Temperature-dependent mechanisms of DOM removal by biological activated carbon filters

Nashita Moona, Urban J. Wünsch, Mia Bondelind, Olof Bergstedt, Tugba Sapmaz, Thomas J. R. Pettersson and Kathleen R. Murphy

Seasonal variability in the removal of dissolved organic matter (DOM) by drinking water biological activated carbon (BAC) filters is often attributed to temperature changes. However, it can be rather difficult to directly relate temperature to treatment efficiency at full scale due to seasonal variations in other influential parameters like DOM concentration and character, and microbial activity. Furthermore, processes in BAC filters include adsorption, desorption and biodegradation within biofilms while each respond differently to temperature. This study aimed to decouple these processes by studying the removal of various DOM fractions from coagulated and settled drinking water when in contact with aged (>3 years) BAC filter material at different water temperatures. DOM removal was measured as changes in dissolved organic carbon (DOC), ultraviolet absorbance at 254 nm (UV\textsubscript{254}) and fluorescence. Under the particular experimental conditions there was little evidence of biological removal; instead, removal of DOM fractions emitting at longer wavelengths ("humic-like", >430 nm) was consistent with chemisorption, removal of DOM emitting at intermediate wavelengths ("humic-like", 390–420 nm) was consistent with physisorption, and multiple mechanisms were indicated for "protein-like" (<380 nm) DOM. Non-biological mechanisms of DOM removal by aged BAC filters are often assumed to be unimportant; however, these results suggest they are important for some DOM fractions, especially during periods of reduced microbial activity.

1. Introduction

Dissolved organic matter (DOM; organic material that passes through a 0.45 \( \mu \)m filter) is present in all-natural waters where it is formed from various complex biotic and abiotic reactions affecting organic molecules from a range of sources.1–3 DOM is undesirable in drinking water production and distribution since it forms harmful disinfection by-products (DBPs) during disinfection with chlorine, fuels bacterial regrowth in the distribution system, and can cause taste- and odor-related problems.4,5 Adsorption onto granular activated carbon (GAC) in fixed-bed filters is a common treatment step for removing DOM from drinking water. GAC adsorbs DOM and organic micropollutants to a degree that is influenced by factors like DOM concentration and type, presence of other organic micropollutants, pH, ionic strength and the age and surface properties of the GAC.6–8

During the operation of fixed-bed GAC filters, the filter media gradually reaches a state of saturation whereby essentially all available adsorption sites are occupied. A naturally-occurring biofilm starts to develop on the porous GAC surface. Microbes in the biofilm utilize organic matter that accumulates on the surface as a food source, prolonging the service life of the fixed-bed GAC filter through its conversion to a biological activated carbon (BAC) filter. BAC filters preferentially reduce biodegradable organic matter, including some organic micropollutants via a complex coexistence of adsorptive and desorption and biodegradation processes.9,10 Since these processes are temperature-dependent, for treatment plants located in temperate and polar regions where there is a large seasonal temperature variation, the processes
controlling BAC-mediated removal of DOM would be expected to vary seasonally.

Four processes describe the removal mechanisms for DOM in BAC filters under different temperature regimes. First, physisorption is a physical process that is relatively weak in nature, exothermic and potentially reversible. Thermodynamic considerations predict that physisorption is favored by decreasing temperature.\(^1\)\(^1\) Second, chemisorption involves chemical reactions between the adsorbate and the surface functional groups on BAC. Chemisorption is rather strong in nature and typically irreversible,\(^1\)\(^1\) and chemisorbed species tend to accumulate on the BAC surface reducing its adsorption capacity. Higher temperatures favor chemisorption (until saturation point) as this provides the activation energy required to form adsorbate–adsorbent bond.\(^6\)\(^1\)\(^2\)\(^1\) Third, biodegradation occurs when microbes use the surfaces provided by GAC to metabolize biodegradable substances in their surroundings. Biological degradation is governed by enzyme activity, which increases with temperature up to a species-dependent tolerance limit.\(^1\)\(^3\) Finally, desorption from BAC can be a source of reversibly-attached DOM if there is a lower concentration of DOM in the water than on the BAC surface.\(^1\)\(^4\)

It is difficult to distinguish between DOM removal processes in practice since they occur simultaneously. Furthermore, DOM is a complex mixture that in treatment plants, is usually assessed by monitoring its overall abundance using bulk parameters like color, total/dissolved organic carbon (TOC/DOC) or UV absorbance at 254 nm (UV\(_{254}\)).\(^1\)\(^5\)\(^1\)\(^6\) However, such bulk indicators do not distinguish between different DOM fractions, although for example, lower-molecular-weight DOM fractions are known to be more efficiently removed by adsorption, and protein-like components, known to be removed more effectively by biodegradation.\(^1\)\(^7\)\(^1\)\(^8\) Lower-molecular-weight “protein-like” fractions can be distinguished from bulk DOM sensitively and accurately using fluorescence spectroscopy.\(^1\)\(^7\)\(^1\)\(^9\) However, to the best of our knowledge, fluorescence spectroscopy has yet to be used to investigate the mechanisms controlling the removal of different DOM fractions at different temperature in BAC filters.

The goal of this study was to evaluate the interaction of DOM with BAC filters in drinking water treatment. Biological removal is thought to be the dominant mechanism; however, in this study two additional removal mechanisms (physisorption and chemisorption) and one release mechanism (desorption) were considered.

The specific aims were to:
1. Identify the most likely removal mechanisms of different DOM fractions through their temperature-dependent behavior.
2. Identify the susceptibility of different DOM fraction to back-diffusion during times of rapidly changing operational conditions.
3. Evaluate fluorescence spectroscopy as a tool to identify removal mechanisms and assess back-diffusion of different DOM fractions.

2. Materials and methods

BAC filter media

Batch tests were performed using full-scale BAC filter media obtained from Lackarebäck drinking water treatment plant (DWTP), which is the largest plant supplying water to the city of Gothenburg, Sweden. Filter material was collected separately for each experiment on five occasions between
July–October 2018 from a single randomly-selected filter that had been in operation for over three years. This filter contained coal-based GAC (Filtrasorb TL 830; Chemviron Carbon) with an iodine number of 900 mg g$^{-1}$ operated at a contact time of 15–20 min and a surface load of 3.9–4.4 m$^{-1}$ with a filter depth of 0.9–1.0 m. Compared to new filter material, the three year old BAC filter media had a lower BET surface area (657.4 m$^{2}$ g$^{-1}$ vs. of 1039 m$^{2}$ g$^{-1}$ for old vs. new) and low pore volume (0.30 cm$^{3}$ g$^{-1}$, $p/p_{0}$: 0.990 vs. 0.63 cm$^{3}$ g$^{-1}$, $p/p_{0}$: 0.990), respectively. Fresh BAC was collected at the beginning of each experiment and at the same time interval after backwashing (three days), as a slurry from the top 5 cm of the bed. After removing excess slurry water, the filter material was immediately homogenized and used within one day of sampling.

**Experimental design**

Experiments (Fig. 1, Table 1) were performed by adding 0.4 g of BAC (wet weight) to 35 mL of settled water in replicate flasks ($n = 5$ replicates) and placed on a shaker table in a temperature-controlled room. DOM concentration was measured before and after exposing the water to the BAC for 20 hours. The kinetics of adsorption of methylene blue onto the BAC filter material was investigated prior to the DOM sorption experiments. In all tests, the steady-state equilibrium was reached within 20 hours.

The experiments were performed in summer and fall (Table 1) to allow for both seasonal changes in water quality and seasonal changes in microbial community composition. Between these two seasons there was a large drop in ambient temperature (from 20 ºC in summer to 10 ºC during fall) and slight change in incoming water quality (DOC increased from 3.8 to 4.8 mg L$^{-1}$ and UV$_{254}$ from 0.033 to 0.038 cm$^{-1}$). In each experiment, the ambient temperature at the treatment plant was designated as the reference temperature and experiments were run by increasing and/or decreasing water temperature by 10 ºC relative to the reference temperature (experiment 1: ambient –10 ºC, experiment 2: ambient, experiment 3: ambient +10 ºC). Experiment 1 was performed only in summer while experiments 2 (ambient) and 3 (ambient +10 ºC) were repeated for both summer and fall. The highest water temperature tested (30 ºC) exceeds the maximum water temperature for water in the DWTP (up to 24 ºC in summer) and slightly exceeds the projected maximum temperature under climate change (25–28 ºC). Our motivation for experimenting a larger temperature range was in order to be confident in detecting significant differences between treatments.

In experiment 4 (ambient) and 5 (ambient +10 ºC), fresh BAC material (0.4 g) was placed in 35 mL ultrapure water at 10 ºC and 20 ºC for 20 hours, allowing investigation of the effect of a negative concentration gradient.

**Dissolved organic matter characterization**

Samples ($N = 132$) were filtered through pre-washed 0.45 µm membrane filters (cellulose acetate). DOM absorbance and fluorescence was measured using a Horiba Aqualog spectrophotometer. Fluorescence excitation-emission matrices (EEMs) were obtained in a 1 cm cell by scanning the excitation wavelengths from 240–500 nm while emission was detected from 250–650 nm. At the same time, absorbance measurements were obtained corresponding to the fluorescence excitation wavelengths. Processing of fluorescence data followed established methodologies.

Briefly, this included spectral correction and blank subtraction to remove Raman and Rayleigh scatter as well as correction for primary and secondary inner filter effects. Fluorescence intensities were normalized to the area under the water Raman peak at 350 nm thereby converting fluorescence to Raman units (R.U.).

DOC was measured using the high-temperature catalytic combustion method. Filtered samples were measured using a Shimadzu TOC-VCPH carbon analyzer. DOC concentrations were calculated using a five-point calibration curve of potassium phthalate standard solutions (1.0–10.0 mg C L$^{-1}$).

**Data analysis**

The underlying components of fluorescent DOM measured in 132 samples were isolated with Parallel Factor Analysis (PARAFAC) using the dREEM toolbox. Models with four to seven components and non-negative loadings and scores were explored and cross-validated. Ultimately, a split-half validated seven-component PARAFAC model with an explained variance of 99.9% and a core consistency of 0.2% was found to best represent the data set. The obtained spectra representing independently-varying fluorescence

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<table>
<thead>
<tr>
<th>Experiment</th>
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<th>Temperature</th>
<th>Parameters</th>
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<td>Ambient</td>
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<td>10 ºC</td>
</tr>
<tr>
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<td>Summer</td>
<td>Ambient</td>
<td>20 ºC</td>
<td>10 ºC</td>
</tr>
<tr>
<td>3</td>
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<td>Ambient</td>
<td>10 ºC</td>
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</tr>
<tr>
<td>5</td>
<td>Fall</td>
<td>Ambient</td>
<td>+10 ºC</td>
<td>20 ºC</td>
</tr>
</tbody>
</table>

* Desorption test with ultrapure water.
fractions were compared to previously published studies using the OpenFluor database.  

Concentrations of fluorescent DOM fractions at different temperature were determined relative to initial settled water concentrations. Thus, a relative DOM concentration close to 1 indicated zero removal, values >1 indicated release and <1 indicated removal by BAC filter material.

One-way analysis of variance (ANOVA) was conducted to investigate effects of temperature on fluorescence intensities. Mean values and standard deviation of measurements (n = 5) were calculated for each experiment and statistical significance was determined by calculating p-values at a significance level of α = 0.05 using MATLAB® (v9.6, R2019a).

3. Results and discussion

DOM composition

The initial settled water (pH 6.3–6.7) had low UV absorbance (approx. 0.046 ± 0.02 cm⁻¹) and a SUVA value between 0.97 and 1.2 L mg⁻¹ m⁻¹. This indicates that the initial settled water mainly consisted of DOM with low hydrophobicity and low molecular weight which would be difficult to remove by conventional water treatment.  

The PARAFAC model of the fluorescence datasets featured seven fluorescence components; these had emission maxima near 430, 390, 460, 520, 420, 320 and 340 nm (Fig. 2). The fluorescence components are henceforth referred to according to their emission maximum, e.g. F₄₃₀ refers to the component with an emission peak near 430 nm. The first five components (F₄₃₀, F₃₉₀, F₄₆₀, F₅₂₀ and F₄₂₀) were dominated by visible-wavelength emission while F₃₂₀ and F₃₄₀ emitted light in the UVA region (300–380 nm). Visible wavelength fluorescence components are usually described as “humic-like” components in published literature. Fluorescence components similar to F₃₂₀ and F₃₄₀ have been shown to correlate with tryptophan- and tyrosine concentrations and are typically referred to as “protein-like” in published literature. Fluorescence components similar to F₃₂₀ have also been identified in soluble microbial products produced during the microbial degradation of DOM.  

Comparison with the OpenFluor database revealed that all identified fluorescence components were statistically congruent to published spectra in the database (Tucker congruence exceeding 0.95 for both excitation and emission spectrum). Matches across diverse aquatic environments were found, including when compared to samples from the Baltic sea (F₃₂₀ with C5 in Stedmon et al. 2006), recycled wastewater, (F₃₄₀ with C4 in Murphy et al. (ref. 1)), and drinking water (F₃₉₀ with C2 in Stedmon et al. 2006).

Temperature dependence of BAC performance

Removal of different fluorescence fractions. The fluorescence components could be separated into four Groups (Fig. 2, Table 2) based on their responses to temperature. ANOVA results indicated that all fluorescence components were significantly influenced by temperature (p < 0.05) except component F₃₄₀ [F(1, 17) = 1.74, p = 0.204, 95% confidence interval [CI] = 0.043, 0.082]. In previous studies, visible fluorescence components similar to group 1, 2 and 3 have been reported to resist biodegradation and be adsorbed onto BAC material. However, type of adsorption mechanisms were not elucidated in these studies. Fig. 3 shows the relative change in fluorescence intensities during 20 hours of BAC contact, with C/C₀ > 1 indicating release of DOM and C/C₀ < 1 indicating removal. Increases in C/C₀ with temperature therefore indicate a decrease in DOM removal efficiency with temperature, and vice versa. Biological
degradation should be favored by warmer temperatures\textsuperscript{32,33} and would be recognized by increasing DOM removal (decreasing $C/C_0$) with increasing temperatures up until the maximum growth temperature for the BAC microorganisms (typically 45 °C for mesophilic microbes\textsuperscript{25}). For group 1 ($F_{430}$ and $F_{460}$) fluorescence components, removal followed a v-shaped curve with respect to temperature (Fig. 3a). Thus, removal efficiency decreased with both an increase and decrease of temperature relative to the ambient temperature. This trend suggests that the primary removal was by chemisorption whereby adsorption increases with increasing temperature until an equilibrium is reached, then decreases with further temperature increase.\textsuperscript{6} Previously, Schreiber, Brinkmann et al. 2005 (ref. 33) found that adsorption of water molecules onto BAC surface decreases with increasing temperature, leading the BAC surface to favor the adsorption of hydrophobic, aromatic DOMs at elevated temperatures. In our study, the enhanced removal of group 1 aromatic and hydrophobic fluorescent DOM at 20 °C (ambient) compared to 10 °C (ambient - 10 °C) is therefore likely to have been due to increased numbers of hydrophobic interactions between the BAC surface and aromatic DOM structures. For group 2 components ($F_{390}$ and $F_{420}$), removal decreased with increasing temperature and resulted in a release of group 2 components at ambient +10 °C during summer but not during fall (Fig. 3b). Relative fluorescence was lowest (and removal was greatest) at 10 °C with $C/C_0 = 0.8$ in both summer and fall and decreased to $C/C_0 = 1.2$ (release) at 30 °C (Fig. 3b). This suggests that the predominant removal mechanism for group 2 components was an exothermic process, probably physisorption. Note that the observed removal trend is exactly opposite to what would be expected if removal had been due to a biological process.\textsuperscript{34} Group 3 consisted solely of component $F_{520}$. $F_{520}$ fluorescence responded weakly to temperature changes in both summer and fall experiments, following a similar pattern as group 2 but with a smaller range ($C/C_0 = 0.8-0.9$) (Fig. 3c). It has been hypothesized that $F_{520}$ tends to be associated with DOM of large molecular-size relative to the remaining fluorescent fractions.\textsuperscript{35,36} Previous studies have established that large molecular weight DOM is poorly removed by microbes since these compounds are not easily transported across the cell membrane and cannot be attacked by metabolic enzymes.\textsuperscript{37,38} Our results suggest that weakly exothermic physisorption may be the dominant removal mechanism for this DOM fraction. However, it should be noted that fluorescent DOM tracks a large number of molecular species.\textsuperscript{36,39} The resulting broad molecular size distributions thus hinder the assignment of a distinct size to each fluorescent fraction.\textsuperscript{40,41} The exact extent to which molecular size influenced the temperature dynamics of group 3 thus remains unclear. Group 4 ($F_{320}$ and $F_{340}$) “protein-like” components showed limited and variable response to temperature changes in summer and fall experiments (Fig. 3d). Earlier studies reported

<table>
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<tr>
<th>Groups</th>
<th>Components</th>
<th>Temperature behaviors</th>
<th>Possible mechanism</th>
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<tbody>
<tr>
<td>Group 1</td>
<td>$F_{430}$, $F_{460}$</td>
<td>Removal of DOM reached an equilibrium point above which removal declined. Showed strong temperature effect.</td>
<td>Chemisorption</td>
</tr>
<tr>
<td>Group 2</td>
<td>$F_{390}$, $F_{420}$</td>
<td>Less DOM removal at elevated temperature (exoeritic reaction). Showed strong temperature effect.</td>
<td>Physisorption</td>
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<tr>
<td>Group 3</td>
<td>$F_{520}$</td>
<td>Weakly influenced by temperature.</td>
<td>Weak chemisorption</td>
</tr>
<tr>
<td>Group 4</td>
<td>$F_{320}$, $F_{340}$</td>
<td>$F_{320}$ Removed at the temperature the microbial community acclimatized at. $F_{340}$ did not show any temperature-dependent pattern.</td>
<td>Chemisorption</td>
</tr>
</tbody>
</table>

**Table 2** Identified fluorescence components and their probable removal mechanism
decreasing protein-like fluorescence through BAC filters, presumably due to microbial degradation,\textsuperscript{31,42,43} although microbial degradation can also produce this signal.\textsuperscript{29,44,45} In agreement with this inconsistent picture, we found no statistically significant effects of temperature on group 4 components. Warmer temperatures promote faster biological degradation\textsuperscript{32,33} and would lead to increased removal and lowered \( \frac{C_{BAC}}{C_{CMB}} \) for protein-like DOM. Additionally, biological degradation produces microbial protein-like by-products.\textsuperscript{46} However, compared to other components the abundance of group 4 components was highly variable between replicates. It cannot be excluded that the observed patterns represent the sum of simultaneous microbial uptake and release. Additionally, given the relatively short duration of our experiments (20 hours), we suspect that microbial activity alone would not have led to the release of complex metabolites at the relatively high observed levels (20–25% increase above background fluorescence). Furthermore, high variability is also consistent with measurement, modeling, and interpreting fluorescence at protein-like wavelengths.\textsuperscript{47} A diverse group of phenolic compounds, freely dissolved amino acids, or amino acids in peptides may account for the fluorescence at these wavelengths; their varying fluorescence efficiencies\textsuperscript{48} and changing abundance between samples may be responsible for larger variance in signals between replicates. It was therefore not possible to unambiguously attribute a primary mechanism to the dynamics of group 4 fluorescence components.

Since fluorescence was measured at 10 °C and 20 °C in both summer and fall, it is possible to compare the removal of DOM fluorescence between seasons at the same temperature. For group 2 and 3 fluorescence components, the fraction removed was consistent between seasons at both temperatures (approx. 8 ± 3% at 10 °C and 5 ± 2% at 20 °C, Fig. 3). Also, for \( F_{340} \) in group 4, removal was very similar at the same temperature between seasons, while for \( F_{330} \) in group 4, a seasonal difference was observed at 10 °C only. For only group 1 components was there a clear difference between seasons, whereby 20% removal was observed at 10 °C in fall but at 20 °C in summer, \textit{i.e.} only in experiments performed at the ambient water temperature. This might indicate that biodegradation contributed to removing group 1 components, but only when microbes were incubated at their original water temperature.

\textbf{Response of bulk dissolved organic matter.} Previous studies identified the main mechanisms of DOC removal by BAC filters to be a combination of physio-chemical adsorption onto GAC surface and biofilm, together with biodegradation of the biodegradable organic matter fraction within the biofilm.\textsuperscript{49} Additionally, previous studies established that warmer temperatures favor microbial removal processes due to faster metabolism of organic pollutants within the biofilm.\textsuperscript{49,50}

In this study, bulk DOM abundance in terms of DOC measurements available for fall experiments (ambient temperature at 10 °C) facilitate comparisons with previous studies. The average relative concentration \( \left( \frac{C_{BAC}}{C_{CMB}} \right) \) of DOC was 0.9 ± 0.1 at 10 °C and increased to 0.98 ± 0.1 at 20 °C indicating that DOC removal decreased from 10% to 2% along with a 10 °C increase in temperature. The observed removal rate at 10 °C is similar to previously reported values of 8–14% in pilot-scale experiments performed on BAC filters receiving coagulated/flocculated/sand-filtered incoming water.\textsuperscript{10,51} Because DOC removal by BAC decreased with increasing temperature, the dominant removal mechanism for bulk DOC was exothermic in nature (Fig. 4a), consistent with physiosorption and confirming the presence of remaining adsorption capacity in the BAC filter material. This result deviates from the general consensus that, after operating for a certain number of years (>3 years in this study), the adsorption capacity of a GAC filter is reduced to effectively zero and all further removal is attributable to biological processes.\textsuperscript{52–56} The DOC data also suggest that different types of continuously-ongoing regeneration mechanisms within the filter may have freed up previously occupied adsorption sites for physiosorption.

In contrast to bulk DOC, UV-absorbing DOM did not show a significant response to changing temperature \((F(3,18) = 1.15, p = 0.35, \text{Fig. 4b})\). This differs from results in the study by Lohwacharin, Yang \textit{et al.} 2014 \textsuperscript{(ref. 57)} where old (>6 years) BAC filters released aromatic UV absorbing DOM fractions and specific UV absorbance (SUVA) increased slightly from 0.9 to 1.2 L mg\(^{-1}\) m\(^{-1}\) with temperature. However, this slight shift in SUVA value did not alter character of DOM; since values remained well below 2 L mg\(^{-1}\) m\(^{-1}\) indicating low average aromaticity.\textsuperscript{58} The insignificant effect of temperature on the removal of aromatic DOM as measured by UV\(_{354}\) via BAC filter in our study is noteworthy. Fluorescence indicates that some fractions are significantly influenced by temperature, but this cannot be tracked using UV absorbance because it is less sensitive and less specific, \textit{i.e.} it only shows their combined abundance.

\textbf{DOM desorption from BAC}

A recent study by Di Tommaso \textit{et al.} (2019)\textsuperscript{59} measured aromatic fractions at much higher concentrations in biofilm
than in the water phase. This implies that biofilm can accumulate a large portion of aromatic organic material, and as a result, the concentration of aromatics in the water phase could be much lower. Desorption from activated carbon is an important mechanism affecting BAC and GAC performance when operating conditions change suddenly.\textsuperscript{14} Desorption can occur by two mechanisms: displacement and/or back-diffusion. Displacement occurs when adsorbed compounds are displaced by compounds with a higher adsorption affinity, releasing the less adsorptive compounds back into solution. Back-diffusion occurs when the concentration of DOM in water surrounding the BAC material decreases rapidly. The concentration gradient is addressed by diffusion of compounds back into solution.\textsuperscript{60} While displacement may occur constantly during the operation of a BAC filter system, back-diffusion is most likely only noticeable during times of sudden changes in operating conditions, e.g. following rainfall events or clean water backwashing during which DOM concentrations in the water phase decrease rapidly.

Desorption due to back-diffusion was evaluated in this study by placing BAC filter material in contact with ultrapure water. All but components $F_{340}$ and $F_{520}$ showed a significant release of DOM at 10–20 °C, with a greater release at 20 °C than at 10 °C ($p < 0.001$, Fig. 5). The release of DOM was greatest for long-wavelength humic-like fluorescence components $F_{430}$, $F_{390}$, $F_{460}$ and $F_{4120}$. This is consistent with increased diffusion rate at higher temperature. This release of long emission wavelength humic-like components could present a mechanism that frees previously-occupied adsorption sites and makes them available to other organics. This mechanism would prolong the bed life of GAC by biologically regenerating the biodegradation capacity and chemisorption capacity when the concentration changes rapidly.\textsuperscript{61}

In contrast, “protein-like” $F_{320}$ and “humic-like” $F_{520}$ showed less back diffusion with increasing temperature. Since this result is inconsistent with the expected increase in diffusion rate at higher temperatures, it is likely that a combination of mechanisms explains the dynamics of these two fluorescence components with back-diffusion not being the most important of these. For example, the increased number of free adsorption sites may have led to some adsorption of these two components. However, it is presently unclear why this would have been observed only for $F_{320}$ and $F_{520}$ and not the other fluorescence components.

Our results for DOC and UV-absorbing DOM are in line with the observations by Suidan et al. (1993),\textsuperscript{62} who also reported increasing back-diffusion with increasing temperature. This was interpreted as evidence that increased temperatures results in the weakening and ultimate breaking of intermolecular forces between bulk DOM and BAC. However, our use of fluorescence in combination with PARAFAC demonstrates that different mechanisms control adsorption of different DOM subfractions.

Based on the amount and type of DOM that desorbs from a BAC filter due to a lower concentration in water than BAC surface, BAC filters can have beneficial or detrimental effects on the outgoing water quality. For example, in the pilot-scale study done by Qu, F., et al. (2018),\textsuperscript{63} BAC filters were found to release high molecular weight organics that caused increased fouling potential in the following ultrafiltration process. Similarly, the desorption of a labile fraction like $F_{340}$ could free up adsorption sites and thus promote the adsorption of more recalcitrant fractions of DOM. Conversely, if absorbable and non-biodegradable refractory organics similar to $F_{430}$, $F_{390}$, $F_{460}$ and $F_{4120}$ are desorbed, adsorption of more labile DOM may be promoted.\textsuperscript{64} Depending on which fraction is released into the water, the potential for subsequent microbial growth may change depending on changes in the reactivity of DOM in the outgoing water.

The batch-desorption tests in this study are greatly simplified relative to actual conditions affecting BAC filters in a treatment facility. Since these tests do not simulate the plug-flow condition of full-scale BAC filters they cannot be reliably upscaled to predict the amount of DOM that would be removed under full-scale conditions. The lack of evidence for biological removal in this study was surprising and suggests that the biology was either suppressed due to a stress response, or that the experimental conditions were otherwise unfavorable for microbes, for example due to too low encounter rates. This would explain why previous

![Fig. 5 Desorption of fluorescence components, DOC and UV-absorbing DOM from BAC in ultrapure water. Error bars represent the standard error across five replicate samples.](image)
research indicates that BAC filters typically function better at warmer temperatures when microbial activity is high, while the reverse was typically true in this study. Our batch test results may therefore be most informative about mechanisms that could be observed at full scale during periods of very low biological activity.

Our tests suggest that during summer when surface water temperatures can be around 20–25 °C in Sweden, sorption is reversible for most types of fluorescent DOM and will occur in the presence of a negative concentration gradient. At times when there are rapid increases in temperature, decreases in source water DOM or during backwashing with clean water, the BAC filters could work as a source instead of a sink of organic pollutants. The effect of temperature could also be of importance if another intake depth or a reserve water source is used with a different temperature than the main water source or if a blend of groundwater and surface water is used causing temperature fluctuations. Under climate change, global average temperatures are increasing and precipitation patterns are affected. Sweden is experiencing an increase in both temperature and precipitation. Such increases affect the occurrence and duration of stratification in lakes and disproportionately affect shallow surface waters.

The results of this study highlight some ways that changing water temperatures are likely to affect the DOM removal performance of BAC filters.

4. Conclusions

This study investigated the interactions of DOM and BAC filters in drinking water treatment. The temperature dependent behavior of BAC was studied in several batch experiments and the impact of BAC treatment on DOM quality was assessed with fluorescence spectroscopy. Fluorescence spectroscopy was able to provide more in-depth compositional information of different DOM fractions compared to UV and bulk DOC; however, for some signals and in some experiments, an unambiguous assignment of mechanisms was difficult due to removal and release occurring simultaneously.

For aged BAC, the general assumption is that biological degradation is the dominant factor affecting DOM removal, so that BAC filters tend to function best at higher temperatures when microbial respiration is greatest. However, our results suggest that physical and chemical interaction between BAC and DOM also occur and may be important for some DOM fractions, especially during periods when biological activity is low. Our results further suggest that BAC can be a source of DOM under negative concentration gradients and in times of sudden temperature shifts. Such conditions can be met when water sources or intake depths are changed during the operation of drinking water treatment plants.

Conflicts of interest

The authors declare no competing financial interest.

Acknowledgements

This research was funded by the national drinking water research centre DRICKS hosted at Chalmers University of Technology, Swedish Water and Wastewater Association (SVU), Göteborg Stad (Kretsslopp och Vatten), Västvatten AB, VIVAB, Trollhättan Energi, Sydvatten and Norrvatten. KRM and UJW acknowledge funding by the Swedish Research Council for Environment, Agricultural Sciences and Spatial Planning (FORMAS grants 2013-1214 and 2017-00743). The authors thank staff at Lackarebäck DWTP for their valuable assistance.

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