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Molecular diversity of riverine alkaline-extractable sediment organic matter and its linkages with spectral indicators and molecular size distributions

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ABSTRACT

Few studies have been conducted to examine the spatial heterogeneity of riverine sediment organic matter (SOM) at the molecular level. The present study explored the chemical and molecular heterogeneity of alkaline-extractable SOM from riverine sediments via multiple analytical tools including molecular composition, absorption and fluorescence spectra, and molecular size distributions. The riverine SOM revealed complex and diverse characteristics, exhibiting a great number of non-redundant formulas and high spatial variations. The molecular diversity was more pronounced for the sediments affected by a higher degree of anthropogenic activities. Unlike the cases of aquatic dissolved organic matter, highly-unsaturated structures with oxygen (HUSO) of SOM were more associated with the spectral and size features of humic-like (or terrestrial) substances than aromatic molecules were, cautioning the interpretation of the SOM molecules responsible for apparent indicators. Noting that a higher detection rate (DR) produces fewer common molecules, the common molecules of 23 different SOMs were determined at a reasonable DR value of 0.35, which accounted for a small portion (5.8%) of all detected molecules. They were mainly CHO compounds (>98%), which positively correlated with spectral indicators of biological production. Despite the low abundance, however, the ratios of aromatic to aliphatic substances could be indexed to classify the common molecules into several geochemical molecular groups with different degrees of the associations with the apparent spectral and size indicators.

1. Introduction

Sediment organic matter (SOM) is not only an important reservoir of particulate organic carbon in aquatic environments (Hedges and Keil, 1995), but it also operates as dynamic sources of organic matter to the bottom/overlying water (Komada et al., 2002). In riverine ecosystems, dissolved organic matter (DOM) tends to become aged SOM sources upon abiotic and biotic transformations during its transport from upstream to downstream (Benner et al., 2004; Raymond and Bauer, 2001). SOM can be mobile through sorption/desorption (Perez et al., 2011) and easily transformed upon further photochemical dissolution and oxidation (Schiebel et al., 2014; Porcal et al., 2013; Simon et al., 2002). Moreover, riverine SOM likely remains exposed to direct (e.g., organic matter discharge from different land use) and indirect anthropogenic activities (e.g., algae bloom caused by eutrophication) (Wilson and Xenopoulos, 2009). Given the aforementioned situations, it is possible to hypothesize that molecular diversity of riverine SOM is highly site-dependent.

Due to the capability of resolving thousands of individual molecules with varying elemental compositions (Stenson et al., 2002), ultra-high resolution Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR-MS) has been employed to examine the molecular diversity of the DOM from aquatic environments such as overlying water (Kellerman et al., 2014, 2015), deep water (Dittmar and Koch, 2006), pore water (Riedel et al., 2013; Schmidt et al., 2009), and glacier-melting water (Spencer et al., 2014; Singer et al., 2012). With the aid of FT-ICR-MS, the sources (Spencer et al., 2014), the degradation behaviors (Ward et al., 2013; Tfaily et al., 2013), the microbial alternation (Osterholz et al., 2015), and the photo-induced transformations of DOM (Rossel et al., 2013; Chen et al., 2014) have been successfully examined at the

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molecular level. By contrast, the molecular diversity of particulate organic matter (POM) or solid phase SOM has received much less attention (Schmidt et al., 2014). Furthermore, previous studies considered only water-soluble fraction of SOM, which accounted for a small portion of organic composition in sediments when compared with the alkaline-extractable fraction of sediments (Kuwatsuka et al., 1992; Hur et al., 2014). Exploring molecular diversity of solid phase SOM via the FT-ICR-MS analyses of alkaline-extractable organic matter (AEOM) could thus provide a better insight into the similarities and differences between POM and DOM, as well as the sources of sediments. Based on previous literature, chemical composition at the molecular level is closely associated with many spectral indicators including carbon specific ultraviolet absorbance ($SUVA_{254}$), fluorescent indices, and fluorescence excitation emission matrix (EEM) parallel factor components (PARAFAC), and also with the size distributions (Kellerman et al., 2015; Singer et al., 2012; Stubbins et al., 2014). However, it is questionable but as yet unexplored whether or not many relationships previously reported for aquatic DOM are still applicable to riverine SOM pool.

In order to answer such fundamental questions and to test the hypothesis above, we collected riverine SOM samples (or AEOM of sediments) from many locations affected by different land cover and different degrees of anthropogenic activities, and determined FT-ICR-MS, absorption and fluorescence spectra, and size exclusion chromatography (SEC) coupled with organic carbon detector (SEC-OCD). The objectives of this study were (1) to explore the heterogeneous molecular composition of riverine SOM through FT-ICR-MS, spectroscopic features, and size distributions, and (2) to identify the linkages of the molecular composition with spectral indicators and molecular sizes.

2. Materials and methods

2.1. Sample collection and treatment

Fifty five sediments were initially collected from different rivers and streams distributed in four major watersheds of South Korea (including the Han River, Nakdong River, Geum River, and Yeongsan River Watersheds), and twenty three of them were used for this study based on comprehensive consideration for the spectral indicators, geographic distribution, and anthropogenic activities (He et al., 2016a). To test the spatial heterogeneity of SOM, some samples were replicated at the same locations (e.g., GP3 & GP4, HJ1 & HJ2, DY1 & DY2). The geographical information concerning the samples is summarized in Supporting Information (SI) (Tables S1–S2 and Fig. S1). The sampling information is provided in a previous study (Chen et al., 2015) and briefly in SI Text S1. The extraction and cleanup methods of SOM are fully described in SI Text S1 (Hur et al., 2014; Osburn et al., 2012). In brief, dried sediments were soaked in 0.1 N NaOH solution, shaken for 24 h before centrifugation and filtration using a pre-washed 0.45 μm pore-sized membrane and passed through cation exchange resin. The purified SOM solution (or AEOM) was freeze-dried and stored in desiccator until solid phase extraction (SPE) followed by FT-ICR-MS analysis. A portion of the eluate was freeze-dried and re-dissolved using ultrapure water prior to the measurements of dissolved organic carbon (DOC), ultraviolet–visible absorption spectra (UV–Vis), fluorescence EEM, and SEC-OCD.

2.2. Spectral indicators and SEC-OCD analyses

DOC was determined by a Shimadzu V-CPH TOC analyzer with a relative precision of <3% (Yang and Hur, 2014). The pH of the purified SOM was adjusted to ~3 prior to UV–Vis and EEM determinations. The absorption spectra (200–800 nm) were scanned by a Shimadzu UV-1300 spectrometer with 1-cm cuvette. $SUVA_{254}$ was calculated as 100-fold ratios of absorbance at 254 nm to DOC concentration, and spectral slope ratio (S_R) was estimated based on the spectral slope over 275–295 nm relative to 350–400 nm (Chen et al., 2015; Yang et al., 2014).

EEM spectra were scanned at the excitation/emission wavelengths of 220–500/280–550 nm with excitation at a 5-nm step and emission at a 0.5-nm step using a luminescence spectrometer (Perkin Elmer LS55). According to an inter-laboratory standard method, EEM data were corrected for water blank and inner filter effect using automatical Matlab code, namely, FDOMcorrect.m (Murphy et al., 2010). Humification index (HIX) and biological index (BIX) were calculated, respectively, as a ratio of the areas under the emission spectra over 435–480 nm to 300–345 nm with an excitation wavelength of 255 nm and a ratio of the fluorescence intensity at the emission wavelength of 380 nm–430 nm with an excitation wavelength of 310 nm (Zsolnay et al., 1999; Huguet et al., 2009). PARAFAC modelling was performed with the EEM data set for the AEOM of the original 55 sediments using Matlab toolbox, namely, DOMFluor (Stedmon and Bro, 2008). According to core consistency diagnostic (Table S3), three PARAFAC components were finally extracted for the present study (Fig. S2). One protein-like component (C1) and two humic-like components (C2 and C3) were quantitatively identified using a self-edited Matlab (He and Hur, 2015). Further details on the procedure are described in Text S2 and Table S3.

SEC-OCD results provided the quantities of five different size fractions from a bulk SOM sample, which include biopolymers (BP), humic substances (HS), building blocks (BB), low molecular-weight acids (LMWA), and low molecular-weight neutrals (LMWN) in the order of larger to smaller sizes (Huber et al., 2011). Aromaticity (ARM) and molecular weight (MW) of HS were also estimated by both UV and OCD detectors of the SEC system. The experimental setup for SEC-OCD and additional information on the five size fractions are provided in Text S3 (Huber et al., 2011).

2.3. FT-ICR-MS analysis

SPE was performed following a recommended process (Dittmar et al., 2008), and a previously optimized method was adopted for the FT-ICR-MS analyses of this study (Bae et al., 2011; Koch et al., 2007; Chen et al., 2016). Detailed descriptions of the extraction and the FT-ICR-MS determination are given in Text S4. Briefly, the freeze-dried AEOM samples were re-dissolved, filtered, and adjusted to pH ~2 before they were placed on top of a styrene-divinylbenzene (Agilent Bond Elut PPL) solid phase extraction (SPE) cartridge, which were previously washed with ultrapure water and sequent HCl-acidified ultrapure water. The samples were passed through the conditioned PPL-SPE. After removing salts and drying the PPL-SPE cartridge, methanol was added to elute the PPL-extracted SOM (PPL-SOM). The same sample procedure was applied to ultrapure water blanks to check for potential contamination. All the samples and blanks were stored at −20 °C until FT-ICR-MS determination.

The PPL-SOM, after dilution with methanol: ultrapure water at a ratio of 1:1 (v/v) and filtered, was measured using a 15-T FT-ICR-MS interfaced with an Apollo II electrospray ionization source in negative mode (EST, Bruker Daltonik, Germany). The details of the instrument condition are described in Text S4. To achieve a mass accuracy of <0.03 ppm, external calibrations were made with arginine clusters and Suwannee River fulvic acid (SRFA). Solvent blanks were run between samples to avoid cross-contamination. Procedural blanks were also performed to exclude the background molecules. The peaks with signal to noise ratios (S/N) > 4