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Molecular and structural characterization of dissolved organic matter during and post cyanobacterial bloom in Taihu by combination of NMR spectroscopy and FTICR mass spectrometry

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ABSTRACT

Seasonal molecular changes in dissolved organic matter (DOM) isolated from Tai Lake (Taihu) both during (June) and following (November) an algal bloom event in 2007 were characterized by nuclear magnetic resonance spectroscopy (NMR) and Fourier transform ion cyclotron resonance (FTICR) mass spectrometry. Considerable biosignatures were present in summer DOM, yet with a near absence of algal extract compounds. Extensive molecular alteration resulting from multistep and massively parallel biotic and subordinated abiotic transformations of algal biomass to DOM included loss and synthesis of carbohydrates, fundamental changes of aromatic compounds and progressive formation of carboxyl-rich alicyclic compounds (CRAM). The DOM transformation from summer to fall resulted in smaller molecules, increased abundance of CHNO continuous molecular series and overall molecular diversity. Analysis of MS-derived compositional networks placed summer DOM in-between the algal extract and fall DOM. Metabolic pathway annotation by means of high-resolution mass analysis provided a wide range of pathways associated with secondary metabolites in DOM and more basic ones like carbohydrate metabolism characteristic of algal extract compounds. Overall, the time-dependent molecular signature of Taihu DOM was likely dominated by microbial metabolism rather than abiotic chemical transformations. Results from this study indicate that high-resolution organic structural spectroscopy resolves meaningful structural detail out of complex environmental mixtures and has the potential to contribute significantly to future functional biodiversity studies.

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1. Introduction

Aquatic dissolved organic matter (DOM), the environmentally most significant sub-fraction of natural OM (NOM), ranges among the most heterogeneous mixtures on earth and is likely composed of millions of organic compounds (Hertkorn et al., 2008; Koch et al., 2005). Both concentration and composition of DOM result from a complex interplay of abiotic (e.g. redox and photochemistry) and biotic (e.g. photosynthesis, heterotrophic microbial metabolism) reactions (Kujawinski et al., 2004, 2009; Minor et al., 2007). NOM connects the living and non-living world from nano- to continental scales (Battin et al., 2009; Hedges and Oades, 1997; Hertkorn et al., 2007; Opsahl et al., 1999) and plays a key role in the transfer of energy and organic molecules in aquatic environments. Most heterotrophic microorganisms in aquatic systems use DOM as a key source of energy and micronutrients (Amon and Benner, 1996a,b; Hertkorn et al., 2002a), implying a close link between biodiversity of organisms and biogeochemical processes.

Algal blooms in fresh and marine waters are environmentally significant events worldwide. While seasonal blooms are prominent features of many ecosystems and provide an important source of energy to upper trophic levels, they also have the potential to impair key ecological functions and services, including freshwater supply, fisheries, and flood mitigation when production exceeds system capacity (i.e. eutrophication) or when blooms are dominated by toxic or harmful species (Duan et al., 2009). Such events can be considered population breakouts, often with a few dominating species (Jester et al., 2009; Michaloudi et al., 2009), and genuine algal and successive food web metabolites are expected to affect DOM composition and concentration (Xing and Kong, 2007; Gao et al., 2007; McCarthy et al., 2007; Lehman et al., 2010). Algal blooms therefore offer the opportunity to follow real ecosystem DOM dynamics and the

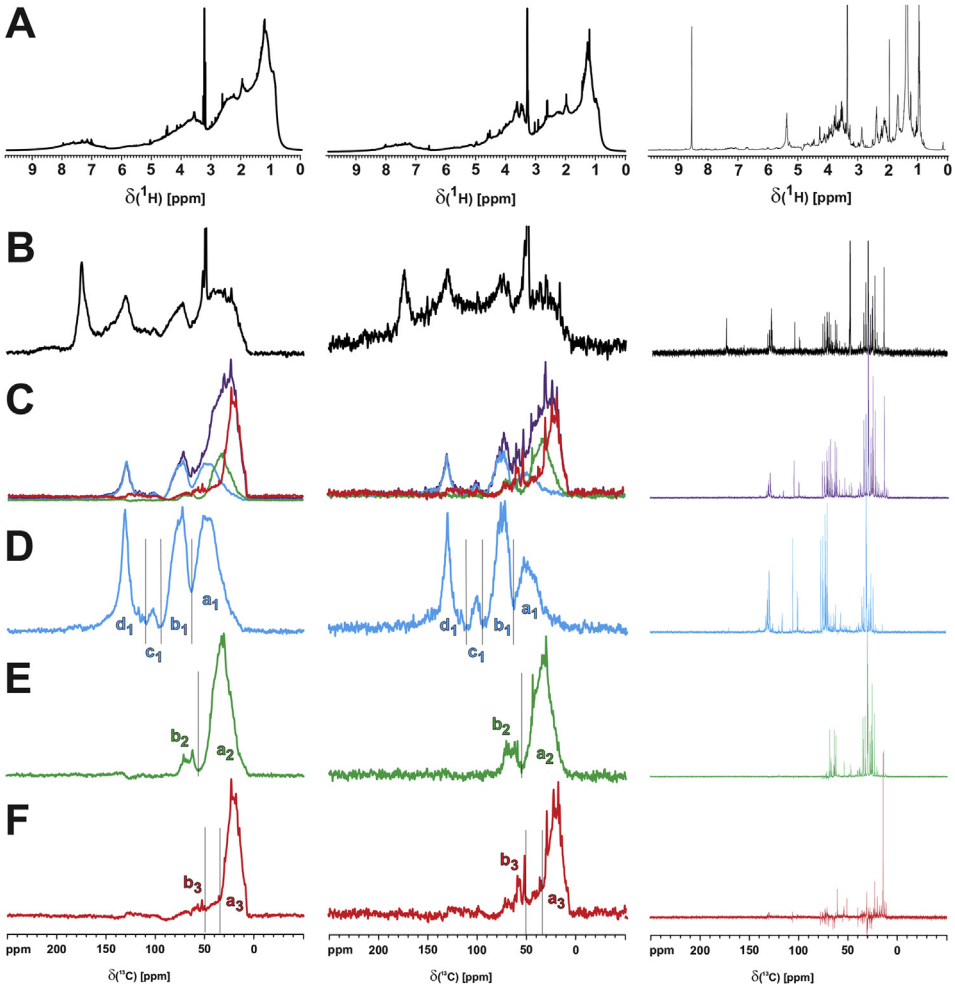

Fig. 1 – (A) ^{1}H NMR spectra; (B) ^{13}C NMR spectra of non-bloom DOM (November; left column), bloom DOM (June; middle column) and direct extract of algal dry matter extract (right column); (C) superimposed protonated carbon NMR resonances (CH_{123}; DEPT-45 ^{13}C NMR spectra) together with proportionately scaled individual carbon multiplicity traces; (D, E, F) multiplicity-edited ^{13}C NMR spectra are indicated in blue (CH; methine), green (CH_2; methylene) and red (CH_3; methyl). Indices denote certain chemical environments of protonated carbon described in the text. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)