Molecular Investigation of Surface Water Chemistry in the Munson Slough/Lake Munson Watershed in St. Marks-Wakulla River Basin by FT-ICR Mass Spectrometry

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Introduction

The chemical composition of dissolved organic matter (DOM) is shaped by its source materials and biogeochemical processing. Wastewater, storm water, and agricultural runoff carry pesticides, pharmaceuticals, and nutrients. While these chemicals serve important functions in crop production or treatment of disease in livestock and humans, they become pollutants when discharged into surface waters.

DOM in aquatic system can originate, in a broad sense, from two distinct sources. Autochthonous DOM is produced within the aquatic environment, and essentially derived from bacteria, algae or aquatic macrophytes growing in the water body. Allochthonous DOM is imported from outside the aquatic environment by processes such as riverine inflow and atmospheric deposition, and is of mostly terrestrial (or terrigenous) origin. Biogeochemical processes such as microbial degradation and photochemical oxidation also alter the physicochemical characteristics of DOM. The disparity in the sources of DOM, and in the biogeochemical processes controlling its transport and alteration, is expected to lead to structural differences in DOM from different environments. Organic matter has historically been difficult to analyze due to compositional complexity and high oxygen content. Only advanced analytical techniques can illuminate compositional changes in DOM that affect water quality.

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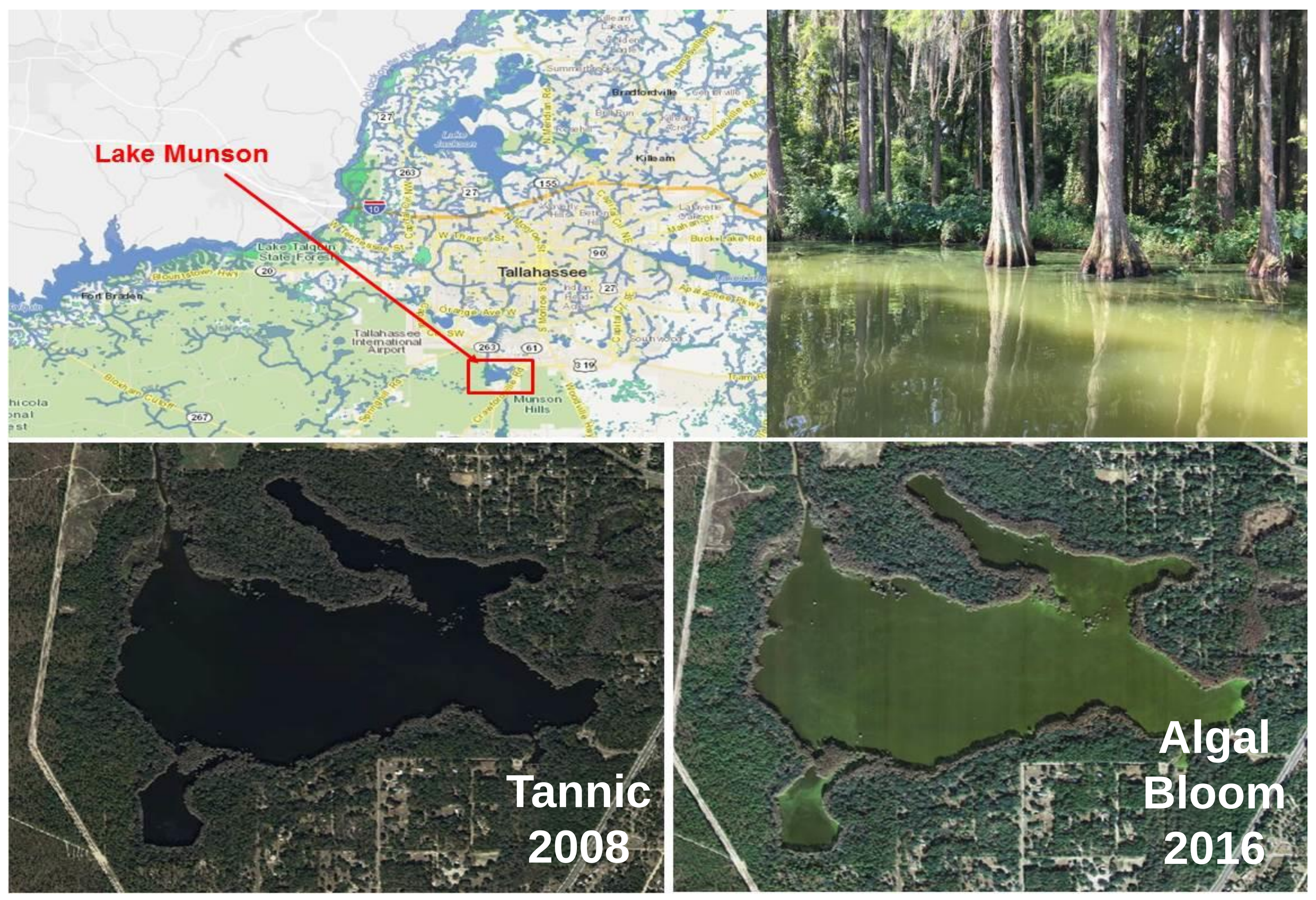

Figure 1. Lake Munson is a 255 acre cypress-rimmed, eutrophic water body located in the St. Marks river watershed in Leon County Florida. The lake experiences frequent algal blooms as recent as August 3016 (bottom, right) compared to slightly tannic water (bottom, left).

Lake Munson is an approximately 255 acre, cypress-rimmed, nitrogen-limited lake located south of the City of Tallahassee,[1,2] believed to originally be a cypress swamp currently impounded and functioning as a shallow, man-made lake. Lake Munson received the majority of input from heavily-altered Munson Slough and tributaries, and flows southward ultimately draining into Ames Sink, and for over 50 years has been a major watershed for the City of Tallahassee.[3] Therefore, Lake Munson has been ranked as the seventh most degraded lake in the state of Florida by the Florida Department of Environmental Protection (FDEP),[4] with a history of severe water quality and ecological problems (e.g., fish kills, algal blooms, exotic vegetation and snails, high nutrient and bacterial levels) and received a TMDL (Total Maximum Daily Load) by the FDEP in 2013, which requires significant reduction in total nutrients (total nitrogen 32%; total phosphorus 76%; dissolved oxygen 50%) and turbidity (32%).[1] Organic and nutrient-rich sediments in Lake Munson contribute to poor water quality, and previous sediment removal and drawdowns (2010) have been effective at consolidating the sediments but have little to no effect on nutrient reduction.

We will highlight a temporal study on the compositional changes in DOM derived from the Munson Slough/Lake Munson Watershed, an impaired water body in Leon County Florida. Samples collected each quarter from February 2016-current will catalogue the compositional variation in the chemical cycling that occurs in lake inputs and in-lake sampling locations as a function of time. Correlations will be made to the water quality criteria established by the Florida Department of Environmental Protection, and measured by the Leon County Stormwater Management. This project is in collaboration with Leon County Florida, and Florida A&M University School of the Environment.

FDEP Mandated TMDL Targets for Lake Munson and Munson Slough (2013) [1]

	Munson Slough	Lake Munson
Total Phosphorus	0.15 mg/L	0.044 mg/L
Total Nitrogen	0.752 mg/L	0.765 mg/L

Map of Lake Munson

Figure 2. Map of Lake Munson and Munson Slough in Leon County , Florida. MS1 is the input from the City of Tallahassee drainage; LMU7 and LMU8 are tow in-lake sampling sites; MS2 is sampled as the southern outflow; MS4 is sampled south of 319 as the water heads to Ames Sink.

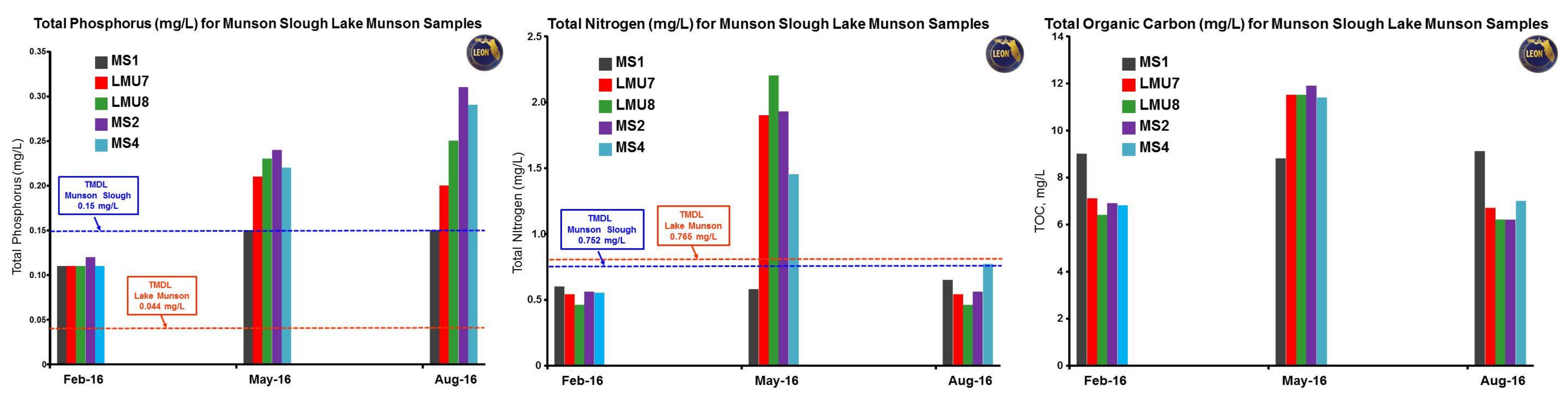

Figure 3. Total nutrient (phosphorus and nitrogen) and total organic carbon for 2016 samples. Additional time points from 2017 in progress.

Samples from MS1, LMU7, LMU8, MS2 and MS4 were provided each quarter by the Leon County Stormwater Management department, shown in Table 1. Each samples was filtered through a 0.2 μm filter prior to solid-phase extraction (SPE) of the dissolved organic matter.[5] Samples were analyzed with negative-ion electrospray ionization Fourier transform ion cyclotron resonance mass spectrometry at 9.4 tesla.[6]

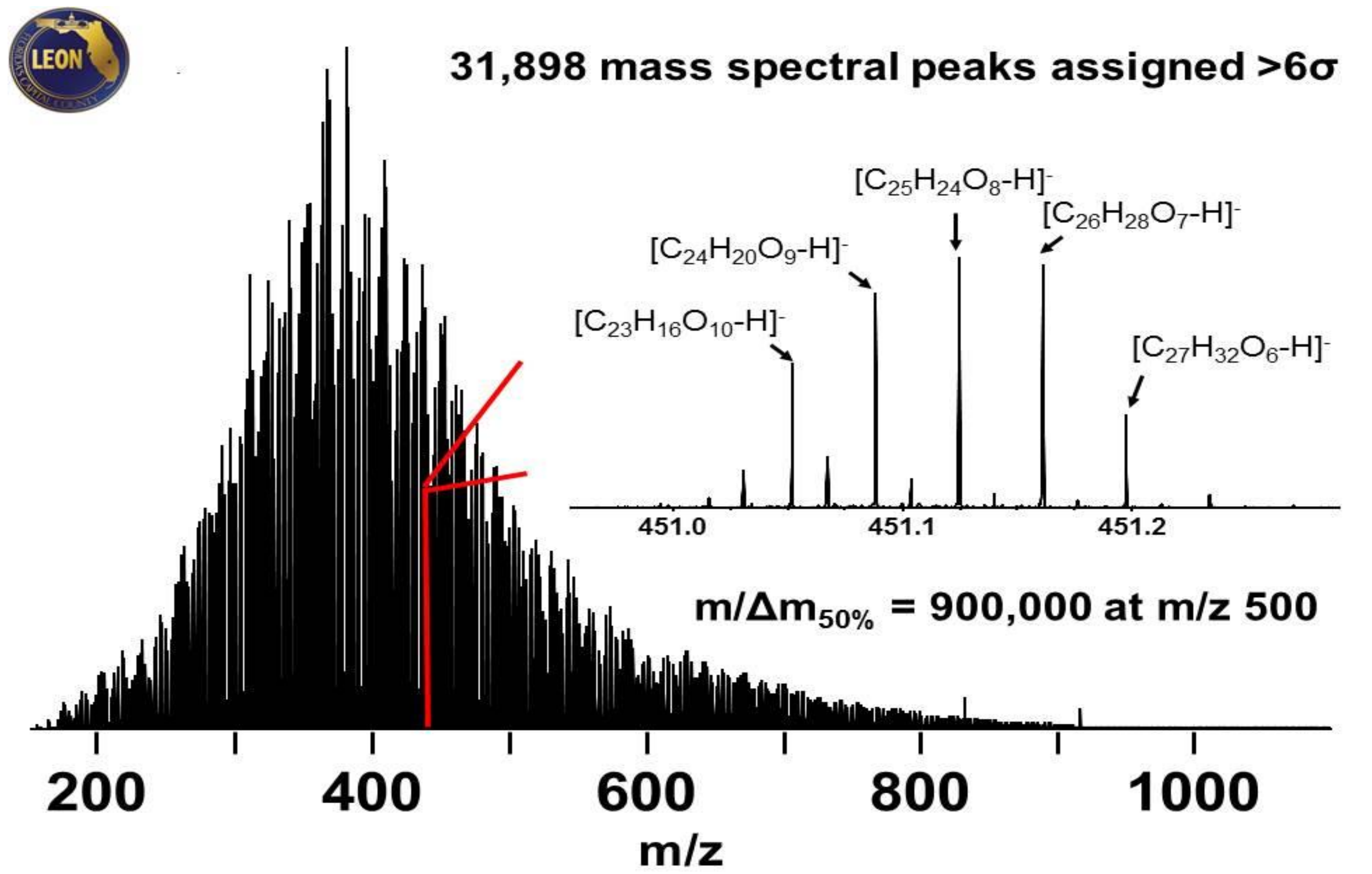

Figure 3. Negative-ion electrospray ionization FT-ICR mass spectrum at 9.4 tesla of a Lake Munson (LMU7) sample collected on May 16, 2016 (Tallahassee, Florida). More than 31,000 unique mass spectral peaks are detected across the mass range 150 < *m/z* < 1000. A mass-scale expanded zoom inset illustrates the achieved resolving power ($m/\Delta m_{50\%}$ = 900,000 at *m/z* 500), sufficient to resolve numerous peaks that have the same nominal mass but differ in exact mass by three-to-four times the mass of an electron.[7] The most abundant compound class for all Munson samples contain between O_7-O_{12} oxygens per molecule, in agreement with previous reports for terrestrial-derived DOM. However, compositional variation occurred between in-lake samples and slough samples over the 18 mos sampling campaign. Sampling will continue for the five sites noted above through summer of 2018.

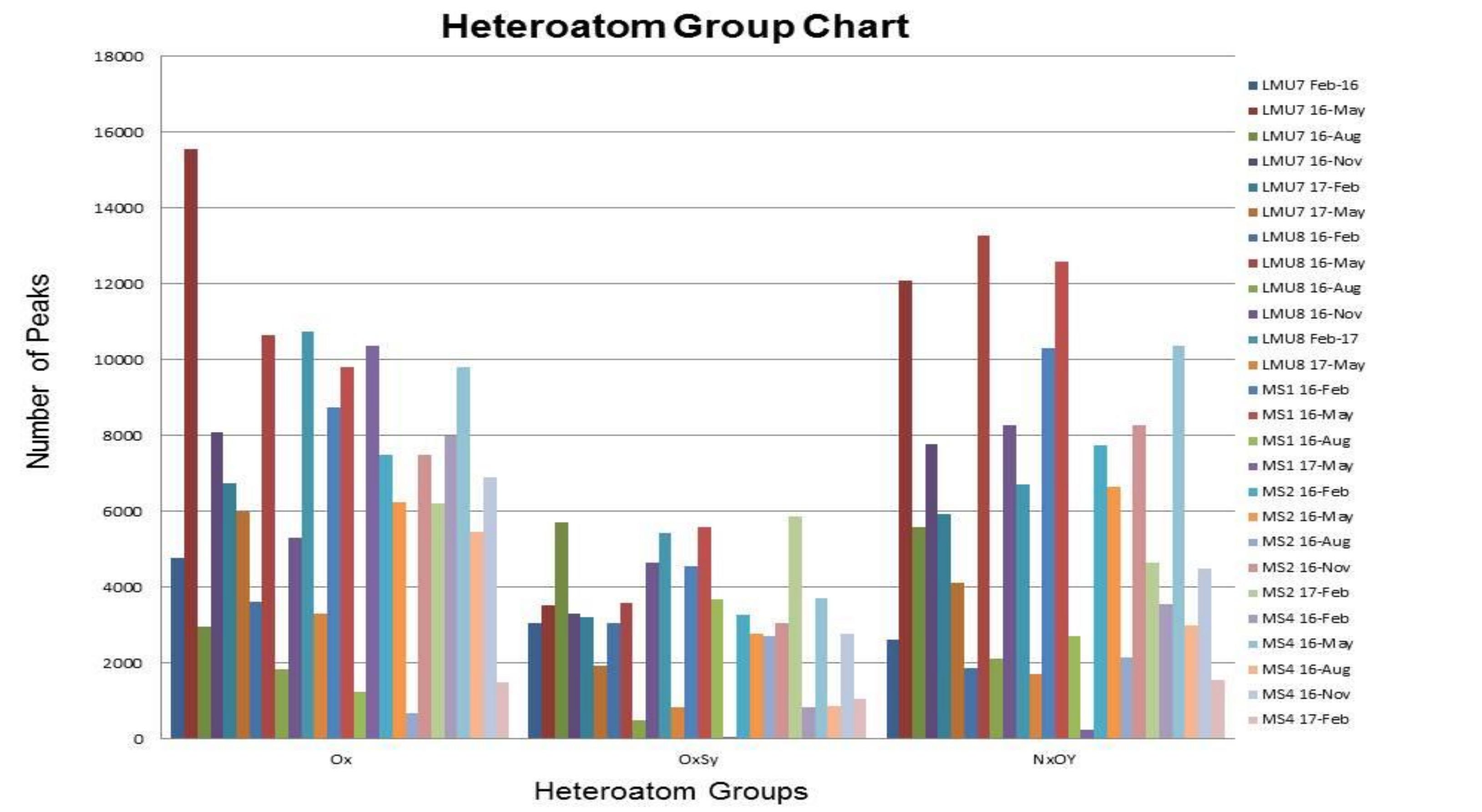

Figure 4. Heteroatom group distribution for Lake Munson and Munson Slough samples that highlight the compositional variation between the input (MS1), in-lake (LMU7 and LMU8) and outlet (MS2, MS4) as a function of time. Each heteroaotm class is the combination of all compounds that contain carbon and hydrogen in addition to oxygen (O_x), oxygen and sulfur (O_xS_y), and nitrogen and oxygen (N_xO_y).

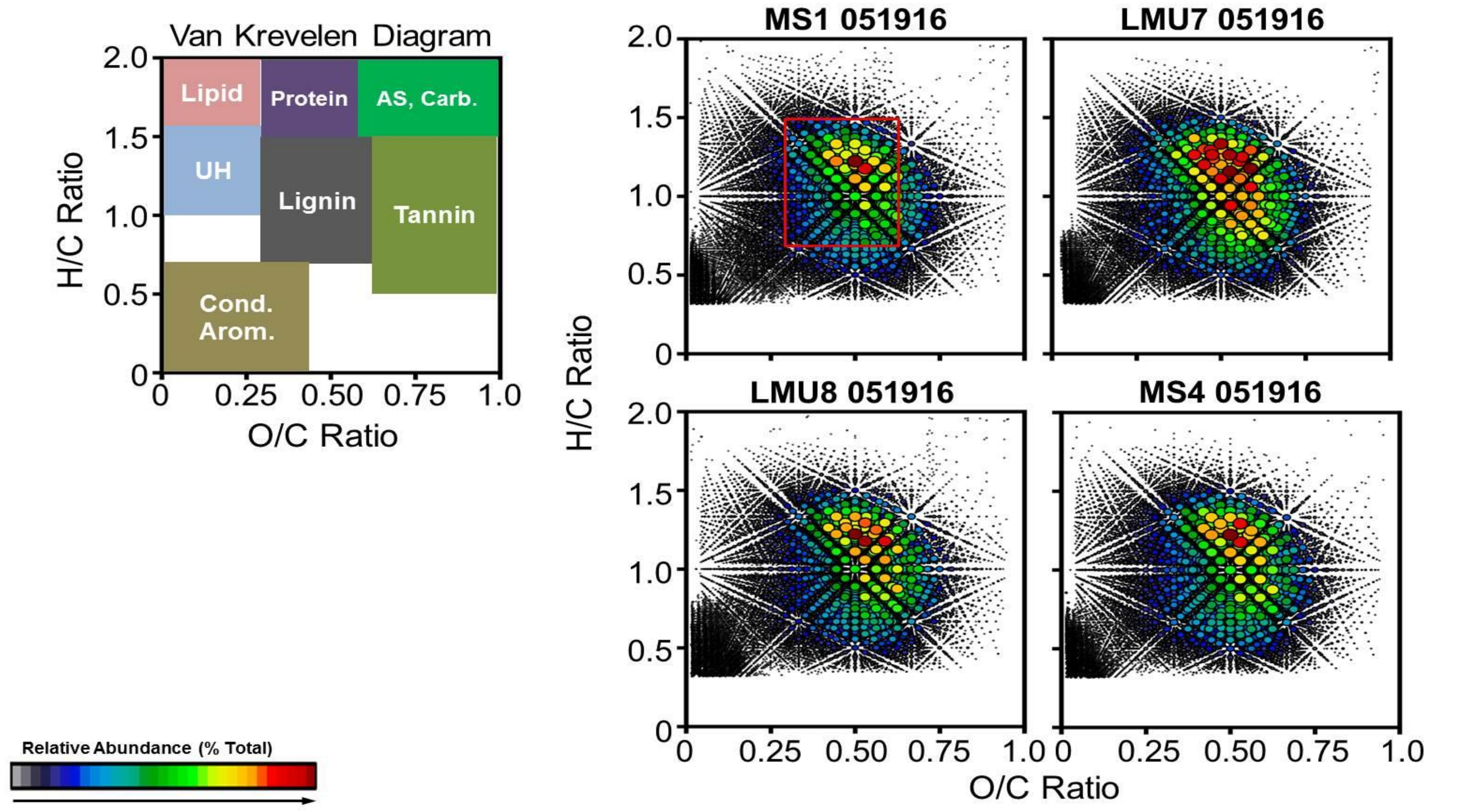

Figure 5. van Krevelen diagrams derived from elemental compositions identified by FT-ICR mass spectral characterization of MS1 (input), LMU7 and LMU8 (In-lake) and MS4 (output) collected in May 2016. Elemental compositions categorize into compound groups based on H/C and O/C ration, and include lipid-like, protein-like, aminosugar and carbohydrate-like (AS, carb.), unsaturated hydrocarbon (UH), condensed aromatic, lignin-like and tannin-like compounds. [8,9] The most abundant compounds in all samples correlate to lignin-like compounds, structural biopolymers unique to vascular plants, that serve as biomarkers of plant-derived DOM. Microbial activity can change DOM composition through preferential mineralization of labile compounds, alteration of existing compounds or assimilation into microbial biomass. Lignin, for example, is one compound enriched as other compounds degrade, and can only be degraded aerobically. Therefore, for the Munson basin, naturally a peatland marsh, this indicates that lignin and tannin-like compounds dominate DOM across all sampling sites.

Future Work

Future studies will correlate bulk water chemistry parameters (e.g. chlorophyll, turbidity, pH, water clarity) with compositional changes that occur in Lake Munson and its tributaries through December 2017. In addition, biology will be correlated to chemical properties to characterize at heavy metal gene distribution among bacteria in Lake Munson.

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Acknowledgements

Work supported by (NSF DMR-1157490), the State of Florida, and the BP/Gulf of Mexico Research Initiative. The authors would like to thank John P. Quinn, Greg T. Blakney for their continued assistance in instrumental maintenance, Yuri E. Corilo for data processing and imaging software, and Huan Chen.