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Water residence time is an important predictor of dissolved organic matter composition and drinking water treatability

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ABSTRACT

Freshwater ecosystems are critical resources for drinking water. In recent decades, dissolved organic matter (DOM) inputs into aquatic systems have increased significantly, particularly in central and northern Europe, due to climatic and anthropogenic drivers. The associated increase in dissolved organic carbon (DOC) concentration can change lake ecosystem services and adversely affect drinking water treatment processes. In this study, we examined spatial and temporal patterns of DOM treatability with granular activated carbon (GAC) and biological reactivity based on 14-day bacterial respiration incubations at 11 sites across Mälaren during six-time points between July 2019 and February 2021. Mälaren is the third largest lake in Sweden and provides drinking water for over 2 million people including the capital city Stockholm. In our spatio-temporal analysis, we assessed the influence of phytoplankton abundance, water chemistry, runoff, and climate on DOM composition, GAC removal efficiency, and biological reactivity. Variations in DOM composition were characterized using optical measurements and Orbitrap mass spectrometry. Multivariate statistical analyses indicated that DOM produced during warmer months was easier to remove by GAC. Removal efficiency of GAC varied from 41 to 87 %, and the best predictor of treatability using mass spectrometry was double bond equivalents (DBE), while the best optical predictors were specific UV absorbance (SUVA), and freshness index. The oxygen consumption rate (k) from the bacterial respiration incubations ranged from 0.04 to 0.71 d^{-1} and higher in warmer months and at deeper basins and was associated with more aliphatic and fresh DOM. The three deepest lake basins with the longest water residence time (WRT) were temporally the most stable in terms of DOM composition and had the highest DOC removal efficiency and k rates. DOM composition in these three lake basins was optically clearer than in basins located closer to terrestrial inputs and had a signature suggesting it was derived from in-lake processes including phytoplankton production and bacterial processing of terrestrial DOM. This means that with increasing WRT, DOM derived from terrestrial sources shifts to more aquatically produced DOM and becomes easier to remove with GAC. These findings indicate WRT can be highly relevant in shaping DOM composition and thereby likely to affect its ease of treatability for drinking water purposes.

1. Introduction

Freshwater ecosystems are highly valued in terms of ecosystem services, particularly as a critical drinking water source (Fisher et al., 2009). The growing global demand for drinking water implies a need to maintain and understand the internal biogeochemical cycling of such resources (Boretti and Rosa, 2019). However, freshwater ecosystems have been impacted by numerous anthropogenic activities, including socioeconomic development, climate change, and land use (Jenny et al., 2020), leading to a considerable increase in dissolved organic matter (DOM) inputs (Evans et al., 2005). There have been significant increases in the terrestrial input of DOM to surface waters, particularly in central and northern Europe and parts of North America (Evans et al., 2005; Kritzberg and Ekström, 2012; Monteith et al., 2007). This increase in DOC concentration is a greater concern to drinking water providers in northern countries that depend on surface waters for drinking water

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(Eikebrokk et al., 2004; Ledesma et al., 2012), including Sweden, where 50 % of the drinking water is from surface waters (http://www.svensktvatten.se) (Kritzberg et al., 2020). Analogously, several studies suggest that warming conditions driven by climate change have led to higher bacterial activity (e.g., in-lake heterotrophic metabolism) and phytoplankton productivity, thereby increasing the aquatically produced DOM in freshwaters (Angeler et al., 2010; Creed et al., 2018; Karlsson et al., 2009; Woolway et al., 2020).

DOM contributes to several challenges for drinking water treatment plants (DWTPs) including the re-growth of harmful bacteria and the formation of biofilms in the distribution system, and contributing to the unpleasant taste and odor of water (Kenefick et al., 1992; Ledesma et al., 2012). The presence of DOM can alter the fate and transport of contaminants like heavy metals and micropollutants in DWTPs by changing their reactivity and solubility or by forming associations with DOM (Aiken et al., 2011; Ledesma et al., 2012). High concentrations of dissolved organic carbon (DOC) can lead to the production of toxic disinfection by-products (e.g., trihalomethanes) during chlorination (Chow et al., 2003). Therefore, understanding the best strategies for removing DOM from source waters and optimizing treatment processes is highly relevant.

There have been several treatment processes for DOM removal including flocculation/coagulation (Matilainen et al., 2010), chemical oxidation (Wenk et al., 2013), membrane filtration (Zhang et al., 2018), and adsorption (Zusman et al., 2020), GAC is an adsorbent that is increasingly used for the removal of DOC as a filtration step after flocculation and coagulation. GAC has a high hydraulic conductivity, surface area and sorption capacity to help remove DOM (Jamil et al., 2020; Zusman et al., 2020). Studies have shown the selective removal of different DOM compounds by GAC (Andersson et al., 2020; Moona et al., 2018; Moreno-Castilla, 2004). Different treatment methods can target two main types of DOM, namely terrestrially-derived and aquatically-produced DOM, and the removal efficiency can depend on DOM quality and composition (Lavonen et al., 2015). For instance, coagulation and flocculation selectively target terrestrial and aromatic DOM (SUVA >4) (Edzwald and Tobiason, 1999; Lavonen et al., 2015). WRT is one of the critical factors that can control DOM quality and its molecular composition. As WRT increases the optical signatures associated with terrestrial DOM diminish, whereas those characteristics linked to aquatic sources comprise a greater fraction of the DOM (Kellerman et al., 2014; Köhler et al., 2013; Kothawala et al., 2014). Therefore, WRT can potentially play an important role in shaping the molecular composition of DOM which in turn could affect the treatability of DOM.

Mälaren is located in southeast Sweden and is the third-largest lake in the country. It holds particular societal significance as it provides drinking water for over two million people including the greater Stockholm area (Rehrl et al., 2020). In recent decades, lake water quality has been impacted by urbanization, temperature increases, precipitation changes, and anthropogenic activities (Ledesma et al., 2012; Peacock et al., 2023; Rehrl et al., 2020). The impacts of these alterations on lake water quality can be limited or exaggerated, depending on the WRT (Algesten et al., 2004; Hanson et al., 2011). Mälaren is a lake comprised of several hydrodynamically connected lake basins, and thus, changes to water quality can be detected with movement spatially across the lake as WRT increases from basin to basin (Köhler et al., 2013; Weyhenmeyer et al., 2004). This unique feature of Mälaren provides an opportunity to link DOM sources and composition to treatability and reactivity (Kellerman et al., 2018, 2015; Matilainen et al., 2010). In a previous study of Mälaren (Köhler et al., 2013), WRT was found to strongly control DOC concentration and composition, and shift the molecular weight (MW) of DOM. However, there is still a lack of information about seasonally-driven hydrological effects on the dynamics of DOM composition, treatability with GAC and biological reactivity in different basins of Mälaren with different WRT. In addition, including analysis of DOM with high-resolution mass spectrometry can provide deeper insights into DOM composition including information about elemental composition (C:H:O), which goes beyond bulk optical metrics.

In this study, we aim to provide a comprehensive understanding of spatial and temporal DOM composition dynamics in 11 basins of Mälaren characterized with various WRT using multiple analytical methods including absorbance, fluorescence and mass spectrometry. We investigated the biological reactivity of DOM over 14 days based on the oxygen consumption rate (k) using an optode technique (Soares et al., 2019). We hypothesize that DOM in the eastern lake basins with longer WRT during summer months will be more biologically active than in western basins during winter months. In previous studies using activated carbon, higher removal efficiency was observed for more colored, high molecular weight and aromatic DOM compounds (Jamil et al., 2020; Moreno-Castilla, 2004; Schreiber et al., 2005). Accordingly, we expect that DOM in basins with shorter WRT, having more influence from terrestrial sources, will be easier to remove with GAC than DOM in higher WRT basins.

2. Materials and methods

2.1. Study site: lake Mälaren

Mälaren is a large lake (1140 km^2) in southeast Sweden (59°30′N, 17°12′E), and provides drinking water for over 2 million people in the greater Stockholm area and surrounding towns (Fig. S1). The mean depth is 12.8 m, with a maximum depth of 63 m and water retention time of 2.8 years (Köhler et al., 2013).

Water samples were collected as part of the routine Mälaren lake monitoring program (Fölster et al., 2014) from 11 basins: Galten, Blacken, Granfjärden, Svinnegarnsviken, Ulvhällsfjärden, Prästfjärden, Västeråsfjärden, Södra (S) Björkfjärden, Ekoln, Skarven and Görväln. The main direction of water flows from the west (Galten) to the east (S. Björkfjärden), and secondly from the north (Ekoln) to the south (Görväln). The water drains out of Mälaren at the south-east end of the lake into the Baltic Sea. Lake basins were grouped into three subgroups based on their WRT (Fig. S2) (Liungman et al., 2010), DOM characteristics and their proximity to inflows. Group A included basins close to major inflows, Galten, Ekoln, and Skarven; Group B comprised sites with intermediate WRT, Blacken, Västeråsfjärden, Granfjärden, Svinnegarnsviken, and Ulvhällsfjärden; and Group C consisted of three basins with the longest WRT that are the deepest basins, Prästfjärden, S. Björkfjärden, and Görväln (Fig. 1).

Water samples were taken from a depth of 0.5 m at six-time points: July 2019, August 2019, September 2019, February 2020, September 2020, and February 2021. Samples were collected in 1 L pre-washed polyethylene bottles and stored in the dark at 4 °C until analysis (maximum one week after), and were filtered with precombusted glass fiber filters (Whatman GF/C, pore size 1.2 μm) before chemical, optical, and mass spectrometry analyses. Stream discharge and temperature data were downloaded from the Swedish Meteorological and Hydrological Institute (https://vattenwebb.smhi.se/modelarea/). Water discharge for five major stream inflows was used to generate a cumulative hydrograph for Mälaren over the study period of January 2019 to February 2021 (Fig. S3). Cumulative runoff (Q) pertaining to the six sampling dates was used in further analyses to evaluate differences in the hydrological conditions of the lake.

2.2. Hydrological model for water residence times

We obtained WRT data from an existing 3D hydrodynamic model that was developed to study the circulation and exchange between various sub-basins of Mälaren (Liungman et al., 2010). Calibration and validation of the model were conducted against temperature profiles at multiple stations, water levels observed at two stations, and combined outflows through Stockholm and an internal age tracer was also used for validation purposes (detailed in Liungman et al. 2010, also see Köhler

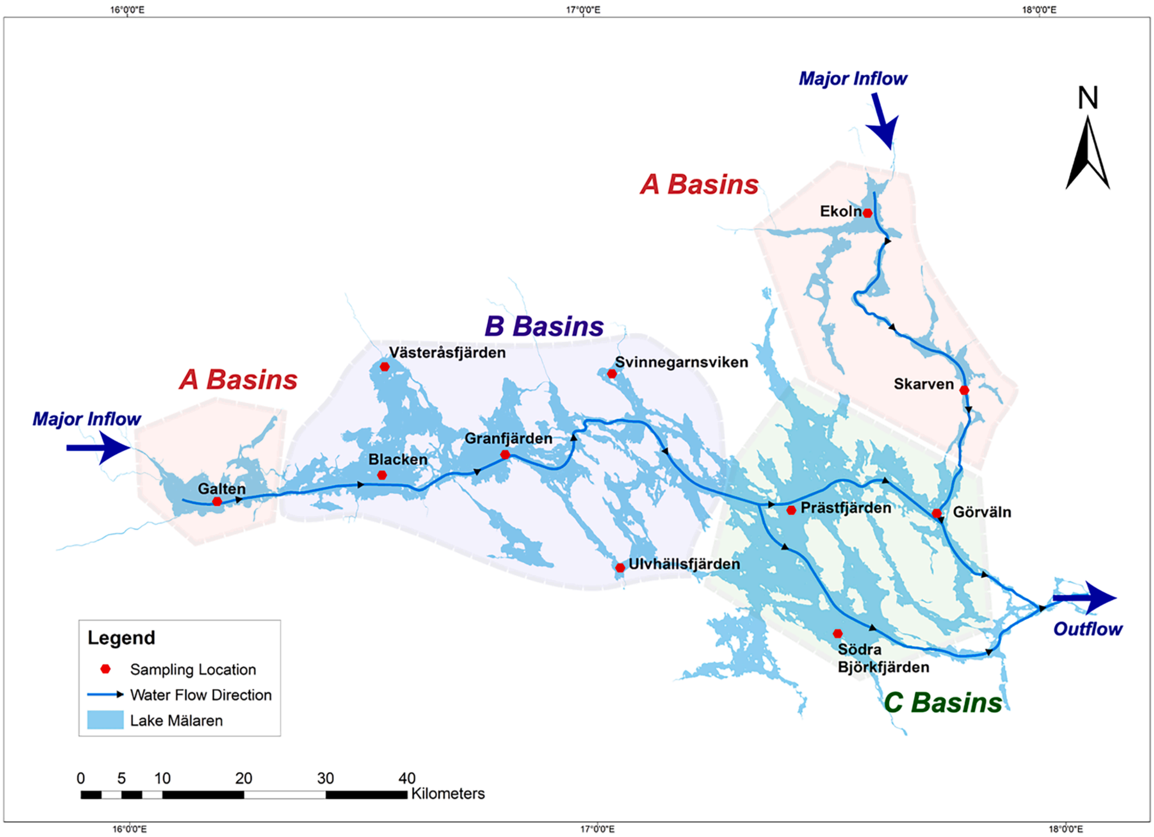

Fig. 1. Map of Mälaren with red dots showing the 11 lake basins sampled across the lake, with black arrows on the blue lines showing the dominant direction of water flow. The major inflows and outflow are shown with large blue arrows, and the subgrouping of basins A, B, and C are shown in shaded areas of the map.

et al. 2013). We used the WRT model to identify basins with longer or shorter WRT relative to each other and to help recognize the sizable differences in WRT between lake basins. Simulated age of surface waters in different basins is provided in supporting information (SI) (Fig. S2).

2.3. Monitoring dataset

We obtained water chemistry data from an accredited lab on the 11 long-term monitoring sites in this study, including concentrations of total nitrogen (TN, total dissolved nitrogen (TDN), nitrite (NO$_2^-$), nitrate (NO$_3^-$), ammonium (NH$_4^+$), total phosphorus (TP), anions (Cl$^-$, and SO4^{2-}), cations (K^+, Mg^{2+}, Na$^+$, and Ca^{2+}), iron content (Fe), and chlorophyll-a in different basins and times using open access data provided by the Swedish University of Agricultural Sciences (SLU) and the Mälaren Water Conservation Association (Fölster et al., 2014; Miljödata-MVM, 2024). Dissolved organic nitrogen (DON) was calculated based on the difference between TDN and inorganic N (NH$_4^+$, NO$_2^-$, and NO$_3^-$). Likewise, total organic nitrogen (N.org) was calculated as the difference between TN and inorganic N (NH$_4^+$, NO$_2^-$, and NO$_3^-$). Phytoplankton biovolume data was also collected but was limited to four of the six-time points and less than 50 % of lake basins used in this study (Fig. S3).

2.4. Characterization of DOM

DOC concentration was determined using a total organic carbon (TOC) analyzer (Sievers M9 Laboratory Analyzer, GE Analytical Instruments, Boulder, Colorado, USA). UV–Visible absorbance spectra (200 to 600 nm) were measured in a 1 cm quartz cuvette using a Lambda35 UV–Vis Spectrometer (PerkinElmer Lambda 25, Perkin Elmer, Waltham, USA). The specific UV absorbance values (SUVA; L mg C^{-1} m^{-1}), used as indicators of aromaticity, were determined by dividing the UV absorbance at 254 nm over a pathlength of 1 cm by the DOC concentration (mg C L^{-1}) (Weishaar et al., 2003). Higher values of SUVA indicate more aromatic, colored, and terrestrially-derived inputs of DOM.

Fluorescence excitation-emission matrices (EEM) were measured on filtered samples in a 1 cm quartz cuvette using a Spectrofluorometer (FluoroMax-4, Jobin Yvon, Horiba, Kyoto, Japan) at excitation wavelengths (Ex$_\lambda$) from 250 to 445 nm at 5 nm increments, emission wavelengths (Em$_\lambda$) from 300 to 600 nm at 4 nm increments. All EEMs were blank subtracted using the spectra of Milli-Q water, and corrected for instrument biases and inner filter effects (Kothawala et al., 2013). Fluorescence intensities were converted from counts per second (cps) to water Raman units (R.U.) by division of each data point with the area under the water Raman peak (integrated at Ex$_\lambda$ = 350 nm, Em$_\lambda$ from 380 to 420 nm) (Lawaetz and Stedmon, 2009). Three commonly used optical indices were calculated from the EEM data including the humification index (HIX = ratio of areas under the emission curve at 435–480 nm and 300–345 nm plus 435–480 nm at an excitation wavelength 254 nm) (Ohno, 2002), fluorescence index (FI = emission intensity at 470 nm divided by 520 nm at 370 nm excitation) (Cory and McKnight, 2005), and freshness index (ratio of emission intensity at 380 nm and maximum intensity between 420 and 435 nm at an excitation wavelength of 310 nm) (Parlanti et al., 2000). DOM with higher freshness and FI contains more microbially produced organic matter. Also, relative intensity of peak T, C, and M was determined across all the samples and calculated as %peaks. Peak T represents protein-like DOM, while peak C and M indicate humic-like DOM (Fellman et al., 2010). Locations of the peaks were determined within Ex$_{270–280\ (<240)}$, Em$_{330–368}$ for peak T, Ex$_{320–360}$, Em$_{420–460}$ for peak C, and Ex$_{290–325\ (<250)}$, Em$_{370–430}$ for peak M. The DOMcorr toolbox was used for all pre-processing of the fluorescence data, including blank subtraction, correction for inner filter effects, and Raman normalization (Murphy et al., 2010). Parallel factor analysis

(PARAFAC) was also used to characterize DOM fluorescence signals in a way that decomposes fluorescence excitation–emission matrices (EEMs) into trilinear components that explain the variability of the fluorescence characteristics of DOM in the samples (Bro, 1997; Stedmon and Bro, 2008). The detailed method used for PARAFAC analysis is provided in the SI (Section S.1.1, Fig. S9).

The DOM composition of water samples was measured by direct infusion electrospray ionisation (ESI) Orbitrap mass spectrometry (Fleury et al., 2017; Hawkes et al., 2016). Details of the analysis are provided in the SI (Section S.1.2). Identified molecules were categorized into different compound groups based on the elemental composition found in their molecular formula (Kellerman et al., 2014; Koch and Dittmar, 2006). Different compounds were grouped based on the modified aromaticity index (AI_{mod}), double bond equivalent (DBE), H/C and O/C ratios (Koch and Dittmar, 2006). DBE is a well-established index showing aromatic or condensed aromatic structures. We defined condensed aromatic compounds as present at $AI_{mod} > 0.67$. Compounds with $0.5 < AI_{mod} \leq 0.67$, were considered highly unsaturated compounds (HUS), and aliphatic compounds were defined as having $H/C \geq 1.5$. Oxygen-rich-unsaturated (O-rich-unsaturated) compounds were considered to have $AI_{mod} < 0.5$, $H/C < 1.5$, and $O/C > 0.5$, while oxygen-poor-unsaturated (O-poor-unsaturated) compounds were defined as $AI_{mod} < 0.5$, $H/C < 1.5$, and $O/C < 0.5$. Refractory carboxyl-rich alicyclic molecules (CRAM) were defined as peaks with $DBE/C > 0{,}3$, $DBE/C < 0{,}68$, $DBE/H > 0{,}2$, $DBE/H < 0{,}95$, $DBE/O > 0{,}77$, $DBE/O < 1{,}75$ (Figs. S10, S11).

2.5. DOM treatability with column adsorption experiments

We assessed the treatability of DOM by measuring DOC concentration before and after exposure to GAC in column experiments. Here we used GAC Filtrasorb 400® (Calgon Carbon Corporation, Feluy, Belgium) which is a steam-activated bituminous coal, pulverized and reagglomerated with a particle size of 0.55–0.75 mm, and a specific surface area of 1050 $m^2\ g^{-1}$. The column experiments were performed in acid-washed 3 mL columns. The columns were packed with 1 g dried GAC, and the bottom and top of the columns were packed with precombusted glass wool. The GAC columns were washed with MQ water, and then preconditioned by soaking in MQ water for 24 h, followed by rinsing with 100 mL of MQ water. Then, 100 mL of lake water was added to the syringe and allowed to pass through the GAC columns with a three-way stopcock regulating at a flow rate of approximately 1 mL per minute, to mimic the flow rate of 15 min exposure time at local DWTPs. GAC effluents were analyzed for DOC concentration and optical analyses.

2.6. Biological reactivity of DOM

To determine DOM reactivity, the *k* rates were measured by continuous monitoring of O_2 concentration over 14 days in filtered (0.7 um glass fiber) water samples (5 mL glass PreSens vials containing a sensor spot (SDR SensorDish® Reader, PreSens)). The initial oxygen reading was conducted once the incubation temperature stabilized after 12 h, and all samples were allowed to reach the ambient temperature inside the incubator. Oxygen measurements were recorded as %air saturation of oxygen at intervals of 30 min over 14 days at 20 °C in the dark, and the samples were run in duplicate. Milli-Q controls were used to monitor and ensure background O_2 consumption was minimal. The *k* values were obtained by fitting an exponential decay model with a residual pool to our data over the incubation period of 14 days (Koehler et al., 2012).

$$O_t = O_{demand}\ e^{-kt} + O_{residual} \tag{1}$$

2.7. Statistical analyses

We conducted non-metric multidimensional scaling (NMDS) analysis to explore how chemical, hydrological, and climatic lake characteristics relate to each other, alongside %DOC removal by GAC and biological reactivity (*k*). Additionally, we employed a partial least square (PLS) model to identify the ambient lake characteristics best able to predict DOC removal by GAC and biological reactivity (*k*). Due to limited data of phytoplankton biovolume, we did not include biovolume in the NMDS or PLS analyses. Analysis with the subset of data including phytoplankton biovolume did not reveal strong connections with DOM composition metrics. Furthermore, we used a linear mixed-effects model to explore how the optical composition of DOM changed before and after exposure to GAC considering the relative importance of spatial, temporal and interactive effects between space and time. Finally, we tested the linear correlation between %DOC removal by GAC and optical and mass spectrometry indices using Pearson's correlation analysis.

To get an overview of interrelationships across the entire dataset of measured variables, NMDS analysis was performed using all climate and hydrological data, water chemistry, DOM composition variables, %DOC removal by GAC and biological reactivity (*k*). The ordination was based on the Bray−Curtis dissimilarities across the 66 samples over 11 basins at 6-time points. All the variables were fit to the ordination plot with *p*-values calculated over 999 permutations. The NMDS allows the exploration of patterns across all input variables across space and time. NMDS was performed using the "vegan" package in R software version 4.3.1.

PLS analysis was used to determine the main contributing factors in predicting %DOC loss by GAC adsorbent. The %DOC loss was considered a dependent variable (Y) in the PLS analysis, and all climate, hydrological, chemical, optical and molecular characteristics were independent variables (X). Data were mean-centered and scaled to unit variance prior to analysis, and skewed predictor variables were log-transformed. Some variables were grouped including anions (Cl^-, and $SO4^{2-}$) and cations (K^+, Mg^{2+}, Na^+, and Ca^{2+}). Nitrogen and phosphorus species were excluded from these two ion groupings to investigate their role as nutrients. PLS analysis was particularly suitable for our dataset since it is not affected by correlations between the predictor variables. The importance of predictor variables is determined by the variable influence on projections (VIP) scores. Variables with VIP scores higher than 1 were considered as highly influential. The predictive power of the model (Q^2Y) was assessed by cross-validation, and random permutation tests (100 permutations) were run to assess the statistical significance of the estimated predictive power. PLS modelling was performed in SIMCA 15.0 (Umetrics AB, Umeå, Sweden).

A linear mixed-effects model was used to determine univariate relationships for six optical indices including SUVA, freshness, FI, HIX, %peak T, %peak M and %peak C, with lake basin and time to establish the effect of GAC treatment. GAC treatment, site, and season groups were fixed effects with interaction and site and date were random effects. In the model, we categorized the basins into the three subgroups of A, B, and C (Fig. 1). The sampling time points of July 2019, August 2019, September 2019 and September 2020 were grouped as warm months, and February 2020 and 2021 were defined as cold months. The analysis was done using "lmerTest" package in R software version 4.3.1.

3. Results

3.1. Spatiotemporal dynamics of DOC

The spatial and temporal dynamics in DOC concentration (Fig. 2a) were similar to DOM composition (Fig. 2b) across Mälaren with increasing WRT.

DOC concentration has a generally decreasing trend with increasing WRT as water moves from the major river inflows into western lake basins (Galten, Blacken and Västeråsfjärden) and continues to the eastern and deeper lake basin (S. Björkfjärden) (Fig. 2a). Likewise, DOC

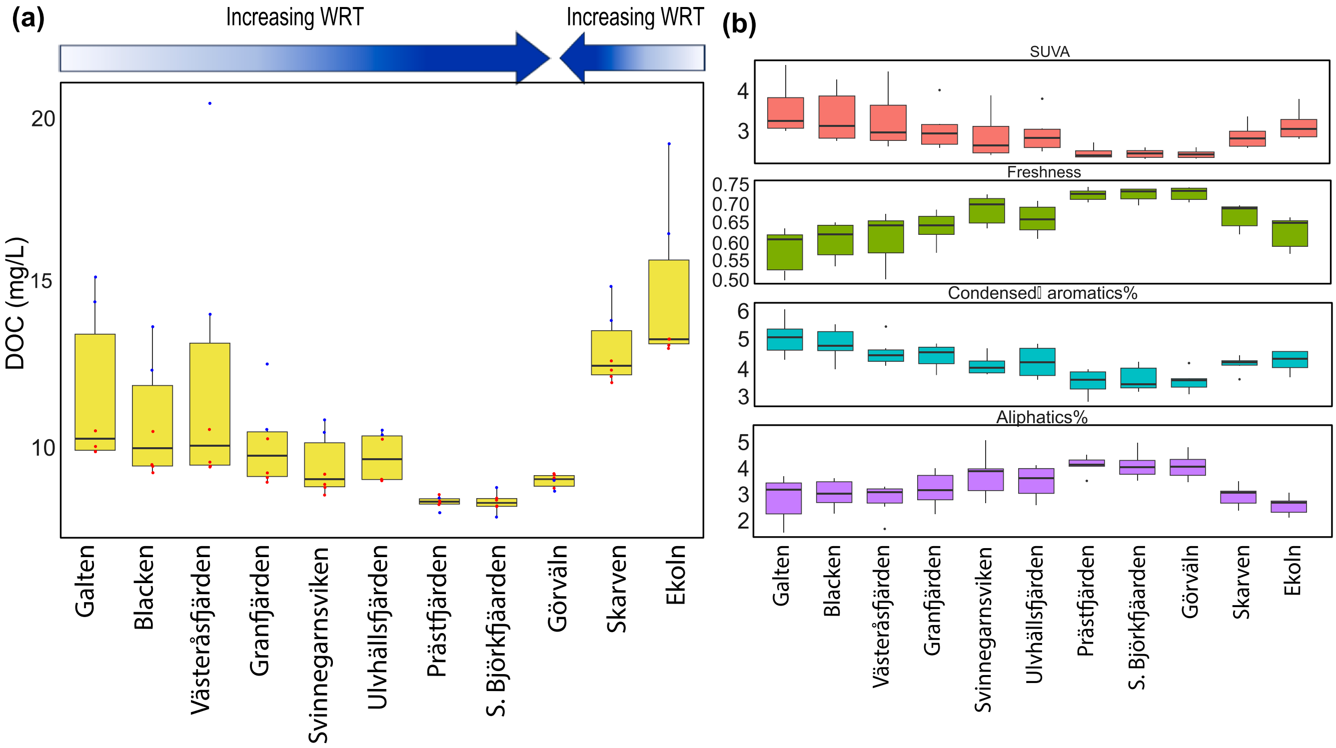

Fig. 2. Seasonal variation across the lake in (a) DOC concentration at 11 sites and (b) DOM composition using optical and mass spectrometry analysis for 11 basins of Mälaren. Note that the box and whiskers plots represent temporal variability in each basin, and show the median, first and third quartiles, with the whiskers set at ±1.5 times the interquartile range. The sites are arranged based on increasing WRT as shown with the arrow on top of panel (a).

concentration was highest at northern lake basins of Ekoln and Skarven, and decreased at Görväln, where water from the north mixes with water from the western basin (Fig. 2a). DOC concentration ranged from 7.1 to 20.4 mg L^{-1} with a mean of 10 ± 2.8 mg L^{-1}. The greatest temporal variability was observed in western and northern basins while the most stable DOC concentrations were observed at the three deepest sites, Prästfjärden, S. Björkfjärden and Görväln, associated with having the longest WRT and lowest DOC concentrations (Table S2).

SUVA is higher in basins with shorter WRT and greater direct inputs from large rivers, including Galten (3.5 ± 0.7) and Ekoln (3.1 ± 0.39) (Fig. 2b). There is a decrease of 33 % in mean aromaticity moving from Galten with highest SUVA to the eastern basin, Görväln with lowest SUVA (2.3 ± 0.11). In agreement with the SUVA data, freshness index is greater in older water indicating a shift in DOM composition to more internally produced and optically clear DOM. An increase of 20 % in mean freshness was observed with increasing WRT moving from basin Galten to Görväln. The three deepest basins with the longest WRT were temporally the most stable in terms of SUVA and freshness index, while lake basins with shorter WRT had more temporal variability (Fig. 2b, Table S2).

Additionally, mass spectrometry results also illustrate a shift in the presence of aliphatic and condensed aromatic compounds along the lake and over time (Fig. 2b). Notably, the three basins with longer WRT contain higher percentages of aliphatic compounds and lower percentages of condensed aromatic compounds. Collectively, results from optical analysis and mass spectrometry mutually validate each other and indicate a consistent pattern of terrestrially-derived DOM shifting to a more internally processed DOM across the lake. Similar to DOC concentration dynamics, the trends confirm that the temporal variations of DOC composition in different time points are more consistent (lower standard deviation, Table S2) in the three deepest basins with longer WRT (Fig. 2b).

3.2. *Seasonality impacts on DOC dynamics across different basins*

Bray-Curtis dissimilarity (NMDS, stress: 0.1, K:2) using all environmental data, optical measurements, mass spectrometry, %DOC loss by GAC, and *k* rates gave a non-metric fit of R^2=0.99 between observed dissimilarity and ordination distance. We observed a clear separation diagonally along the first and second dimensions (indicated with a dashed line in Fig. 3a) between colder months (February 2020, 2021) and warmer months (July 2019, August 2019, September 2019, September 2020).

The colder months (February 2020, 2021) were associated with higher runoff, PO_4^{-3}, DOC: DON, oxygen-rich unsaturated compounds, A_{420}, SUVA, and O/C. Both winter sampling dates (February 2020, 2021) were found distinctly in the upper right side of the NMDS (Fig. 3a), suggesting that seasonality was a predominant factor for separating data across the dataset. Lake basins did pair up together in the winter region of the NMDS, and the three deepest basins with the longest WRT clustered together, and were more closely associated with DOC removal by GAC and *k* (Fig. S4), suggesting that lake basins also grouped based on WRT (Fig. 3b). Basins with greatest inputs from river inflows (Galten, Ekoln, and Skarven) were more closely associated with highly aromatic and colored DOM, with high SUVA and A_{420}.

Conversely, DOM in the warmer months exhibited a greater proportion of aliphatic compounds, higher H/C ratios, and more fresh organic matter, and were characterized by higher chlorophyll-a and pH. The full range of pH across this dataset spanned from 6.7 to 8.4, and thus remained within the circumneutral range regardless of basin or season. Water temperature spanned from 2.2 to 14 °C and chlorophyll-a from 0.7 to 35 μg l^{-1}. The DOM composition, GAC treatability and *k* across the section of the NMDS associated with warmer months, did cluster by lake basin (Fig. 3b). The top left side of the NMDS was associated with DOM that was aliphatic, with higher H/C, freshness index and O-poor unsaturated compounds, and was the easiest to remove with GAC. The NMDS showed that the source of this DOM group was the three deepest lake

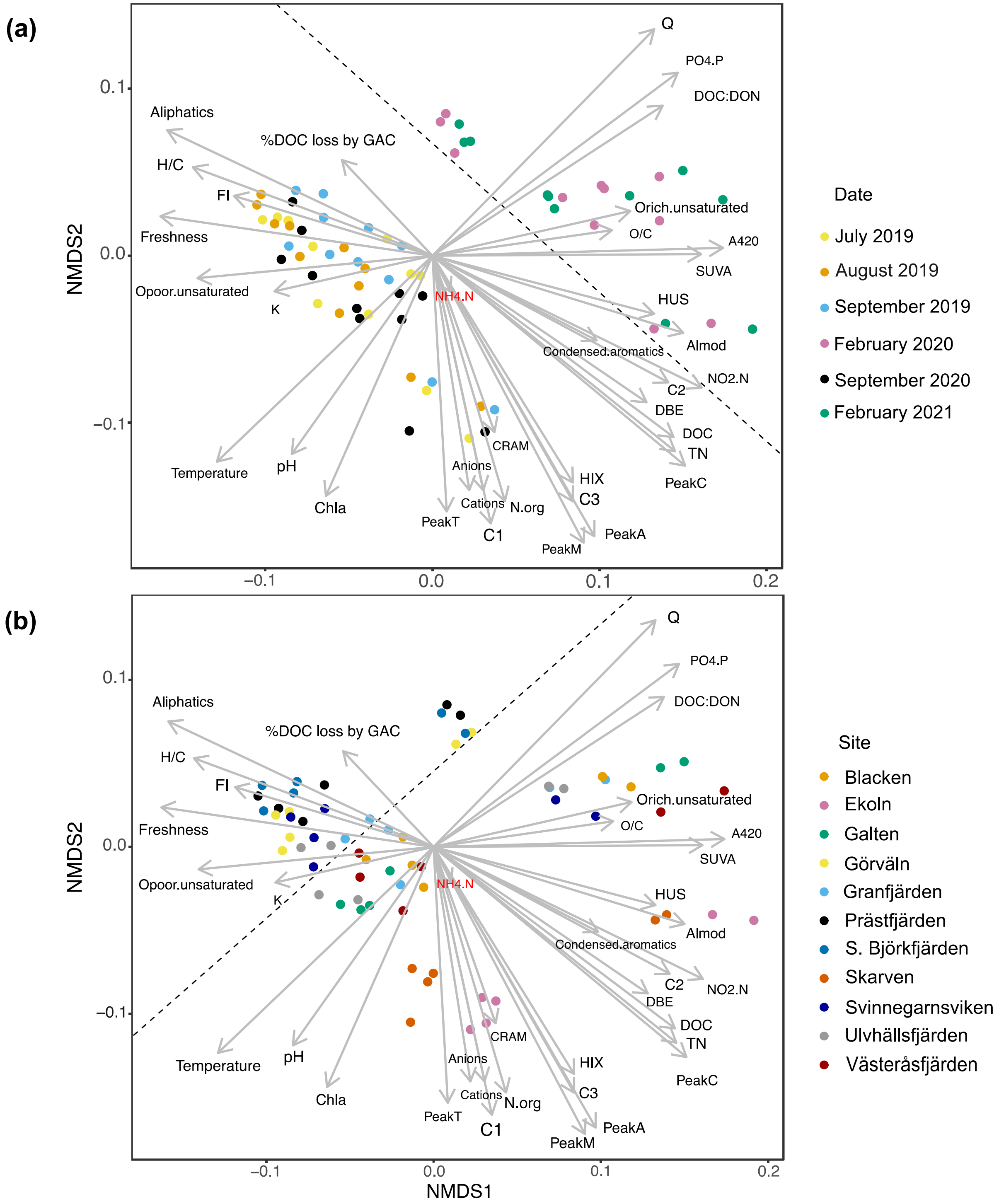

Fig. 3. Non-metric multidimensional scaling (NMDS) of the DOM composition metrics, water chemistry and environmental factors in Mälaren with (a) data points colored based on six different time points and the dashed line separates warmer drier months from cooler wetter months and (b) data points colored based on 11 lake basins, with dashed line separating three basins with the highest WRT (Prästfjärden, S. Björkfjärden and Görvaln). Chla = chlorophyll-a; N. org = Total organic nitrogen; Q= runoff; C1, C2 and C3 = 3 PARAFAC components; DON= dissolved organic nitrogen, *k* = oxygen consumption rate.

basins with the longest WRT. Opposite to this were Ekoln and Skarven where DOC was harder to remove with GAC and the molecular composition was associated with higher HIX, peak T and N. org, fluorescence component C1 and CRAM.

On the second dimension of the NMDS plots (Fig. 3b), corresponding to the Skarven and Ekoln basins, peak T, N. org, cations, and anions exert perpendicular influence in contrast to SUVA and the freshness index, which primarily affect the first dimension. The *k* rates (Figs. 3a, S4b, S5) are higher during the warmer months when fresh DOM is more available, reflecting the relationship between temperature and microbial activity.

3.3. *Relative importance of factors influencing %DOC loss by GAC*

A PLS model was used to identify the best predicting factors contributing to %DOC loss by GAC adsorbent. The first PLS component explained 49 % of the variance in %DOC loss (Fig. 4) and the second PLS component explained 9 %. Model predictivity (Q^2) was 0.43 and R^2Y was 0.53. The PLS model was validated using a permutation test with 100 runs and produced as $Q^2 = -0{,}182$ and a small background correlation of R^2Y of 0.0752.

The loading plot (Fig. 4) and VIP values (SI, Fig. S6) showed that NH_4^+, temperature, DBE, CRAM, AI_{mod}, H/C, optical indices (freshness and fluorescence indices, A420, SUVA, HIX,) were highly influential variables related to DOC removal by GAC. Organic compounds with higher freshness, FI and H/C were preferentially removed by GAC while more colored organic matter with higher AI_{mod}, SUVA, DBE and CRAM flowed through the GAC column and did not adsorb as well to GAC surfaces. Based on the scores labeled by site and sampling time (Fig. S7), we observed a distinct clustering pattern on the top right side of the figure, indicating that the three deepest lake basins with longer WRT, are associated with a higher level of DOC removal through GAC treatment. In contrast, basins with a greater abundance of aromatic compounds and with shorter WRT, especially during colder months, are located on the left side of the score plots (Fig. S7), indicating lower DOC removal by GAC. Seasonality (warmer versus colder months) plays a more prominent role than spatial dynamics across the lake's basins. However, it is important to highlight that the three deepest basins, particularly Görväln, exhibit remarkable stability both over time and space in terms of treatability (Fig. S7). Linear regressions of %DOC loss by GAC and SUVA, freshness index and DBE (Fig. 5) confirmed the relationships of the most influential optical and mass spectrometry indices predicted by PLS analysis.

3.4. Compositional changes of DOC after GAC treatment

Alterations to optical indices and fluorescence peaks before and after exposure to GAC provide an overview of selective adsorption and changes to the resulting molecular composition of DOM (Fig. 6).

Based on the linear mixed-effects model, changes in FI, freshness, and SUVA (Fig. 6a–c) show significant decreases, particularly within C basins which are the three deep basins (p-values of GAC treatment in Table S1). The lowering of FI and freshness index after the GAC treatment indicates the removal of the microbially produced DOM (bacteria and phytoplankton) and the most freshly produced DOM, respectively. The three C basins with higher initial values of FI and freshness had greater decreases after GAC treatment (Fig. 6a, b) based on the linear mixed-effects model, as indicated in Table S1. Likewise, lake basins with lower SUVA had the greatest decreases after GAC treatment (Fig. 6c). However, the decrease in SUVA was relatively consistent across all the group basins (p-values of GAC treatment in Table S1). In terms of GAC removal, FI and freshness were better able to distinguish between lake basin groups compared to SUVA which was less sensitive to differences between basin groups.

Changes to the relative abundance of fluorescence peaks give further support that GAC selectively removed DOM that is protein-like, represented by %Peak T (Fig. 6d). It becomes apparent that the three deep basins exhibited the highest %Peak T values across the lake (before GAC treatment), confirming in-lake production of DOM. The decrease in % Peak T after GAC treatment was most significant at the three deepest basins with the longest WRT (p-values of GAC treatment in Table S1). The %peak M and %peak C (Fig. 6e, f) exhibited strong trends of decreasing values after GAC treatment across all sites, suggesting the removal of humic-like DOM. However, the decrease in such peaks was higher, particularly at the three basins with longer WRT, where those peaks had lower initial values. Our results show that GAC is effective for the removal of both aromatic and aliphatic compounds, but it is noteworthy that GAC is highly effective at removing fresh and clear DOM. Considering the changes in optical indices (except FI) and fluorescence peaks, Görväln, stands out for its remarkable temporal consistency both before and after GAC treatment.

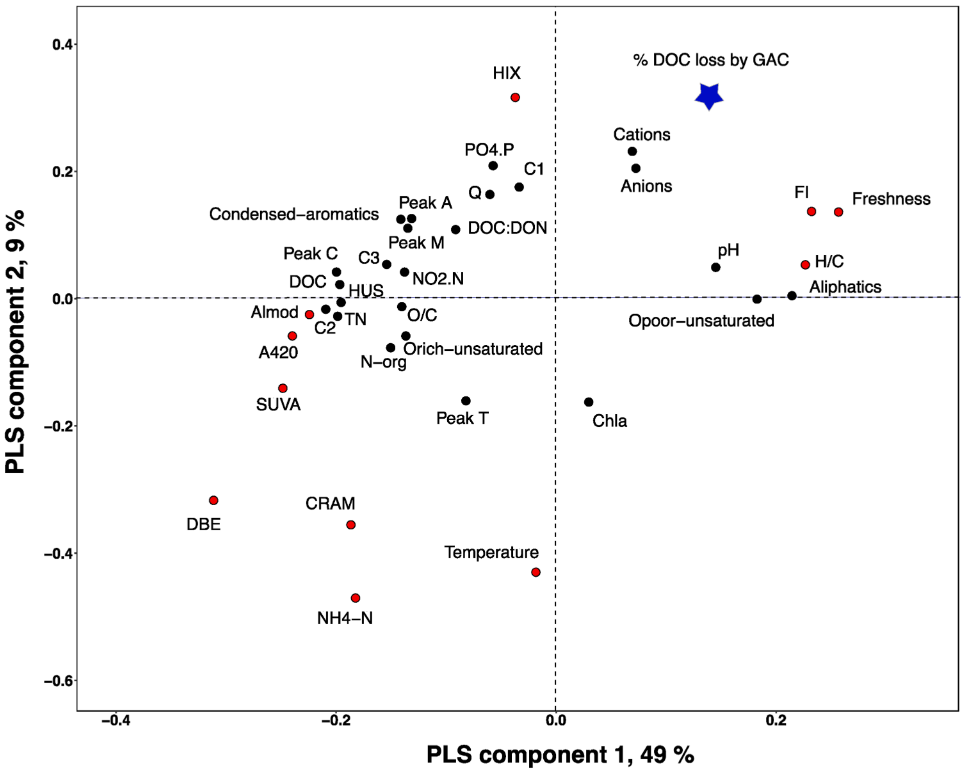

Fig. 4. Loading plot of the PLS analysis predicting %DOC loss by GAC. The graph shows the correlation structures of the independent (X) variables (circles) and the dependent (Y) variable %DOC loss by GAC (blue star). Red dots are highly influential variables with VIP > 1. Chla = chlorophyll-a; N. org= Total organic nitrogen; Q= runoff; C1, C2 and C3 = 3 PARAFAC components; DON= dissolved organic nitrogen; remaining black dots are less influential with VIP ≤ 1.

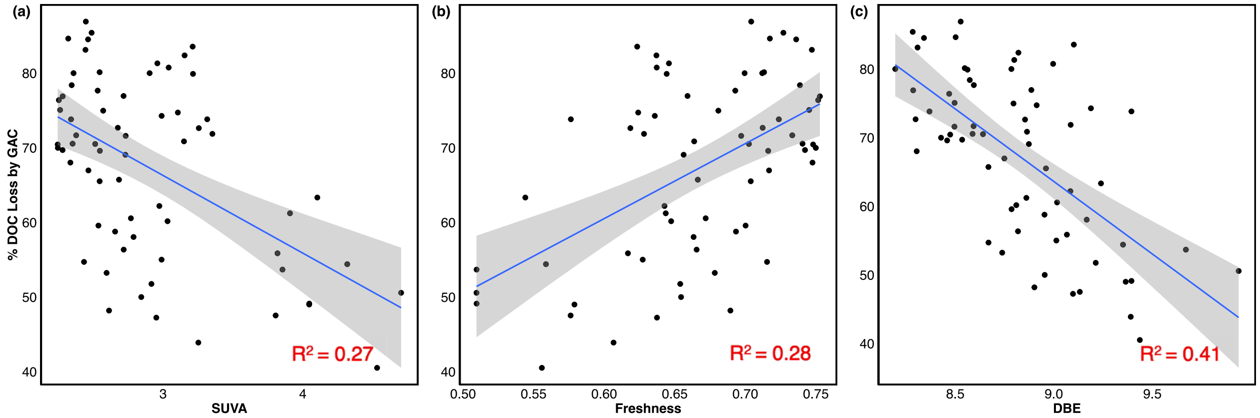

Fig. 5. Linear regression of %DOC loss and influential optical and mass spectrometry indices including (a) specific UV absorbance (SUVA), (b) Freshness index, and (c) double bond equivalents (DBE).

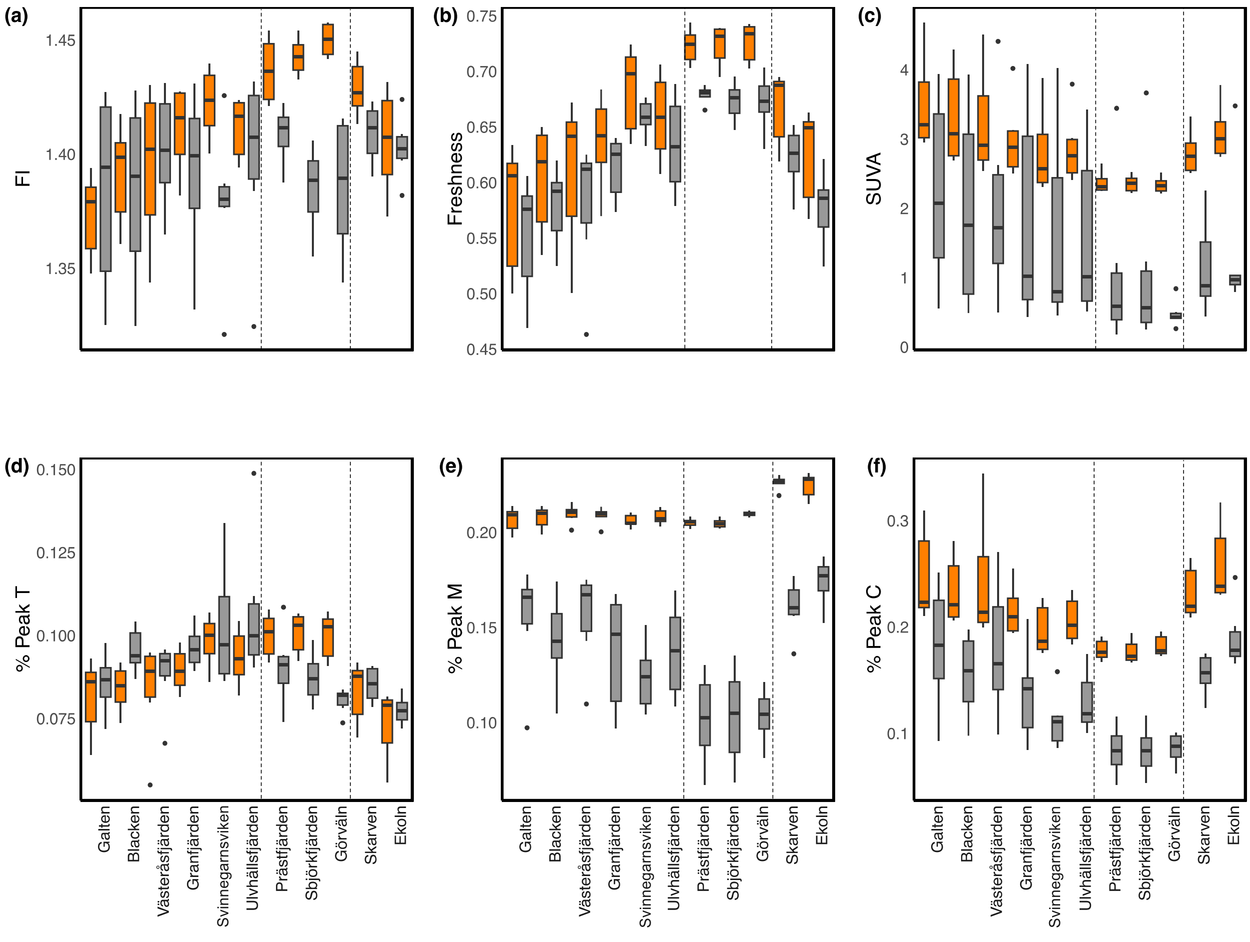

Fig. 6. Relative quantitative changes before (orange) and after (light gray) GAC treatment for DOM optical indices (a) Fluorescence index, (b) Freshness index, (c) specific UV absorbance (SUVA), (d) %Peak T, (e) %Peak M, and (f) %Peak C. Three C basins of Prästfjärden, S. Björkfjärden, and Görväln are marked by dashed lines. Error bars represent the temporal variation of optical indices (median ± standard deviation).

4. Discussion

4.1. *Spatiotemporal factors on the dynamics of DOM in Mälaren*

The three deepest basins in Mälaren with the longest WRT, referred to as C basins (Prästfjärden, S.Björkfjärden, and Görväln) were temporally the most stable in terms of DOC concentration and DOM composition. The C basins had a strong signature of aquatically-produced DOM and additionally, this DOM was the easiest to remove with GAC (Fig. S4a). Conversely, basins closer to terrestrial stream inputs, referred to as A basins, including Galten, Ekoln and Skarven, with shorter WRT were temporally dynamic, had a distinct terrestrial signature and were harder to remove by GAC (Figs. 1, S1). These results suggest that terrestrial inputs contributed to the spatio-temporal dynamics of DOM in terms of concentration and composition, while highlighting the critical role of WRT. Specifically, longer WRT is associated with a decrease in the terrestrial fraction of DOM and an increase in the fraction derived from aquatic sources.

The deeper basins with the longest WRT contain DOM that is less aromatic, more fresh, non-colored and with a higher fraction of aliphatic compounds. This indicates that a larger fraction of DOM in these basins was derived from in-lake processes and are metabolic by-products of terrestrially-derived DOM (Köhler et al., 2013; Tranvik and Jansson, 2002). Additionally, higher *k* rates (Figs. S5, S4b) in these basins are associated with higher degradability of aliphatic compounds, which are energetically rich for microbial consumption (D'Andrilli et al., 2015; Mostovaya et al., 2017; Spencer et al., 2015).

In addition to WRT, DOC concentration and DOM composition were influenced by seasonality. Seasonal trends in DOC concentration and composition were attributed to higher runoff in the colder months of February 2020 and 2021(Fig. S3), which could be associated with higher inputs of terrestrial-derived DOM as previously observed (Freeman et al., 2001; Kellerman et al., 2014; Peacock et al., 2023; Tranvik and Jansson, 2002). Colder months were positively correlated with lake color (higher A_{420}) and aromaticity (higher SUVA, AI_{mod} and abundance of oxygen-rich unsaturated compounds), which can be explained by the increase in delivery of terrestrial DOM originating from decomposition and leaching of plant and soil organic matter in such months (Helms et al., 2008; Kellerman et al., 2018, 2014; Mcknight et al., 2001; Weishaar et al., 2003). Additionally, our results show higher concentrations of phosphate in colder months, which is associated with higher export of phosphate from catchment soils and less microbial activity due to lower rates of metabolism (Jeppesen et al., 2009).

In warmer months, we observed a higher fraction of aliphatic compounds with higher H/C ratio, and optical properties, which represents microbially produced DOM (Kellerman et al., 2018). This is due to a warmer water temperature that promotes primary production and microbial activity (Thornton, 2014), and thus releases a greater extent of microbially produced DOM. This is confirmed by our observation demonstrating that temperature and chlorophyll-a are two influential factors in warmer months coupled to higher production of aquatically derived DOM in warmer months. The associated increase in pH observed during warmer months is likely associated with higher autotrophic productivity whereby rates of photosynthesis are highest and sequentially consumes CO_2 as carbonic acid in the water column and increases the pH (Fig. 3) (Schindler et al., 1972).

4.2. Drinking water treatability of DOM spatially and temporally across Mälaren

Mälaren serves as an important natural drinking water resource in Sweden. Treatability of DOM in this lake, therefore, is of high importance. Changes in DOC concentration and composition can affect the efficiency of DOC removal (Rehrl et al., 2020). There have been studies regarding DOM removal by GAC showing effective removal of hydrophobic and smaller-sized low molecular weight DOM compounds and higher affinity of aromatic compounds to the adsorbent surface (Jamil et al., 2020; Moona et al., 2018; Moreno-Castilla, 2004; Schreiber et al., 2005; Ofri B Zusman et al., 2020). These variations in the selective removal of DOM by GAC could be due to distinct types of GAC that show higher affinity to particular organic compounds or may indicate variations in the composition of DOM and chemistry of solution (Moona et al., 2018; Moreno-Castilla, 2004). We originally hypothesized that aromatic DOM would be easier to treat than optically clear and aliphatic DOM as previous work has found aromatic DOM to be easier to remove with GAC (Schreiber et al., 2005). However, we observed removal of both aliphatic and aromatic DOM which is in line with recent studies (Andersson et al., 2020; Jamil et al., 2020; Moona et al., 2018). Specifically, this was seen in deeper basins with more optically clear and fresh DOM with higher aliphatic compounds.

We also found a temporal trend in DOM removal by GAC, which is more effective in warmer months than colder months based on NMDS analysis (Fig. 3). In the future as summers get warmer and evaporation increases, many lakes will have longer WRTs (Woolway et al., 2020). GAC will be a good option for DWTPs to treat and remove the aquatically produced DOM derived from phytoplankton and bacterial decomposition of terrestrial DOM. We recommend further studies including more measurements during colder months and analysis of GAC removal efficiency after treatment by coagulation and flocculation. This would help evaluate if GAC is effective at removing the fraction of DOM that resists coagulation and flocculation.

Treatability of the aliphatic fraction of DOM is important for drinking water treatment purposes. Such compounds are highly hydrophobic and less soluble, and are sourced mostly from bacterial and algal exudates (Gough et al., 2015). They are also challenging to remove by conventional methods such as flocculation and they primarily contribute to poor taste and odour problems (Matilainen et al., 2011). However, flocculation is not efficient for removal of aliphatics (Edzwald and Tobiason, 1999). Our results are highly promising in removing smaller, more hydrophobic and aliphatic compounds using GAC. This is particularly beneficial for Görväln as one of the three deep basins located near a DWTP.

4.3. Mechanisms of DOM removal by GAC

The factors controlling adsorption depend on properties of the adsorbent, adsorbate as well as the chemistry of the solution (Moreno-Castilla, 2004). Pore size and surface chemistry of the adsorbent, the molecular composition of DOM, degree of hydrophobicity, pH and ionic strength are all factors that can control the adsorption of DOM to GAC surfaces (Moreno-Castilla, 2004). GAC has a large number of micropores and mesopores which can provide a large adsorption capacity for organic compounds (Newcombe et al., 1997; Yuan et al., 2022). It was found that the adsorption capacity on activated carbon rises as molecular weight decreases (Cheng et al., 2005). A lower SUVA represents DOM of a lower molecular weight (Edzwald and Tobiason, 1999). Therefore, in deeper basins with higher WRT, where there is a greater abundance of low-SUVA, aliphatic DOM derived from higher microbial activity (phytoplankton and recycling of terrestrial DOM by bacteria), is expected to be of lower molecular weight that is likely to have access to a larger fraction of pores across the GAC surface. Similar observations have been made in previous studies (Andersson et al., 2020; Moona et al., 2018).

Chemical mechanisms of DOM adsorption to GAC include Van der Waals forces or π–π interactions depending on the composition of DOM (Moreno-Castilla, 2004). Based on the PLS analysis, pH and ionic strength were positively correlated to %DOC loss by GAC and located closer to aliphatic compounds, which supports Van der Waals interaction theory (Arnarson and Keil, 2000). The mean pH of the lake water was 7.7, and the point of zero charge for the fresh GAC is typically between 7 and 8 (Bjelopavlic et al., 1999). In warmer months, the presence of aliphatic compounds with higher pH values could increase the negative charge of DOM. Accordingly, the net surface charge of GAC becomes slightly more negative. This means that electrostatic repulsion becomes greater, which reduces the adsorption of negatively charged aliphatic compounds to GAC. However, adsorption of DOM can be controlled by variations in ionic strength as well. Higher ionic strength, as observed here, can lead to the compression of electro double-layer thickness, decreasing the electrostatic repulsion force between the negatively charged GAC surface and DOM, and therefore enhancing Van der Waals interactions (Arnarson and Keil, 2000). An increase in adsorption at higher ionic strength and pH indicates that Van der Waals interactions could be the dominant mechanism involved in the adsorption of aliphatic compounds. While we found a dominant removal of aliphatic compounds, our results also show that some aromatic compounds were removed by GAC. The dominant mechanism for removing compounds with higher aromaticity is mostly controlled by π–π interactions between hydrophobic molecules on the surface of the GAC and π bond associated with aromatic functional groups on DOM (Jamil et al., 2020; Moreno-Castilla, 2004; Schreiber et al., 2005; Tran et al., 2017).

4.4. Relative importance of factors contributing to DOM removal by GAC

Statistical analyses show that the mass spectrometry index, DBE, was the most relevant factor contributing to DOC loss by GAC, with lower % DOC loss at higher DBE. This is confirmed by PLS analysis (VIP of 1.6, Fig. S6), high Pearson's correlation coefficient ($r = -0.64$) and significant *p*-value (Fig. S8). Additionally, optical indices (Freshness and SUVA) and molecular composition of DOM (H/C ratio) had higher VIP and significant p-values, showing that DOM with higher aliphatic compounds adsorb more to GAC surfaces. SUVA is a commonly used metric for DWTPs to assess the removal efficiency of DOM with coagulation and flocculation whereby DOM with a SUVA > 4, is easier to remove, and DOM with SUVA < 4 is more difficult to remove (Matilainen et al., 2010). We observed that 90 % of DOM across Mälaren had SUVA < 4 with the mean removal efficiency of 69 % ± 3.1, whereas the remaining samples with SUVA > 4 exhibited lower removal efficiency (mean 51 % ± 1.5). This confirms that SUVA can also be used as a predictor of GAC removal efficiency whereby lower SUVA results in higher removal of DOM by GAC ($r = -0.52$) (Figs. 6c, S6, and S8). As SUVA is straightforward to measure relative to DBE, we suggest it as a useful proxy for monitoring changes of DOM composition in DWTPs before GAC treatment. Finally, it is noteworthy that DOC concentration had a lower influence on GAC removal efficiency (Fig. S6), suggesting that DOM concentration is less relevant than the compositional characteristics of DOM.

4.5. Conclusions and future implications of climate change

Climate scenarios for Sweden and the boreal ecozone anticipate a warmer and wetter climate (Gauthier et al., 2015). Warmer climate will likely lengthen the WRT of lakes and contribute to more aquatic- produced DOM signature (Kellerman et al., 2014). With an increase in temperature, the decomposition of soil organic matter is expected to contribute to greater inputs of terrestrially-derived DOM and to increase heterotrophy of boreal lakes (Algesten et al., 2004). Increasing terrestrial inputs also pose a concern for surface waters used for drinking water (Leenheer and Croué, 2003). However, in a warmer climate with lower precipitation, and longer WRT, there will also be an increase in degradation rates and transformation of imported aromatic terrestrial DOM into aquatically produced aliphatic compounds (Köhler et al., 2013; Kothawala et al., 2014; Stubbins et al., 2010). Under future climate scenarios, many lakes can be expected to have higher evaporative losses during summer months and longer WRT. Therefore, these lakes become more stable in terms of DOC concentration and DOM composition. This has implications for potentially increasing the biological availability of DOM to the microbial loop and being a source of CO_2 to the atmosphere. The shift in composition is also likely to impact ecosystem services including treatability for drinking water providers. This study found that GAC was more effective at removing the colorless and more aliphatic DOM compounds found in lake basins with longer WRT, which tend to be more resistant to treatment by flocculation and coagulation. Our findings suggest that with an increase in microbial and phytoplankton-derived DOM in freshwater systems, using adsorbents such as GAC after flocculation and coagulation can be very promising in the removal of both aromatic and aliphatic compounds for drinking water treatment purposes.

CRediT authorship contribution statement

Mona Abbasi: Writing – review & editing, Writing – original draft, Visualization, Software, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Mike Peacock:** Writing – review & editing, Project administration, Investigation, Conceptualization. **Stina Drakare:** Writing – review & editing, Resources, Investigation, Conceptualization. **Jeffrey Hawkes:** Writing – review & editing, Software, Methodology, Investigation. **Elizabeth Jakobsson:** Writing – review & editing, Methodology, Investigation, Formal analysis. **Dolly Kothawala:** Writing – review & editing, Supervision, Project administration, Investigation, Funding acquisition, 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

Data will be made available on request.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.watres.2024.121910.

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