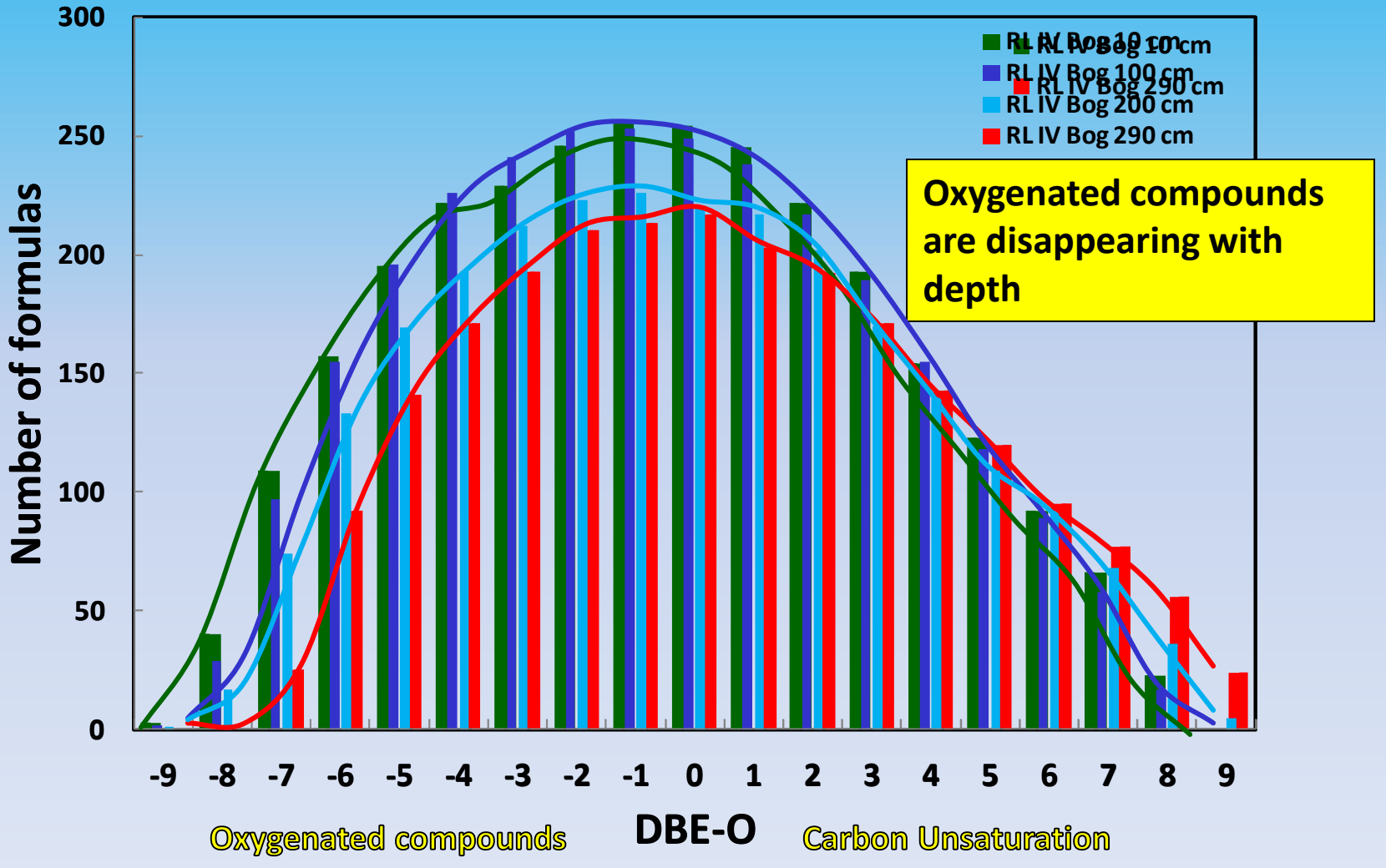




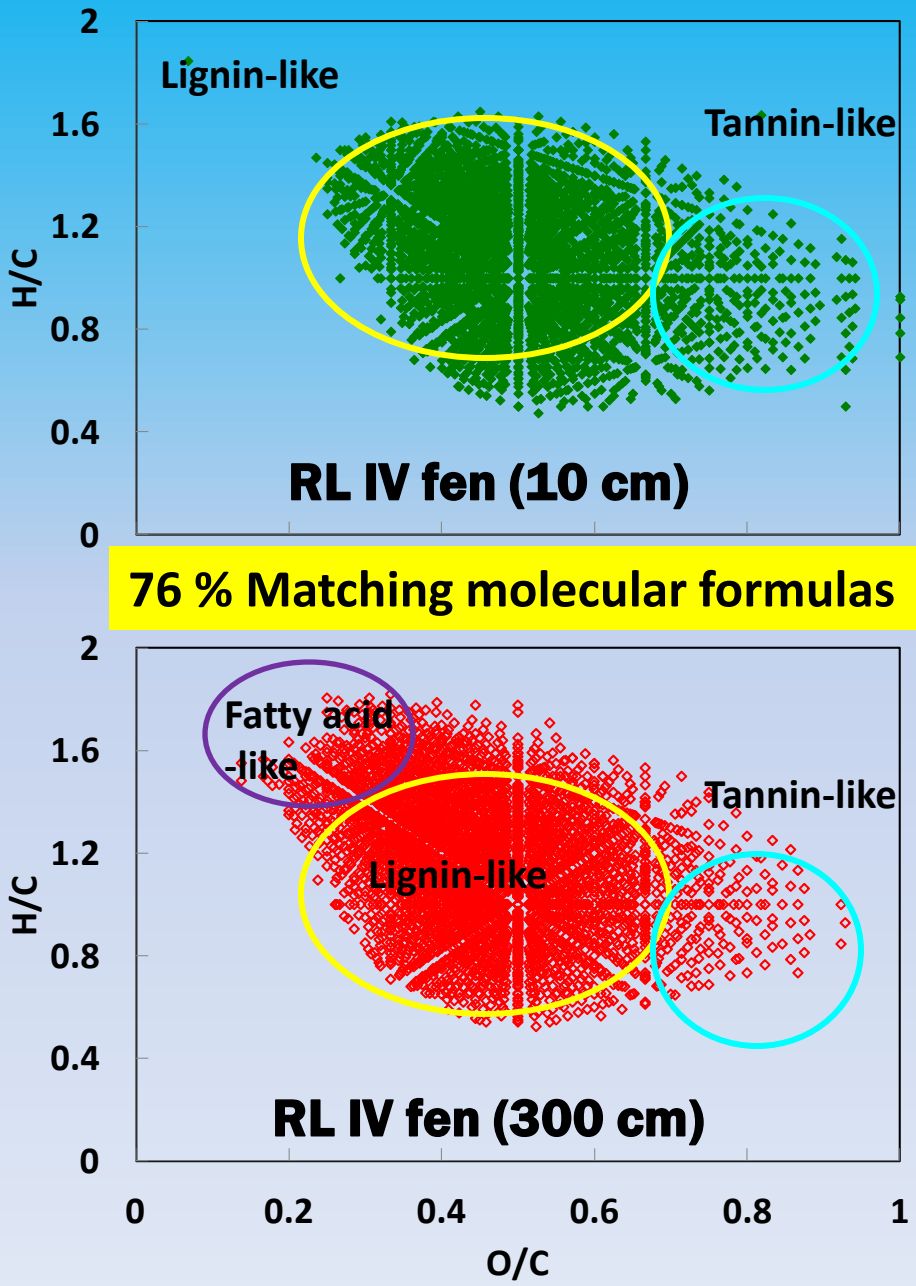
Bog DBE-O

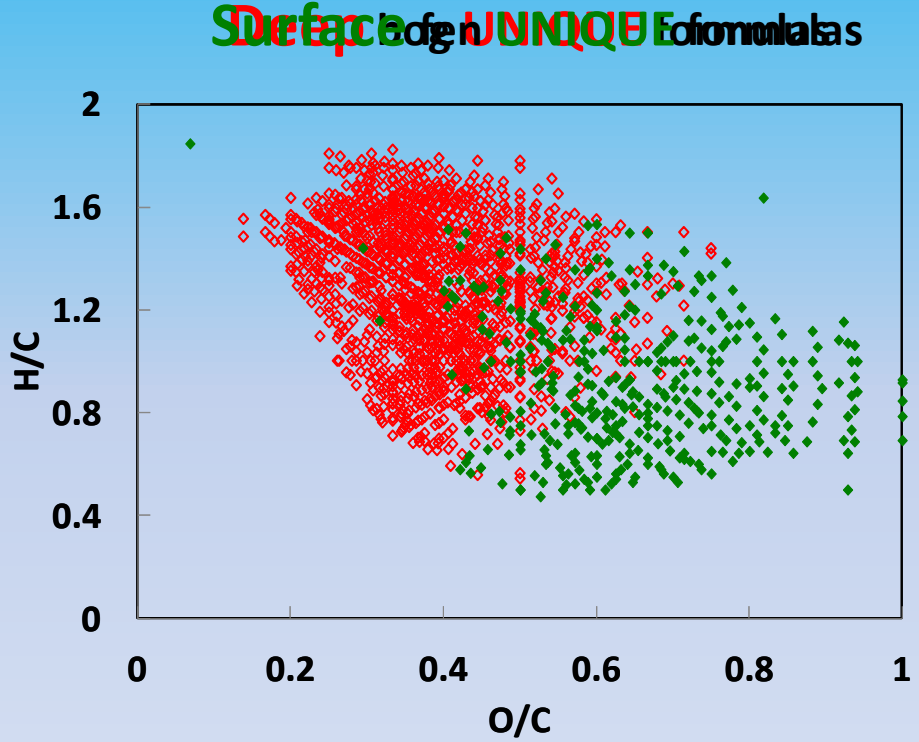
DBE = C – (H/2) + (N/2) +1

DBE-O represents C=C bonds by subtracting out the C=O contribution: measures carbon unsaturation

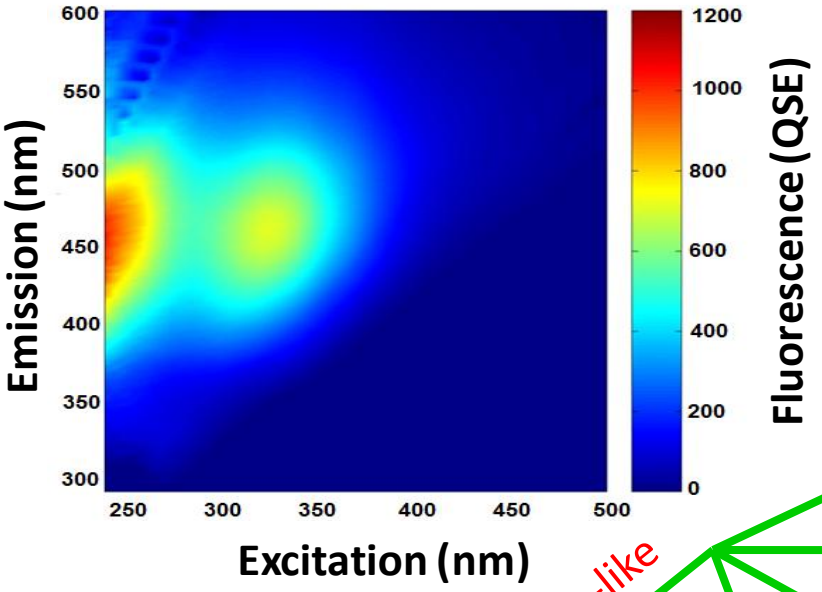


Fen vK diagrams





PARAFAC-EEMS



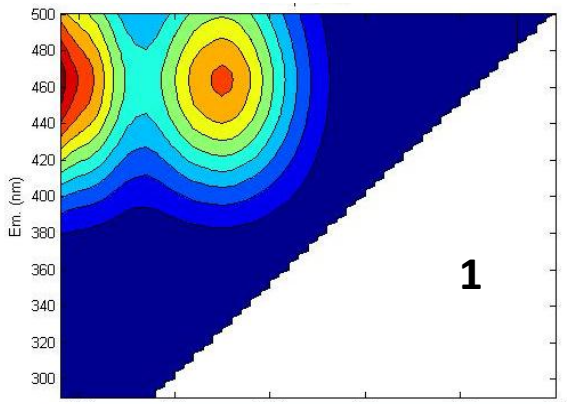
Terrestrial Humic-like

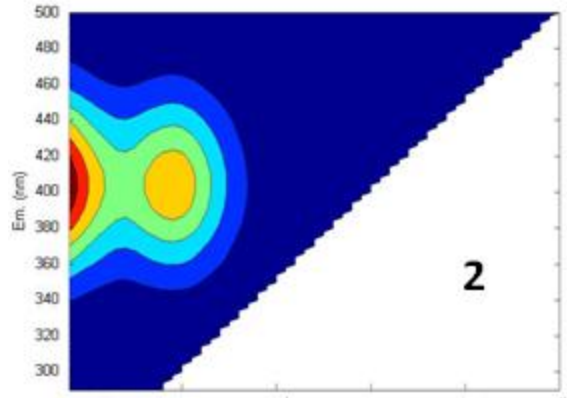
Microbial Humic-like

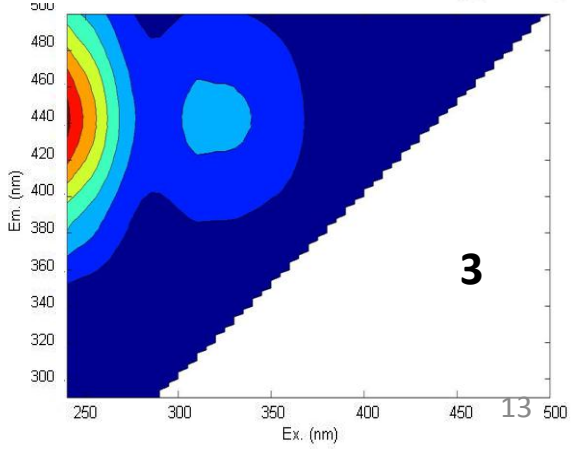
Microbially - assimilated

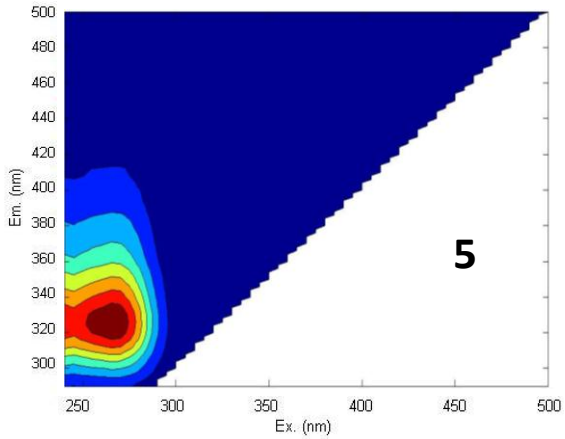
Terrestrial Humic-like

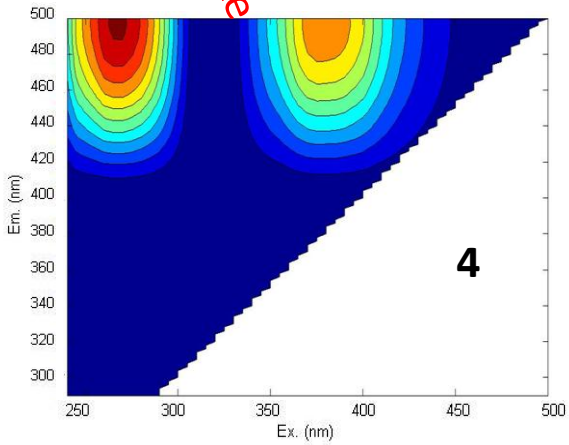
Protein-like











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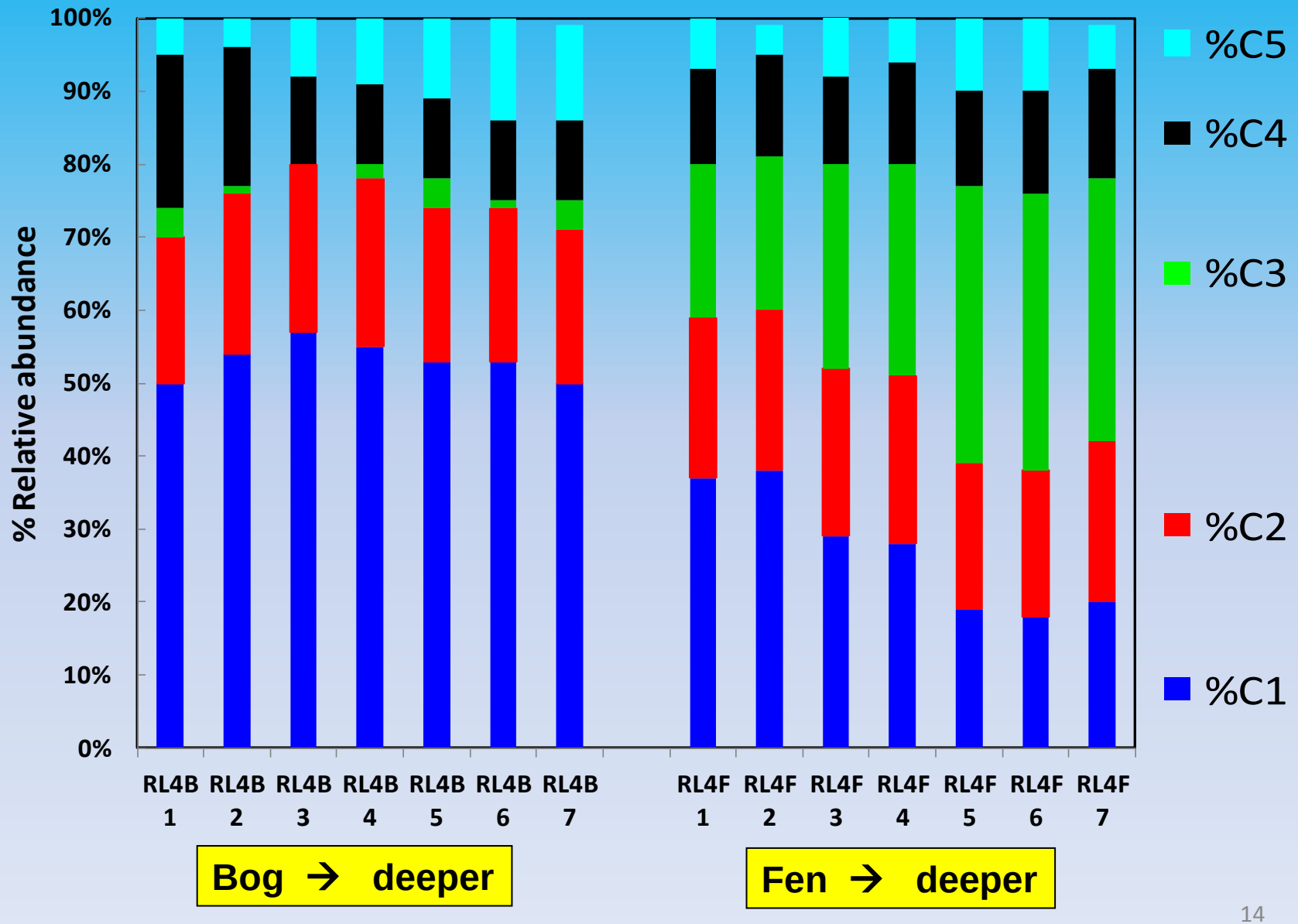

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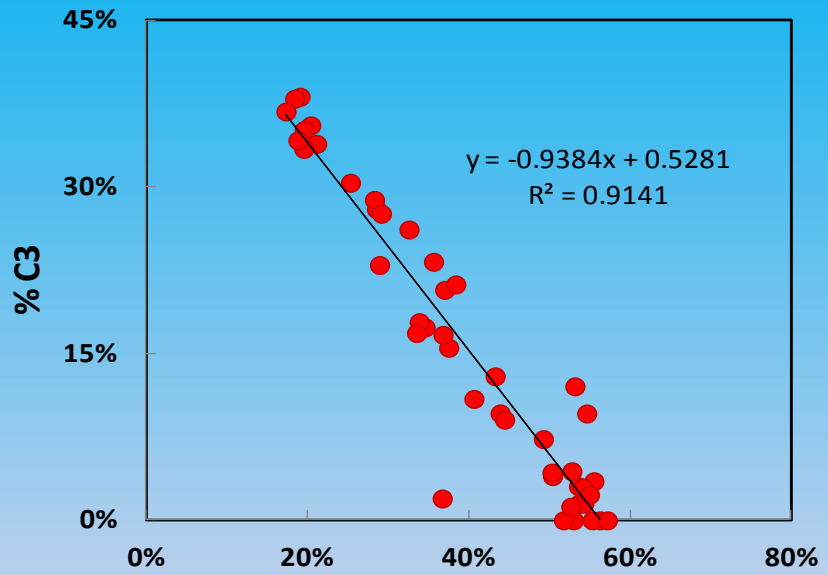
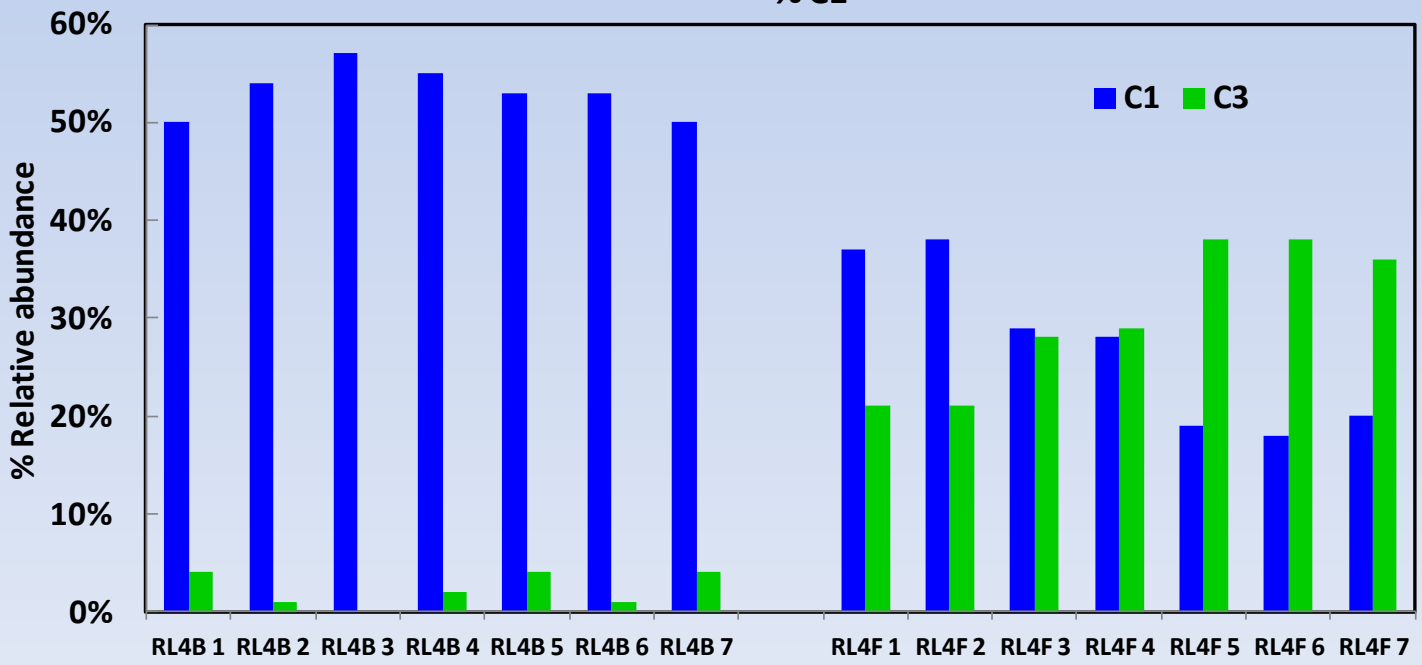
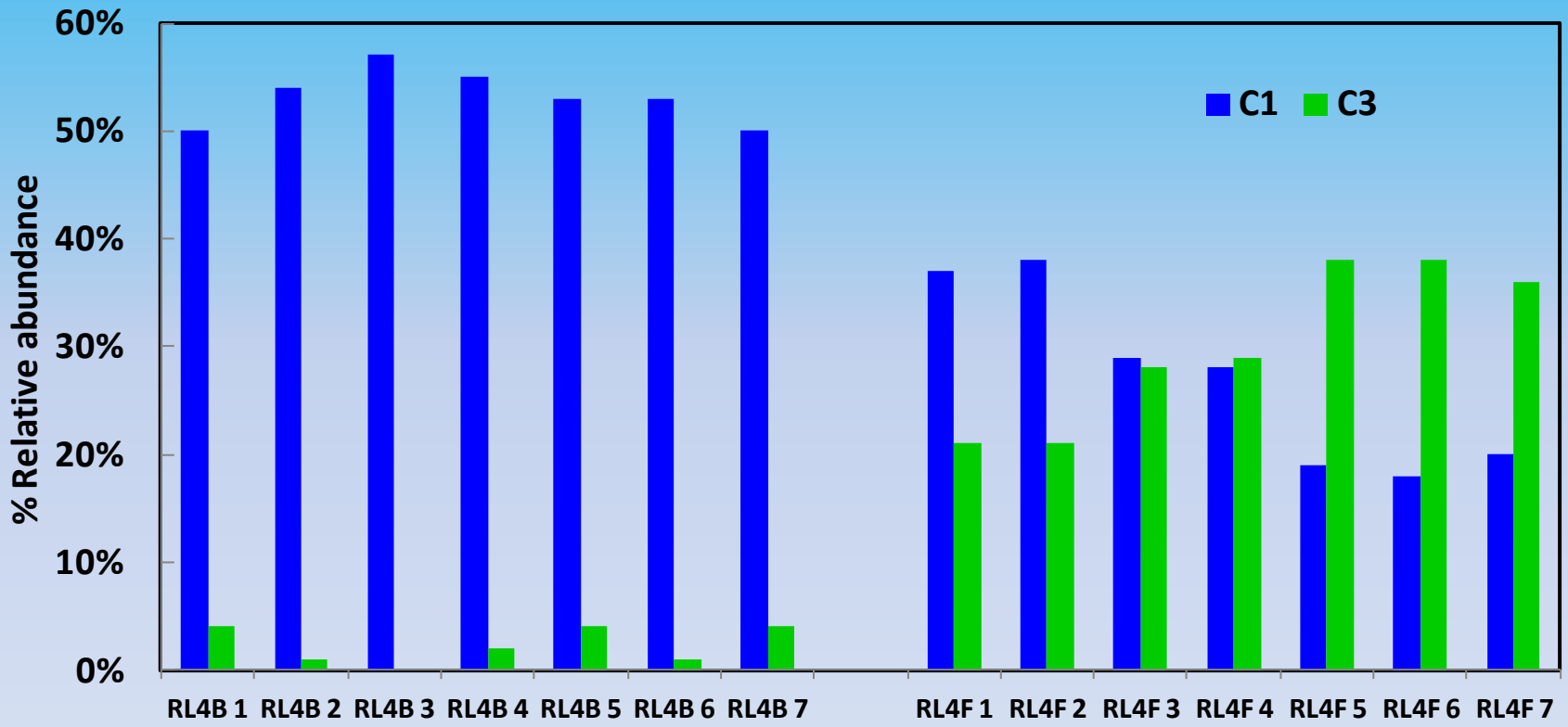




PARAFAC

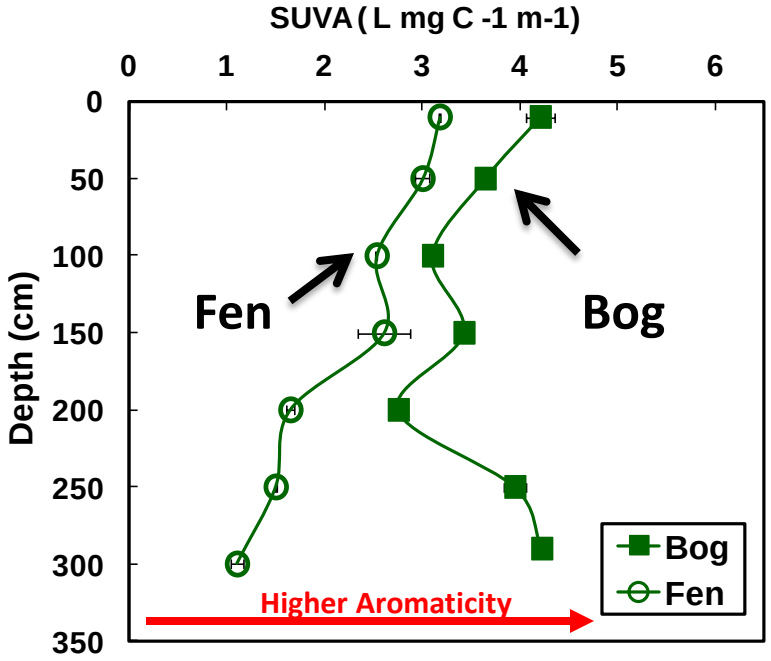
➢ **Anearobic bacteria mainly feed on the terrestrial humic-like component, C1, to produce the microbial component, C3.**

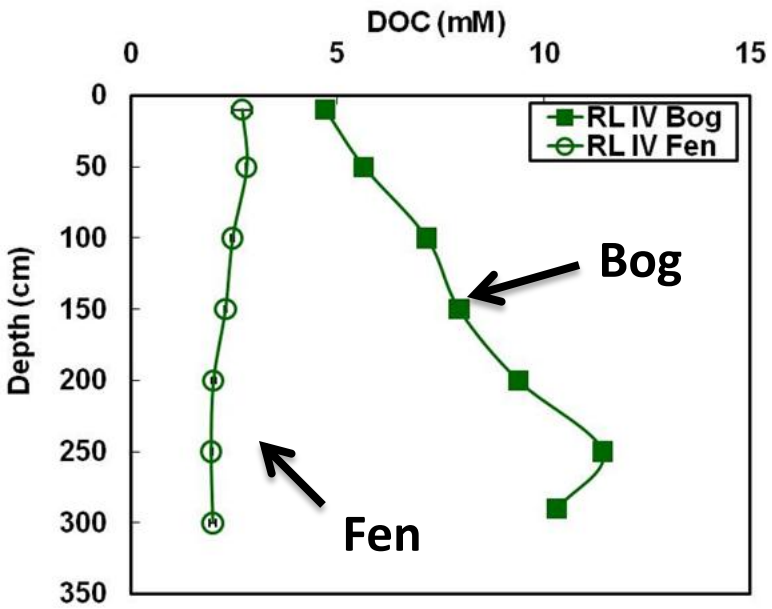


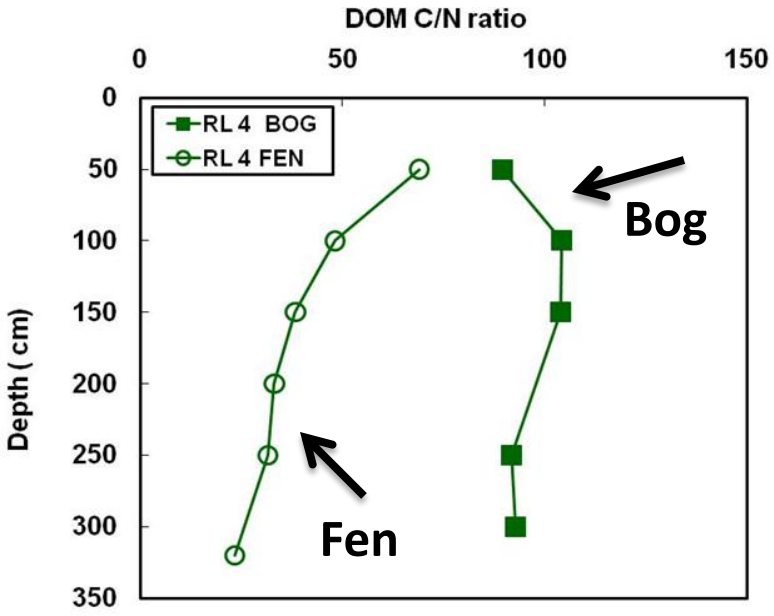
Bog DOM → Mainly refractory

Fen DOM →Reactive & supports fermentation

DOM characterization



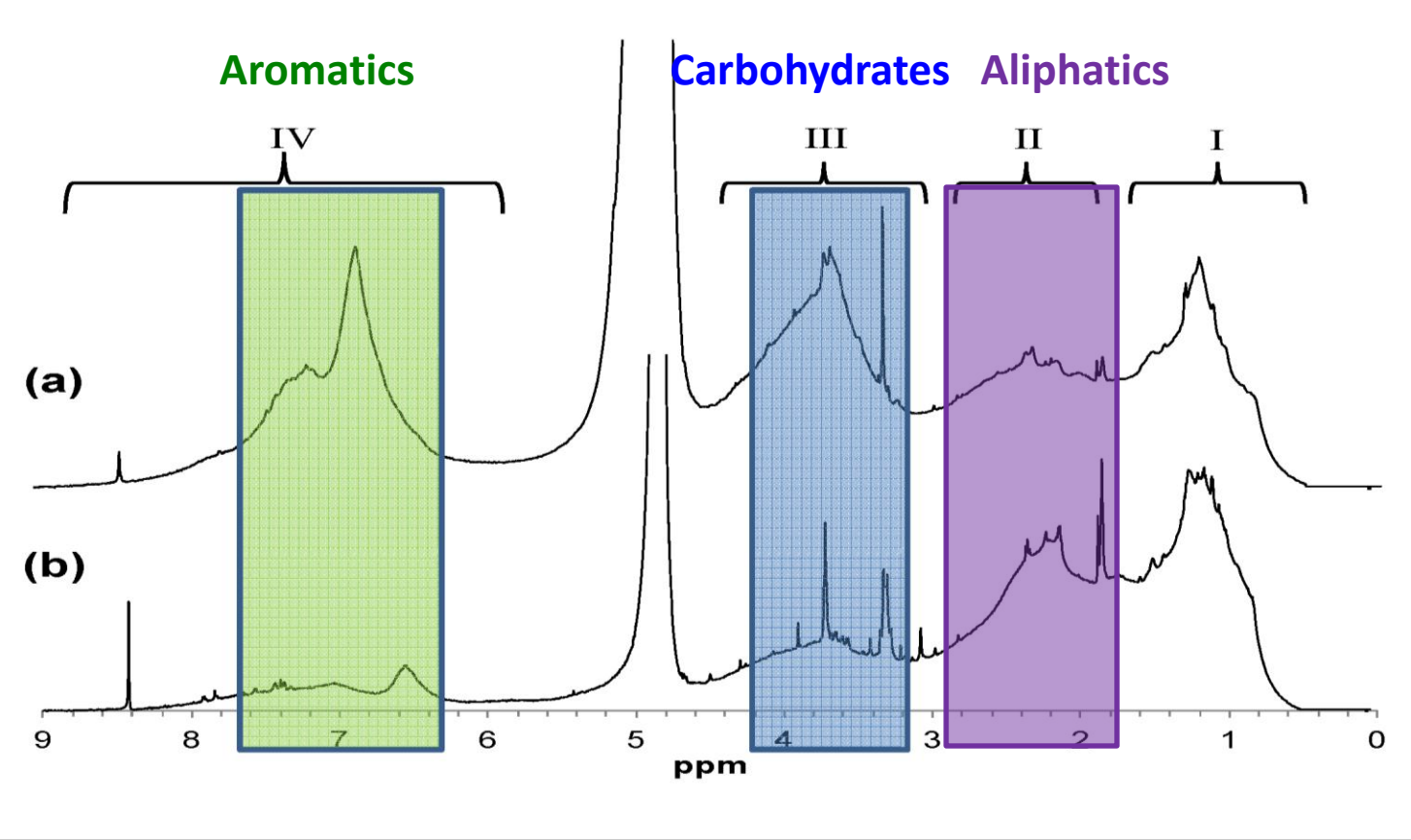




H- Nuclear Magnetic resonance (NMR)

Bog

Fen



- Aromatic and carbohydrate components represented up to 70% of deep bog DOM but comprised a much smaller proportion of deep fen DOM

Summary

- **Organic matter held under sub-oxic conditions sheds organically bound oxygen to produce CO_2 associated with fermentation**

- **This observation was more pronounced at the fen than at the bog**

- **Differences in source materials and / or environmental factors**

Acknowledgments

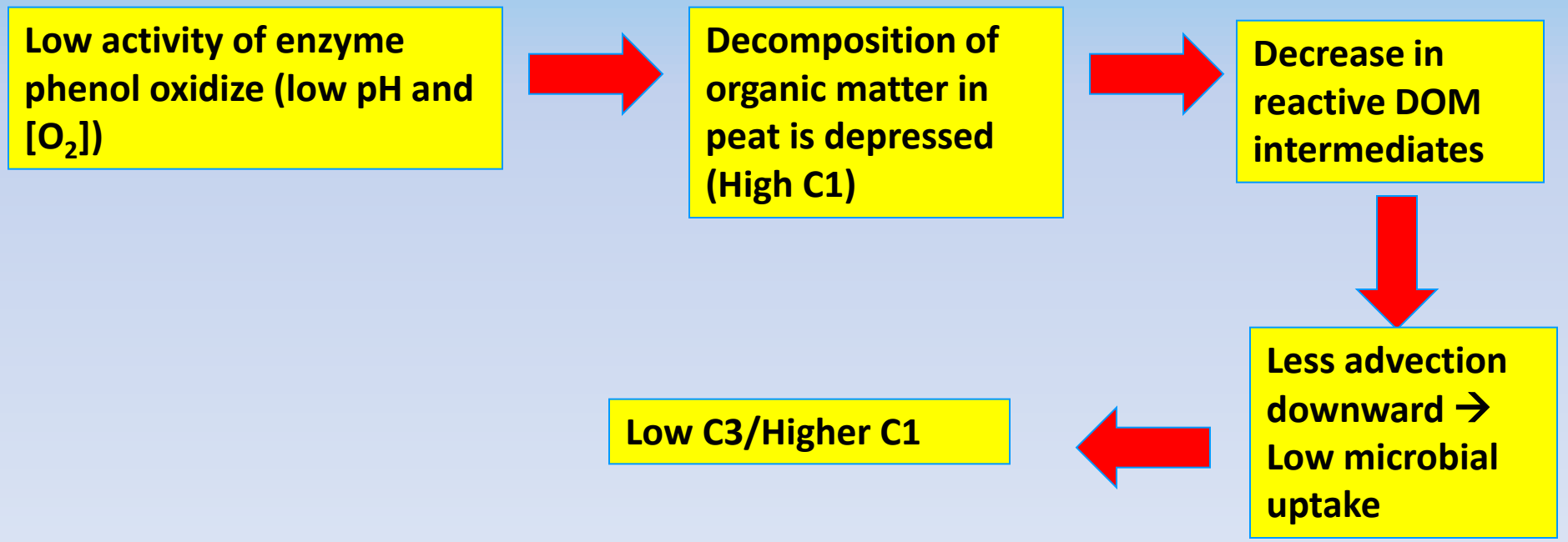
- The Florida State University
- Bill Cooper
- Jeffrey Chanton
- Paul Glaser
- David Burdige
- Donald Siegel

NSF Grant # EAR 0628349

Nature vs Nuture

- Occurrences that follow DOM postproduction

Enzymatic "latch model"



SUVA

SUVA = $A_{254\ (m-1)}$ / $[DOC]_{(mg\ C/L)}$ = Correlated with DOM aromaticity