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Dynamics of dissolved organic matter: A view from two dimensional correlation spectroscopy techniques

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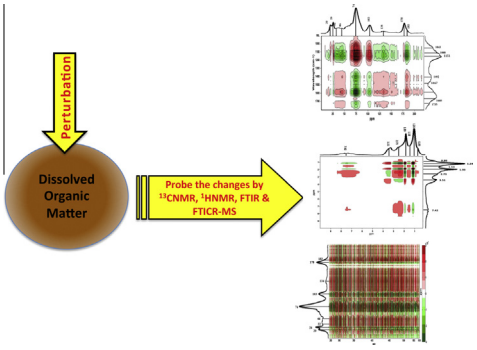
HIGHLIGHTS

- Using two dimensional correlation spectroscopy analysis (2D correlations) to study the dynamic of DOM.
- Using the multi probes 2D correlations techniques gives more insight on the dynamics of DOM.
- Six different compounds classes of DOM identified along salinity transect.

GRAPHICAL ABSTRACT



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ABSTRACT

Dissolved organic matter (DOM) is the most reactive organic carbon pool in earth. However, the heterogeneity of this organic mixture makes it difficult to investigate its dynamics under different external perturbations. In this review, we present the potential of using the two dimensional correlation spectroscopy analysis (2D correlations) as a tool to study the dynamic of DOM. We demonstrate the application of the 2D correlation analysis on high molecular weight DOM (HMW-DOM) with the salinity as perturbation parameter. We used four different chemical probes: Carbon nuclear magnetic resonance spectroscopy (^{13}C NMR), Fourier transform infrared spectroscopy (FTIR), proton nuclear magnetic resonance spectroscopy (^{1}H NMR) and Fourier transform ion cyclotron resonance mass spectrometry (FTICR-MS).

Introduction

Dissolved organic matter (DOM) is a dynamic mixture of natural organic compounds found in all types of natural waters. DOM plays many important ecological and environmental roles; these include acting as a short-term sink of atmospheric CO_2 [1], a bacterial food source [2], and as a reactant and absorbent of man-made pollutants [3]. Characterizing the chemical codes that have been imprinted in DOM pool by different biogeochemical processes is the key to understanding the dynamics of one of the largest organic matter reservoirs in the global carbon cycle. Unfortunately,

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little is known about its chemical composition due to the chemical complexity of DOM, the low concentration of DOM and the high concentration of co-dissolved inorganic species in many natural waters.

In the last three decades, the use of state-of-the-art instrumentation have made substantial breakthroughs in our understanding of the chemical composition of DOM; for example use of solid-state nuclear magnetic resonance spectroscopy with cross polarization magic angle spinning (CP/MAS ^{13}CNMR) have provided for measuring the relative distribution of the major chemical functional groups of DOM, and shows that marine DOM has higher polysaccharides and lower aromatic contents compared with terrestrial DOM [4]. Analyzing marine DOM by proton nuclear magnetic resonance spectroscopy (^{1}H NMR) has revealed that acetylated polysaccharides like N-acetyl aminosugars accounts for a major fraction of marine DOM [5,6]. Fourier transform infrared spectroscopy (FTIR) provides spectral information that allows us to deconvolute the relative distributions of amide, ester and carboxyl functional groups in DOM [3,7]. Chemical characterization of DOM by Direct temperature-mass spectrometry (DT-MS) shows that marine DOM is characterized by highly branched and cross-linked polysaccharides including a large fraction of N-acetyl and deoxy-aminosugars [8], which is verified by two-dimensional proton nuclear magnetic resonance correlation spectroscopy (^{1}H COSY) and heteronuclear single-quantum correlation spectroscopy (^{1}H–^{13}C HSQC) analysis [9]. Characterization of DOM by Fourier transform ion cyclotron resonance mass spectrometry (FTICR-MS) significantly enhances our knowledge about the chemical heterogeneity of the thousands of organic compounds within the DOM pool [10]. Hertkorn et al. [11] integrated the data from (FTICR-MS, ^{13}C NMR and ^{1}H NMR) to speculate about the presence of carboxyl-rich alicyclic molecules (CRAM) in marine DOM.

Although, with all these remarkable efforts in DOM characterization, the ultimate goal of understanding the dynamics of DOM as it changes when subjected to external perturbations is far from being achieved. For example, attempts to measure the lability of DOM under different biogeochemical processes is a challenge because of the extreme heterogeneous nature of DOM and the difficulty of extracting subtle chemical compositional changes from the large DOM chemical background. One of the chemometric techniques that shows great potential for highlighting subtle changes in a complex mixture under specific external perturbations is the two dimensional correlation spectroscopy techniques (2D correlation spectroscopy). From the time that Noda [12] introduced this approach, it has been applied widely to understand the chemical behavior of different chemical mixtures exposed to wide varieties of perturbations.

In this overview and integration, we demonstrate the potential of using 2D correlation to investigate the dynamics of DOM, by summarizing and drawing together in an integrative fashion the recent studies [13–15] that applied 2D correlation techniques to highlight the changes in high molecular weight DOM (HMW-DOM) isolated along a salinity transect ($n = 24$ samples) using four different spectroscopic probes. These studies employed (1) Solid-state nuclear magnetic resonance spectroscopy with cross polarization magic angle spinning (CP/MAS ^{13}C NMR), (2) Fourier transform infrared spectroscopy (FTIR), (3) proton nuclear magnetic resonance spectroscopy (^{1}H NMR) and (4) Fourier transform ion cyclotron resonance mass spectrometry (FTICR-MS). In this paper we will focus mainly on how 2D correlation allows us classify different chemical components of DOM based on their biogeochemical reactivity and how hetero-spectral 2D correlations between different spectroscopic probes along the same perturbation (salinity) complements the power of each spectroscopic probe and overcomes the limitations of using a single spectroscopic probe. While previous studies used the 2D correlations to one or two spectral probes, the attempt is made here to integrate across all spectral probes.

Solid-state nuclear magnetic resonance spectroscopy (^{13}C NMR)

Applying the 2D correlation technique on the 24 reduced-noise and normalized ^{13}C NMR spectra with salinity as the perturbation (as described in details in Abdulla et al. [13]) generates two types of maps (synchronous and asynchronous). Along the diagonal line of the synchronous map (Fig. 1), eight major ^{13}C NMR bands show the following significant changes along the salinity transect: two bands in the paraffinic carbon region (^1CH_n and ^2CH_n at 0–29 ppm and 29–40 ppm, respectively), one band in the methoxy and amino group region (^1CH_n—O at 40–55 ppm), a major band in the middle of the O-alkyl region (HC—OH at 62–90 ppm), the anomeric carbon band of polysaccharides (O—C—O at 90–115 ppm), a broad aromatic band (C=C/Ar at 115–140 ppm), the oxygen-substituted aromatic carbon band (Ar—O at 140–160 ppm), and a band at the higher chemical shift side of the carboxylic acid, ester and amide region (COO/CON; centered at 183 ppm).

Based on the off-diagonal peaks correlation (cross peaks) in the synchronous map, these eight major ^{13}C NMR bands are classified into two types of chemical components that have a different biogeochemical reactivity along the salinity transect. The first component contains the first paraffin carbon region (^1CH_n at 0–29 ppm), the O-alkyl region band (HC—OH at 62–90 ppm) and the anomeric carbons band (O—C—O at 90–115 ppm). All these bands of the first component show negative correlations (green color cross peaks) with the other five ^{13}C NMR bands: the second paraffinic carbon band (^2CH_n at 29–40 ppm), the methoxy and amino group band (^1CH_n—O at 40–55 ppm), the two aromatics bands (C=C/Ar and Ar—O at 115–140 ppm and 140–160 ppm, respectively) and the carboxylic acid, ester and amide band (COO/CON; centered at 183 ppm). Taking a closer look at the synchronous map (Fig. 1)

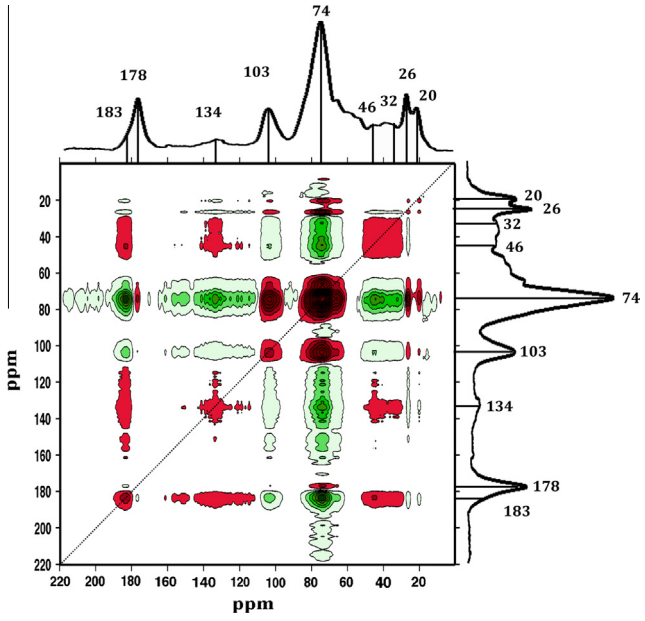

Fig. 1. The generated synchronous contour map from all the ^{13}C NMR ($n = 24$) of HMW-DOM spectra, the top and the right side are the average ^{13}C NMR spectra (included as reference). Red represents positive correlations and green represents negative correlations; higher color intensity indicates a stronger positive or negative correlation. (Reprinted with permission from Ref. No. 13. Copyright (2010) American Chemical Society). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)