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Carbon Budget and Molecular Structure of Natural Organic Matter in Bank Infiltrated Groundwater

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Abstract

Managed aquifer recharge (MAR) provides means to remove natural organic matter (NOM) from surface waters. Recent studies have explored the degree of NOM removal in groundwater. In this study, we further elaborate the NOM removal at a lakeside natural bank infiltration site that functions as a surrogate for MAR. Our objective was to quantify the carbon budget in the aquifer based on concentration measurements of dissolved (in)organic carbon, and the molecular changes in NOM using Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS). According to the carbon budget, only 25% of the dissolved carbon entering the aquifer was organic, and it predominantly originated from lake water. Of the inorganic majority, on average 40% was produced in the vadose zone above the groundwater table, 31% in the lake bank, 22% in the aquifer as a result of degrading organic matter of lake water, and 7% in the lake. Seasonal concentration variations suggested that the lake bank was the main carbon source in the summer, increasing the carbon concentration of infiltrating lake water, that is, 3.0 mg/L to 7.9 mg/L. FT-ICR MS results showed 4960 to 5330 individual compounds in lake and groundwater. NOM removal in the aquifer was selective: the relative abundance of oxygen-containing species decreased from 75 to 31%, while the relative abundance of sulfur-containing species increased from 15 to 57%. The average molecular weights of both species remained unchanged. The study highlighted the role of lake bank processes and sulfur-containing species in groundwater quality.

Introduction

Managed aquifer recharge (MAR) refers to an intentional recharge of water into an aquifer. It is a common method for removing natural organic matter

(NOM) from surface water in drinking water production. Groundwater overuse and the growing awareness of its impacts on ecosystems have led to an increasing interest in MAR in drinking water production, water storage, and treatment. Bank infiltration (BF) is the most widespread version of MAR (Sprenger et al. 2017; Dillon et al. 2019). Other common methods being well injection and infiltration ponds. The main NOM removal process in BF is mineralization, that is, aerobic or anaerobic biodegradation of NOM to dissolved inorganic carbon (DIC) (Dillon et al. 2019). The removal efficiency of NOM in MAR varies from approximately 30 to 100% (e.g., Maeng et al. 2011; Jokela et al. 2017). The most intensive reactions are known to occur along the first meters of the infiltration flow path (e.g., Diem et al. 2013; Henzler et al. 2016).

NOM plays an important role in geochemical processes in soil and groundwater. NOM mineralization in the infiltrating lake water consumes oxygen in the aquifer, which impacts the redox conditions and easily leads to anoxic groundwater. Degradation of particulate organic matter (such as plant litter) in lake or river bottom sediment causes additional oxygen consumption at the beginning of the flow path of the infiltrating water (e.g., Diem et al. 2013; Regnery et al. 2017; Bayarsaikhan et al. 2018;

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Hellauer et al. 2019). Oxygen depletion is undesirable, as anoxic conditions lead to reductive dissolution of Fe and Mn minerals from the soil material, which is a common quality problem in drinking water (e.g., Massmann et al. 2006; Grishenk and Paufler 2017). NOM also affects the transport and degradation of pollutants (e.g., Regnery et al. 2017; Yu et al. 2020). Investigations of NOM removal and organic matter composition at the molecular level are needed to understand the key processes in groundwater in which organic matter is involved. The beginning of the flow path after infiltration is of special interest because of rapid degradation reactions and impact of the lake bottom sediments on oxygen consumption.

There are several established methods for characterizing organic matter. The concentration of organic matter in water can be measured by bulk parameters such as total organic carbon (TOC) and dissolved organic carbon (DOC), and the amount of degradation products can be measured as DIC and methane. The origin of organic carbon can be traced by analyzing the stable carbon isotope ratios (Clark and Fritz 1997; Kendall and McDonnell 1998; Appelo and Postma 1999). Structural analyses of NOM include spectroscopic techniques like fluorescence, ultraviolet–visible spectroscopy (UV–Vis) or Fourier-transform infrared (FT-IR) spectroscopy, chromatographic techniques like size exclusion chromatography (SEC), and mass spectrometric methods like liquid chromatography mass spectrometry (LC-MS). Alternatively, NOM can be directly characterized from water samples by using high-resolution mass spectrometry, such as Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) (Matilainen et al. 2011) and nuclear magnetic resonance spectroscopy (NMR) (Hertkorn et al. 2016; Masoom et al. 2016). NOM is a complex organic mixture, comprising hundreds or thousands of heteroatom-containing compounds (Thurmann 1985; Nebbioso and Piccolo 2013; Masoom et al. 2016). With FT-ICR MS, thousands of chemical constituents in a given sample can be separated, and their chemical formulae can be assigned due to the high resolving power and mass accuracy of the technique. Even though FT-ICR MS is a semi-quantitative method, differences in samples' chemical constituents and their relative proportions can be determined (Marshall 2000; Koch et al. 2007).

FT-ICR MS has previously been applied to the characterization of NOM in water obtained from various natural environments like oceans (Sleighter and Hatcher 2008; Kujawinski et al. 2009; D'Andrilli et al. 2010a), pore water (Tremblay et al. 2007; Schmidt et al. 2009; D'Andrilli et al. 2010b), rainwater (Mead et al. 2013), streams (Kim et al. 2006), paddy soils (Li et al. 2018), groundwater (Yu et al. 2020), lakes (Kellerman et al. 2014; Butturini et al. 2020), and forests (Roth et al. 2015; Ide et al. 2017). It has also been applied to study the NOM removal in surface water treatment plants (Lavonen et al. 2015; Raeke et al. 2017). The key value of FT-ICR MS is the distinctive information it provides about the molecular signature of samples at different phases of the

water cycle or treatment process. Such information is in our study expected to refine the knowledge about organic matter removal in BF.

Jylhä-Ollila et al. (2020) studied groundwater quality in terms of NOM at a natural lakeside bank filtration site functioning as a surrogate for MAR. They quantified rapid changes in DOC and TOC concentrations after water infiltrated to the aquifer. This study expands their analysis to include concentrations of both DOC and DIC in lake and groundwater samples, as well as the molecular signature of the samples by FT-ICR MS. At the BF site, infiltration of lake water occurs through the lake bottom sediment to the groundwater reservoir. The objective is to quantify the carbon budget of the aquifer and to reveal the changes in the molecular structure of NOM during the different stages of the NOM removal process. The main questions were: (1) How much dissolved organic and inorganic carbon enters the groundwater reservoir from the different sources including the lake, the lake bottom sediment, and the vadose zone above the groundwater table? How much organic carbon degrades in the aquifer? (2) What is the molecular composition of NOM in the lake water, and how does the bank filtration and the transport through the aquifer impact the composition? The data analysis presented in this study is among the first detailed investigations of changes in the molecular structure of dissolved organic matter during bank infiltration by FT-ICR MS.

Research Method

There are many different names and acronyms used for NOM in fresh waters (Filella 2009). In this article, we use the following terminology. Natural organic matter (NOM) is a broad term for all organic matter in a reservoir other than living organisms and man-made compounds (Filella 2009). Total organic carbon (TOC) refers to the analysis result of bulk organic carbon in a water sample (mg/L). Dissolved organic carbon (DOC) refers to the analysis result of bulk organic carbon in a water sample that has been filtered through a 0.45 μm filter (mg/L). Dissolved inorganic carbon (DIC) refers to the sum of CO_2 , HCO_3^- and CO_3^{2-} ions in water (mg/L). Total dissolved carbon (TDC) is the sum of DOC and DIC (mg/L). Dissolved organic matter (DOM) refers to the soluble fraction of NOM that is observable by FT-ICR MS.

Site Description

The study site is a groundwater aquifer bordered on Lake Iso Tiilijärvi in southern Finland (Figure 1). It is located on an end moraine composed mainly of glaciofluvial sand and gravel, and the total thickness of the aquifer is approximately 40 m (Jylhä-Ollila et al. 2020). The infiltrated water flows through the aquifer and is discharged from several springs northeast of the lake. The average fraction of water in the aquifer that stems from the lake is 0.95–0.96 near the shore, and it decreases to 0.75–0.76 at the springs (Jylhä-Ollila et al. 2020). Outside the main flow path, the relative proportion of

Table 1
Water Quality of the Infiltrating Water from Lake Iso Tiilijärvi (Jylhä-Ollila et al. 2020)

Parameter	Average Value and Standard Deviation
Turbidity (NTU)	0.6 ± 0.03
pH	5.9 ± 0.5
O ₂ (mg/L)	11 ± 1.5
TOC (mg/L)	3.0 ± 0.2
DOC (mg/L)	2.6 ± 0.2

infiltrated lake water is lower. The total retention time from the lake through the 160 m long groundwater flow path is about 1 year (Jylhä-Ollila et al. 2020), which corresponds to an average flow velocity of 0.44 m/d. Based on 15 lake water samples gathered from 2016 to 2018, the infiltrating lake water is characterized by low turbidity, almost saturated with oxygen, and an average TOC concentration of 3.0 ± 0.2 mg/L (Table 1). The lake water temperature varies between 22 °C in the summer and 0 °C in the winter.

Sampling

Water samples from Lake Iso Tiilijärvi were taken from locations L1 (1 m depth) and L2 (7 m depth) using a Limnos water sampler (Figure 1). Groundwater samples were collected from observation wells OW4, OW5, OW30, OW40, OW50, and OW60 (Figure 1). Samples from OW4, OW5, and OW30 were collected with a suction pump (Honda) and from OW40, OW50, and OW60 with a submersible pump (Mini Monsoon). The diameter of the wells was either 32 mm or 50 mm, and the length of the screens ranged from 1 to 10 m. Prior to the sampling, a minimum of 100 L of water were pumped from each groundwater well to clear the water of turbidity.

DIC and the Stable Carbon Isotopes

Sampling for the DIC analysis and stable carbon isotope analyses was conducted at observation locations L1, L2, OW30, OW40, OW60, OW4, and OW5. The DIC samples were taken in June 2017 and in December 2017 to represent warm summer and cold winter conditions, as the degradation processes in lake sediments are known to be temperature-dependent (e.g., Gross-Wittke et al. 2010; Diem et al. 2013).

Samples were taken following the method described by Schilder et al. (2015), using helium instead of nitrogen to flush the sample bottles. In brief, 60 mL of water was sampled using a syringe connected with a tube to the groundwater pump or to the Limnos lake water sampler. A three-way valve was used to expel water samples containing gas bubbles until a gas bubble free sample could be taken. This 60 mL of water was injected into a 118 mL glass vial with a thick butyl rubber stopper (Apodan, Denmark). These vials were prepared to contain

no carbon and with phosphoric acid to purge the DIC from the water sample. The vials were prepared and analyzed using a gas chromatograph (Agilent 7890B with a stainless steel HayeSep Q 80/100 packed column, equipped with a TCD). The preparation of the vials and the analysis of the samples were conducted at the University of Jyväskylä's Department of Biological and Environmental Science.

Stable carbon isotope ratios were used to characterize organic and inorganic carbon, as the isotopic composition of carbon originating from plants differs from that of the atmospheric carbon (e.g., Vogel 1993). The stable carbon isotope ratios of DIC were analyzed from the head-space of the 60 mL vials of the DIC concentration measurements, using an isoprime trace gas pre-concentrator coupled to an isoprime IRMS. The stable carbon isotope ratios of DOC were, for their part, analyzed from the freeze-drying residue of 1 L of water that was slightly acidified with hydrochloric acid to purge most DIC from the water. This was done using a Carlo Erba Flash EA1112 elemental analyzer connected to a Thermo Finnigan DELTAplusAdvantage continuous flow stable isotope-ratio mass spectrometer (CF-IRMS).

The results of the stable carbon isotope analyses were presented as $\delta^{13}\text{C}$ values which were calculated from the isotope ratios (the heavier against the lighter):

$$\delta_{\text{sample}} = (R_{\text{sample}}/R_{\text{std}} - 1) \quad (1)$$

where R_{sample} is the $^{13}\text{C}/^{12}\text{C}$ ratio of the sample and R_{std} is the $^{13}\text{C}/^{12}\text{C}$ ratio in the standard (V-PDB; Craig 1957).

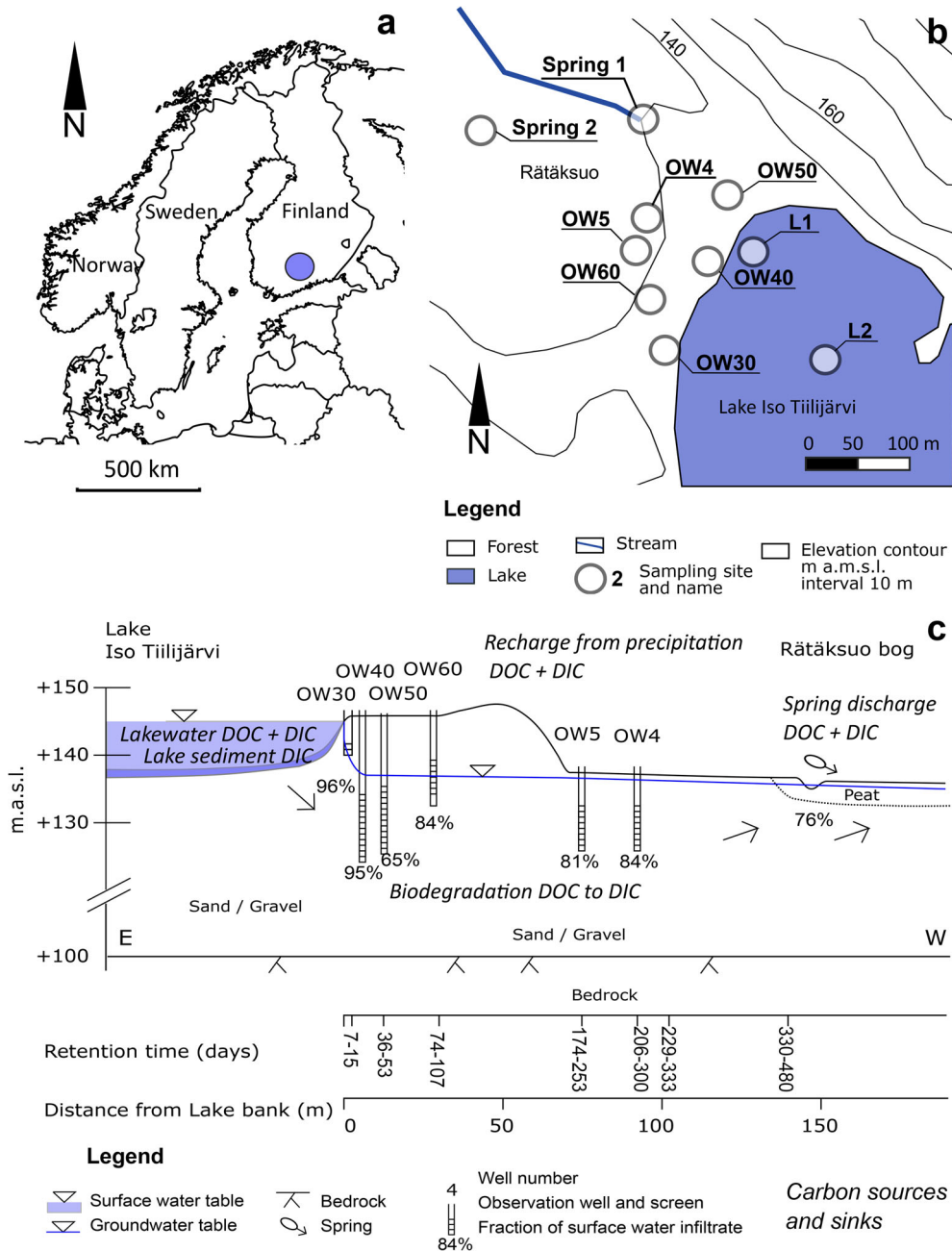
Carbon Budget

The calculation of the annual carbon budget of the aquifer was based on the following equations:

$$M_{\text{DOClake}} + M_{\text{DOCrain}} = M_{\text{DOCspring}} + M_{\text{DOCdegr}} \quad (2)$$

$$M_{\text{DIClake}} + M_{\text{DICsed}} + M_{\text{DICrain}} + M_{\text{DOCdegr}} = M_{\text{DICspring}} \quad (3)$$

where M_{DOClake} and M_{DIClake} , are the organic and inorganic carbon fluxes, respectively, to the aquifer from the lake water (kg/year), M_{DOCrain} and M_{DICrain} are the organic and inorganic carbon fluxes to the aquifer from the soil solid phase in the vadose zone overlaying the entire aquifer, leached down by the infiltrating rainwater (kg/year), M_{DICsed} is the inorganic carbon flux originating from the degradation of solid organic matter in the lake bottom sediment (kg/year), $M_{\text{DOCspring}}$ and $M_{\text{DICspring}}$ are the organic and inorganic carbon fluxes discharging from the springs (kg/year), and M_{DOCdegr} is the degradation of DOC to DIC in the aquifer (kg/year) (cf. Figure 1). The lake sediment was only considered to function as a DIC source for the aquifer based on the findings of, for example, Diem et al. (2013) and Henzler et al. (2016), according to which DOC concentrations decrease during the infiltration in lake bank sediments. In addition, carbon exchange between the atmosphere and the inorganic carbon pool in the aquifer was considered



negligible in the scale of the overall budget. Based on Jylhä-Ollila et al. (2020), sorption of DOC on mineral material and carbon dissolution from the aquifer were also considered negligible. The calculations and the data used are presented in Appendix S1.

For the carbon budget calculation, the DOC data were taken from Jylhä-Ollila et al. (2020).

Fourier Transform Ion Cyclotron Resonance Mass Spectrometry

For the FT-ICR MS analysis, water samples were collected from the monitoring locations L1, OW30,

OW40, OW50, and OW60 in September 2017. As NOM was observed to degrade rapidly after infiltration, sampling was targeted at the first 50 m of the flow path. Organic matter isolation from the samples was conducted at the laboratory of the Department of Built Environment at Aalto University. The samples were first filtered using the Whatman GF/F glass fiber filters and acidified to pH 2 with 2 M HCL. Then, DOM was extracted using Agilent Bond Elut PPL solid phase extraction (SPE) cartridges, where 1 g of polar functionalized polystyrene divinylbenzene acted as an adsorbent. The extraction was conducted following Dittmar et al. (2008).

The FT-ICR MS analyses of the NOM samples were performed on a 12-T Bruker solariX XR FT-ICR mass spectrometer (Bruker Daltonics, Bremen, Germany), equipped with an Apollo-II electrospray ionization (ESI) source, which was operated in a negative-ion mode. For the MS analyses, the samples were dissolved in methanol (HPLC grade) to a DOC concentration of 10 $\mu\text{g/mL}$. The samples were directly infused into the ion source at a flow rate of 2 $\mu\text{L/min}$. The ESI-generated ions were accumulated in the hexapole ion trap and subsequently transferred into the ICR cell for trapping, excitation, and detection. Dry nitrogen was used as the drying and nebulizing gas. The data were acquired at an m/z range of 100–2000 with three hundred 8 MWord time-domain transients summed for each spectrum. The data acquisition was accomplished using the Bruker Compass ftmsControl 2.1 software (Bruker Daltonics, Bremen, Germany).

The external mass calibration was carried out with sodium trifluoroacetate (STFA) clusters. The data were then internally recalibrated with respect to the known O_x and S_1O_x compounds. The initial spectral inspection was done with the Bruker DataAnalysis 4.4 SR1 software. Further data processing and molecular formula assignments were carried out with the PetroOrg 16.0 software (Omics LLC, Tallahassee, Florida). Briefly, peaks with a signal-to-noise ratio (S/N) ≥ 5 were taken into account, and the molecular formulae were limited to $^{13}\text{C}_{1-100}$ $^{1}\text{H}_{1-200}$ $^{14}\text{N}_{0-4}$ $^{16}\text{O}_{0-30}$ $^{30}\text{P}_{0-1}$ $^{32}\text{S}_{0-2}$ $^{34}\text{Cl}_{0-2}$ with a double bond equivalent (DBE) of 0–80 and a mass error of ≤ 0.6 ppm. For the molecules containing the above listed elements, DBE was calculated from (Koch and Dittmar 2006):

$$\text{DBE} = c - \frac{h}{2} + \frac{p}{2} + \frac{n}{2} + 1 \quad (4)$$

where c , h , p and n are the numbers of C, H, P, and N atoms, respectively. (The divalent atoms, like O and S, do not contribute to DBE.)

From the FT-ICR MS data, the detected compounds were characterized by of their relative abundance, heteroatom class, carbon number ($C\#$), and DBE. Furthermore, the aromaticity index (AI) was calculated for each molecule according to Koch and Dittmar (2006):

$$\text{AI} = \frac{1 + c - O - s - 0.5h}{c - O - s - n - p} \quad (5)$$

where s and O are the numbers of S and O atoms. If the numerator or denominator in Equation 5 is ≤ 0 , then $\text{AI} = 0$. Both DBE and AI provide information on the degree of unsaturation in a molecule. The AI values can also be used to broadly categorize the molecules into aliphatic ($\text{AI} < 0.5$), aromatic ($\text{AI} > 0.5$), or condensed aromatic structures ($\text{AI} > 0.67$) (Koch and Dittmar 2006). Spearman rank correlations were calculated between the DOC concentration and the average molecular weight (MW_{av}) of the compounds, the number of identified species in each sample, the average carbon number ($C\#_{\text{av}}$), and the average DBE of the molecular mixture (DBE_{av}).

The MS data visualizations were done with the PetroOrg and Microsoft Excel softwares. A principal component analysis (PCA) for the molecular composition between the samples of all molecules and O_y molecules was performed with PetroOrg, using a nonlinear iterative partial least squares (NIPALS) algorithm.

Results

DIC Concentration and Stable Carbon Isotopic Composition

The DIC concentration in the lake water ranged between 0.5 and 1.0 mg/L (Figure 2). In OW30, the DIC concentrations showed seasonal variation with a high DIC concentration in the summer (7.0 mg/L) and a low concentration in the winter (1.6 mg/L). At longer distances, the DIC concentrations ranged between 5.8 and 8.8 mg/L with the seasonal signal smoothed. TDC was higher in the groundwater than in the lake, although seasonal variation could be observed due to fluctuations in the DIC concentrations near the lake bank (Figure 2b). In the lake water, the fraction of DIC in TDC was 14–28%, and at the end of the groundwater flow path it was 96%.

The $\delta^{13}\text{C}_{\text{DOC}}$ values in all samples ranged between -28.3 and -25.1 ‰ (Figure 2c). The $\delta^{13}\text{C}_{\text{DIC}}$ values in groundwater showed a similar range (-26.3 to -24.1 ‰). In the lake water the inorganic carbon was richer in ^{13}C , as $\delta^{13}\text{C}_{\text{DIC}}$ was -14.8 ‰ at a depth of 1 m and -18.3 ‰ at a depth of 7 m.

Carbon Budget

The main DOC source to the aquifer was lake water leading to a carbon influx between 854 kg/year and 1234 kg/year (Figure 3, Appendix S1). The estimated DOC input from the groundwater formed from precipitation only ranged between 12 kg/year and 18 kg/year. The main DOC sink was its degradation to DIC in the aquifer, which ranged between 723 kg/year and 1044 kg/year, while only a smaller fraction of DOC discharged from the springs, in the range between 151 kg/year and 220 kg/year. Unlike for DOC, there were several sources of DIC to the aquifer. The two main DIC sources were from precipitation and organic matter degradation. Input from precipitation ranged between 1267 kg/year and 1901 kg/year. Organic matter degradation in lake bottom sediment ranged between 1038 kg/year and 1499 kg/year. Other sources were lake water, with DIC input ranging between 243 kg/year and 351 kg/year and lake bottom sediment which produced DIC ranging between 723 kg/year and 1044 kg/year. The only DIC sink was the discharge from springs, ranging between 3489 kg/year and 5058 kg/year.

Molecular Composition of DOM

Negative-ion ESI FT-ICR mass spectra for L1, OW30, OW40, OW50, and OW60 are plotted as line spectra, comprising all detected and assigned species, except for a few highly abundant S_1O_3 and S_1O_4 species that were tentatively identified (relying on their $C\#$ and DBE

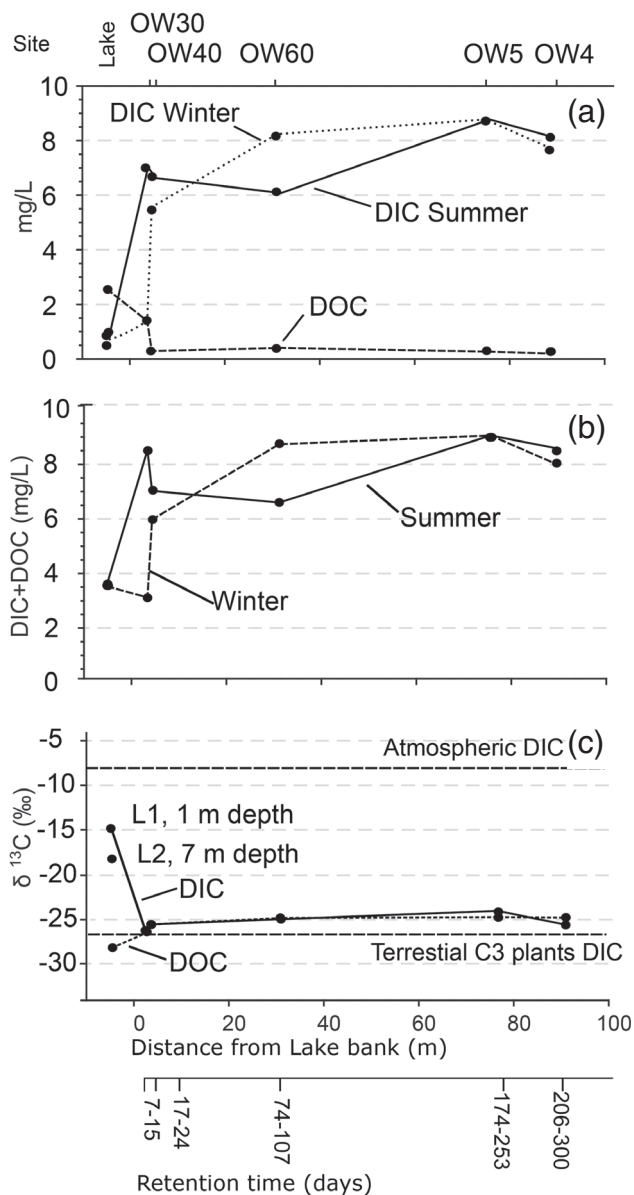


Figure 2. (a) winter and summer DIC concentrations and average DOC concentrations, (b) the sum of DIC and DOC concentrations (TDC) in winter and summer, and (c) $\delta^{13}\text{C}$ values of DIC and DOC in lake and groundwater samples. The values for atmospheric DIC and terrestrial C3 plants DIC are from Deines (1980), Schiff et al. (1997), and Vogel (1993). The values of DOC are from Jylhä-Ollila et al. (2020).

values) as alkylbenzene sulfonates (Figure 4). They are common anionic surfactants that most likely originate from the materials that have been in contact with the samples during the sample preparation (e.g., plastic/rubber hardware). All the mass spectra exhibited either bimodal or trimodal mass distributions (Figure 4). In the samples L1 and OW30, the compounds within 300–400 Da were more dominant while the compounds of size 600–700 Da were relatively more abundant in the rest of the samples.

The major heteroatom containing compound classes identified were O_y , S_zO_y , N_xO_y , O_yCl_1 , and $\text{N}_x\text{O}_y\text{S}_z$

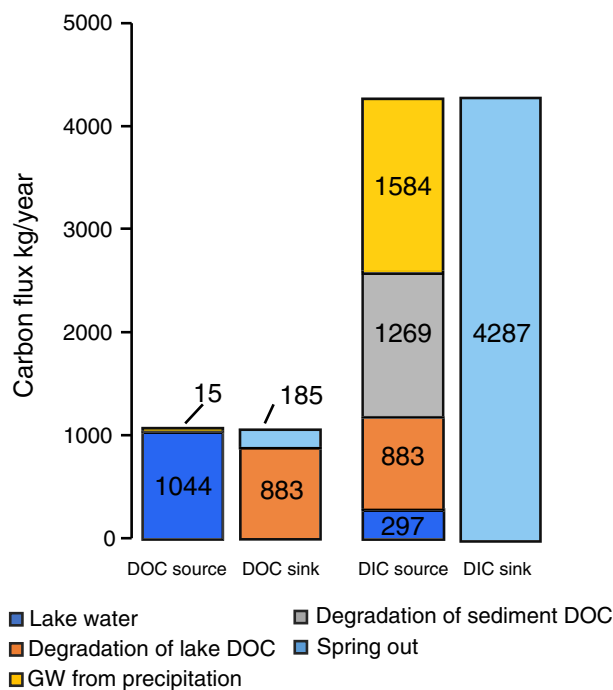


Figure 3. Average values of calculated carbon sources and sinks in the aquifer.

(Figure 5a). No phosphorus-containing compounds were detected. The lake water sample L1 and the groundwater sample OW30 were dominated by O_y class molecules, with a relative abundance of approximately 73–75%. For the other three samples the abundance of O_y class molecules was lower, 25–50%. The proportion of the S_zO_y class in samples OW40, OW50 and OW60 was greater (38–60%) than in samples from L1 and OW30 (15–18%). The relative amounts of N_xO_y , $\text{N}_x\text{O}_y\text{S}_z$, and chlorinated O_y species were minor in all samples.

Chemical differences among the five samples were illustrated by presenting the data as van Krevelen (VK) diagrams (van Krevelen 1950; Kim et al. 2003) (Figure 5b and Figure S1). Two main regions are seen in the VK diagram of L1, which is shown as an example in Figure 5b. Plotting separately the heteroatom-containing compound classes (Figure 6) illustrates the regions of S_zO_y and O_y compounds. The O_y species were more abundant in L1 and OW30, while the relative intensity of the O_y species was lower in OW40, OW50, and OW60. On the other hand, the intensity of the S_zO_y species did not change much between samples.

The number of unique compounds in each sample ranged between 4960 and 5330 (Table 2). The molecular composition clearly differed among the samples. After infiltration to location OW60, the number of O_y species had decreased by 40%, that is, from 3150 compounds in the lake water to 1900 in OW60, and the number of S_zO_y species increased by 97%, that is, from 900 to 1770 compounds. A total of 2385 compounds out of all identified compounds were present in all samples. From these shared compounds, 1517 compounds were

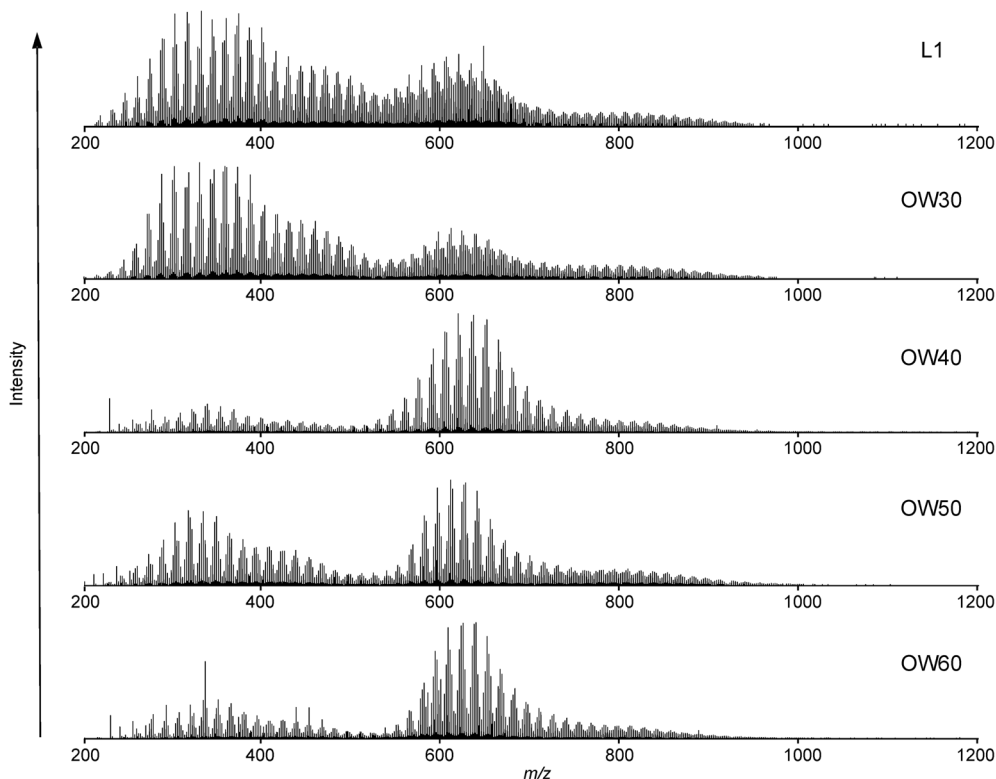


Figure 4. The mass spectra of natural organic matter detected by negative-ion ESI FT-ICR-MS. L1 represents lake water and OW30, OW40, OW50, and OW60 groundwater in the bank infiltration zone.

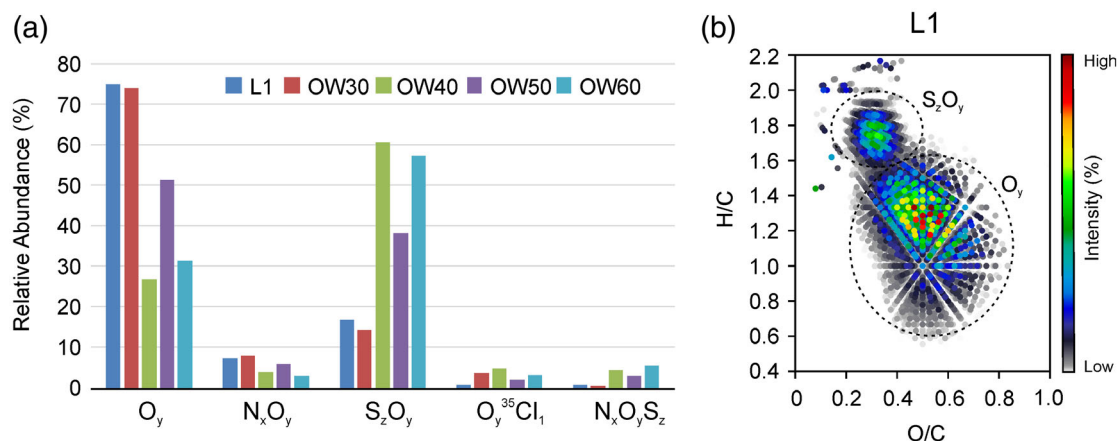


Figure 5. Relative abundance of the identified heteroatom containing compound classes O_y , S_zO_y , N_xO_y , O_yCl_1 , and $N_xO_yS_z$ (a) and Van Krevelen diagram of all species in lake water (b).

O_y species and 566 were S_zO_y species. The intensity-weighted average molecular weights ($C\#_{av}$) of the O_y species ranged between 560 and 700 Da, and the MW_{av} of the S_zO_y species ranged between 626 and 700 Da. For all species, MW_{av} of the assigned compounds was approximately 580 Da for samples L1 and OW30, and approximately 670 Da for OW40, OW50, and OW60 (Table 2). There was a positive correlation between the DOC concentration and the total number of O_y species, and a negative correlation between the DOC concentration

and MW_{av} of all species, $C\#_{av}$ of all species, $C\#_{av}$ of the O_y species, and the number of S_zO_y species.

The two-dimensional PCA analysis demonstrated the molecular (dis)similarity of the samples and thereby the change in the relative intensities of the compounds in relation to the distance from the lake (Figure 7). Samples L1 and OW30 were clearly clustered in the PCA scores plots, indicating a similar molecular composition in these samples. Also, the samples OW40 and OW60 were clustered and distinguished from the first mentioned

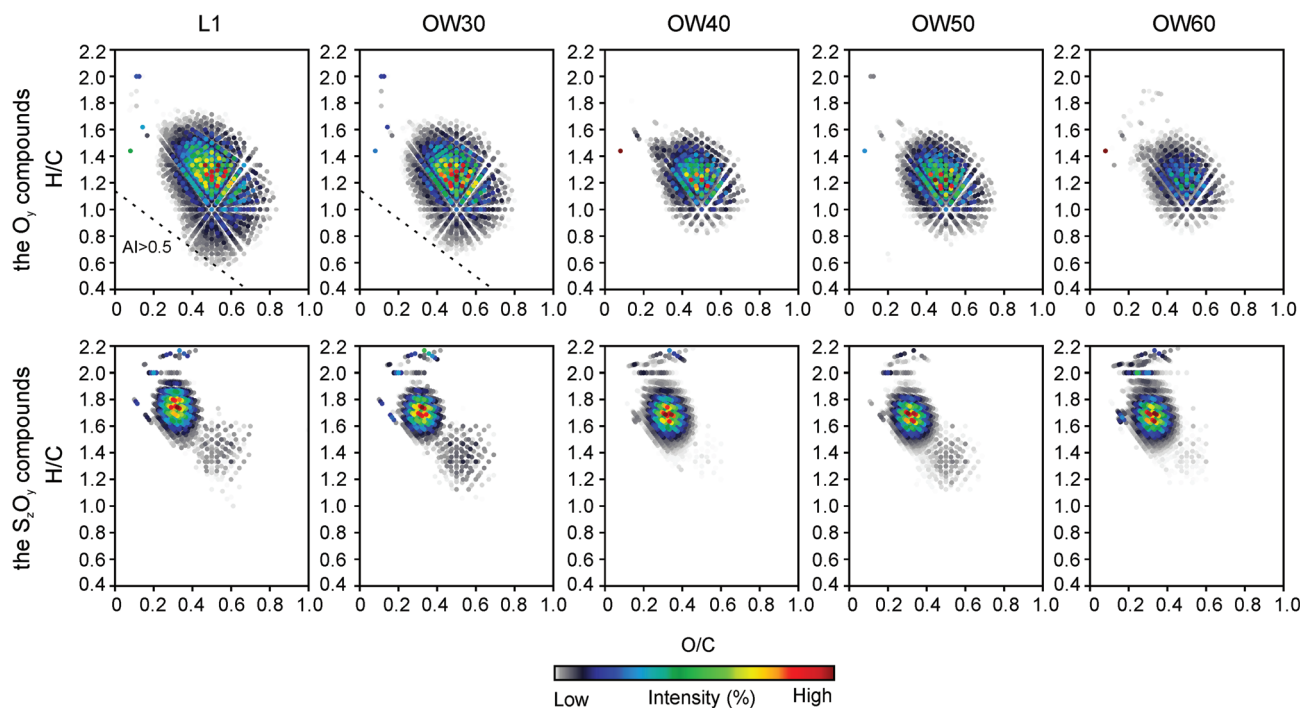


Figure 6. Van Krevelen diagrams for the two identified main compound classes in the samples: O_y and S_zO_y .

Table 2
Molecular Properties (Number of Species, Average Molecular Weight MW_{av} , Average Carbon Number $C\#_{av}$, Average Double Bond Equivalence DBE_{av}) of NOM in Lake Water L1 and Groundwater Samples OW30–OW60

Sample	DOC Removed (%)	Number of Species	MW_{av} (Da)	$C\#_{av}$	DBE_{av}
All species					
L1	0	5170	578	28.6	11.0
OW30	50%	4960	578	28.7	11.0
OW40	85%	5330	667	33.8	10.2
OW50	70%	5070	666	33.4	11.6
OW60	87%	5180	667	33.7	10.2
% change		0	15%	18%	-7%
r		-0.70	-0.95	-0.99	0.63
p		0.28	0.28	0.28	0.28
O_y species					
L1	0	3150	560	28.1	11.6
OW30	50%	2740	568	28.3	11.5
OW40	85%	1850	575	32.2	13.0
OW50	70%	2250	596	32.0	13.1
OW60	87%	1900	578	31.8	12.9
% Change		-40%	3%	13%	11%
r		1.00	-0.60	-0.90	-0.60
p		0.28	0.28	0.28	0.28
S_zO_y species					
L1	0	900	626	31.8	6.1
OW30	50%	820	638	32.5	6.6
OW40	85%	1780	687	35.0	7.5
OW50	70%	1410	700	35.7	7.9
OW60	87%	1770	690	35.2	7.6
% Change		97%	10%	11%	25%
r		-0.90	-0.60	-0.60	-0.60
p		0.04	0.28	0.28	0.28

Note: Percentual change between lake water L1 and the most distant sampling location OW60 in groundwater, Spearman's rank correlation (r and p -value) between DOC concentration and the molecular properties in the samples.

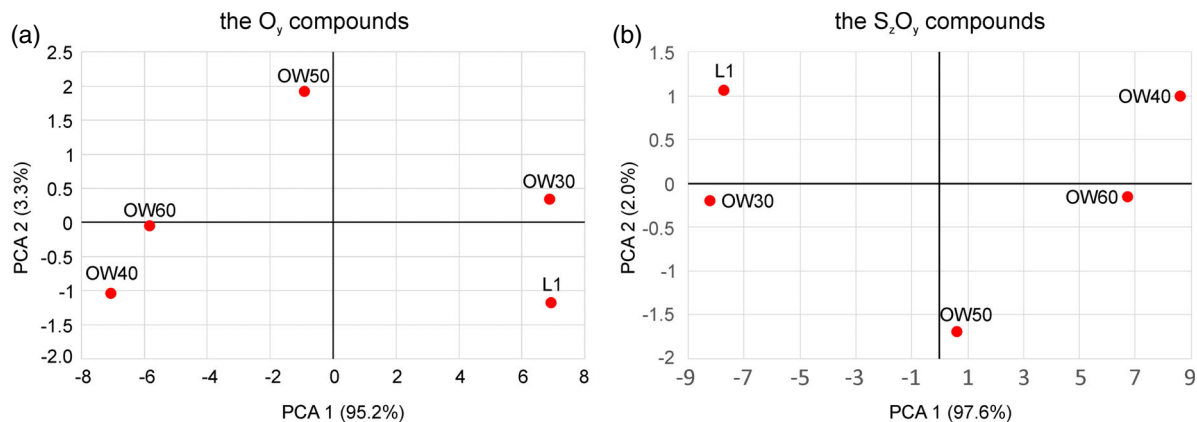


Figure 7. PCA analysis between the results of FT-ICR-MS of (a) O_y compounds and (b) S_zO_y compounds.

cluster (Figure 7). Sample OW50 was located away from both of the mentioned clusters, indicating a distinct, anomalous molecular composition.

Discussion

The stable carbon isotopic composition in groundwater resembled the isotopic composition of terrestrial C3 plants (Figure 2, Deines 1980; Schiff et al. 1997; Vogel 1993), showing that the dissolved carbon observed in the aquifer originated from the surrounding nature. In the lake water, the inorganic carbon was richer in ^{13}C , which showed that DIC in lake water partly originated from atmospheric carbon dioxide.

Determination of the carbon budget expanded the results of Jylhä-Ollila et al. (2020) by providing a more complete quantification of the degradable and residual organic C, as well as the main inorganic C mass fluxes in bank infiltration with a retention time of several months. Earlier research demonstrated that degradation of particulate organic matter in the lake or river sediment and the subsequent additional oxygen consumption can have a major impact on groundwater quality in bank infiltration (e.g., Diem et al. 2013; Regnery et al. 2017; Bayarsaikhan et al. 2018; Hellauer et al. 2019). At the Iso Tiilijärvi study site, the calculation of the carbon budget provided a quantitative estimate of the amount of organic matter degradation in the lake sediment. As DOC degradation is commonly observed by oxygen consumption, it is limited to aerobic conditions, whereas DIC measurements also provide information on the amount of degradation in anoxic conditions.

The measured DIC and DOC concentrations revealed an increase in the summertime TDC concentration from 3.6 to 8.5 mg/L after the first meters of lake water infiltration (Figure 2b). This suggests that a total of 4.9 mg/L carbon was added to the groundwater from the lake sediment as a result of degradation of organic matter in the sediment, and the lake sediment had more impact on the oxygen consumption than the degradation of DOC originating from the lake water (2.9 mg/L). In the winter,

the conditions were different. The TDC decreased after infiltration to OW30, which suggests that when the lake water temperature is close to the freezing point, bacterial activity in the lake sediment is negligible, and some of the organic matter is filtered without degradation at the beginning of the flow path.

According to the carbon budget, only 25% of dissolved carbon entering the aquifer was organic, and 75% was already in the inorganic form. This is partly due to the relatively low DOC concentration in Lake Iso Tiilijärvi, compared to the global estimate of 5.3 mg/L DOC (Meybeck 1993). 99% of the DOC originated from the lake water, and 83% of this DOC degraded to inorganic carbon in the groundwater, while 17% traveled through the aquifer without degradation and discharged from the springs. The lake sediment was assumed not to leach organic carbon in the aquifer. The rapid decrease in DOC after infiltration, and the fact that the molecular composition of DOM was similar in the lake water (L1) and in the groundwater (OW30) support the assumption. If there is leakage of organic matter from the sediment, the amount is minor compared to the DIC production, and the chemical properties of the leaking material are similar to the lake DOM.

The sources of DIC inflow to the aquifer were lake water (7%), biodegradation of lake DOC in the aquifer (22%), biodegradation of organic matter in the lake sediment (31%) and DIC originating from the vadose zone due to groundwater recharge by precipitation (40%). The DIC concentration of groundwater recharge was estimated at 12.6 mg/L, which is within the range of observed values in similar aquifers in Finland, that is, 2.4–21.6 mg/L based on Kortelainen and Karhu (2006) and Kortelainen and Karhu (2009).

Based on the PCA analysis, after a DOM removal of approximately 50% in OW30, the molecular composition of organic matter was still close to the lake water composition (L1), whereas after a DOM removal of over 80% in OW40 and OW60, the molecular composition became clearly different. The molecular composition of OW50 was not similar to either of these groups because

of a bank infiltrate fraction that was lower than in the other observation wells, and because OW50 is located outside the main flow path (Jylhä-Ollila et al. 2020).

O_y compounds dominated in the lake water, which is typical for surface waters (e.g., Lavonen et al. 2015; Lu et al. 2015; Raeke et al. 2017). Furthermore, the O_y compounds were efficiently removed during bank infiltration, and the S_zO_y compounds were enriched in the water in low DOC concentrations (Figure 5a). A relative enrichment of S_zO_y compounds was also observed in the average properties of DOM. The values of MW_{av}, DBE_{av}, and C#_{av} of all species in the lake water were close to the values of the O_y species, but with a decreasing DOC concentration in OW40, OW50, and OW60, the values shifted toward the values of the S_zO_y species (Table 2). For example, in the lake water sample L1, the MW_{av} of all moieties (578 Da) is close to the MW_{av} of O_y compounds (560 Da), whereas in OW60, the MW_{av} of all moieties (667 Da) is close to the MW_{av} of S_zO_y compounds (690 Da). The results from a surface treatment by flocculation have shown a similar enrichment of S_zO_y compounds in treated water (Raeke et al. 2017). From the O_y compounds, unsaturated molecules with a low H/C ratio were removed most efficiently in the infiltration (Figure S1).

According to the H/C and O/C ratios (Figure 6), the O_y compounds represent conventional NOM found in bogs and lake waters, which mainly consist of comprised polyphenols, carbonyl-rich alicyclic molecules (CRAM), or carbohydrate-like compounds (D'Andrilli et al. 2013; Cao et al. 2018). Only few carbohydrates, lipids, amino acids, or other aliphatic compounds were observed. Compounds with a H/C ratio of 0.6–1.6 and an O/C ratio of 0.2–1.8 may contain a variety of compounds, including carbonyl-rich alicyclic molecules (CRAMs), tannins, and condensed aromatics (D'Andrilli et al. 2013, Hockaday et al. 2009; Ohno et al. 2010). Based solely on their molecular formulae, the exact structure of a compound or its possible aromatic nature could not be determined. The aromatic index (AI) provides a conservative criterion for the identification of aromatics (AI > 0.5) and condensed aromatics (AI > 0.67) present in NOM samples (Koch and Dittmar 2006). There were only a few compounds with AI > 0.5 in the L1 sample, but none in the other samples. This indicates that the O_y species were not condensed aromatics or polyphenols/tannins. Anyhow, the AI of both CRAMs and lignin-derived compounds is typically below 0.5 even if they are aromatic. Thus, Equation 5 is not suited for the lignin-derived compounds due to the large amount of oxygen in the aliphatic side chains (Stubbins et al. 2010). The S_zO_y compounds represent less condensed (larger H/C ratio) and more oxygenated compounds, most likely different sulfoxides or sulfones.

The molecular diversity with 1900 to 3150 O_y species, and 4960 to 5330 species in total in each sample corresponds to earlier observations of DOM diversity in rainwater (Mead et al. 2013), forest soils (Roth et al. 2015), and surface waters (Kim et al. 2006; Kellerman et al. 2014; Lavonen et al. 2015; Lu et al. 2015). In

contrast, Ide et al. (2017) reported in a study by FT-ICR MS the molecular diversity of organic compounds in water fluxes in a boreal forest ecosystem to be lower, 1293 ± 307 SD per sample. As the methodology might differ between investigations, the results related to molecular diversity may not be comparable. In our study, molecular diversity did not decrease with a decreasing DOC concentration, which is consistent with Ide et al. (2017) and Lavonen et al. (2015), but in contrast with Roth et al. (2015).

Unlike earlier observations by HPSEC from surface water treatment plants or MAR (Nissinen et al. 2001; Lindroos et al. 2002; Matilainen et al. 2002), bank filtration did not affect MW_{av} of DOM. The molecular weights of NOM by different methods are not directly comparable. Mass spectrometry of NOM indicate masses lower than 1000 Da for most compounds, whereas results from HPSEC suggest much larger macro molecules, typically in the range of 500–10,000 Da (Nissinen et al. 2001; Lindroos et al. 2002; Matilainen et al. 2002; Nebbioso and Piccolo 2013). The discrepancy between the molecular size determined by different methods has been explained by the hypothesis that non-covalently bound aggregates remain intact during membrane size fractionation, but they separate in electro spray ionization with ultra-high-resolution mass spectrometry (Gonsior et al. 2014). The molecular properties of NOM are under discussion, and the existence of large macromolecules has been questioned (e.g., Schmidt et al. 2011; Lehmann and Kleber 2015; Janzen 2019).

Research on DOM characterized by FT-ICR MS has so far focused on describing the properties of DOM in different environments (e.g., Kim et al. 2006; Mead et al. 2013; Ide et al. 2017), but not enough is known about the and key underlying environmental factors behind to explain the observations. Soil pH, iron complexing index and C/N ratio, as well as temperature, are known to be factors controlling the DOM profiles in soils (Roth et al. 2015; Li et al. 2018). Roth et al. (2015) observed that the molecular diversity and saturation of the molecules increase in winter and with low pH in soils. They propose that when the bacterial activity slows down by low pH or low temperature, the easily degradable DOM fractions (i.e., the saturated molecules of DOM) are not degraded. Even if the total molecular diversity of all compounds was not reduced in the bank infiltration at Iso Tiilijärvi, the molecular diversity of the main compounds (O_y) was reduced and the saturated compounds were removed.

Conclusions

Determination of the carbon budget demonstrated the relative importance of different DOC and DIC sources for groundwater quality, while FT-ICR MS provided a novel way to describe the diversity of dissolved carbon compounds and changes in their molecular composition during the transport from the lake to the aquifer.

According to the carbon budget, the majority of dissolved carbon compounds entering the aquifer are

inorganic (75%), and most of this inorganic carbon originates from the soil solid phase in the vadose zone above the groundwater table (40%) and from the lake bottom sediment (31%). Degradation of DOC originating from the lake water to the inorganic form in the aquifer constitutes only 22% and the DIC originating directly from the lake water constitutes 7%. Of the total DOC entering the aquifer, as much as 99% originates from the lake water and only 1% from the soil solid phase above the groundwater table.

The biodegradation of organic matter in the lake bottom sediment was observed as a DIC addition to groundwater after infiltration through the sediment. The seasonal temperature variation had an influence on this DIC production: in temperatures close to 0 °C, the production of additional carbon from the lake bank sediment was negligible, whereas in the summer temperatures around 22 °C, a carbon addition of 4.9 mg/L was measured, which led to anoxic conditions from surface water with oxygen saturation. The results strengthened the assumption that leakage of DOC from the lake bank is small or negligible, as the DOC concentration decreased after infiltration, and the molecular composition of DOM resembled the composition of the lake water DOM after infiltration through the lake sediment; Changes in the molecular properties of DOM were only evident after longer residence times in the aquifer.

The main finding from FT-ICR MS was that bank infiltration selectively removed natural organic matter. O_y compounds, which made 75% of the boreal lake DOM, were removed efficiently, whereas S_zO_y compounds traveled through the aquifer and were enriched in groundwater as the TOC concentration decreased. These results suggest that the O_y compounds are easily removed by bank infiltration through degradation, but the S_zO_y compounds are resilient to degradation in the aquifer. Observations on the selectivity of NOM removal demonstrate that the final efficiency of organic matter removal depends on the quality of the organic matter in the surface water, and a better knowledge of NOM quality on the molecular level in surface waters would help in estimating the total removal efficiency of MAR. The results highlighted the importance of lake bank processes in MAR. To achieve better groundwater quality in drinking water production by MAR, methods to minimize the impact of the sediment should be developed.

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Authors' Note

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Supporting Information

Additional supporting information may be found online in the Supporting Information section at the end of the article. Supporting Information is generally *not* peer reviewed.

Appendix S1. Carbon budget calculation.

Figure S1. Van Krevelen diagrams of all samples.

References

- Appelo, C.A.J., and D. Postma. 1999. *Geochemistry, Groundwater and Pollution*. Rotterdam: A.A. Balkema.
- Bayarsaikhan, U., J. Filter, U. Gernert, M. Jekel, and A.S. Ruhl. 2018. Fate of leaf litter deposits and impacts on oxygen availability in bank filtration column studies. *Environmental Research* 164: 495–500. <https://doi.org/10.1016/j.envres.2018.03.033>
- Butturini, A., P. Herzsprung, O.J. Lechtenfeld, S. Venturi, S. Amalfitano, E. Vazquez, N. Pacini, D.M. Harper, F. Tassi, and S. Fazi. 2020. Dissolved organic matter in a tropical saline-alkaline lake of the East African Rift Valley. *Water Research* 173: 115532. <https://doi.org/10.1016/j.watres.2020.115532>
- Cao, X., G.R. Aiken, K.D. Butler, J. Mao, and K. Schmidt-Rohr. 2018. Comparison of the chemical composition of dissolved organic matter in three lakes in Minnesota. *Environmental Science and Technology* 52, no. 4: 1747–1755. <https://doi.org/10.1021/acs.est.7b04076>
- Clark, I., and P. Fritz. 1997. *Environmental Isotopes in Hydrogeology*. Boca Raton, Florida: Lewis Publishers.
- Craig, H. 1957. Isotopic standards for carbon and oxygen and correction factors for mass-spectrometric analysis of carbon dioxide. *Geochimica et Cosmochimica Acta* 12, no. 1–2: 133–149. [https://doi.org/10.1016/0016-7037\(57\)90024-8](https://doi.org/10.1016/0016-7037(57)90024-8)
- D'Andrilli, J., C.M. Foreman, A.G. Marshall, and D.M. McKnight. 2013. Characterization of IHSS pony lake fulvic acid dissolved organic matter by electrospray ionization fourier transform ion cyclotron resonance mass spectrometry and fluorescence spectroscopy. *Organic Geochemistry* 65: 19–28. <https://doi.org/10.1016/j.orggeochem.2013.09.013>
- D'Andrilli, J., T. Dittmar, B.P. Koch, J.M. Purcell, A.G. Marshall, and W.T. Cooper. 2010a. Comprehensive characterization of marine dissolved organic matter by fourier transform ion cyclotron resonance mass spectrometry with electrospray and atmospheric pressure photoionization. *Rapid Communications in Mass Spectrometry* 24, no. 5: 643–650. <https://doi.org/10.1002/rcm.4421>
- D'Andrilli, J., J.P. Chanton, P.H. Glaser, and W.T. Cooper. 2010b. Characterization of dissolved organic matter in northern peatland soil porewaters by ultra high resolution mass spectrometry. *Organic Geochemistry* 41, no. 8: 791–799. <https://doi.org/10.1016/j.orggeochem.2010.05.009>

- Deines, P. 1980. The isotopic composition of reduced organic carbon. In *Handbook of Environmental Isotope Geochemistry*, Vol. 1, ed. P. Fritz, and C.H. Fontes, 329–406. Amsterdam, The Netherlands: Elsevier (Chapter 9).
- Diem, S., M.R. Von Rohr, J.G. Hering, H.-P. Kohler, M. Schirmer, and U. von Gunten. 2013. NOM degradation during river infiltration: Effects of the climate variables temperature and discharge. *Water Research* 47, no. 17: 6585–6595. <https://doi.org/10.1016/j.watres.2013.08.028>
- Dillon, P., P. Stuyfzand, T. Grischek, M. Lloria, R.D.G. Pyne, R.C. Jain, J. Bear, J. Schwarz, W. Wang, E. Fernandez, C. Stefan, M. Pettenati, J. van der Gun, C. Sprenger, G. Massmann, B.R. Scanlon, J. Xanke, P. Jokela, Y. Zheng, R. Rossetto, M. Shamruk, P. Pavelic, E. Murray, A. Ross, J.P. Bonilla Valverde, A. Palma Nava, N. Ansems, K. Posavec, K. Ha, R. Martin, and M. Sapiano. 2019. Sixty years of global progress in managed aquifer recharge. *Hydrogeology Journal* 27, no. 1: 1–30. <https://doi.org/10.1007/s10040-018-1841-z>
- Dittmar, T., B. Koch, N. Hertkorn, and G. Kattner. 2008. A simple and efficient method for the solid-phase extraction of dissolved organic matter (SPE-DOM) from seawater. *Limnology and Oceanography: Methods* 6, no. 6: 230–235. <https://doi.org/10.4319/lom.2008.6.230>
- Filella, M. 2009. Freshwaters: Which NOM matters? *Environmental Chemistry Letters* 7, no. 1: 21–35. <https://doi.org/10.1007/s10311-008-0158-x>
- Gonsior, M., P. Schmitt-Kopplin, H. Stavklint, N. Hertkorn, and D. Bastviken. 2014. Changes in dissolved organic matter during the treatment processes of a drinking water plant in Sweden and formation of previously unknown disinfection byproducts. *Environmental Science and Technology* 48, no. 21: 12714–12722. <https://doi.org/10.1021/es504349p>
- Grishenk, T., and S. Pauffler. 2017. Prediction of iron release during riverbank infiltration. *Water* 9, no. 5: 317. <https://doi.org/10.3390/w9050317>
- Gross-Wittke, A., G. Gunkel, and A. Hoffmann. 2010. Temperature effects on bank filtration: Redox conditions and physical-chemical parameters of pore water at Lake Tegel, Berlin, Germany. *Journal of Water and Climate Change* 1, no. 1: 55–66. <https://doi.org/10.2166/wcc.2010.005>
- Hellauer, K., S. Martínez Mayerlen, J.E. Drewes, and U. Hübner. 2019. Biotransformation of trace organic chemicals in the presence of highly refractory dissolved organic carbon. *Chemosphere* 215: 33–39. <https://doi.org/10.1016/j.chemosphere.2018.09.166>
- Henzler, A.F., J. Greskowiak, and G. Massmann. 2016. Seasonality of temperatures and redox zonation during bank filtration—A modeling approach. *Journal of Hydrology* 535: 282–292. <https://doi.org/10.1016/j.jhydrol.2016.01.044>
- Hertkorn, N., M. Harir, K.M. Cawley, P. Schmitt-Kopplin, and R. Jaffé. 2016. Molecular characterization of dissolved organic matter from subtropical wetlands: A comparative study through the analysis of optical properties, NMR and FTICR/MS. *Biogeosciences* 13, no. 8: 2257–2277. <https://doi.org/10.5194/bg-13-2257-2016>
- Hockaday, W.C., J.M. Purcell, A.G. Marshall, J.A. Baldock, and P.G. Hatcher. 2009. Electrospray and photoionization mass spectrometry for the characterization of organic matter in natural waters: A qualitative assessment. *Limnology and Oceanography: Methods* 7, no. 1: 81–95. <https://doi.org/10.4319/lom.2009.7.81>
- Ide, J., M. Ohashi, K. Takahashi, Y. Sugiyama, S. Piirainen, P. Kortelainen, N. Fujitake, K. Yamase, N. Ohte, M. Moritani, M. Hara, and L. Finér. 2017. Spatial variations in the molecular diversity of dissolved organic matter in water moving through a boreal forest in eastern Finland. *Scientific Reports* 7: 42102. <https://doi.org/10.1038/srep42102>
- Janzen, H. 2019. The future of humic substances research: Preface to a debate. *Journal of Environmental Quality* 48, no. 2: 205–206. <https://doi.org/10.2134/jeq2019.01.0001c>
- Jokela, P., T. Eskola, T. Heinonen, U. Tantt, J. Tyrväinen, and A. Artimo. 2017. Raw water quality and pretreatment in managed aquifer recharge for drinking water production in Finland. *Water* 9, no. 2: 138. <https://doi.org/10.3390/w9020138>
- Jylhä-Ollila, M., H. Laine-Kaulio, P. Niinikoski-Fusswinkel, J. Leveinen, and H. Koivusalo. 2020. Water quality changes and organic matter removal using natural bank infiltration at a boreal lake in Finland. *Hydrogeology Journal* 28, no. 4: 1343–1357. <https://doi.org/10.1007/s10040-020-02127-9>
- Kellerman, A.M., T. Dittmar, D.N. Kothawala, and L.J. Tranvik. 2014. Chemodiversity of dissolved organic matter in lakes driven by climate and hydrology. *Nature Communications* 5: 3804. <https://doi.org/10.1038/ncomms4804>
- Kendall, C., and J.J. McDonnell. 1998. *Isotope Tracers in Catchment Hydrology*. Amsterdam: Elsevier Science.
- Kim, S., L.A. Kaplan, and P.G. Hatcher. 2006. Biodegradable dissolved organic matter in a temperate and a tropical stream determined from ultra-high resolution mass spectrometry. *Limnology and Oceanography* 51, no. 2: 1054–1063. <https://doi.org/10.4319/lo.2006.51.2.1054>
- Kim, S., R.W. Kramer, and P.G. Hatcher. 2003. Graphical method for analysis of ultrahigh-resolution broadband mass spectra of natural organic matter, the van Krevelen diagram. *Analytical Chemistry* 75, no. 20: 5336–5344. <https://doi.org/10.1021/ac034415p>
- Koch, B.P., T. Dittmar, M. Witt, and G. Kattner. 2007. Fundamentals of molecular formula assignment to ultrahigh resolution mass data of natural organic matter. *Analytical Chemistry* 79, no. 4: 1758–1763. <https://doi.org/10.1021/ac061949s>
- Koch, B.P., and T. Dittmar. 2006. From mass to structure: An aromaticity index for high-resolution mass data of natural organic matter. *Rapid Communications in Mass Spectrometry* 20, no. 5: 926–932. <https://doi.org/10.1002/rcm.2386>
- Kortelainen, N.M., and J.A. Karhu. 2009. Geochemical and isotopic evolution of high-pH groundwater in a carbonate-bearing glacial aquifer, SW Finland. *Hydrology Research* 40, no. 1: 19–31. <https://doi.org/10.2166/nh.2009.032>
- Kortelainen, N.M., and J.A. Karhu. 2006. Tracing the decomposition of dissolved organic carbon in artificial groundwater recharge using carbon isotope ratios. *Applied Geochemistry* 21, no. 4: 547–562. <https://doi.org/10.1016/j.apgeochem.2006.01.004>
- van Krevelen, D.W. 1950. Graphical-statistical method for the study of structure and reaction processes of coal. *Fuel* 29: 269–284.
- Kujawinski, E.B., K. Longnecker, N.V. Blough, R. Del Vecchio, L. Finlay, J.B. Kitner, and S.J. Giovannoni. 2009. Identification of possible source markers in marine dissolved organic matter using ultrahigh resolution mass spectrometry. *Geochimica et Cosmochimica Acta* 73, no. 5: 4384–4399. <https://doi.org/10.1016/j.gca.2009.04.033>
- Lavonen, E.E., D.N. Kothawala, L.J. Tranvik, M. Gonsior, P. Schmitt-Kopplin, and S.J. Köhler. 2015. Tracking changes in the optical properties and molecular composition of dissolved organic matter during drinking water production. *Water Research* 85: 286–294. <https://doi.org/10.1016/j.watres.2015.08.024>
- Lehmann, J., and M. Kleber. 2015. The contentious nature of soil organic matter. *Nature* 528, no. 7580: 60–68. <https://doi.org/10.1038/nature16069>
- Li, X.-M., G.-X. Sun, S.-C. Chen, Z. Fang, H.-Y. Yuan, Q. Shi, and Y.-G. Zhu. 2018. Molecular chemodiversity of dissolved organic matter in paddy soils. *Environmental*

- Science and Technology* 52, no. 3: 963–971. <https://doi.org/10.1021/acs.est.7b00377>
- Lindroos, A., V. Kitunen, J. Derome, and H.-S. Helmisaari. 2002. Changes in dissolved organic carbon during artificial recharge of groundwater in a forested esker in southern Finland. *Water Resources Research* 36, no. 20: 4951–4958. [https://doi.org/10.1016/S0043-1354\(02\)00226-9](https://doi.org/10.1016/S0043-1354(02)00226-9)
- Lu, Y., X. Li, R. Mesfioui, J.E. Bauer, R.M. Chambers, E.A. Canuel, and P.G. Hatcher. 2015. Use of ESI-FTICR-MS to characterize dissolved organic matter in headwater streams draining forest-dominated and pasture-dominated watersheds. *PLoS One* 10, no. 12: e0145639. <https://doi.org/10.1371/journal.pone.0145639>
- Maeng, S.K., S.K. Sharma, K. Lekkerkerker-Teunissen, and G.L. Amy. 2011. Occurrence and fate of bulk organic matter and pharmaceutically active compounds in managed aquifer recharge: A review. *Water Research* 45: 3015–3033. <https://doi.org/10.1016/j.watres.2011.02.017>
- Marshall, A.G. 2000. Milestones in Fourier transform ion cyclotron resonance mass spectrometry technique development. *International Journal of Mass Spectrometry* 200, no. 1–3: 331–356. [https://doi.org/10.1016/S1387-3806\(00\)00324-9](https://doi.org/10.1016/S1387-3806(00)00324-9)
- Masoom, H., D. Courtier-Murias, H. Farooq, R. Soong, B.P. Kelleher, C. Zhang, W.E. Maas, M. Fey, R. Kumar, M. Monette, H.J. Stronks, M.J. Simpson, and A.J. Simpson. 2016. Soil organic matter in its native state: Unravelling the most complex biomaterial on earth. *Environmental Science and Technology* 50, no. 4: 1670–1680. <https://doi.org/10.1021/acs.est.5b03410>
- Massmann, G., J. Greskowiak, U. Dünbier, S. Zuehlke, A. Knappe, and A. Pekdeger. 2006. The impact of variable temperatures on the redox conditions and the behaviour of pharmaceutical residues during artificial recharge. *Journal of Hydrology* 328, no. 1: 141–156. <https://doi.org/10.1016/j.jhydrol.2005.12.009>
- Matilainen, A., E.T. Gjessing, T. Lahtinen, L. Hed, A. Bhatnagar, and M. Sillanpää. 2011. An overview of the methods used in the characterisation of natural organic matter (NOM) in relation to drinking water treatment. *Chemosphere* 83, no. 11: 1431–1442. <https://doi.org/10.1016/j.chemosphere.2011.01.018>
- Matilainen, A., N. Lindqvist, S. Korhonen, and T. Tuhkanen. 2002. Removal of NOM in the different stages of the water treatment process. *Environment International* 28, no. 6: 457–465. [https://doi.org/10.1016/S0160-4120\(02\)00071-5](https://doi.org/10.1016/S0160-4120(02)00071-5)
- Mead, R.N., K.M. Mullaugh, G. Brooks Avery, R.J. Kieber, J.D. Willey, and D.C. Podgorski. 2013. Insights into dissolved organic matter complexity in rainwater from continental and coastal storms by ultrahigh resolution Fourier transform ion cyclotron resonance mass spectrometry. *Atmospheric Chemistry and Physics* 13, no. 9: 4829–4838. <https://doi.org/10.5194/acp-13-4829-2013>
- Meybeck, M. 1993. C, N, P and S in rivers: From sources to global inputs. In *Interactions of C, N, P and S Biogeochemical Cycles and Global Change*, ed. R. Wollast, F.T. Mackenzie, and L. Chou, 163–193. Berlin: Springer.
- Nebbioso, A., and A. Piccolo. 2013. Molecular characterization of dissolved organic matter (DOM): A critical review. *Analytical and Bioanalytical Chemistry* 405, no. 1: 109–124. <https://doi.org/10.1007/s00216-012-6363-2>
- Nissinen, T.K., I.T. Miettinen, P.I. Martikainen, and T. Vartiainen. 2001. Molecular size distribution of natural organic matter in raw and drinking waters. *Chemosphere* 45, no. 6–7: 865–873. [https://doi.org/10.1016/S0045-6535\(01\)00103-5](https://doi.org/10.1016/S0045-6535(01)00103-5)
- Ohno, T., Z. He, R.L. Sleighter, C.W. Honeycutt, and P.G. Hatcher. 2010. Ultrahigh resolution mass spectrometry and indicator species analysis to identify marker components of soil- and plant biomass-derived organic matter fractions. *Environmental Science and Technology* 44, no. 22: 8594–8600. <https://doi.org/10.1021/es101089t>
- Raake, J., O.J. Lechtenfeld, J. Tittel, M.R. Oosterwoud, K. Bornmann, and T. Reetsma. 2017. Linking the mobilization of dissolved organic matter in catchments and its removal in drinking water treatment to its molecular characteristics. *Water Research* 113: 149–159. <https://doi.org/10.1016/j.watres.2017.01.066>
- Regnery, J., C.P. Gerba, E.R.V. Dickenson, and J.E. Dreves. 2017. The importance of key attenuation factors for microbial and chemical contaminants during managed aquifer recharge: A review. *Critical Reviews in Environmental Science and Technology* 47, no. 15: 1409–1452. <https://doi.org/10.1080/10643389.2017.1369234>
- Roth, V.-N., T. Dittmar, R. Gaupp, and G. Gleixner. 2015. The molecular composition of dissolved organic matter in forest soils as a function of pH and temperature. *PLoS One* 10, no. 3: e0119188. <https://doi.org/10.1371/journal.pone.0119188>
- Schiff, S.L., R. Aravena, S.E. Trumbore, M.J. Hinton, R. Elgood, and P.J. Dillon. 1997. Export of DOC from forested catchments on the Precambrian Shield of Central Ontario: Clues from ¹³C and ¹⁴C. *Biogeochemistry* 36, no. 1: 43–65.
- Schilder, J., D. Bastviken, M. van Hardenbroek, M. Leuenberger, P. Rinta, T. Stötter, and O. Heiri. 2015. The stable carbon isotopic composition of *Daphnia ephippia* in small, temperate lakes reflects in-lake methane availability. *Limnology and Oceanography* 60: 1064–1075. <https://doi.org/10.1002/lno.10079>
- Schmidt, M.W.I., M.S. Torn, S. Abiven, T. Dittmar, G. Guggenberger, I. Janssens, M. Kleber, I. Kögel-Knabner, J. Lehmann, D. Manning, P. Nannipieri, D. Rasse, S. Weiner, and S. Trumbore. 2011. Persistence of soil organic matter as an ecosystem property. *Nature* 478, no. 7367: 49–56. <https://doi.org/10.1038/nature10386>
- Schmidt, F., M. Elvert, B.P. Koch, M. Witt, and K.-U. Hinrichs. 2009. Molecular characterization of dissolved organic matter in pore water of continental shelf sediments. *Geochimica et Cosmochimica Acta* 73, no. 11: 3337–3358. <https://doi.org/10.1016/j.gca.2009.03.008>
- Sleighter, R.L., and P.G. Hatcher. 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, no. 3–4: 140–152. <https://doi.org/10.1016/j.marchem.2008.04.008>
- Sprenger, C., N. Hartog, M. Hernández, E. Vilanova, G. Grützner, F. Scheibler, and S. Hannappel. 2017. Inventory of managed aquifer recharge sites in Europe: Historical development, current situation and perspectives. *Hydrogeology Journal* 25, no. 6: 1909–1922. <https://doi.org/10.1007/s10040-017-1554-8>
- Stubbins, A., R.G.M. Spencer, H. Chen, P.G. Hatcher, K. Mopper, P.J. Hernes, V.L. Mwamba, A.M. Mangangu, J.N. Wabakanghanzi, and J. Six. 2010. Illuminated darkness: Molecular signatures of Congo River dissolved organic matter and its photochemical alteration as revealed by ultrahigh precision mass spectrometry. *Limnology and Oceanography* 55, no. 4: 1467–1477. <https://doi.org/10.4319/lo.2010.55.4.1467>
- Thurmann, E.M. 1985. *Organic Chemistry of Natural Waters*. Dordrecht: Springer Science & Business Media.
- Tremblay, L.B., T. Dittmar, A.G. Marshall, W.J. Cooper, and W.T. Cooper. 2007. Molecular characterization of dissolved organic matter in a North Brazilian mangrove porewater and mangrove-fringed estuaries by ultrahigh resolution Fourier transform-ion cyclotron resonance mass spectrometry and excitation/emission spectroscopy. *Marine Chemistry* 105,

- no. 1–2: 15–29. <https://doi.org/10.1016/j.marchem.2006.12.015>
- Vogel, J.C. 1993. Variability of carbon isotope fractionation during photosynthesis. In *Stable Isotopes and Plant Carbon—Water Relations*, ed. J.R. Ehrlinger, A.E. Hall, and G.D. Farguhar, 29–38. San Diego, California: Academic Press.
- Yu, K., Y. Duan, Y. Gan, Y. Zhang, and K. Zhao. 2020. Anthropogenic influences on dissolved organic matter transport in high arsenic groundwater: Insights from stable carbon isotope analysis and electrospray ionization Fourier transform ion cyclotron resonance mass spectrometry. *Science of the Total Environment* 708: 135162. <https://doi.org/10.1016/j.scitotenv.2019.135162>