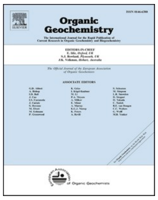
Organic Geochemistry 196 (2024) 104846

Contents lists available at ScienceDirect

Organic Geochemistry

journal homepage: www.elsevier.com/locate/orggeochem



Comparison of dissolved organic matter composition from various sorbents using ultra-high resolution mass spectrometry

Oriane M. Yvin [a,*], Martin R. Kurek [a,*], Amy M. McKenna [b,c], Jon R. Hawkings [d], Robert G.M. Spencer [a]

[a] National High Magnetic Field Laboratory Geochemistry Group and Department of Earth, Ocean and Atmospheric Science, Florida State University, Tallahassee, FL 32306, United States
[b] National High Magnetic Field Laboratory Ion Cyclotron Resonance User Facility, Tallahassee, FL 32310, United States
[c] Department of Soil and Crop Sciences, Colorado State University, Fort Collins, CO, United States
[d] Department of Earth & Environmental Science, University of Pennsylvania, Philadelphia, PA, United States

ARTICLE INFO

Guest editor: Hussain Abdulla; guest associate editor: Jeffrey Hawkes

Keywords:
Sorbent
SPE
DOC
pH
FT-ICR MS

ABSTRACT

Solid phase extraction (SPE) of a variety of diverse dissolved organic matter (DOM) endmembers through eight commercially available sorbents was examined (ENV, PLEXA, PPL, HLB, Isolute 101, C18/ENV+, C18, EnvirElut) representing styrene divinylbenzene polymer (SDVB) and silica-based sorbents. We assessed dissolved organic carbon (DOC) recovery and DOM composition via 21T Fourier transform-ion cyclotron resonance mass spectrometry (FT-ICR MS). DOC recoveries and SPE-DOM composition differed more by endmember type than by sorbent. Silica-based sorbents retained DOM with many N-containing formulae, while SDVB-based sorbents retained DOM with more S-containing formulae. Extraction pH exerted a greater influence on DOM composition, notably through the presence of strong groupings composed of saturated and lowly oxygenated formulae at basic pH, and of aromatic and highly oxygenated formulae at pH 2, irrespective of endmember or sorbent. There was above 25% DOC recovery, regardless of sorbent or endmember; >90% of the relative abundance (RA) of molecular formulae were shared with PPL, which is currently the most commonly utilized sorbent for DOM. This clearly highlights the ability of the selected sorbents to retain representative DOM across diverse endmembers. Such findings may be useful for future targeted DOM studies (e.g., bioincubations, wastewater and drinking water applications) interested in focusing on specific compositional changes and will provide a better understanding of how organic carbon cycling is impacted by anthropogenic processes.

1. Introduction

Dissolved organic matter (DOM) is composed of a complex mixture of organic molecules with around 50% carbon content and heteroatoms such as oxygen, nitrogen, phosphorus, and sulfur, covering a wide range of molecular weights, structures, and physiochemical properties (Hertkorn et al., 2007; Perdue and Ritchie, 2003; Raeke et al., 2016; Li et al., 2017). DOM is both a reactant and a product of biogeochemical processes; it is considered an important carbon and energy source for biota, and impacts water quality parameters such as dissolved oxygen, acidity, concentration of nitrogen, phosphorus, sulfur and numerous trace metals (Leenheer and Croué, 2003). The transportation of organic or inorganic contaminants is facilitated through binding with DOM, which can also produce undesirable water disinfection byproducts (Leenheer and Croué, 2003). DOM is one of the largest contributors to the global carbon pool and is actively involved in many key aquatic ecosystem processes such as biodegradation, photodegradation, and complexation with trace elements (Duarte and Duarte, 2015; Goldberg et al., 2015; Lucas et al., 2016; Mann et al., 2016; Osterholz et al., 2016; Li et al., 2017; Kellerman et al., 2018). Due to its relevance in many chemical and biological processes, DOM has become the focal point of studies addressing environmental and water quality issues.

Solid phase extraction (SPE) is commonly used to separate and concentrate DOM, and employs sample-, sorbent-, and solvent-dependent interactions to temporarily retain DOM, which is then eluted into concentrated solutions (Thurman and Malcolm, 1981; Minor

---

[*] Corresponding authors at: National High Magnetic Field Laboratory Geochemistry Group and Department of Earth, Ocean and Atmospheric Science, Florida State University, Tallahassee, FL 32306, United States.

E-mail addresses: oyvin@fsu.edu (O.M. Yvin), mkurek@fsu.edu (M.R. Kurek).

https://doi.org/10.1016/j.orggeochem.2024.104846
Received 27 November 2023; Received in revised form 25 July 2024; Accepted 25 July 2024
Available online 28 July 2024

et al., 2014; Li et al., 2016). In the late 1970s, the macromolecular amberlite XAD resins were the first generation of sorbents used for the isolation of DOM, with high recoveries of natural organic matter from waters (Junk et al., 1974; Aiken, 1985; Lara and Thomas, 1994; Dittmar et al., 2001, 2008). XAD-1 and XAD-2 were the most effective sorbents for the isolation of humic substances from seawater while XAD-2 was the most effective for the isolation of these substances from river water (Aiken et al., 1979; Spencer et al., 2010a, 2010b). More recently, XAD resins were replaced by a newer generation of silica-based sorbents bonded with different hydrocarbon chains, as well as styrene divinylbenzene polymer (SDVB) sorbents, which are stable over a wide pH range and require relatively simple extraction procedures (Dittmar et al., 2006, 2008; Hertkorn et al., 2013; Li et al., 2016). The use of prepackaged Bond Elut PPL cartridges (Agilent Technologies) for DOM extraction has become increasingly popular due to its high recovery across a broad range of aquatic environments and relative ease of use (Dittmar et al., 2008; Perminova et al., 2014). For instance, SPE-PPL for DOM isolation yields up to 89 % dissolved organic carbon (DOC) recovery for terrestrial DOM and 45 % for marine DOM (Dittmar et al., 2008; Minor et al., 2014; Sandron et al., 2015; Li et al., 2016). In addition, PPL retains various compound fractions such as hydrophobic and polar compounds including an abundance of aliphatic compounds and phenols, and has exhibited both appreciable DOM recovery and diverse molecular DOM formulae inherent to specific sources across a range of aquatic environments including rivers, groundwater, lakes, and seawater (Li et al., 2016).

Despite its popularity and utility in isolating DOM, the specific retention properties of PPL target a select DOM composition that may not necessarily represent the entire sample. For instance, DOM contains many non-polar organic compounds which were extracted in various proportions by sorbents that differ in their non-polar retention properties, such as C18, HLB, and ENV resins (Li et al., 2017). Depending on the different mechanisms of these sorbents and the analytical conditions (e.g., pH, sample matrix), SPE efficiency can vary. SDVB and silica-based sorbents for example are widely used but have several limitations such as instability when the aqueous matrix is not circumneutral (Augusto et al., 2013). Another limitation is the aqueous matrix itself that can contain highly polar and high molecular weight compounds. The partition coefficient of these compounds may not necessarily favor the transfer of the targeted compounds to the sorbent bed or irreversible sorption may occur. Thus, a fraction of the DOM molecular composition may remain in the sample due to not absorbing to the sorbent or due to being permanently stuck on the sorbent (Buszewski and Szultka, 2012; Augusto et al., 2013; Andrade-Eiroa et al., 2016). A comparison between SDVB polymer type sorbents, and silica-based sorbents, such as C18, showed that silica-based sorbents were the least efficient of all sorbents for the extraction of marine DOM (Dittmar et al., 2008). ENV resins were employed to generate DOM fractions such as hydrophilic, transphilic, and hydrophobic acids, neutrals, and bases with up to 85% DOC recovery in total for freshwaters (Malcolm and MacCarthy, 1992; Knulst et al., 1998; Croué, 2004; Dittmar et al., 2008; Ratpukdi et al., 2009; Green et al., 2014; Sandron et al., 2015; Li et al., 2016). Thus, it is readily apparent that, depending on the goals of a study, various sorbents may target relevant components of the DOM pool.

Ultra-high resolution mass spectrometry, via electrospray ionization (ESI) is commonly utilized to characterize DOM in complex mixtures with SPE prior to analysis often used as a pre-concentration step. Since various ionization modes produce distinct ions, and sample matrixes are becoming more complex, the choice of a mass detector necessitates its ability to achieve resolving powers across a wide molecular weight range. The use of negative-ion mode ESI (−ESI), targets species of acidic oxygen and neutral nitrogen species, therefore increasing the heteroatom class complexity (Smith et al., 2018). The currently highest available resolution mass analyzer in the world is Fourier transform-ion cyclotron mass spectrometry (FT-ICR MS), and since resolving power, dynamic range, and sensitivity all improve with magnetic field (Bahureksa et al., 2022), we leveraged the high resolving power ($m/\Delta m_{50\ \%} > 2{,}000{,}000$ at m/z 400), and high mass accuracy of 21T FT-ICR MS, which resolves peaks < 1 mDa apart (Hendrickson et al., 2015; Smith et al., 2018) to assess isolated DOM composition (Koch et al., 2007; Lam et al., 2007; Hertkorn et al., 2008; Li et al., 2016; Kurek et al., 2020). Compositional analysis of DOM species ionized by −ESI provides insight into ecosystem characteristics and is highly dependent on its origin (Hertkorn et al., 2008; Kruger et al., 2011; Li et al., 2017). The combined approach of −ESI with FT-ICR MS can offer compositional information such as aromaticity, aliphaticity, oxygenation and heteroatom content of DOM isolates.

Therefore, utilizing the ultra-high resolution of 21T FT-ICR MS, a diverse range of DOM samples and SPE sorbents were examined to assess molecular-level composition of DOM, as well as their extraction efficiency quantitatively as DOC recovery. In this study we extracted DOM from six diverse aquatic endmembers using eight different sorbents varying in functional groups (SDVB vs silica) and targeted polarities (non-polar, polar). Furthermore, to address uncertainties regarding pH on molecular-level DOM composition, we investigated the effects of extraction pH (2, native, and 10) on the FT-ICR MS spectra from samples representing a high DOC, terrestrially dominated riverine endmember and a low DOC, microbially dominated groundwater endmember. Finally, we compared all sorbent DOC recoveries and DOM compositions against PPL due to its high utility and widespread use. Overall, this study examines several analytical parameters and their impact on the molecular composition of the DOM pool revealed via 21T FT-ICR MS. Samples encompassing a wide variety of natural DOM sources were used, hence this study provides a benchmark for future studies investigating specific components of the DOM pool, as well as sorbents other than PPL.

2. Materials and methods

2.1. Study sites and sampling

Natural waters across a wide range of DOM compositional endmembers were selected to assess the recoveries and selectivities of different sorbents. Water samples were collected into acid washed polypropylene bottles and filtered through 0.45 μm capsule filters using Nalgene tubing and a peristaltic pump. Filtered samples were kept cold (4 °C) and in the dark during transport and stored at −20 °C prior to SPE. The DOM endmembers encompassed terrestrially dominated aromatic-rich waters to autochthonously dominated sources. This selection captures a wide range of DOM composition, from blackwater rivers such as the Congo River, one of the largest rivers in the world and a major source of DOM to the ocean, permafrost thaw known to contain more saturated DOM (Spencer et al., 2015; Ward and Cory, 2015), coastal and groundwater endmembers, and an anthropogenically impacted urban river.

The six DOM endmembers utilized in this study included a clear groundwater site (groundwater) dominated by microbially sourced DOM (Luzius et al., 2018), which was sampled at Sally Ward Spring, Florida, USA (30.2416°N, 84.3108°W) and two aromatic-rich DOM sites, the Ochlocknee River, a blackwater river (blackwater-1) which was sampled near Havana, Florida, USA (30.5857°N, 84.3592°W; Textor et al., 2018), and the Congo River (blackwater-2), which was sampled at a site upstream of the cities of Kinshasa-Brazzaville on the mainstem of the Congo, and downstream of the Malebo Pool (04.1815°S, 15.2058°E; Spencer et al., 2016). Coastal marine water (coastal) was sampled from the Florida State University Coastal & Marine Laboratory, located at St. Teresa, Florida, USA (29.9317°N, 84.4567°W). An anthropogenically impacted river (urban river), the Schuylkill River, was sampled near Philadelphia, USA (39.95189°N, 75.18109°W; Albert, 1988). Finally, a permafrost thaw water stream sample (permafrost) was collected from the Duvannyi Yar exposure near the Northeast Science Station in Cherskiy, Russia (68.6305°N, 159.1501°E; Stubbins et al., 2017).

2.2. DOC analysis

After acidification (HCl, pH 2), filtered samples were analyzed for DOC concentration using a Shimadzu TOC-L CPH high temperature catalytic oxidation total organic analyzer, and the non-purgeable organic carbon method was employed to eliminate dissolved inorganic carbon. Following established methodology, a five-point calibration curve was used to determine the DOC concentration of each sample which was calculated as the mean of three injections (Spencer et al., 2009; Mann et al., 2012, 2014; Kurek et al., 2022).

2.3. Solid phase extraction

All six DOM samples (groundwater, blackwater-1, blackwater-2, coastal, urban river, permafrost) were adjusted to pH 2 (HCl) before SPE extraction. Additionally, groundwater and blackwater-1 samples were extracted at their native pH and at pH 10 (NaOH) to study the effects of extraction pH on DOC recovery and DOM composition. Eight commercially available sorbents were studied, ENV, PLEXA, PPL, HLB, Isolute 101 as styrene divinylbenzene polymer (SDVB) sorbents, C18/ENV+ as an SDVB and silica-based sorbent and C18 and EnvirElut as silica-based sorbents (Table S1). All sorbents were prepacked by the manufacturer.

The extraction process adhered to the same technique used in PPL extractions (Dittmar et al., 2008; Minor et al., 2014; Li et al., 2016; Raeke et al., 2016; Kurek et al., 2020), in order to guarantee consistency across the various sorbents and comparability to PPL. The extraction procedure was as follows: The sorbents contained in the columns were prepared by soaking them overnight in methanol, then rinsing them once with methanol, twice with Milli-Q water, rinsing once with methanol again, and lastly rinsing twice with acidified Milli-Q (HCl, pH 2). During the extraction of native pH samples, Milli-Q was used in place of acidified Milli-Q. In basic extractions, Milli-Q at pH 10 was prepared with the use of NaOH. Approximately 100 μg organic C was isolated onto the sorbents, which is considerably below the limit employed by Dittmar et al., (2008) (2 mmol DOC/g of sorbent) and dried with ultrapure N_2. Before analysis, DOM from each sorbent was eluted with 1 mL of methanol, into precombusted glass vials (550 °C, ≥ 4h) before being stored at −20 °C. Using methanol to prepare the sorbents, blanks for each sorbent were obtained by extracting Milli-Q water using the same amount of sample and eluted with 1 mL of methanol. Methanol was used as it is a protic solvent and enables the deprotonation or protonation to occur on acidic functional groups, thereby resulting in gas-phase anions in negative ion electrospray ionization or gas-phase cations in positive-ion mode. Due to analytical constraints, each sample was prepared with a single extraction. Although we recognize the potential variability within replicate extractions, we posit that the variability between end-members of this study is greater than the analytical variability between replicates (e.g., Dittmar et al., 2008).

2.4. DOC recovery

To calculate the DOC recovery for each sample, 300 μL of methanol eluent was collected into precombusted glass vials (550 °C, ≥ 4h) and stored at −20 °C prior to analysis. The methanol contained in the glass vials was evaporated for each sample, by using a drying oven overnight (55 °C). The remaining residue was redissolved in 15 mL of acidified Milli-Q (pH 2) and shaken for several hours before DOC analysis. DOC recovery was calculated by dividing the sum of DOC concentrations in the methanol extract (adjusted for dilutions) and permeate (volume of sample that passed through the SPE sorbent), to the concentration in the original sample.

2.5. FT-ICR MS

Methanolic extracts were analyzed on a custom-built hybrid linear ion trap FT-ICR MS equipped with a 21T superconducting solenoid magnet at the National High Magnetic Field Laboratory (Tallahassee, FL). The sample solution was infused via a microelectrospray source at 500 nL/min using a syringe pump. The parameters for the formation of negative ions were as follows, emitting voltage was −2.70 to −3.09 kV, S-lens RF (45%), and the heated metal capillary temperature was 350 °C (Emmett et al., 1998). The mass spectra were obtained with time-domain transients of 3.1 s using the Predator data station that handled excitation and detection only, initiated by a TTL trigger from the commercial Thermo data station, with 100 time domain acquisitions conditionally co-added (averaged) for all experiments (Blakney et al., 2011). Mass spectra were phase-corrected with absorption mode data processing (Xian et al., 2010) and internally calibrated based on the “walking” calibration method (Savory et al., 2011) of several highly abundant O-containing Kendrick series. Elemental composition assignment and data visualization were performed with PetroOrg© software constrained by $C_{4-45}H_{4-150}O_{1-30}N_{0-4}S_{0-2}P_{0\text{-}1}$ and did not exceed 0.2 ppm error. Calibrated mass spectra typically resulted in 12,000–23,000 assigned species with an average RMS error of 70 ppb. All FT-ICR MS raw and processed data are publicly available via the Open Science Framework (https://osf.io/awy27/). Given the large range of extraction pH and sorbent material, sodiated adducts ($C_{4-45}H_{4-150}O_{1-30}Na_{0\text{-}1}$) were also considered for assignment (Koch et al., 2005).

2.6. Data analysis and statistical methods

The assigned formulae obtained via FT-ICR MS were post-processed and data visualized using Microsoft Excel and R using the ggplot2 and eulerr packages. The FT-ICR MS data at pH 2, pH native, and pH 10 were preprocessed to remove high abundance peaks from blank spectra in each sorbent, prior to analysis. According to Koch and Dittmar, (2006; 2016) the double bond equivalence (DBE and DBE/C) and the modified aromaticity index (AI_{mod}) were calculated. The nominal oxidation state of carbon (NOSC; LaRowe and Van Cappellen, 2011) were calculated as means of all molecular formulae in a singular DOM sample. For each molecular formula, the O/C, H/C, N/C, and S/C ratios were determined and calculated as the sum of all corresponding atoms divided by the sum of all C atoms. By averaging all molecular formulae ratios (intensity weighted averages) in the DOM samples, the average formulaic O/C, H/C, N/C, and S/C were determined for all DOM samples, based on previous calculations. Molecular formulae were assigned to heteroatom groups (CHO, CHON, CHOS, CHONS, CHOP) and separated into compound classes (condensed aromatics, polyphenolic, highly unsaturated low O/C, highly unsaturated high O/C, and aliphatic; Šantl-Temkiv et al., 2013). Unless stated otherwise, all mean FT-ICR MS parameters were calculated using intensity weighted averages and any sodiated adducts were eliminated from the final processed formulae lists in each sample. Isotopologues (e.g., ^{13}C), were included in molecular formulae assignments but not considered during the calculation of FT-ICR MS parameters and analysis. Principal Component Analysis (PCA) was conducted on the FT-ICR MS data to assess the relationships between sample types, sorbents, and extraction pH using the factoextra package in R (Kassambara and Mundt, 2020).

3. Results and Discussion

3.1. SPE DOC recovery

DOC recovery was determined on six different water types using eight commercially available sorbents that were separated into SDVB- and silica-based sorbents. As described earlier, the use of PPL has become somewhat the de facto standard method for the isolation of aqueous DOM due to its favorable carbon recovery in terrestrial and marine environments (Dittmar et al., 2008; Minor et al., 2014; Sandron et al., 2015; Li et al., 2017) and was thus used as a reference point in this study. Within the PPL isolates, the coastal sample had the lowest DOC recovery (26%) and blackwater-1 and blackwater-2 yielded over 80%

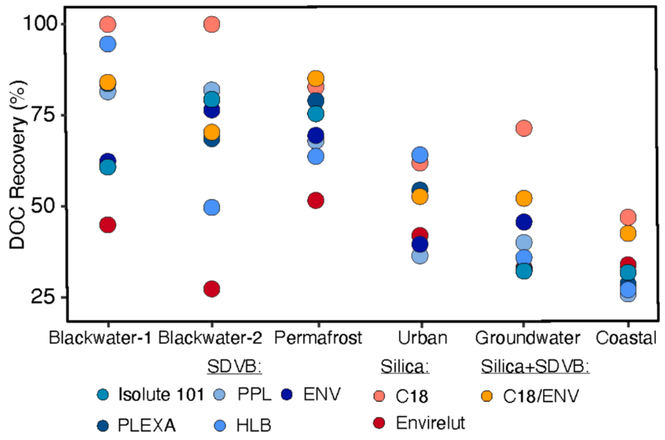


Fig. 1. Scatterplot representing DOC recoveries (%) of DOM extracts obtained with eight commercially available columns.

recoveries (Fig. 1; Table 1). When considering the other sorbents, the most consistent differences were between sample type. The blackwater rivers and permafrost leachate recovered more DOC on average than the groundwater, coastal, and urban river DOM samples, regardless of sorbent (Fig. 1; Table S2).

Aromaticity metrics derived from FT-ICR MS analysis of SPE extracts have been related to bulk optical aromaticity (Kellerman et al., 2018), suggesting that the extractable DOM from the endmembers can represent the aromaticity of the DOM sample. Given that the blackwater rivers may have contained more extractable aromatic DOM than the other endmembers (Table 1; Table S2) this suggests that extraction efficiency increases with aromaticity and is more efficient for DOM originating from terrestrial sources across the studied sorbents. This is consistent with previous measurements of specific UV absorbance at 254 nm ($SUVA_{254}$) of the blackwater rivers (blackwater-1: 4.4 L mg $C^{-1}m^{-1}$; blackwater-2: 3.26 L mg $C^{-1}m^{-1}$; Spencer et al., 2010b; Textor et al., 2018) compared to groundwater (0.99 L mg $C^{-1}m^{-1}$; Kurek et al., 2020) and marine sources (0.6–1.8 L mg $C^{-1}m^{-1}$; Kellerman et al., 2018).

Comparing DOC recovery between sorbents, C18 with its non-polar characteristics had the highest yield for all sorbents (blackwater-1, blackwater-2: 100%; permafrost: 83%; urban river: 62%; groundwater: 71%; coastal: 47%; Fig. 1; Table S2). High extraction efficiencies were observed for blackwater-1 and the urban river with the HLB sorbent (blackwater-1: 95%; urban river: 64%; Table S2). DOM from the groundwater, coastal and permafrost samples were relatively less aromatic, more aliphatic, and were extracted in highest efficiency by the C18/ENV sorbent (groundwater: 52%; coastal: 43%; permafrost: 85%; Table S2). There were no consistent differences in DOC yield between SDVB and silica-based sorbents.

DOC recoveries of blackwater samples showed larger ranges and therefore a wider distribution between samples, while DOC recoveries of the urban river, groundwater and coastal samples had less variance (Fig. 1; Table 1). Extraction of DOM from terrestrial samples were surprisingly low using the EnvirElut sorbent, which has a non-polar retention mechanism. It has been demonstrated that SPE sorbents preferentially extract certain compound groups (Perminova et al., 2014; Tfaily et al., 2015; Chen et al., 2016; Li et al.,2017), however little is known of the effects of various DOM sources on DOC recovery. According to Chen et al., (2016) sorbent selectivity is source-dependent, with identified compound groups being seemingly source-specific. Aliphatic compounds were more abundant in samples of microbial and algal origin (e.g., permafrost, coastal), while phenolic compounds (tannin and lignin-like) were more abundant in terrestrial samples (e.g., blackwater rivers).

DOC recovery results of the sampled endmembers were variable,

Table 1
DOC concentrations, DOC recoveries, and mean FT-ICR MS parameters for the blackwater-1, blackwater-2, permafrost leachate, urban river, groundwater, and coastal samples extracted through PPL columns at pH 2. CHO, CHON, CHOS, CHONS, and CHOP are all reported as percent relative abundances (%RA). Compound classes (CA: Condensed Aromatics; PPh: Polyphenolics; HU low O/C: highly unsaturated and phenolic low O/C; HU high O/C: highly unsaturated and phenolic high O/C; Ali: Aliphatics) are all reported as percent relative abundances (%RA). Standard deviations of replicate DOC recoveries were typically ± 6%.

Sample	DOC (mg/L)	DOC Recovery (%)	CHO	CHON	CHOS	CHONS	CHOP	CA	PPh	HU (low O/C)	HU (high O/C)	Ali	Formulae	Mass	H/C	O/C	N/C ($x10^3$)	S/C ($x10^3$)	AI_{mod}	NOSC
Blackwater-1	7.8	82	81.0	14.5	4.3	0.2	0.0	2.2	14.7	33.3	45.3	4.5	11,730	523.1641	1.08	0.52	10.5	2.3	0.33	0.00
Blackwater-2	6.5	82	78.1	18.1	3.6	0.1	0.0	2.0	17.9	25.7	52.3	2.1	12,227	586.0408	1.01	0.55	10.7	1.7	0.36	0.12
Permafrost	98.7	68	69.4	21.3	7.8	1.4	0.0	0.5	5.2	28.1	59.0	7.3	13,831	532.7774	1.19	0.54	14.8	4.9	0.24	−0.05
Urban	3.5	36	62.9	17.7	18.0	1.4	0.0	0.7	7.9	45.6	35.2	10.7	11,212	532.3907	1.19	0.47	12.4	9.7	0.27	−0.19
Groundwater	0.5	40	75.4	14.8	8.1	1.7	0.1	1.5	9.9	45.5	38.6	4.5	15,786	501.8230	1.13	0.48	11.6	5.0	0.31	−0.13
Coastal	3.4	26	73.5	16.8	9.0	0.8	0.0	2.6	7.9	42.7	40.5	6.3	8,965	537.8324	1.17	0.49	12.0	4.3	0.28	−0.14

depending on the chemical and the physical properties of these sorbents (Table S1), such as adsorption of specific molecular groups. Differences in pore sizes and sorbent mass should also be considered with respect to differences in DOC recovery results (Denis et al., 2017). The silica-based sorbents, C18 and EnvirElut have a higher bedload (200 mg C, 500 mg C, Table S1) than the SDVB sorbent, HLB (60 mg C, Table S1), making methanol elution more complicated due to potential solvent retention in the sorbent. Dittmar et al., (2008) demonstrated that pore size affects DOC recovery, with the smaller pore sizes found in the C18 sorbent (60 Å, Table S1) retaining smaller molecules than PPL (150 Å, Table S1) or ENV (450 Å, Table S1). In addition, a single extraction procedure was conducted for all sorbents, which deviates from some of the manufacturer's recommendations (2–10 bed volumes of solvent), with differing sizes and volume of head space between sorbents. Sorbent extractions were carried out following the PPL extraction from Dittmar et al., (2008) in order to obtain a comparison point with the most commonly used sorbent.

3.2. *Sorbent impacts on DOM composition*

The DOM composition of different endmembers was variable, and highly dependent on watershed landcover and source (Wagner et al., 2015; Melendez-Perez et al., 2016; Lechleitner et al., 2017; Kellerman et al., 2018; Drake et al., 2019; Zhang et al., 2023). The molecular composition of PPL extracts for the blackwater-1 sample was consistent with that observed previously in terrestrially dominated aromatic-rich waters (Textor et al., 2018) and was comprised of 81% CHO, 14.5% CHON, 4.3% CHOS, and 0.2% CHONS by relative abundance (RA; Table 1). This sample contained the most polyphenolic compounds (14.7% RA; Table 1) as well as condensed aromatics (2.2% RA; Table 1). The blackwater-2 sample was mainly composed of CHO and CHON-containing formulae (Table 1). The blackwater-2 sample had a H/C ratio of 1.01 with a modified aromaticity index of 0.36, highly comparable to past studies on terrestrially dominated river samples (Textor et al., 2018; Kurek et al., 2022; Table 1). Both these rivers are allochthonous, with molecular formulae containing high O/C ratios, low H/C ratios, and high aromaticity, characteristic of terrestrial inputs from plant and soil-derived compounds (Hertkorn et al., 2006, 2008; Koch and Dittmar, 2006; Sleighter and Hatcher, 2007; D'Andrilli et al., 2010; Wagner et al., 2015).

Low O/C and high H/C ratios with decreasing aromaticity can indicate autochthonous sourcing, with more aliphatic formulae (Stenson et al., 2003; Koch and Dittmar, 2006; Sleighter and Hatcher, 2007, 2008; Wagner et al., 2015; Powers et al., 2021), such as in groundwater and coastal DOM (Table 1). For both groundwater and coastal DOM, heteroatomic composition was similar. However, differences were observed in aromaticity and in %CHONS. Due to the export of terrestrial DOM to coastal waters (Raymond et al., 2007), aromaticity was higher for the coastal sample than marine DOM (Kellerman et al., 2018; Table 1). The urban river, an anthropogenically impacted endmember, was enriched in S-containing formulae with high H/C ratios, similar to DOM originating from wastewater effluent (Gonsior et al., 2011; Wagner et al., 2015; Table 1) as well as high proportions of N-containing formulae (Table 1). Furthermore, N-containing formulae originating from agricultural runoff is an anthropogenic input shown to influence primary production in aquatic ecosystems (Mattsson et al., 2005, 2009; Wilson and Xenopoulos, 2009; Williams et al., 2010; Wagner et al., 2015). Results obtained for permafrost DOM (Table 1) were consistent with past studies. These previous studies reported low proportions of aromatic carbon, higher average H/C ratios and lower average O/C ratios, compared to other DOM sources (Spencer et al., 2015; Ward and Cory, 2015).

To evaluate the compositional differences between the endmembers and the different SPE sorbents, a PCA was conducted on DOM samples originating from all the aquatic endmembers at pH 2 (silica-based, SDVB, silica and SDVB). PC1 and PC2 explained 59.5% of the variance between the samples using bulk properties derived from the mass spectra (Fig. 2A, B). PC1 had a strong positive correlation with H/C and was most negatively correlated with AI_{mod} and mass; therefore, an indicator of aromaticity and molecular weight (Fig. 2A, B). In contrast PC2 was positively correlated with S-containing heteroatoms (%CHOS, %CHONS), and negatively with %CHOP, %CHON and %CHO, suggesting it describes divergent behavior between P and N- composition versus S-composition (Fig. 2A, B). Samples extracted from different sorbents clustered together based on endmember type, with terrestrial samples, such as the blackwater rivers, clustering together based on aromaticity, molecular weight, and oxygenation (Fig. 2A). In contrast, samples with autochthonous or anthropogenically impacted DOM were positively scored along PC1 with larger differences in heteroatom content within each endmember due to the individual sorbents (Fig. 2A). We did not observe any clear trends between individual sorbents, but instead saw groupings between different sorbent material types (i.e., silica-based vs SDVB based; Fig. 2B).

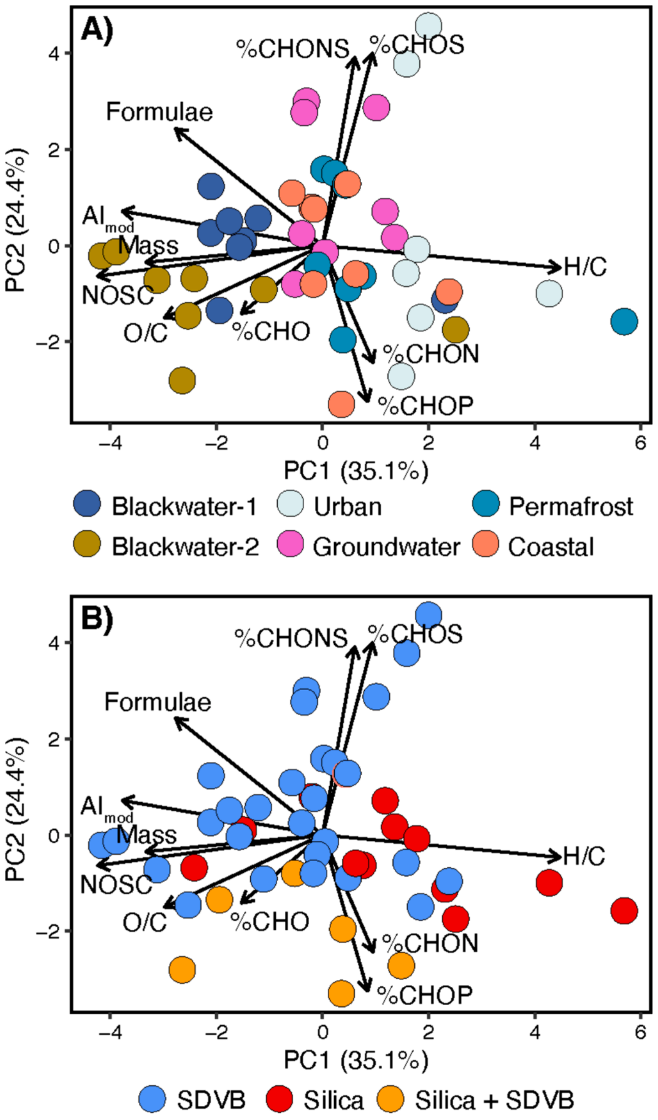


Fig. 2. A) Principal component analysis (PCA) biplot of DOM samples derived from negative ESI FT-ICR mass spectra. Variables from the FT-ICR spectra are represented by black vectors. B) PCA biplot of DOM samples extracted using SDVB columns (blue dots), silica columns (red dots), and silica + SDVB column (orange dots). Variables from the FT-ICR spectra are represented by black vectors. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

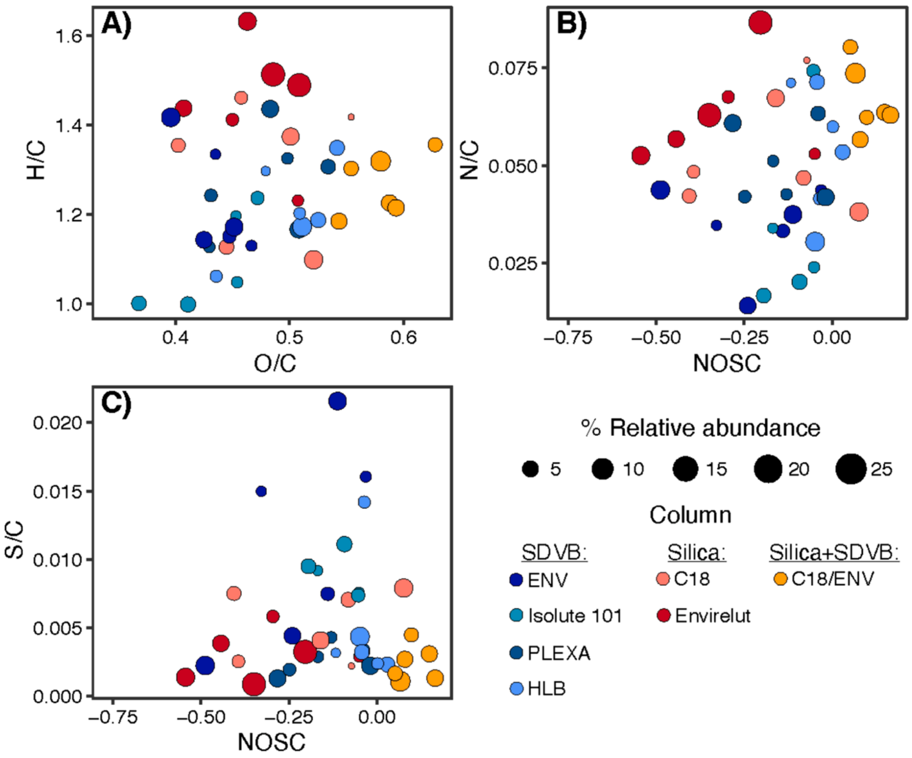


Fig. 3. A) Average H/C and O/C elemental ratios of DOM endmember extracts derived from negative ESI FT-ICR mass spectra. B) Average N/C elemental ratio and NOSC parameter of DOM endmember extracts derived from negative ESI FT-ICR mass spectra. C) Average S/C elemental ratio and NOSC parameter of DOM endmember extracts derived from FT-ICR mass spectra. Bubble size indicates the percent relative abundance of unique formulae in each sample not present in PPL.

SDVB sorbents had a higher affinity for aromatic compounds, as well as formulae with S-bearing DOM, particularly, from autochthonous and anthropogenically impacted samples (Fig. 2B; Fig. S1). Silica-based sorbents retained DOM with greater %RA of aliphatic composition (Fig. 2B; Fig. S1). While the mixed silica and SDVB sorbents had no preference for aromaticity or oxygenation but extracted formulae with greater overall N-content (Fig. 2B; Fig. S1). Strong groupings can be visualized between endmembers, but groupings between sorbent material was also apparent regardless of the differences in DOM composition between endmembers. Raeke et al., (2016) demonstrated that selectivity of compound groups depended on the sorbent material and was related to the molecular composition of the sample. Permeates and size distribution of SPE-DOM extracted using PPL, C18 and HLB in freshwater samples were analyzed using FT-ICR MS and compared to the initial sample. It was demonstrated that the degree of similarity between the original sample and the DOM extracts varied between the sorbents.

3.3. Unique DOM signatures between sorbents

Van Krevelen diagrams of PPL-extracted samples were compared to van Krevelen diagrams of non-PPL extracted samples to observe compositional similarities and differences.

For the blackwater-1 non-PPL extracts, the observed molecular composition is very similar to that of the PPL-extract, differences in composition were observed in the EnvirElut sorbent and the C18/ENV sorbent, which had very little CHOS and CHONS formulae (Fig S2; Table S2). In addition, the EnvirElut sorbent was compositionally distinct due to the presence of highly oxygenated CHOP formulae (Fig S2; Table S2). The blackwater-2 PPL-extract had very few high O/C and H/C formulae (Fig S3). These high O/C and H/C formulae were present in all sorbents, except the Isolute 101 sorbent (Fig S3). The non-polar sorbents C18, EnvirElut and ENV, had few or no CHONS formula around an O/C ratio of 0.50, however almost all the sorbents but Isolute 101, C18 and HLB, had a group of aromatic CHONS of lower O/C ratios (Fig S3). The PPL-extract had no CHOP formulae, however several other sorbents extracted CHOP formulae such as C18/ENV, ENV, PLEXA, and EnvirElut (Fig S3; Table S3).

The permafrost leachate non-PPL extracts are similar to the PPL extract, differences lie in more CHON, high O/C and H/C containing formulae in the other sorbents as well as CHOP containing formulae, in the Envirelut, PLEXA, and C18/ENV sorbent (Fig S4; Table S2). The PPL extract had CHONS containing formulae around an O/C ratio of 0.6, comparable to almost all the sorbents (Fig S4). However, the EnvirElut sorbent had little CHONS (Fig S4; Table S2). In addition, the C18/ENV, PLEXA, and EnvirElut sorbents had a cluster of CHONS of low O/C ratio and of aromatic nature, which was not extracted by the PPL sorbent (Fig S4). The presence of CHOS and CHONS compounds in the urban river PPL extract is apparent, with the ENV sorbent following the same trends (Fig S5). However, the other sorbents had very few CHONS formulae, which is a visible difference with the PPL sorbent (Fig S5; Table S2). The groundwater extracts all had a similar molecular composition (Fig S6; Table S2).

For the coastal DOM, there are many similarities between the various sorbents (Fig S7). Differences with the PPL-extract are notable in CHONS %RA, with few formulae in the Envirelut, PLEXA, C18/ENV, and Isolute 101 sorbents (Fig S7; Table S2). The presence of CHOS and CHONS compounds in the urban river PPL extract is apparent, with the ENV sorbent following the same trends (Fig S7). However, the other sorbents had very few CHONS formulae, which is a visible difference with the PPL sorbent (Fig S7; Table S2).

The DOM extracts of each sorbent were compared to the PPL sorbent by examining the formulae that were unique to each sorbent (i.e., not shared with PPL spectra). The results obtained in Table S3 represent the mean FT-ICR MS parameters unique to these extracts as well as the total %RA shared with PPL. The molecular composition of heteroatom classes (CHO, CHON, CHOS, CHONS, CHOP) were displayed in van Krevelen diagrams (Figs. S8-S13). The %RA unique to the fractions obtained by each sorbent for all endmember samples is relatively low with most of

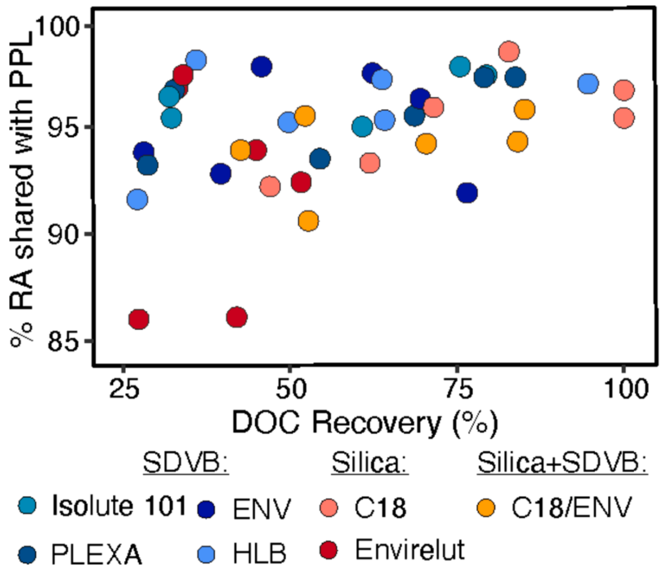


Fig. 4. Percent relative abundance (%RA) of molecular formulae from each sample that are shared with PPL and DOC recovery of aquatic extracts derived from negative ESI FT-ICR mass spectra. DOM extracts are colored according to column type.

the %RA shared between each sorbent and PPL (Table S3). All sorbents extracted relatively similar DOM compositions, although it is noted there were also molecular formulae unique to each individual sorbent (Table S3).

Terrestrial endmembers, blackwater-1 and blackwater-2, spanned a wide range of molecular composition for all sorbents (Fig. S8; Fig. S9). Formulae extracted by both samples had a higher AI_{mod} with values ranging from 0.19 to 0.41 for blackwater-1 extracts and 0.14–0.37 for blackwater-2 extracts (Table S3). Blackwater-1 contained formulae with higher proportions of S-containing DOM, and the blackwater-2 higher proportions of N-containing DOM (Table S3). The permafrost thaw, groundwater, and coastal endmembers had a more homogeneous molecular composition than the terrestrial endmembers and groundwater (Fig S10-S13). Coastal DOM had fewer aliphatic formulae ($H/C \geq 1.5$; Fig. S13; Kellerman et al., 2014), but was more aromatic than the groundwater and urban river samples (Table S3). Across all sorbents, groundwater DOM had a similar molecular signature to coastal DOM (Fig. S12), but with fewer CHONS formulae (Fig.S12). Permafrost thaw had a similar molecular signature to both blackwater samples (Fig. S10), with high N/C ratios and lower aromaticity (Table S3). For the urban river sample, all sorbents had a cluster of low O/C formulae with high S-content at O/C ratios ranging from 0.125 to 0.375 and H/C ratios ranging from 0.55 to 1.25 (Fig. S11), with very few aromatic formulae (Table S3).

The molecular composition of endmember samples was also highly dependent on extraction sorbent. Comparing the unique molecular composition extracted (Fig. 3A) by various sorbent materials for all endmembers, the silica-based sorbent, EnvirElut, primarily extracted aliphatic formulae, depleted in oxygen. SDVB sorbents, HLB, PLEXA, ENV, and the silica sorbent, C18, clustered around similar H/C and O/C ratios, extracting unsaturated formulae, rich in oxygen (Fig. 3A). The exception to the SDVB sorbents was Isolute 101, which primarily extracted low oxygen-containing aromatic formulae (Fig. 3A). The C18/ENV sorbent containing silica and SDVB materials, extracted DOM with H/C ratios similar to the other SDVB sorbents but with formulae highly enriched in oxygen. The C18 and HLB sorbent, popular sorbents used for the extraction of DOM (Dittmar et al., 2008; Li et al., 2016; Raeke et al., 2016), both extracted unsaturated formulae enriched in oxygen, but C18 extracted at higher O/C values (Fig. 3A). N-containing formulae were more abundant for silica-containing sorbents, with higher N/C ratios

Table 2
DOC recoveries and mean FT-ICR MS parameters for blackwater-1 and groundwater samples extracted through PPL columns at acidic, native, and basic pH conditions. CHO, CHON, CHOS, CHONS, and CHOP are all reported as percent relative abundances (%RA). Compound classes (CA: Condensed Aromatics; PPh: Polyphenolics; HU low O/C: highly unsaturated and phenolic low O/C; HU high O/C: highly unsaturated and phenolic high O/C; Ali: Aliphatics) are all reported as percent relative abundances (%RA). Standard deviations of replicate DOC recoveries were typically ± 6%.

Sample	pH	DOC Recovery (%)	CHO	CHON	CHOS	CHONS	CHOP	CA	PPh	HU (low O/C)	HU (high O/C)	Ali	Formulae	Mass	H/C	O/C	N/C $(x10^3)$	S/C $(x10^3)$	AI_{mod}	NOSC
Blackwater-1	2	82	81.0	14.5	4.3	0.2	0.0	2.2	14.7	33.3	45.3	4.5	11,730	523.1641	1.08	0.52	10.5	2.3	0.33	0.00
	7	17	84.4	9.2	6.0	0.3	0.0	0.5	5.3	71.1	7.3	15.8	11,650	510.7830	1.29	0.37	6.6	3.3	0.26	−0.53
	10	10	89.4	3.2	6.5	0.9	0.0	0.1	2.4	42.8	2.1	52.6	5,214	401.1498	1.58	0.23	2.3	5.3	0.16	−1.10
Groundwater	2	40	75.4	14.8	8.1	1.7	0.1	1.5	9.9	45.5	38.6	4.5	15,786	501.8231	1.13	0.48	11.6	5.0	0.31	−0.13
	8	17	80.3	8.5	9.7	1.1	0.4	0.2	2.4	69.9	4.0	23.5	6,355	456.0512	1.36	0.34	6.8	6.8	0.24	−0.65
	10	7	83.3	10.5	4.8	1.4	0.0	0.0	2.6	33.9	0.3	63.1	4,126	374.9641	1.66	0.21	6.8	3.6	0.14	−1.22

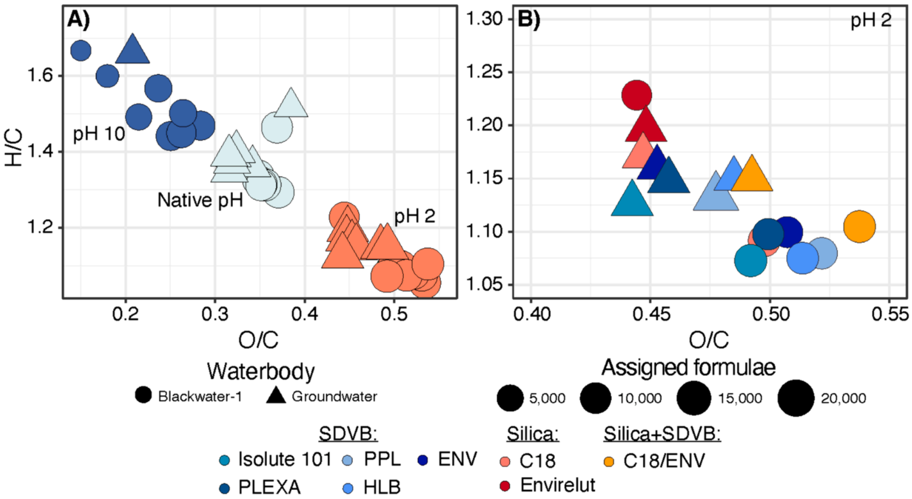


Fig. 5. A) Average H/C and O/C elemental ratios of blackwater-1 and groundwater extracts at various pH (pH 2, pH native, pH 10) derived from negative ESI FT-ICR mass spectra. B) Average H/C and O/C elemental ratios of blackwater-1 and groundwater extracts from various SPE columns derived from negative ESI FT-ICR mass spectra at pH 2. Bubble size indicates the number of assigned formulae obtained by FT-ICR mass spectra.

(Fig. 3B; Table S3), the exception being C18, which clustered around the same N/C values as SDVB sorbents. Roughly, all sorbents converged on the same S/C ratios (ratios varying from a little above 0.0 to 0.0055; Fig. 3C). The Isolute 101 and ENV sorbents extracted formulae at high S/C ratios and are therefore the most appropriate for the extraction of S-containing formulae (Table S3).

3.4. Commonality between PPL and other sorbent DOM

We observed a general increase between DOC recovery and the %RA of molecular formulae in each sample that were shared with PPL (Fig. 4). These molecular formulae represent ions that were found in mass spectra from both PPL and non-PPL extracted samples. The sorbents with the highest shared relative abundance with PPL were C18 and C18/ENV. Although the material of these sorbents varied (silica-based vs SVDB/silica-based), bulk chemical properties and detailed compositional information of the C18, and PPL SPE-DOM spectra were similar. The C18/ENV sorbent extracts fractions specific to C18 and ENV, with the ENV sorbent also having similar extraction properties as PPL. These results agree with previous studies that show molecular fractions extracted by PPL and ENV were highly similar (Dittmar et al., 2008).

Typically, above 25% DOC recovery, >90% of the RA of molecular formulae were shared with PPL across all endmembers, with no consistent differences between sample type or sorbent material (SDVB vs silica, Fig. 4). The 90% shared RA between PPL and other sorbents indicates that they all extract a relatively similar DOM composition, even at lower DOC recoveries. Above 25% DOC recovery these sorbents are therefore highly comparable to PPL with respect to DOM composition (Dittmar et al., 2008; Chen et al., 2016; Raeke et al., 2016), and may be used as an alternative to concentrate and extract specific DOM fractions such as N and S-content molecular groups or aliphatic compounds.

The shared %RA of peaks with PPL describes both the number of shared peaks between two given mass spectra and the total sum of the shared peaks' intensity (i.e., the summed peak height). However, this metric does not account for distribution of peak intensities within each mass spectrum, since a common set of peaks can have vastly different peak intensities between different mass spectra. To assess whether the shared %RA of peaks was a suitable indicator of commonality between samples, we conducted a similar analysis utilizing the intensity of peaks from the mass spectra. Peaks from each sorbent were compared to peaks from PPL for each sample endmember (Figure S14) and a resulting r^2 of each comparison was plotted against the %RA of peaks common with PPL for each sample, as depicted on the y-axis in Fig. 4. A monotonic increase was observed between the r^2 of each PPL-comparison and the shared %RA of peaks with PPL (Figure S15). This suggests that the shared %RA describes both the commonality of sorbents with PPL as well as the intensity distribution of shared ions within each mass spectrum between samples (Figure S15).

3.5. pH effects on SPE

Groundwater and blackwater-1 river samples were extracted at pH 2, native pH, and pH 10 to investigate the effects of extraction pH on DOM composition and SPE efficiency. Overall, increasing extraction pH decreased DOC recovery, heteroatom content, aromaticity, number of assigned formulae, and average oxidation state in the PPL sorbents for both samples (Table 2). This trend was similar across all other SPE sorbents and resulted in a near-linear shift from the bottom right to the upper left in van Krevelen space as pH increased from acidic to basic (Fig. 5A; Table S2). Tfaily et al., (2011), observed that an increase in acidification of DOM from porewaters resulted in a shift towards the extraction of highly oxygenated compounds of high molecular weight (Table 2), which are more aromatic, due to the increase in AI_{mod} with acidification (Han et al., 2022; Table 2). As extraction pH increased, the O/C ratios decreased, and H/C ratios increased proportionally (Fig. 5A). There were strong groupings between sorbents extracted at pH 2, native pH, and pH 10, with sorbent material having secondary influence (Fig. 5A,5B). However, samples extracted for both endmembers using C18/ENV at native pH did not follow this general trend (Fig. S16A). At pH 10, there were groupings between sample type, however, there were also differences between sorbent material (Fig. S16B).

Shared formulae between samples extracted at pH 2 and those extracted at native pH were well over 80% RA for all sorbents (Table S4). There were therefore very few distinctions in molecular composition between these pH values (Table S4). Differences became apparent at basic pH, with shared %RA with samples extracted at pH 2, sharply decreasing as pH increased (Table S4). There were no specific similarities in %RA between sorbents, whether that is in sorbent material or in sorbent retention properties (Table S2). Under acidic conditions the extraction efficiency of organic acids and phenols increases. These compounds being aromatic carboxylic acids, their ionization efficiency increases under acidic conditions in ESI negative mode, therefore increasing the overall aromaticity. In the case of highly saturated compounds such as aliphatic compounds, hydrolysis occurring in acidified samples can strongly decrease the presence of these compounds (Han et al., 2022; Fig. 5A).

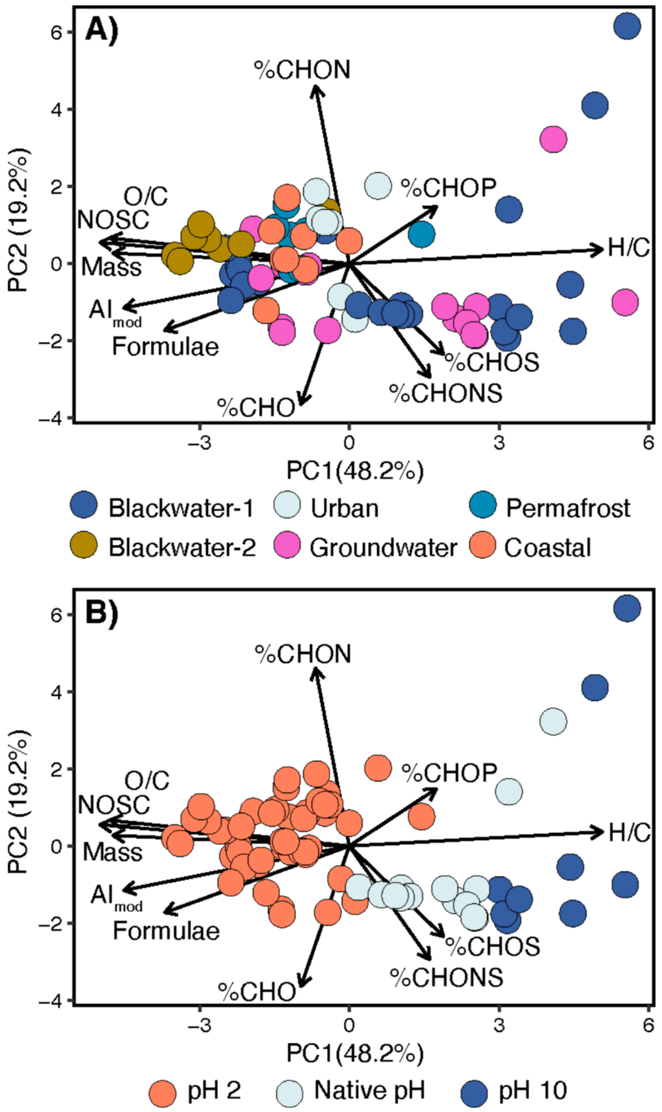


Fig. 6. A) Principal component analysis (PCA) biplot of DOM samples derived from negative ESI FT-ICR mass spectra and colored by waterbody. B) PCA biplot of DOM samples extracted at pH 2 (red dots), native pH (light blue dots), and at pH 10 (dark blue dots). Variables from the FT-ICR mass spectra are represented by black vectors. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

PCA was conducted with all samples from this study to compare the effects of extraction pH in the context of compositionally different DOM endmembers (Fig. 6). PC1 and PC2 together explain 67.4% of the total variance between the samples using bulk properties derived from the FT-ICR MS analysis (Fig. 6A, B). Similar to the vectors in the PCA from Fig. 2, PC1 had strong positive correlations with H/C and was negatively correlated with AI_{mod}, but also had contributions from NOSC and O/C, suggesting it is an indicator of aromaticity and oxygenation (Fig. 6A, B). In contrast PC2 was positively correlated with %CHON and negatively correlated with %CHO, but not strongly with S-content as in Fig. 2, suggesting it is an indicator of N-containing heteroatom content (Fig. 6A, B). Both Fig. 6A and 6B exhibited a large gradient along PC1, with fewer samples spread along PC2, suggesting that the main driver of variance between samples is aromaticity and oxygenation. Allochthonous DOM samples were primarily clustered at PC1 < 0 while autochthonous DOM samples were clustered at PC1 > 0 (Fig. 6A), with tighter groupings than in the PCA of pH 2 extracts (Fig. 2A). The gradient in aromaticity and oxygenation observed in the variable pH PCA is mostly due to extraction pH as it increased along PC1 from 2 to 10 (Fig. 6B). As extraction pH increased there was a greater variability in heteroatom content between different sorbents. At pH 2 there was little variation between samples along PC1 and PC2; however, variability increased at higher pH values where there was greater variation in the %RA of N, S, and P containing formulae (Fig. 6B). There were no consistent differences between sorbents in the context of the various pH extractions, especially at lower pH values (Table S2).

Our study suggests that extraction pH is a strong contributor to FT-ICR MS DOM composition across different endmembers and sorbent types. In the context of all samples (i.e., various aquatic endmembers, extraction pH, sorbent type), extraction pH exerted the greatest influence over the molecular-level composition regardless of DOM source or sorbent material. However, when extractions were performed at pH 2 (as is typical with PPL extractions), sorbent material became the primary influence over DOM composition observed across different aquatic endmembers.

4. Conclusion

This study examined a suite of sorbents across a broad spectrum of DOM sources and highlights that extraction efficiency of DOM is more dependent on the molecular composition of different aquatic endmembers than sorbent type. Extraction efficiency (as indicated by DOC retention on the sorbent) increased with aromaticity, with allochthonous endmembers being more efficiently recovered than autochthonous endmembers, across all SPE sorbents. Above 25% DOC recovery, $> 90\%$ of the RA of molecular formulae were shared with PPL across all endmembers, with no consistent differences between sample type, sorbent, or sorbent material (SDVB vs silica). Additionally, extraction pH influenced DOM molecular composition regardless of DOM sourcing or material. However, at pH 2, sorbent material is clearly the determining factor of DOM composition across all aquatic endmembers. We demonstrated that specific fractions of DOM can be extracted with carefully selected sorbents. For instance, aliphatic molecular formulae were better retained by non-polar sorbents such as EnvirElut. Silica-based functionalized sorbents retained relatively greater N-content than SDVB sorbents and thus appear to be more suitable for the extraction of dissolved organic nitrogen (DON). The specificity of each sorbent may thus be useful in future studies to gain information on compositional changes within the DOM pool including N, S, and P containing formulae.

Credit authorship contribution statement

Oriane M. Yvin: Writing – review & editing, Writing – original draft, Methodology, Formal analysis, Data curation, Conceptualization. **Martin R. Kurek:** Writing – review & editing, Data curation, Conceptualization. **Amy M. McKenna:** Data curation. **Jon R. Hawkings:** Conceptualization. **Robert G.M. Spencer:** Writing – review & editing, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

All FT-ICR MS raw and processed data are publicly available via the Open Science Framework (https://osf.io/awy27/)

Acknowledgements

The conception of the study as well as the selection and collection of the samples was conducted by O.M.Y, M.R.K, J.R.H and R.G.M.S. A.M.K ran the FT-ICR MS analyses, and data processing was conducted by M.R.K. O.M.Y conducted the statistical analyses and wrote the manuscript with comments and suggestions from M.R.K and R.G.M.S. All authors commented on the manuscript. O.M.Y. was partially supported by a Florida Education Fund McKnight Doctoral Fellowship. A portion of this work was performed at the National High Magnetic Field Laboratory Ion Cyclotron Resonance user facility, which is supported by the National Science Foundation Division of Materials Research and the Division of Chemistry through Cooperative Agreement No. DMR-1644779 and the State of Florida.

References

Aiken, G.R. (Ed.), 1985. Humic Substances in Soil, Sediment, and Water: Geochemistry, Isolation, and Characterization. Wiley, New York.

Aiken, G.R., Thurman, E.M., Malcolm, R.L., Walton, H.F., 1979. Comparison of XAD macroporous resins for the concentration of fulvic acid from aqueous solution. Analytical Chemistry 51, 1799–1803.

Albert, R.C., 1988. The historical context of water quality management for the Delaware Estuary. Estuaries 11, 99.

Andrade-Eiroa, A., Canle, M., Leroy-Cancellieri, V., Cerdà, V., 2016. Solid-phase extraction of organic compounds: A critical review (Part I). TrAC Trends in Analytical Chemistry 80, 641–654.

Augusto, F., Hantao, L.W., Mogollón, N.G.S., Braga, S.C.G.N., 2013. New materials and trends in sorbents for solid-phase extraction. TrAC Trends in Analytical Chemistry 43, 14–23.

Kassambara, A., Mundt, F., 2020. Factoextra: Extract and Visualize the Results of Multivariate Data Analyses. R Package Version 1.07.

Bahureksa, W., Borch, T., Young, R.B., Weisbrod, Chad.R., Blakney, G.T., McKenna, A. M., 2022. Improved dynamic range, resolving power, and sensitivity achievable with FT-ICR mass spectrometry at 21 T reveals the hidden complexity of natural organic matter. Analytical Chemistry 94, 11382–11389.

Blakney, G.T., Hendrickson, C.L., Marshall, A.G., 2011. Predator data station: A fast data acquisition system for advanced FT-ICR MS experiments. International Journal of Mass Spectrometry 306, 246–252.

Buszewski, B., Szultka, M., 2012. Past, present, and future of solid phase extraction: A review. Critical Reviews in Analytical Chemistry 42, 198–213.

Chen, M., Kim, S., Park, J.-E., Kim, H.S., Hur, J., 2016. Effects of dissolved organic matter (DOM) sources and nature of solid extraction sorbent on recoverable DOM composition: Implication into potential lability of different compound groups. Analytical and Bioanalytical Chemistry 408, 4809–4819.

Croué, J.-P., 2004. Isolation of Humic and Non-Humic NOM Fractions: Structural Characterization. Environmental Monitoring and Assessment 92, 193–207.

D'Andrilli, J., Chanton, J.P., Glaser, P.H., Cooper, W.T., 2010. Characterization of dissolved organic matter in northern peatland soil porewaters by ultra high resolution mass spectrometry. Organic Geochemistry 41, 791–799.

Denis, M., Jeanneau, L., Pierson-Wickman, A.-C., Humbert, G., Petitjean, P., Jaffrézic, A., Gruau, G., 2017. A comparative study on the pore-size and filter type effect on the molecular composition of soil and stream dissolved organic matter. Organic Geochemistry 110, 36–44.

Dittmar, T., Lara, R.J., Kattner, G., 2001. River or mangrove? Tracing major organic matter sources in tropical Brazilian coastal waters. Marine Chemistry 73, 253–271.

Dittmar, T., Hertkorn, N., Kattner, G., Lara, R.J., 2006. Mangroves, a major source of dissolved organic carbon to the oceans. Global Biogeochemical Cycles 20. https://doi.org/10.1029/2005GB002570.

Dittmar, T., Koch, B., Hertkorn, N., Kattner, G., 2008. A simple and efficient method for the solid-phase extraction of dissolved organic matter (SPE-DOM) from seawater. Limnology and Oceanography: Methods 6, 230–235.

Drake, T.W., Van Oost, K., Barthel, M., Bauters, M., Hoyt, A.M., Podgorski, D.C., Six, J., Boeckx, P., Trumbore, S.E., Cizungu Ntaboba, L., Spencer, R.G.M., 2019. Mobilization of aged and biolabile soil carbon by tropical deforestation. Nature Geoscience 12, 541–546.

Duarte, R.M.B.O., Duarte, A.C., 2015. Unraveling the structural features of organic aerosols by NMR spectroscopy: a review: NMR applications in organic aerosols studies. Magnetic Resonance in Chemistry 53, 658–666.

Emmett, M.R., White, F.M., Hendrickson, C.L., Shi, S.D.-H., Marshall, A.G., 1998. Application of micro-electrospray liquid chromatography techniques to FT-ICR MS to enable high-sensitivity biological analysis. Journal of the American Society for Mass Spectrometry 9 (4), 333–340.

Goldberg, S.J., Ball, G.I., Allen, B.C., Schladow, S.G., Simpson, A.J., Masoom, H., Soong, R., Graven, H.D., Aluwihare, L.I., 2015. Refractory dissolved organic nitrogen accumulation in high-elevation lakes. Nature Communications 6, 6347.

Gonsior, M., Zwartjes, M., Cooper, W.J., Song, W., Ishida, K.P., Tseng, L.Y., Jeung, M.K., Rosso, D., Hertkorn, N., Schmitt-Kopplin, P., 2011. Molecular characterization of effluent organic matter identified by ultrahigh resolution mass spectrometry. Water Research 45, 2943–2953.

Green, N.W., Perdue, E.M., Aiken, G.R., Butler, K.D., Chen, H., Dittmar, T., Niggemann, J., Stubbins, A., 2014. An intercomparison of three methods for the large-scale isolation of oceanic dissolved organic matter. Marine Chemistry 161, 14–19.

Han, H., Feng, Y., Chen, J., Xie, Q., Chen, S., Sheng, M., Zhong, S., Wei, W., Su, S., Fu, P., 2022. Acidification impacts on the molecular composition of dissolved organic matter revealed by FT-ICR MS. Science of the Total Environment 805, 150284.

Hendrickson, C.L., Quinn, J.P., Kaiser, N.K., Smith, D.F., Blakney, G.T., Chen, T., Marshall, A.G., Weisbrod, C.R., Beu, S.C., 2015. 21 Tesla Fourier transform ion cyclotron resonance mass spectrometer: A national resource for ultrahigh resolution mass analysis. Journal of the American Society of Mass Spectrometry 26, 1626–1632.

Hertkorn, N., Benner, R., Frommberger, M., Schmitt-Kopplin, P., Witt, M., Kaiser, K., Kettrup, A., Hedges, J.I., 2006. Characterization of a major refractory component of marine dissolved organic matter. Geochimica et Cosmochimica Acta 70, 2990–3010.

Hertkorn, N., Ruecker, C., Meringer, M., Gugisch, R., Frommberger, M., Perdue, E.M., Witt, M., Schmitt-Kopplin, P., 2007. High-precision frequency measurements: indispensable tools at the core of the molecular-level analysis of complex systems. Analytical and Bioanalytical Chemistry 389, 1311–1327.

Hertkorn, N., Frommberger, M., Witt, M., Koch, B.P., Schmitt-Kopplin, Ph., Perdue, E.M., 2008. Natural organic matter and the event horizon of mass spectrometry. Analytical Chemistry 80, 8908–8919.

Hertkorn, N., Harir, M., Koch, B.P., Michalke, B., Schmitt-Kopplin, P., 2013. High-field NMR spectroscopy and FTICR mass spectrometry: powerful discovery tools for the molecular level characterization of marine dissolved organic matter. Biogeosciences 10, 1583–1624.

Junk, G.A., Richard, J.J., Grieser, M.D., Witiak, D., Witiak, J.L., Arguello, M.D., Vick, R., Svec, H.J., Fritz, J.S., Calder, G.V., 1974. Use of macroreticular resins in the analysis of water for trace organic contaminants. Journal of Chromatography A 99, 745–762.

Kellerman, A.M., Dittmar, T., Kothawala, D.N., Tranvik, L.J., 2014. Chemodiversity of dissolved organic matter in lakes driven by climate and hydrology. Nature Communications 5, 3804.

Kellerman, A.M., Guillemette, F., Podgorski, D.C., Aiken, G.R., Butler, K.D., Spencer, R.G. M., 2018. Unifying concepts linking dissolved organic matter composition to persistence in aquatic ecosystems. Environmental Science and Technology 52, 2538–2548.

Knulst, J.C., Boerschke, R.C., Loemo, S., 1998. Differences in organic surface microlayers from an artificially acidified and control lake, elucidated by XAD-8/XAD-4 tandem separation and solid state ^{13} C NMR spectroscopy. Environmental Science and Technology 32, 8–12.

Koch, B.P., Dittmar, T., 2006. From mass to structure: an aromaticity index for high-resolution mass data of natural organic matter. Rapid Communications in Mass Spectrometry 20, 926–932.

Koch, B.P., Dittmar, T., 2016. From mass to structure: an aromaticity index for high-resolution mass data of natural organic matter. Rapid Communications in Mass Spectrometry 30, 250.

Koch, B.P., Witt, M., Engbrodt, R., Dittmar, T., Kattner, G., 2005. Molecular formulae of marine and terrigenous dissolved organic matter detected by electrospray ionization Fourier transform ion cyclotron resonance mass spectrometry. Geochimica et Cosmochimica Acta 69, 3299–3308.

Koch, B.P., Dittmar, T., Witt, M., Kattner, G., 2007. Fundamentals of molecular formula assignment to ultrahigh resolution mass data of natural organic matter. Analytical Chemistry 79, 1758–1763.

Kruger, B.R., Dalzell, B.J., Minor, E.C., 2011. Effect of organic matter source and salinity on dissolved organic matter isolation via ultrafiltration and solid phase extraction. Aquatic Sciences 73, 405–417.

Kurek, M.R., Poulin, B.A., McKenna, A.M., Spencer, R.G.M., 2020. Deciphering dissolved organic matter: Ionization, dopant, and fragmentation insights via Fourier Transform-Ion Cyclotron Resonance Mass Spectrometry. Environmental Science and Technology 54, 16249–16259.

Kurek, M.R., Stubbins, A., Drake, T.W., Dittmar, T., Moura, M.S., J., Holmes, R.M., Osterholz, H., Six, J., Wabakanghanzi, J.N., Dinga, B., Mitsuya, M., Spencer, R.G.M.,, 2022. Organic molecular signatures of the Congo River and comparison to the Amazon. Global Biogeochemical Cycles 36. https://doi.org/10.1029/2022GB007301.

Lam, B., Baer, A., Alaee, M., Lefebvre, B., Moser, A., Williams, A., Simpson, A.J., 2007. Major structural components in freshwater dissolved organic matter. Environmental Science and Technology 41, 8240–8247.

Lara, R.J., Thomas, D.N., 1994. XAD-fractionation of "new" dissolved organic matter: is the hydrophobic fraction seriously underestimated? Marine Chemistry 47, 93–96.

LaRowe, D.E., Van Cappellen, P., 2011. Degradation of natural organic matter: A thermodynamic analysis. Geochimica et Cosmochimica Acta 75, 2030–2042.

Lechleitner, F.A., Dittmar, T., Baldini, J.U.L., Prufer, K.M., Eglinton, T.I., 2017. Molecular signatures of dissolved organic matter in a tropical karst system. Organic Geochemistry 113, 141–149.

Leenheer, J.A., Croué, J.-P., 2003. Characterizing aquatic dissolved organic matter. Environmental Science and Technology 37, 18A–26A.

Li, Y., Harir, M., Lucio, M., Kanawati, B., Smirnov, K., Flerus, R., Koch, B.P., Schmitt-Kopplin, P., Hertkorn, N., 2016. Proposed guidelines for solid phase extraction of Suwannee River dissolved organic matter. Analytical Chemistry 88, 6680–6688.

Li, Y., Harir, M., Uhl, J., Kanawati, B., Lucio, M., Smirnov, K.S., Koch, B.P., Schmitt-Kopplin, P., Hertkorn, N., 2017. How representative are dissolved organic matter (DOM) extracts? A comprehensive study of sorbent selectivity for DOM isolation. Water Research 116, 316–323.

Lucas, J., Koester, I., Wichels, A., Niggemann, J., Dittmar, T., Callies, U., Wiltshire, K.H., Gerdts, G., 2016. Short-term dynamics of North Sea bacterioplankton-dissolved organic matter coherence on molecular level. Frontiers in Microbiology 7. https://doi.org/10.3389/fmicb.2016.00321.

Luzius, C., Guillemette, F., Podgorski, D.C., Kellerman, A.M., Spencer, R.G.M., 2018. Drivers of dissolved organic matter in the vent and major conduits of the world's largest freshwater spring. Journal of Geophysical Research: Biogeosciences 123, 2775–2790.

Malcolm, R.L., MacCarthy, P., 1992. Quantitative evaluation of XAD-8 and XAD-4 resins used in tandem for removing organic solutes from water. Environment International 18, 597–607.

Mann, P.J., Davydova, A., Zimov, N., Spencer, R.G.M., Davydov, S., Bulygina, E., Zimov, S., Holmes, R.M., 2012. Controls on the composition and lability of dissolved organic matter in Siberia's Kolyma River basin. Journal of Geophysical Research: Biogeosciences 117, 2011JG001798.

Mann, P.J., Spencer, R.G.M., Dinga, B.J., Poulsen, J.R., Hernes, P.J., Fiske, G., Salter, M. E., Wang, Z.A., Hoering, K.A., Six, J., Holmes, R.M., 2014. The biogeochemistry of carbon across a gradient of streams and rivers within the Congo Basin: Aquatic C biogeochemistry in Congo Basin. Journal of Geophysical Research: Biogeosciences 119, 687–702.

Mann, P.J., Spencer, R.G.M., Hernes, P.J., Six, J., Aiken, G.R., Tank, S.E., McClelland, J. W., Butler, K.D., Dyda, R.Y., Holmes, R.M., 2016. Pan-Arctic trends in terrestrial dissolved organic matter from optical measurements. Frontiers in Earth Science 4. https://doi.org/10.3389/feart.2016.00025.

Mattsson, T., Kortelainen, P., Räike, A., 2005. Export of DOM from boreal catchments: Impacts of land use cover and climate. Biogeochemistry 76, 373–394.

Mattsson, T., Kortelainen, P., Laubel, A., Evans, D., Pujo-Pay, M., Räike, A., Conan, P., 2009. Export of dissolved organic matter in relation to land use along a European climatic gradient. Science of the Total Environment 407, 1967–1976.

Melendez-Perez, J.J., Martínez-Mejía, M.J., Awan, A.T., Fadini, P.S., Mozeto, A.A., Eberlin, M.N., 2016. Characterization and comparison of riverine, lacustrine, marine and estuarine dissolved organic matter by ultra-high resolution and accuracy Fourier transform mass spectrometry. Organic Geochemistry 101, 99–107.

Minor, E.C., Swenson, M.M., Mattson, B.M., Oyler, A.R., 2014. Structural characterization of dissolved organic matter: a review of current techniques for isolation and analysis. Environmental Science: Processes and Impacts 16, 2064–2079.

Osterholz, H., Singer, G., Wemheuer, B., Daniel, R., Simon, M., Niggemann, J., Dittmar, T., 2016. Deciphering associations between dissolved organic molecules and bacterial communities in a pelagic marine system. The ISME Journal 10, 1717–1730.

Perdue, E.M., Ritchie, J.D., 2003. Dissolved Organic Matter in Freshwaters. Treatise on Geochemistry. Elsevier, pp. 273–318.

Perminova, I.V., Dubinenkov, I.V., Kononikhin, A.S., Konstantinov, A.I., Zherebker, A.Y., Andzhushev, M.A., Lebedev, V.A., Bulygina, E., Holmes, R.M., Kostyukevich, Y.I., Popov, I.A., Nikolaev, E.N., 2014. Molecular mapping of sorbent selectivities with respect to isolation of Arctic dissolved organic matter as measured by Fourier transform mass spectrometry. Environmental Science and Technology 48, 7461–7468.

Powers, L.C., Lapham, L.L., Malkin, S.Y., Heyes, A., Schmitt-Kopplin, P., Gonsior, M., 2021. Molecular and optical characterization reveals the preservation and sulfurization of chemically diverse porewater dissolved organic matter in oligohaline and brackish Chesapeake Bay sediments. Organic Geochemistry 161, 104324.

Raeke, J., Lechtenfeld, O.J., Wagner, M., Herzsprung, P., Reemtsma, T., 2016. Selectivity of solid phase extraction of freshwater dissolved organic matter and its effect on ultrahigh resolution mass spectra. Environmental Science: Processes and Impacts 18, 918–927.

Ratpukdi, T., Rice, J.A., Chilom, G., Bezbaruah, A., Khan, E., 2009. Rapid fractionation of natural organic matter in water using a novel solid-phase extraction technique. Water Environment Research 81, 2299–2308.

Raymond, P.A., McClelland, J.W., Holmes, R.M., Zhulidov, A.V., Mull, K., Peterson, B.J., Striegl, R.G., Aiken, G.R., Gurtovaya, T.Y., 2007. Flux and age of dissolved organic carbon exported to the Arctic Ocean: A carbon isotopic study of the five largest arctic rivers. Global Biogeochemical Cycles 21. https://doi.org/10.1029/2007GB002934.

Sandron, S., Rojas, A., Wilson, R., Davies, N.W., Haddad, P.R., Shellie, R.A., Nesterenko, P.N., Kelleher, B.P., Paull, B., 2015. Chromatographic methods for the isolation, separation and characterisation of dissolved organic matter. Environmental Science: Processes and Impacts 17, 1531–1567.

Šantl-Temkiv, T., Finster, K., Dittmar, T., Hansen, B.M., Thyrhaug, R., Nielsen, N.W., Karlson, U.G., 2013. Hailstones: A window into the microbial and chemical inventory of a storm cloud. PLoS One 8, e53550.

Savory, J.J., Kaiser, N.K., McKenna, A.M., Xian, F., Blakney, G.T., Rodgers, R.P., Hendrickson, C.L., Marshall, A.G., 2011. Parts-per-billion Fourier transform ion cyclotron resonance mass measurement accuracy with a "walking" calibration equation. Analytical Chemistry 83, 1732–1736.

Sleighter, R.L., Hatcher, P.G., 2007. The application of electrospray ionization coupled to ultrahigh resolution mass spectrometry for the molecular characterization of natural organic matter. Journal of Mass Spectrometry 42, 559–574.

Sleighter, R.L., Hatcher, P.G., 2008. Molecular characterization of dissolved organic matter (DOM) along a river to ocean transect of the lower Chesapeake Bay by ultrahigh resolution electrospray ionization Fourier transform ion cyclotron resonance mass spectrometry. Marine Chemistry 110, 140–152.

Smith, D.F., Podgorski, D.C., Rodgers, R.P., Blakney, G.T., Hendrickson, C.L., 2018. 21 Tesla FT-ICR mass spectrometer for ultrahigh-resolution analysis of complex organic mixtures. Analytical Chemistry 90, 2041–2047.

Spencer, R.G.M., Stubbins, A., Hernes, P.J., Baker, A., Mopper, K., Aufdenkampe, A.K., Dyda, R.Y., Mwamba, V.L., Mangangu, A.M., Wabakanghanzi, J.N., Six, J., 2009. Photochemical degradation of dissolved organic matter and dissolved lignin phenols from the Congo River. Journal of Geophysical Research: Biogeosciences 114, 2009JG000968.

Spencer, R.G.M., Aiken, G.R., Dyda, R.Y., Butler, K.D., Bergamaschi, B.A., Hernes, P.J., 2010a. Comparison of XAD with other dissolved lignin isolation techniques and a compilation of analytical improvements for the analysis of lignin in aquatic settings. Organic Geochemistry 41, 445–453.

Spencer, R.G.M., Hernes, P.J., Ruf, R., Baker, A., Dyda, R.Y., Stubbins, A., Six, J., 2010b. Temporal controls on dissolved organic matter and lignin biogeochemistry in a pristine tropical river, Democratic Republic of Congo. Journal of Geophysical Research 115, G03013.

Spencer, R.G.M., Mann, P.J., Dittmar, T., Eglinton, T.I., McIntyre, C., Holmes, R.M., Zimov, N., Stubbins, A., 2015. Detecting the signature of permafrost thaw in Arctic rivers. Geophysical Research Letters 42, 2830–2835.

Spencer, R.G.M., Hernes, P.J., Dinga, B., Wabakanghanzi, J.N., Drake, T.W., Six, J., 2016. Origins, seasonality, and fluxes of organic matter in the Congo River. Global Biogeochemical Cycles 30, 1105–1121.

Stenson, A.C., Marshall, A.G., Cooper, W.T., 2003. Exact masses and chemical formulas of individual Suwannee River fulvic acids from ultrahigh resolution electrospray ionization Fourier transform ion cyclotron resonance mass spectra. Analytical Chemistry 75, 1275–1284.

Stubbins, A., Mann, P.J., Powers, L., Bittar, T.B., Dittmar, T., McIntyre, C.P., Eglinton, T. I., Zimov, N., Spencer, R.G.M., 2017. Low photolability of yedoma permafrost dissolved organic carbon. Journal of Geophysical Research: Biogeosciences 122, 200–211.

Textor, S.R., Guillemette, F., Zito, P.A., Spencer, R.G.M., 2018. An assessment of dissolved organic carbon biodegradability and priming in blackwater systems. Journal of Geophysical Research: Biogeosciences 123, 2998–3015.

Tfaily, M.M., Podgorski, D.C., Corbett, J.E., Chanton, J.P., Cooper, W.T., 2011. Influence of acidification on the optical properties and molecular composition of dissolved organic matter. Analytica Chimica Acta 706, 261–267.

Tfaily, M.M., Chu, R.K., Tolić, N., Roscioli, K.M., Anderton, C.R., Paša-Tolić, L., Robinson, E.W., Hess, N.J., 2015. Advanced solvent based methods for molecular characterization of soil organic matter by high-resolution mass spectrometry. Analytical Chemistry 87, 5206–5215.

Thurman, E.M., Malcolm, R.L., 1981. Preparative isolation of aquatic humic substances. Environmental Science and Technology 15, 463–466.

Wagner, S., Riedel, T., Niggemann, J., Vähätalo, A.V., Dittmar, T., Jaffé, R., 2015. Linking the molecular signature of heteroatomic dissolved organic matter to watershed characteristics in world rivers. Environmental Science and Technology 49, 13798–13806.

Ward, C.P., Cory, R.M., 2015. Chemical composition of dissolved organic matter draining permafrost soils. Geochimica et Cosmochimica Acta 167, 63–79.

Williams, C.J., Yamashita, Y., Wilson, H.F., Jaffé, R., Xenopoulos, M.A., 2010. Unraveling the role of land use and microbial activity in shaping dissolved organic matter characteristics in stream ecosystems. Limnology and Oceanography 55, 1159–1171.

Wilson, H.F., Xenopoulos, M.A., 2009. Effects of agricultural land use on the composition of fluvial dissolved organic matter. Nature Geoscience 2, 37–41.

Xian, F., Hendrickson, C.L., Blakney, G.T., Beu, S.C., Marshall, A.G., 2010. Automated broadband phase correction of Fourier transform ion cyclotron resonance mass spectra. Analytical Chemistry 82, 8807–8812.

Zhang, Q., Lv, J., He, A., Cao, D., He, X., Zhao, L., Wang, Y., Jiang, G., 2023. Investigation with ESI FT-ICR MS on sorbent selectivity and comprehensive molecular composition of landfill leachate dissolved organic matter. Water Research 243, 120359.