

The Supporting Information is available free of charge at
<https://pubs.acs.org/doi/xxx>

Detailed description of materials and methods including sample preparation and data processing, and gradient elution conditions for the LC-MS analysis (Table S1); peak assignment for Figure 1b (Table S2); elemental compositions calculated by the result from the FT-ICR measurement (Table S3); relative abundances for the O_x class compounds of the LC fractions SW II, SW III, and SW IV (Figure S1); in-cell CID fragmentation spectrum of the precursor ion at *m/z* 267.0544 (C₉H₁₅O₇S⁻, top) and the precursor ion at *m/z* 281.0701 (C₁₀H₁₇O₇S⁻, bottom), with the proposed molecular structure and annotation of fragment ions (Figure S2) (PDF)

Supporting Information

Online Liquid Chromatography and FT-ICR MS Enables Advanced Separation and Profiling of Organosulfates in Dissolved Organic Matter

*Yulin Qi^{1,2}, Chao Ma¹, Shuang Chen¹, Jinfeng Ge¹, Qiaozhuan Hu¹, Si-Liang Li¹,
Dietrich A. Volmer³, Pingqing Fu^{1,2,*}*

¹ Institute of Surface-Earth System Science, School of Earth System Science, Tianjin University, Tianjin 300072, China

² Tianjin Key Laboratory of Earth Critical Zone Science and Sustainable Development in Bohai Rim, Tianjin University, Tianjin 300072, China

³ Department of Chemistry, Humboldt-Universität zu Berlin, Berlin 12489, Germany

*Corresponding author: Pingqing Fu (fupingqing@tju.edu.cn)

Materials and Methods

Sample Preparation

The surface water (SW) sample was collected from the mainstream of the Yongding River, China, and dissolved NOM was collected using the solid-phase extraction (SPE) protocol described by Dittmar et al.^[1] Briefly, Agilent Bond Elut PPL (1 g) cartridges were conditioned with methanol followed by ultrapure water (pH 2). Roughly 1 L of sample was loaded onto the cartridge followed by another rinse with ultrapure water (pH 2). The cartridges were then dried under a stream of N₂ gas followed by elution of NOM in 10 mL of methanol and stored at −20 °C until further analysis.

The rainwater (RW) sample was collected from urban areas of Shanghai. Rainwater was filtered through pre-combusted glass fibre filters (Whatman GFF), then extracted using Waters Oasis HLB (500 mg) cartridges on a Visiprep SPE Vacuum Manifold (Supelco Analytical, USA). The cartridges were preconditioned with methanol and Millipore Q water. The samples were percolated through the cartridges via PTFE tubes. The cartridges were then washed with 5 mL Millipore Q water and dried under a stream of N₂ gas for 1 h, followed by elution of NOM in 6 mL of methanol and stored at −20 °C until further analysis.

HPLC-grade methanol, acetonitrile and ACS-reagent-grade formic acid were purchased from Sigma-Aldrich. For direct-infusion (DI) MS measurement, samples were dissolved in a water/ acetonitrile (50/50, v/v) mixture at a concentration of 50 DI-MS and 200 ppm for LC-MS, respectively.

Data Processing

The acquired datasets were analyzed using a combination of DataAnalysis 5.0 (Bruker) and Composer 1.5.6 (Sierra Analytics) software. The full scan mass spectra were internally calibrated using a series of homologous compounds throughout the m/z range. Elemental formulae were assigned to the peaks inside the calibrated m/z range,

and only peaks with S/N >6 were extracted for DOM formula assignment with the following tolerances: composition was restricted to ^{12}C (1-50), ^1H (1-100), ^{16}O (0-30), ^{32}S (0-2), ^{14}N (0-3) and ^{31}P (0-1); double bond equivalence (DBE) up to 30; $0.3 \leq \text{H/C} \leq 2.5$, $\text{O/C} \leq 1.2$ and $\text{N/C} \leq 0.5$; $-10 \leq \text{DBE-O} \leq 10$; the acceptable mass error was set to ± 0.5 ppm for singly-charged ions.^[2,3] False positive molecular formulas introduced by procedural blanks were excluded from the final mass list.

Table S1. Gradient elution conditions for the LC-MS analysis of the DOM samples

Retention (min)	Flow (ml/min)	A% (H₂O)	B% (ACN)
0	0.1	95	5
5	0.1	95	5
11	0.1	10	90
25	0.1	10	90
28	0.1	95	5
30	0.1	95	5

Table S2. Peak assignment for Figure 1b (right).

No.	Compound	Exp. m/z	Calc. m/z	ppm Error
1	$C_{15}H_{10}O_{11}$	365.01501	365.01504	0.07
2	$C_{19}H_{10}O_8$	365.03028	365.03029	0.03
3	$C_{16}H_{14}O_{10}$	365.05146	365.05142	-0.11
4	$C_{15}H_{14}N_2O_9$	365.06268	365.06265	-0.07
5	$C_{20}H_{14}O_7$	365.06672	365.06668	-0.12
6	$C_{17}H_{18}O_9$	365.08783	365.08781	-0.07
7	$C_{16}H_{18}N_2O_8$	365.09906	365.09904	-0.06
8	$C_{21}H_{18}O_6$	365.10305	365.10306	0.03
9	$C_{18}H_{22}O_8$	365.12421	365.12419	-0.05
10	$C_{17}H_{22}N_2O_7$	365.13541	365.13543	0.04
11	$C_{19}H_{26}O_7$	365.16060	365.16058	-0.06
12	$C_{20}H_{30}O_6$	365.19694	365.19696	0.06
13	$C_{21}H_{34}O_5$	365.23332	365.23335	0.08
14	$C_{15}H_{10}O_7S_2$	364.97934	364.97952	0.49
15	$C_{15}H_{10}O_9S$	364.99726	364.99728	0.04
16	$C_{14}H_{10}N_2O_8S$	365.00849	365.00851	0.05
17	$C_{12}H_{14}O_{11}S$	365.01840	365.01841	0.02
18	$C_{16}H_{14}O_8S$	365.03362	365.03366	0.12
19	$C_{13}H_{18}O_8S_2$	365.03698	365.03703	0.14
20	$C_{15}H_{14}N_2O_7S$	365.04488	365.04490	0.04
21	$C_{13}H_{18}O_{10}S$	365.05479	365.05479	0.00
22	$C_{17}H_{18}O_7S$	365.07001	365.07005	0.10
23	$C_{14}H_{22}O_7S_2$	365.07347	365.07342	-0.14
24	$C_{13}H_{22}N_2O_6S_2$	365.08458	365.08465	0.19
25	$C_{14}H_{22}O_9S$	365.09117	365.09118	0.02
26	$C_{18}H_{22}O_6S$	365.10638	365.10643	0.15
27	$C_{15}H_{26}O_8S$	365.12754	365.12756	0.06
28	$C_{19}H_{26}O_5S$	365.14280	365.14282	0.05
29	$C_{16}H_{30}O_7S$	365.16392	365.16395	0.08
30	$C_{17}H_{34}O_6S$	365.20034	365.20033	-0.02
31	$C_{18}H_{38}O_5S$	365.23672	365.23672	0.00

Table S3. Elemental compositions calculated by the result from the FT-ICR measurement. The values are weight averaged based on peak magnitude.

	C%	O%	S%	N%
DI	57.89	32.76	1.64	1.51
SW2	57.19	34.87	0.46	1.45
SW3	53.39	32.75	6.74	1.32
SW4	62.55	28.89	1.02	0.71

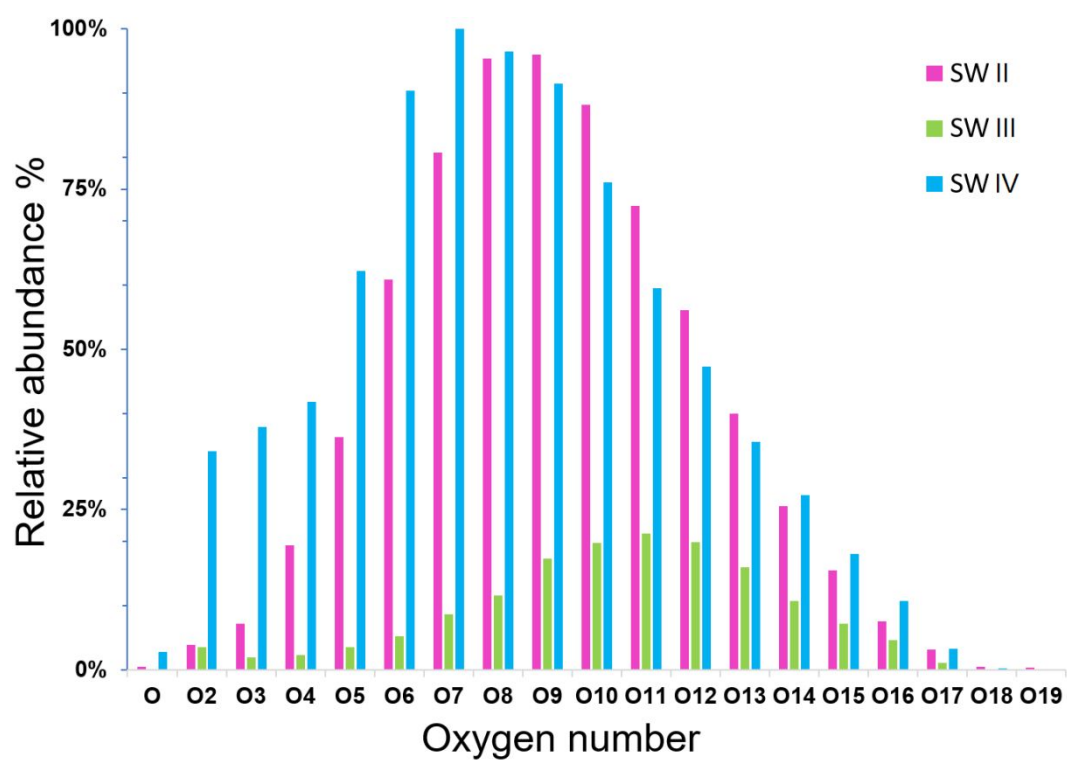


Figure S1. Relative abundances for the Ox class compounds of the LC fractions SW II, SW III, and SW IV

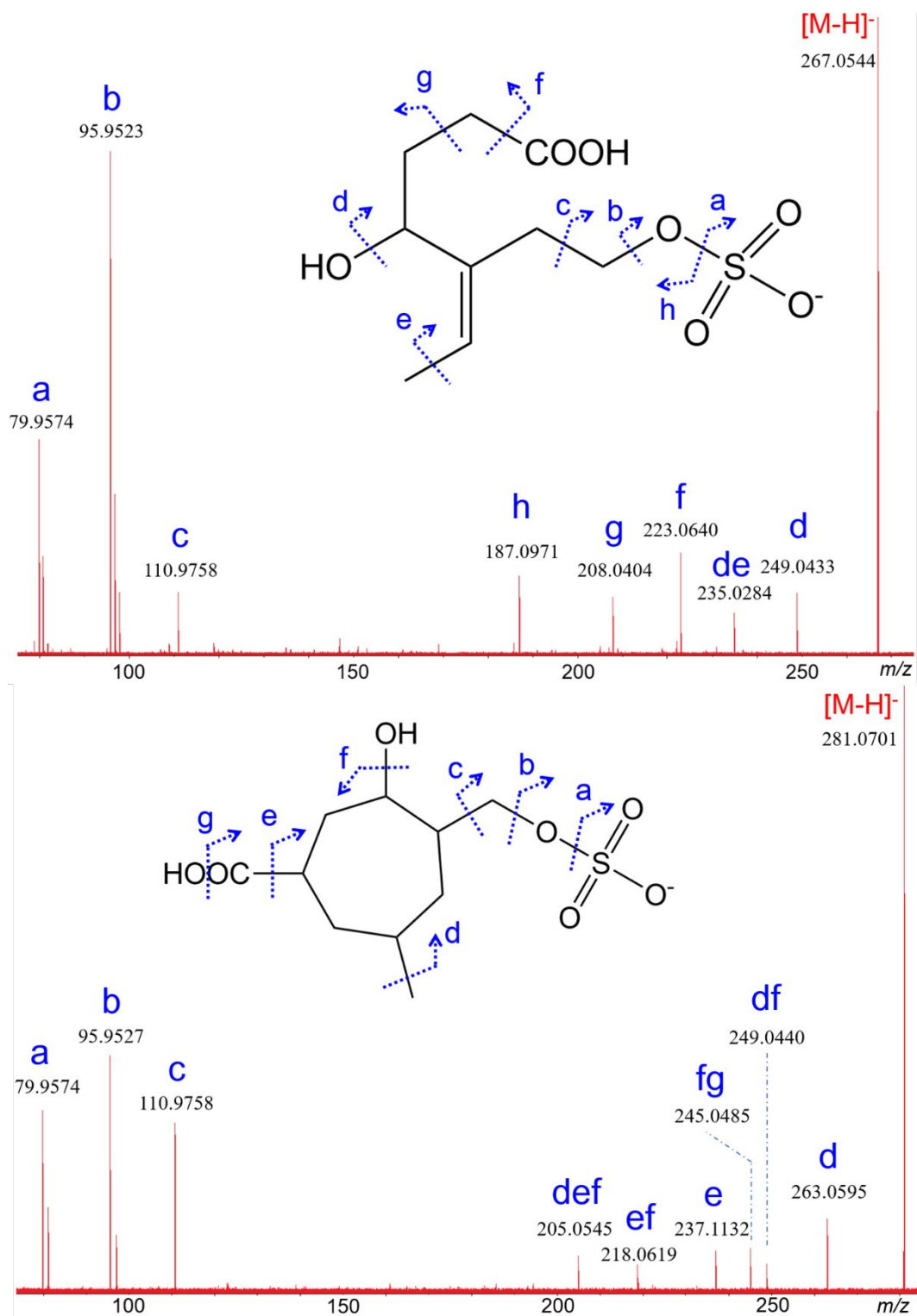


Figure S2. In-cell CID fragmentation spectrum of the precursor ion at m/z 267.0544 ($C_9H_{15}O_7S^-$, top) and the precursor ion at m/z 281.0701 ($C_{10}H_{17}O_7S^-$, bottom), with the proposed molecular structure and annotation of fragment ions.

References

- (1) Dittmar, T.; Koch, B.; Hertkorn, N.; Kattner, G. A Simple and Efficient Method for the Solid-Phase Extraction of Dissolved Organic Matter (SPE-DOM) from Seawater. *Limnol. Oceanogr. Methods* **2008**, 6 (6), 230–235.
- (2) Koch, B. P.; Dittmar, T.; Witt, M.; Kattner, G. Fundamentals of Molecular Formula Assignment to Ultrahigh Resolution Mass Data of Natural Organic Matter. *Anal. Chem.* **2007**, 79 (4), 1758–1763.
- (3) Herzprung, P.; Hertkorn, N.; von Tümpeling, W.; Harir, M.; Friese, K.; Schmitt-Kopplin, P. Understanding Molecular Formula Assignment of Fourier Transform Ion Cyclotron Resonance Mass Spectrometry Data of Natural Organic Matter from a Chemical Point of View. *Anal. Bioanal. Chem.* **2014**, 406 (30), 7977–7987.