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The Fate of Dissolved Organic Matter (DOM) During Bank Filtration under Different Environmental Conditions: Batch and Column Studies

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Abstract: Dissolved organic matter (DOM) in source water highly influences the removal of different contaminants and the dissolution of aquifer materials during bank filtration (BF). The fate of DOM during BF processes under arid climate conditions was analysed by conducting laboratory—scale batch and column studies under different environmental conditions with varying temperature (20–30 °C), redox, and feed water organic matter composition. The behaviour of the DOM fractions was monitored using various analytical techniques: fluorescence excitation-emission matrix spectroscopy coupled with parallel factor analysis (PARAFAC-EEM), and size exclusion liquid chromatography with organic carbon detection (LC-OCD). The results revealed that DOM attenuation is highly dependent ($p < 0.05$) on redox conditions and temperature, with higher removal at lower temperatures and oxic conditions. Biopolymers were the fraction most amenable to removal by biodegradation (>80%) in oxic environments irrespective of temperature and feed water organic composition. This removal was 20–24% lower under sub-oxic conditions. In contrast, the removal of humic compounds exhibited a higher dependency on temperature. PARAFAC-EEM revealed that terrestrial humic components are the most temperature critical fractions during the BF processes as their sorption characteristics are negatively correlated with temperature. In general, it can be concluded that BF is capable of removing labile compounds under oxic conditions at all water temperatures; however, its efficiency is lower for humic compounds at higher temperatures.

Keywords: dissolved organic matter; high temperature; sub-oxic conditions; organic matter composition; PARAFAC-EEM; LC-OCD

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1. Introduction

Pollution of surface water systems and the high cost of treatment have obliged water authorities to extend the use of cost-effective treatment techniques. Therefore, bank filtration (BF) has gained widespread interest in recent years as an economic surrogate for traditional drinking water treatment [1]. This technique has been employed in many European countries as a common method to supply drinking water. Many cities around the Rhine, Elbe, and Danube Rivers were primarily supplied with bank filtrate water for hundreds of years [2,3]. In recent years, BF has been utilized to contribute to the overall drinking water production in many developing countries: e.g., Egypt [4] and India [5], with variable hydrological and environmental conditions. Thus, there is a need to evaluate the effectiveness of the BF process under these hot-semi arid climates conditions. BF is a natural water treatment system in which surface water is induced to flow through a porous media towards a vertical or horizontal pumped well in response to a hydraulic gradient [2]. The riverbed and the underlying aquifer have been proven to act as a natural filter to remove chemical and biological pollutants from the surface water system and thereby improve the pumped water quality. Moreover, the biochemical and physical processes (i.e., adsorption) that occur during subsurface flow have a substantial role in pollutant attenuation [6]. The biochemical process taking place during infiltration is mainly controlled by the abundance and composition of dissolved organic matter (DOM) during the filtration process.

Natural water bodies contain a multitude of DOM types which determine the efficacy of the treatment processes in engineered and natural treatment systems [7]. The organic matter present in surface water systems can be divided into two main categories: (I) non-biodegradable matter (e.g., humics HS), which is mainly formed from the decay of animals and plants in the environment; and (II) biodegradable matter (e.g., protein-like compounds), which principally discharges into the water system from wastewater treatment plants [8]. Although DOM does not have an adverse effect on human health, it negatively impacts the physical properties of the water (e.g., odour, taste, and colour). In addition, it is considered the precursor for disinfection by-products (DBP) carcinogenic compounds formation [9]. Furthermore, DOM components play major roles in the removal of pollutants during the treatment processes [10]. Ma et al. [11] reported that HS has an influential role in the biodegradation of organic micropollutants (e.g., estrogen) in the treatment systems. Due to its high shuttle-electrons capacity, HS might enhance the bacterial growth and thereby the biotransformation of these micropollutants in treatment systems. Moreover, it can act as a redox mediator, thereby stimulating the iron and manganese microbial reduction process and enhancing the release of toxic metals (e.g., As and Cd) from sediment into the filtrate water in natural treatment systems [12]. Recently, Chianese et al. [13] stated that HS absorbs a wide range of wavelengths of UV radiation and thus reducing the available energy for photo-degradation of organic micropollutants. Biodegradable matter, on the other hand, takes part in the following processes: (I) it enhances biofouling in reverse osmosis, nanofiltration, and ultrafiltration membranes [14]; (II) it is used as a substrate for microorganism regrowth in distribution systems; and (III) it serves as a precursor to nitrogenous DBP (N-DBPs) formation in conventional treatment plants [15].

BF is reportedly effective at reducing the labile organic compounds during infiltration, thus increasing the biological stability of drinking water in distribution systems by >60%, as well as reducing the potential for disinfection by-product formation by 40–80% [16]. The natural attenuation of (DOM) during BF processes is primarily due to initial adsorption followed by biodegradation [17]. These processes are highly influenced by subsurface flow area environmental conditions (i.e., temperature, redox conditions, travel time, raw water quality) [18]. Maeng et al. [19] found that more than 50% of the DOM is principally removed during the first 50 cm of infiltration and thus it is highly controlled by raw water temperature. Temperature may affect the DOM behaviour directly by altering the associated soil microbial activity and changing the pollutant adsorption character. Indirectly, DOM may reduce the dissolved oxygen in the infiltrate water and thus increase the potential for developing anoxic and even anaerobic environments in the adjacent aquifer. Adversely, redox alteration may impact the DOM biodegradation rate [20]. Hoehn et al. [21] reported the redox environment turning to Mn(III/IV)—and Fe(III)—reducing conditions during the hot summer of 2003 along the Thur River. Derx et al. [22] observed that a rising water temperature will lead to a lower water viscosity, thereby increasing the infiltration capacity and shortening the travel time, which inversely affects the chemical pollutant removal efficiency. Ray et al. [6] reported that the impact of temperature on water viscosity doubled the infiltration capacity during summer along the Ohio and Danube Rivers. However, this research focussed on the direct influence of temperature and redox conditions on DOM removal during BF processes.

Several field- and lab-scale studies have tracked the behaviour of DOM during BF processes [20,22,23]. However, most research was conducted under cold and moderate-temperature (5–25 °C) conditions. The bank filtrate temperature was recently recorded as 26.4 °C along the Nile River in Egypt [24] and 30 °C along the Yamuna River in India [25]. Moreover, recent climate models predict an increase in average global temperature of 1.4–5.8 °C by 2099 [26]. Therefore, it is highly important to assess the effectiveness of BF to remove DOM under these extreme hot climate conditions. The main objectives of this research are: (1) to study the impact of high temperature (20–30 °C) on bulk organic matter removal during BF processes; (2) to track the behaviour of the DOM fractions during BF processes using innovative analytical tools (i.e., fluorescence spectroscopy coupled with parallel factor analysis (PARAFAC) and liquid chromatography with an on-line organic carbon detection (LC-OCD); (3) to determine which DOM fraction is more impacted by the temperature change and redox conditions; and (4) to quantify the role of biodegradation in DOM removal. To achieve these objectives, laboratory-scale batch studies were conducted to assess the impact of temperature (20, 25, and 30 °C) on DOM behaviour using different influent water sources. Additionally, the impact of redox conditions on the reduction of DOM during BF was tracked in laboratory-scale soil columns at a controlled room temperature (30 ± 2 °C).

2. Materials and Methods

2.1. Batch Experiments

Batch experiments were conducted to study the impact of temperature on effluent and DOM behaviour in a saturated subsurface flow system. The batch reactors were operated (in duplicate) using 0.5 L glass bottles filled with 100 g of sand (grain size 0.8–1.25 mm) and fed with 400 mL of Delft canal water. The reactors were placed on a horizontal reciprocal shaker (shaking speed 100 rpm). Three sets of batch reactors were used at three different temperatures (20, 25, and 30) ± 2 °C. Initially, the reactors were acclimated (with respect to DOC removal) at their respective temperature for 90 days. After the acclimation period, the reactors were fed with four different water types that had a different organic matter composition: (1) Delft canal water, the Netherlands (DC); (2) Delft canal water spiked with secondary treated wastewater effluent from Hoek van Holland, The Netherlands (DCWW); (3) secondary treated wastewater effluent (WW); and (4) water extractable organic matter (WEOM). WEOM was used to simulate the DOM water with a high concentration of humic aromatic compounds. It was prepared using 100 g of clay (obtained from Delftse Hout, Delft, Netherlands) in a 0.5 L glass bottle filled with 400 mL of DC water and placed on a shaker at 150 rpm for 24 h. Then, the extracted solution was centrifuged at 4800 rpm for 30 min, and filtered with 0.45-µm pore-size cellulose acetate filters [27]. Samples were taken from the influent and effluent water and analysed to determine their chemical and physical characteristics. Control samples were taken by filling the glass bottles with the same amount of each influent (without silica sand). Another series of batch reactor studies were performed to estimate the role of biodegradation in the removal of organic matter and to what extent it may be affected by temperature. Maeng et al. [28] suggested sodium azide as a biocide to suppress biological activity. However, this research found that sodium azide enhances fluorescence intensity and UV-absorbance measurements, thus reducing their reliability, as also reported by Park et al. [29]. Alternatively, the batch reactors were spiked with mercuric chloride (20 mm) to develop an abiotic environment inside the reactors [30].

2.2. Column Experiments

A laboratory-scale column study was conducted to assess the impact of redox conditions on the removal of DOM at a high temperature (30 °C) during the BF process. Six columns were established and run under three different redox conditions (oxic, anoxic, and anaerobic). Each column was made of a PVC pipe with a 0.05 m internal diameter and 0.5 m height. The column bottom was packed with a support layer of graded gravel (7 cm), and then with cleaned silica sand (size 0.8–1.25 mm), allowing the media to settle in deionized water and thus ensuring packing homogeneity. The columns were operated in up-flow mode (saturated flow), where a variable speed peristaltic pump was connected to the bottom of each column to introduce the influent water from the tank into the column at a constant hydraulic loading rate of 0.5 m·day^{-1}. Two valves were attached at the inlet and outlet of each column, which allowed the air to dissipate from the system, as well as to collect samples of the influent and effluent water. The oxic environment was maintained through continuous aeration of the influent tanks to keep the dissolved oxygen level at 7 mg·L^{-1}. Anaerobic conditions were developed in the second two columns by degassing the influent tanks with nitrogen to dissipate the air. Anoxic conditions were created through the degassing processes, followed by spiking 5 mg·L^{-1} of nitrate into the influent tank. The columns were acclimated for 70 days until the removal of DOC for three successive measurements was ±1%. Then, three columns were fed with DC and run under the identified redox conditions. The other three columns were fed with WEOM and run under the same redox conditions. All influents were filtered through a microsieve (38 μm) to avoid physically clogging the column inlets. The experiment lasted 30 days, and influent and effluent samples were taken daily.

2.3. Analytical Methods

The collected samples were filtered using 0.45 μm filtration (Whatman, Dassel, Germany) and analysed within three days to avoid organic matter degradation. DOC (in mg·L^{-1}) was measured through the combustion technique using a total organic carbon analyser (TOC-VCPN (TN), Shimadzu, Japan). UV-Absorbance at 254 nm UV254 (cm^{-1}) was measured using a UV/Vis spectrophotometer (UV-2501 PC, Shimadzu, Japan). Specific ultraviolet absorbance SUVA$_{254}$ (L·mg^{-1}·m^{-1}) was used as an indicator for the aromaticity degree and unsaturated structures of the bulk organic matter. It was determined by dividing the UV254 by its corresponding DOC measurement. Adenosine triphosphate (ATP) was measured as an indicator for microbial activity associated with the sand. The sampling and preparation protocols of ATP measurements were explained in [19]. Details of the ATP extraction procedures and the detection method employed are described in Abushaban et al. [31].

The constituents of bulk organic matter were elucidated using different analytical methods, including: Liquid chromatography–organic carbon and nitrogen detection (LC-OCD-OND) (manufacturer DOC-LABOR Dr. Huber, Karlsruhe, Germany) and fluorescence excitation-emission spectrophotometry. LC-OCD is used to separate the pool of DOC into five major fractions: biopolymers BP, humic substances (humic and building blocks) HS, low molecular weight (LMW) acids (LMWa), neutrals (LMWn), and hydrophobic organic carbon (HOC), based on their molecular weight distribution. The measurement procedures were described in detail by Huber et al. [32].

The Fluorescence Emission Excitation Matrices (EEMs) technique was widely used to characterize the bulk organic matter into three main components (humic-, fulvic-, and protein-like fractions) [10]. EEM measurements were conducted at excitation wavelengths from 240 to 452 nm with 4 nm intervals and emission wavelengths ranging between 290 and 500 nm with 2 nm intervals using a Fluoromax-3 spectrofluorometer (HORIBA Jobin Yvon, Edison, NJ, USA). The EEMs were corrected and recorded in Raman units (RU) using MATLAB (version 8.3, R2014a, The MathWorks, Natick, MA, USA).

2.4. PARAFAC Modelling

Fluorescence excitation-emission matrix spectroscopy coupled with parallel factor analysis (PARAFAC-EEMs) is used to decompose the EEMs to independent fluorescent components representing different DOM compositions. PARAFAC-EEMs have been extensively developed to characterize DOM behaviour in natural and treatment systems [10]. PARAFAC is based on decomposing the fluorescence signals into tri-linear components and a residual array using an alternating least squares algorithm [33]:

$$X_{ijk} = \sum_{f=1}^{f} a_{if} b_{jf} c_{kf} + \varepsilon_{ijk},\ i = 1, \ldots\ldots, I;\ j = 1, \ldots\ldots, J;\ k = 1, \ldots\ldots, k;\ f = 1, \ldots\ldots, F \quad (1)$$

where X_{ijk} represents the fluorescence intensity of the ith sample at the kth excitation and jth emission wavelength; f is the number of model components; a_{if} is the score for the fth component and is proportional to the fluorophore f concentration in sample i; b_{jf} is the scaled estimates of the emission spectrum for the fth component; c_{kf} is linearly related to the specific absorption coefficient at excitation wavelength kth; and ε_{ijk} is the residual term representing the unaccounted variation of the model [34].

To further assess the behaviour of different DOM components during the filtration process, a PARAFAC model was developed and validated using the complete measured EEMs dataset (184 samples) from the influent and effluent water of the batch and column experiments. The PARAFAC model with three to seven components was implemented using the N-Way and drEEM MATLAB toolboxes developed by Murphy et al. [35]. The right number of PARAFAC components was selected and validated using diagnostic tools such as split-half validation [36], Tucker′s congruence coefficients [37], and the residual error technique [38,39].

2.5. Statistical Analysis

A two-way analysis of variance (ANOVA) test was applied to assess if an environmental parameter′s influence on the DOM constituent behaviour during the BF process was statistically significant, in which a significant difference was ($p < 0.05$).

3. Results

3.1. PARAFAC Components

PARAFAC analysis successfully decomposed the fluorescence measurements into five components. The validated model explained more than 99.6% of the data variance. The excitation and emission loadings, as well as the contour plots of these fluorescent components in RU, are shown in Figure 1 and Figure S1. The spectral slopes of the identified components were successfully cross-referenced with the OpenFluor database [40] (Table S1).

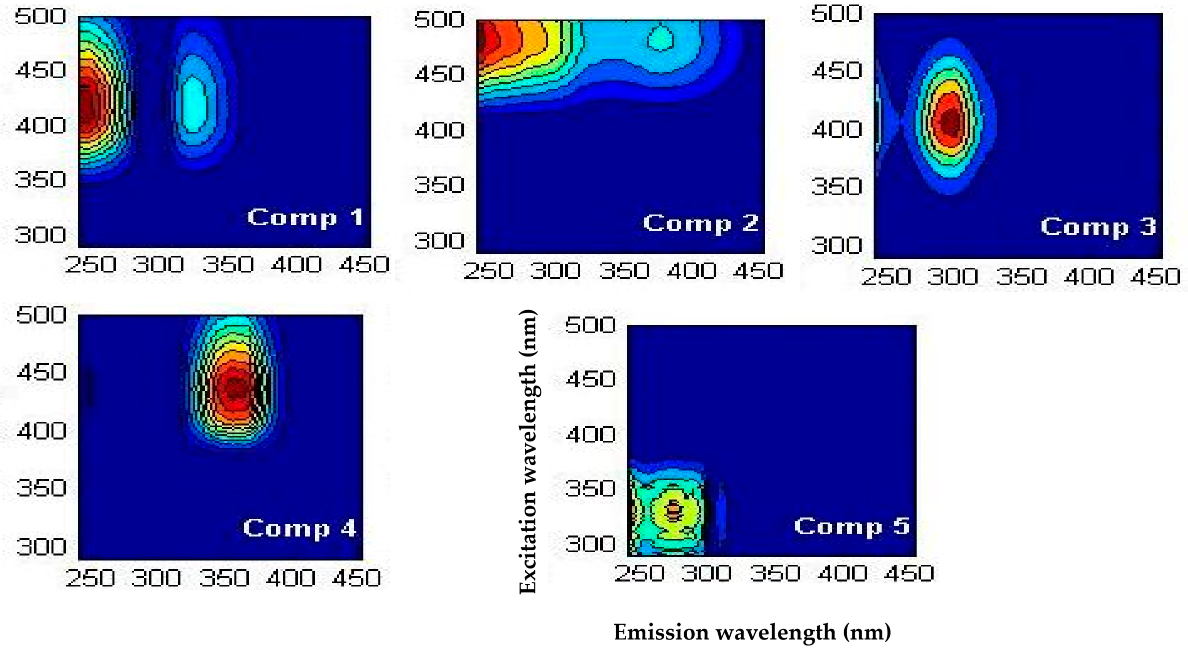


Figure 1. Contour plots of the five components identified from the complete measured F-EEMs dataset for the influent and effluent water of the batch and column experiments.

Four of the PARAFAC components were identified previously as humics: (1) Component 1 (C1) found at (maximum excitation wavelength (λ_{ex})~240 and 320, maximum emission wavelength (λ_{em})~410 nm) and Component 2 (C2) (λ_{ex}~244 and 376, λ_{em}~480 nm(are both associated with humic-like fluorophore substances originating from terrestrial resources, as reported previously in Shutova et al. [41]. It can be seen that component 2 (C2) appeared at longer excitation and emission wavelengths, suggesting it possesses a more condensed and conjugated structure. According to Baghoth et al. [10], these components are characterized by a high molecular weight (>1000 Da).

Moreover, they have low biodegradable matter and are thus principally removed by adsorption and coagulation in water treatment systems. (2) Component 3 (C3) (λ_{ex}~300, λ_{em}~400 nm) mimics microbial humic components in surface water systems [42]. This component is highly related to recent biologically produced fluorescent compounds. It is characterized by an intermediate molecular weight ($650 < C3 < 1000$ Da). (3) Component 4 (C4) (λ_{ex}~360, λ_{em}~440 nm) is related to a humic-like component derived from agricultural activity and it is common in freshwater environments, as reported in Osburn et al. [43]. These compounds mainly contain carboxylic and phenolic moieties in their structures [44]. (4) Component 5 (C5) (λ_{ex}~240 and 270, λ_{em}~320 nm) is spectrally similar to a protein-like fluorophore (tyrosine and tryptophan compounds) identified in Kulkarni et al. [45]. These components are highly correlated with microbial activity in water systems and principally their removal in engineered water treatment systems is attributed to biodegradation [10]. Therefore, it can be used as a surrogate for tracking the manner of bioavailable matter during filtration.

To further investigate the behaviour of the DOM fractions during the filtration process, the maximum fluorescence intensity (F_{max}) was used to characterize the influent and effluent water and to track the behaviour of PARAFAC components during the infiltration process under different environmental conditions. F_{max} fluorescence intensities give an estimation of the proportional contribution of each component to the full fluorescence spectra. This contribution highly relies on the DOM source and the behaviour of the fluorescent components during the filtration process [10].

3.2. Batch Experiments

During this research, laboratory-scale batch studies were employed to assess the impact of temperature (20, 25, 30 ± 2 °C) on the removal of organic matter during the filtration process.

3.2.1. Characteristics of Influent Water DOM

The feed water quality has a clear impact on microbial activity and thus on DOM behaviour during the filtration process [19]. Four different water types were prepared and applied to the batch reactors. The average values of the chemical and physical water quality parameters are presented in Table 1. The results show that WEOM influent water had the highest DOC concentration (14.6 ± 1.6 mg·L^{-1}), followed by DC (11.6 ± 0.7 mg·L^{-1}), DCWW (10.5 ± 0.4 mg·L^{-1}), and WW (9.7 ± 0.6 mg·L^{-1}). Furthermore, the WEOM had a relatively higher $SUVA_{254}$ value (3.56 ± 0.71 L·mg^{-1}·m^{-1}) compared to DC (2.84 ± 0.33 L·mg^{-1}·m^{-1}). This implies that the DOC of the WEOM influent was composed of higher aromatic compounds (i.e., humic substances) than the DC influent water DOC. The average $SUVA_{254}$ values of DCWW and WW were 2.37 ± 0.28 and 2.56 ± 0.42 L·mg^{-1}·m^{-1}, respectively, indicating the relatively low aromatic character of their organic matter composition.

Table 1. Chemical and physical characteristics of the influent water.

	Unit	DC	DCWW	WW	WEOM
pH	-	7.87	7.79	7.66	7.65
DOC	mg·L^{-1}	11.6 ± 0.7	10.5 ± 0.4	9.7 ± 0.6	14.6 ± 1.6
$SUVA_{254}$	L·mg^{-1}·m^{-1}	2.84 ± 0.33	2.37 ± 0.28	2.56 ± 0.42	3.56 ± 0.71
NO_3-N	mg-N·L^{-1}	2.06 ± 0.27	2.10 ± 0.19	1.87 ± 0.15	4.03 ± 0.43
NH_4-N	mg-N·L^{-1}	0.24 ± 0.04	0.21 ± 0.07	0.17 ± 0.03	0.31 ± 0.06
Mn	μg·L^{-1}	46.8	14	14.03	86.74
Fe	μg·L^{-1}	175	87.4	37.6	109.6
Zn	μg·L^{-1}	20.9	30.1	36.6	36.6

Co, Cd, and Pb values were below the limit of detection.

LC-OCD results showed that humic substances (HS) are the dominant fraction of DOC in all influent water. The contributions of HS to total DOC were 74%, 73%, 68%, and 75%, respectively, for DC, DCWW, WW, and WEOM influent. The hydrophobic fraction (HOC) was only 5.7% of the DOC in WEOM influent water, a typical value for surface water systems. However, the HOC of DC, DCWW, and WW influent was 10.3, 9.8, and 13.7% of the total DOC, respectively. This indicates the impact of effluent organic matter (EfOM) on their organic compositions [32]. Though WEOM had the highest concentration of BP, only 42% can be considered protein (assuming the C:N is 3, and all organic nitrogen in BP originates from protein) [46]. However, the protein represents 51, 65, and 82% of the BP for DC, DCWW, and WW influent, respectively, which also reflects the impact of EfOM. Furthermore, WW and DCWW influent contain more LMW (acids and neutrals), which are more subject to biological treatment. However, DC and WEOM contain relatively lower concentrations of LMW.

PARAFAC components (C1–C5) were recorded for all the influent water. F_{max} was lower for protein component C5 than the humic/fulvic components (C1–C4). The maximum and minimum F_{max} of component C5 were observed for WEOM (1.09 ± 0.05 RU) and DC (0.38 ± 0.03 RU), respectively. A humic-like component (C4) exhibited a comparable contribution with a protein-like component to the DOM fluorescence of the influent. The F_{max} of C4 ranged between 0.33 ± 0.04 RU and 0.89 ± 0.1 RU. However, the terrestrial humic-like component (C1) contributed much more highly than other humic/fulvic components. An exception was the WEOM influent, which possessed the highest concentration of conjugated humic component (C2). Microbial humic (C3) contributed moderately to the fluorescence spectrums of the influent water, with a higher contribution (1.39 ± 0.28 RU) observed for the WW influent and a lower contribution (0.99 ± 0.15 RU) for WEOM.

3.2.2. Bulk Organic Matter Parameters

The results demonstrated that the DOC removal during the filtration process is highly dependent ($p < 0.001$) on its concentration in the feed water. Table 2 showed that the DOC removal values for the DC, DCWW, and WW influent were 9.5, 11.4, and 14.7%, respectively, at 30 °C. However, WEOM influent water exhibited the highest DOC removal (44%) at the same temperature and that may be attributed to the higher feed water DOC concentration promoting biomass formation associated with sand. The ATP values of reactor media were measured to be 4.69, 5.21, 5.39, and 7.95 $ng \cdot g^{-1}$ sand at 30 °C for DC, DCWW, WW, and WEOM, respectively. These values increased by 7–9% at 25 °C and 8–16% at 20 °C (Figure 2). However, the statistical analysis revealed that there is no significant ($p > 0.05$) effect of temperature on biological activity (ATP concentration) and thereby DOM biodegradation is not significantly affected by temperature in the range of 20–30 °C. Nevertheless, the results showed a higher DOC removal efficiency at a lower temperature (20 °C) ($p < 0.05$). For instance, the DOC removal for DC increased from 9.5 ± 2.3% at 30 °C to 20.3 ± 3.7% at 20 °C (Table 2). On the other hand, the results of abiotic batch reactors revealed that adsorption mechanisms contributed to the overall removal of DOC for DC influent by 18 ± 2.1% at 30 °C, 38.5 ± 5.4% at 25 °C, and 51 ± 4.7% at 20 °C, and for WEOM influent by 27 ± 3.7% at 30 °C, 42 ± 5.1% at 25 °C, and 58 ± 6.8% at 20 °C (Table 2). In the same regard, $SUVA_{254}$ values exhibited a positive relationship with temperature, increasing from 2.84 ± 0.3 $L \cdot mg^{-1} \cdot m^{-1}$ for the DC influent to 3.71 ± 0.3, 3.59 ± 0.5, and 3.57 ± 0.2 $L \cdot mg^{-1} \cdot m^{-1}$ for the effluent water at 30, 25, and 20 °C, respectively (Table S2). This implies that aromatic compounds are favourably removed at lower temperatures, considering that there is no significant change in the removal of aliphatic compounds at respective temperatures.

Table 2. DOC ($mg \cdot L^{-1}$) values of the batch effluents at different temperatures (20, 25, 30 °C) and biotic/abiotic conditions under oxic conditions.

	30 °C		**25 °C**		**20 °C**	
	Biotic	**Abiotic**	**Biotic**	**Abiotic**	**Biotic**	**Abiotic**
DC	10.5 ± 0.21	11.4 ± 0.35	9.76 ± 0.0.28	10.89 ± 0.61	9.24 ± 0.32	10.4 ± 0.43
DCWW	9.3 ± 0.18	10.29 ± 0.33	9.24 ± 0.37	10.1 ± 0.23	8.18 ± 0.17	9.4 ± 0.29
WW	8.27 ± 0.24	9.42 ± 0.51	7.95 ± 0.27	9.37 ± 0.23	7.37 ± 0.19	8.96 ± 0.18
WEOM	8.18 ± 0.26	12.87 ± 0.37	7.74 ± 0.41	11.7 ± 0.53	6.8 ± 0.27	10.1 ± 0.41

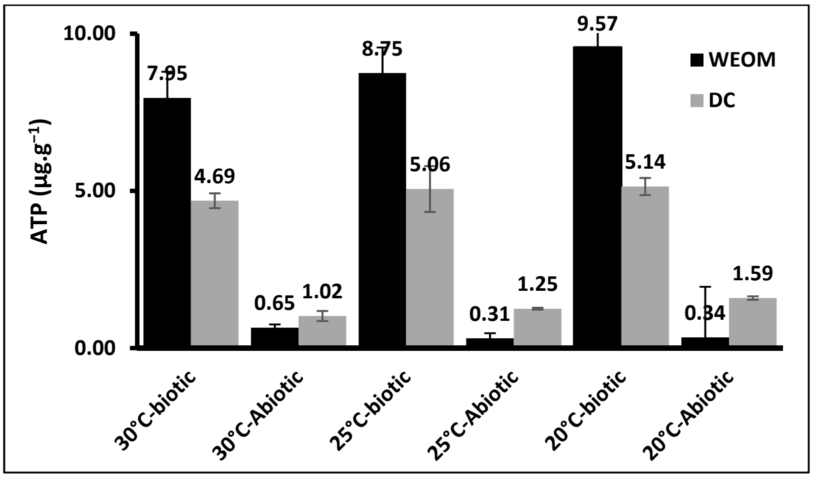
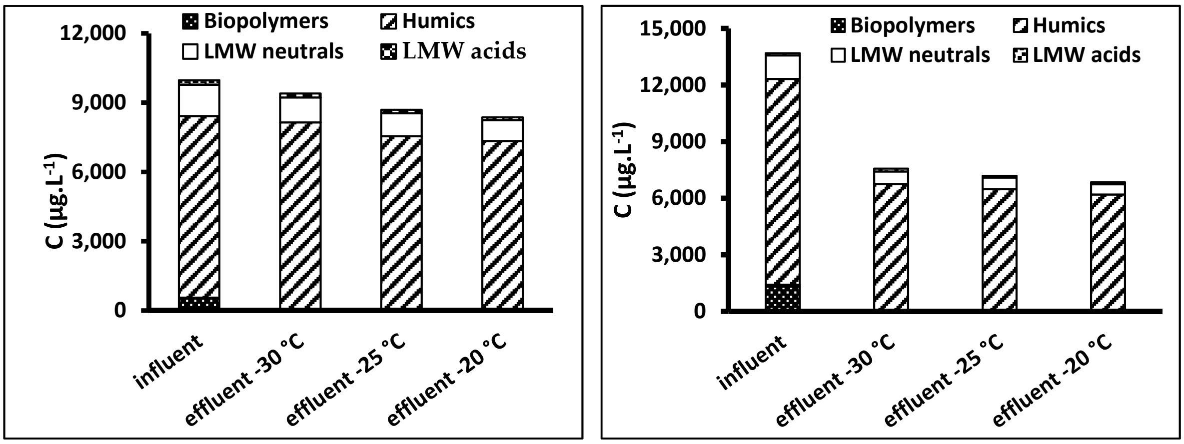


Figure 2. Changes of ATP concentrations (µg·g^{-1}) in a function of temperature and biotic/abiotic conditions during the batch experiment.

3.2.3. LC-OCD Analysis

Total DOC measured by LC-OCD is largely well-matched with the measured values of a conventional TOC analyser to within 0.5 mg·L^{-1}. The changes of DOM fractions at different temperatures are presented in Figure 3 and Table S3. The removal of BP values for DC influent were 87, 94, and 95%; 96, 91, and 88% for DCWW; 94, 86, and 83% for WW; and 98, 97, and 97% for WEOM, at 30, 25, and 20 °C, respectively. However, the statistical analysis revealed that this process is independent of temperature ($p > 0.05$). Other biogenic organic matter fractions (LMWn and LMWa) exhibited lower removal for all the influent water compared to BP. The removal rates of LMWn for DC, DCWW, WW, and WEOM were 20, 16, 6, and 47%, respectively, at 30 °C. This removal increased by 5–16% at 20 °C. Likewise, the LMWa removal ranged between 10–47% for all the influents water at 20 °C. This removal decreased by (6–25%) when the temperature went up by 10 °C. This indicates that the decomposition of higher molecular weight compounds (BP and HS) into LMW hydrophilic compounds is lower than the removal of LWM compounds during filtration. However, this removal is also independent ($p > 0.05$) of temperature. An exception was the LMW acid of WEOM, which increased by 24% at 30 °C.



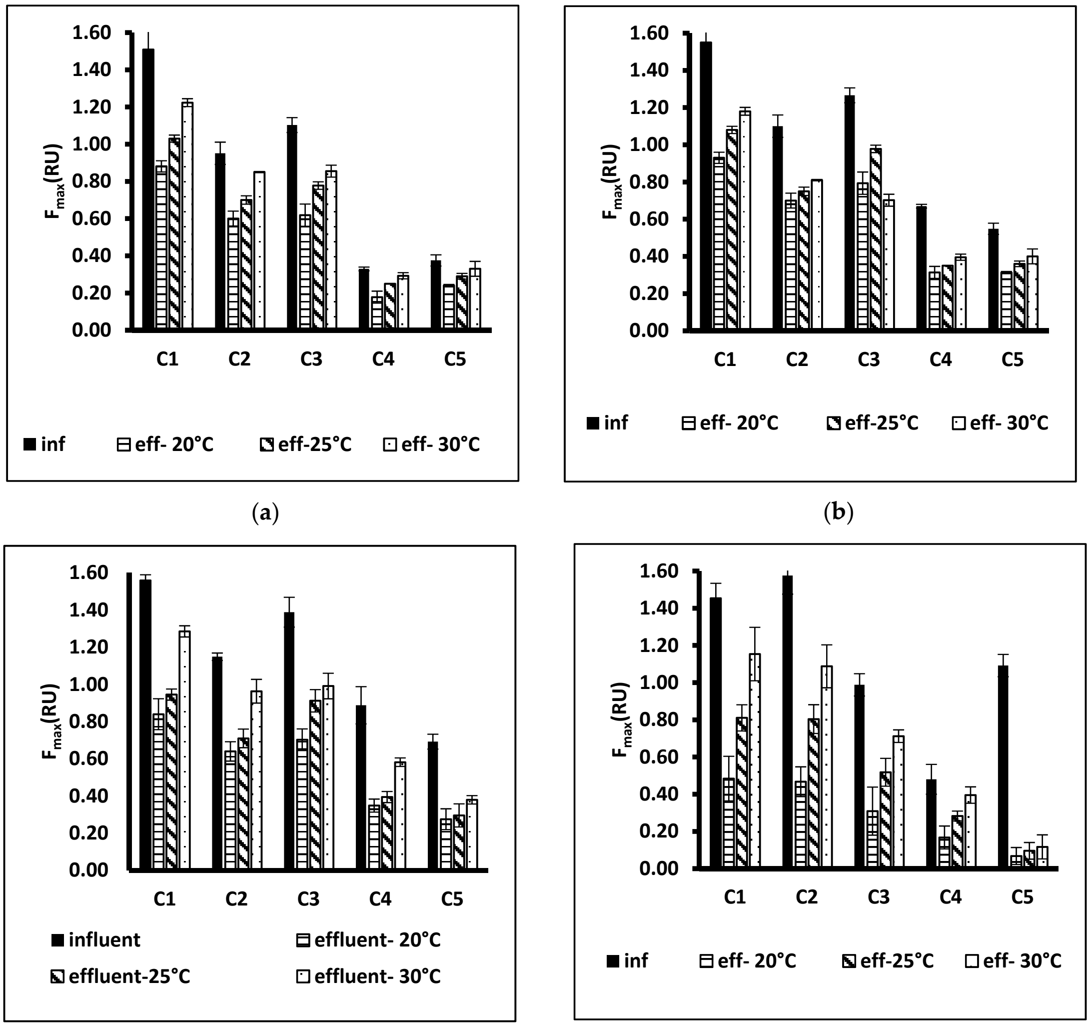
(**a**) (**b**)

Figure 3. Changes in the LC-OCD fractions concentration in batch reactors at different temperatures under oxic conditions: (**a**) DC and (**b**) WEOM.

Humic compound removal exhibited a significant dependency on temperature ($p < 0.05$). Figure 3 displays a highly reduced HS concentration at lower temperatures (20, 25 °C). The HS removal varied between 7–44% at 20 °C and 4–41% at 25 °C for all the influents water. However, an increase in the HS concentration was observed for DC, DCWW, and WW at 30 °C.

3.2.4. PARAFAC-EEM Analysis

The protein-like (C5) component exhibited the highest reduction rate at all three temperatures (Figure 4). The protein-like component removal increased consistently with increasing influent concentration ($p < 0.001$). The highest F_{max} reduction (93.6 ± 2.6%) was recorded for WEOM at 20 °C, followed by WW (60.2 ± 3.2%), DCWW (43 ± 3.8%), and DC (36.1 ± 1.7%), respectively, at the same temperature. Similar to BP removal, these labile compounds exhibited independent behaviour upon temperature variation ($p > 0.05$). The removal percentage was reduced by 23.9 ± 4.8%, 15.9 ± 1.6%, 15.08 ± 5.3%, and 4.5 ± 1.87%, respectively, for DC, DCWW, WW, and WEOM at 30 °C. On the contrary, humic components (C1–C4) removals were impacted significantly by variations in temperature and feed water characteristics ($p < 0.05$). An exception was microbial humic, which showed independent behaviour with temperature variations during the filtration process ($p = 0.09$). Figure 4 illustrates the attenuation of humic components decreasing with rising temperature. The average removal of C1 was 48.6 ± 12.3%, 47 ± 16% for C2, 49.8 ± 13.5% for C3, and 56.2 ± 8.4% for C4, at 20 °C. These removals decreased by 28.4, 26, 19, and 30.4% for C1–C4, respectively, at 30 °C.



(a) (b)

(c) (d)

Figure 4. Changes of PARAFAC components (F_{max}) in the batch reactors at different temperatures (20, 25 and 30 °C) under oxic conditions: (**a**) DC, (**b**) DCWW, (**c**) WW, and (**d**) WEOM (influent = inf and effluent = eff).

3.3. Column Experiments

A column experiment was conducted to assess the impact of redox conditions (oxic, anoxic, and anaerobic) on the behaviour of DOM constituents during the filtration process. The experiment was conducted in a controlled temperature room (30 ± 2 °C) using two different feed water types (DC and WEOM).

3.3.1. Characteristics of Influent Water DOM

The bulk organic characteristics of the feed water are presented in Table 3. It can be shown that WEOM had a higher DOC concentration (14.16 ± 0.73 mg·L^{-1}) than DC influent (10.80 ± 0.51 mg·L^{-1}). Moreover, WEOM possessed higher aromatic characteristics ($SUVA_{254}$ = 3.67 ± 0.21 L·mg^{-1}·m^{-1}) compared to DC influent ($SUVA_{254}$ = 3.05 ± 0.31 L·mg^{-1}·m^{-1}). These results were confirmed with PARAFAC-EEM results, which demonstrated that WEOM had a higher concentration of terrestrial-derived; the average F_{max} values of C1, C2, and C4 for WEOM were 1.52 ± 0.06, 1.61 ± 0.1, and 0.51 ± 0.03 RU, and 1.31 ± 0.04, 0.99 ± 0.07, and 0.41 ± 0.02 for DC influent, respectively. Furthermore, LC-OCD results revealed that the humic fraction was the dominant fraction in the feed water, representing 72 and 73% of the DOM pool for DC and WEOM influents, respectively. However, biogenic fractions (BP, LMWn, and LMWa) represent only 5.9, 11, and 2.3% of DOM for DC influent and 10.7, 8.7, and 1.1% of DOM for WEOM influent, respectively. In addition, PARAFAC-EEM results revealed that DC influent possessed a higher concentration of microbial humic-like component (C3) and lower concentration of protein-like component (C5); the F_{max} values of C3 and C5 were 0.98 ± 0.07 and 0.58 ± 0.03 RU for DC and 0.78 ± 0.06 and 0.92 ± 0.04 RU for WEOM influent, respectively.

Table 3. Characteristics of the influents and effluents water of the columns under different redox conditions.

	DC			**WEOM**		
	pH	**DOC**	**$SUVA_{254}$**	**pH**	**DOC**	**SUVA**
	-	**(mg·L^{-1})**	**(L·mg^{-1}·m^{-1})**	**-**	**(mg·L^{-1})**	**(L·mg^{-1}·m^{-1})**
Influent	7.82	10.80 ± 0.51	3.05 ± 0.31	7.73	14.16 ± 0.73	3.67 ± 0.21
effluent-oxic	7.91	9.49 ± 0.36	4.01 ± 0.24	7.88	7.91 ± 0.17	3.92 ± 0.14
effluent-anoxic	8.08	10.12 ± 0.25	3.06 ± 0.19	8.16	9.37 ± 0.28	3.73 ± 0.33
effluent-anaerobic	8.13	10.26 ± 0.55	3.21 ± 0.27	7.95	10.08 ± 0.39	3.67 ± 0.37

3.3.2. Bulk Organic Matter Parameters

The redox environment significantly ($p < 0.05$) impacts the removal of DOC during filtration. Table 3 shows that the removal of DOC decreased by 5–10% under anoxic, and 7–15% under anaerobic, conditions, compared to oxic conditions. This is highly linked to the biological activity associated with the sand. ATP from active microbial biomass associated with sand was higher for oxic conditions. The average concentrations of ATP in the oxic, anoxic, and anaerobic columns were 5.44 ± 0.64, 3.68 ± 0.37, and 3.21 ± 0.47 for DC and 7.32 ± 0.51, 4.1 ± 0.15, and 4.69 ± 0.21 ng·g^{-1} sand for WEOM, respectively (Figure 5). In the same regard, $SUVA_{254}$ increased from 3.05 ± 0.31 to 4.01 ± 0.24, 3.06 ± 0.19, and 3.22 ± 0.27 L·mg^{-1}·m^{-1} for DC, and from 3.67 ± 0.21 to 3.92 ± 0.14, 3.73 ± 0.33, and 3.67 ± 0.37 L·mg^{-1}·m^{-1} for WEOM, respectively, under oxic, anoxic, and anaerobic conditions.

3.3.3. LC-OCD Analysis

LC-OCD results showed that BP is preferentially removed during soil passage; its removal under anoxic and anaerobic conditions was less than oxic conditions by 20–24% (Figure 6). Similarly, LMWn compounds exhibited higher removal during oxic filtration. The removal was decreased under anoxic and anaerobic conditions by 21 and 50% for WEOM and by 15 and 17% for DC, respectively. The same behaviour was observed for LMWa of DC influent, where its removal decreased by 25–32% under sub-oxic conditions. However, LMWa of WEOM influent exhibited inconsistent behaviour, where its concentration was increased by 15–21% under sub-oxic conditions compared to its concentration in the feed water. In the same way, HS demonstrated a higher removal efficiency under oxic conditions. For WEOM, the average removal of HS under oxic, anoxic, and anaerobic conditions was 36, 29, and 24%, respectively. However, HS removal for DC was only decreased by 2–4% when the environment turned into sub-oxic conditions.

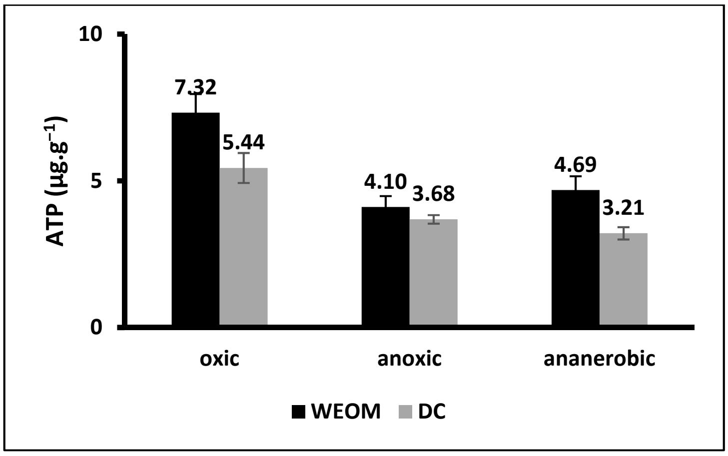
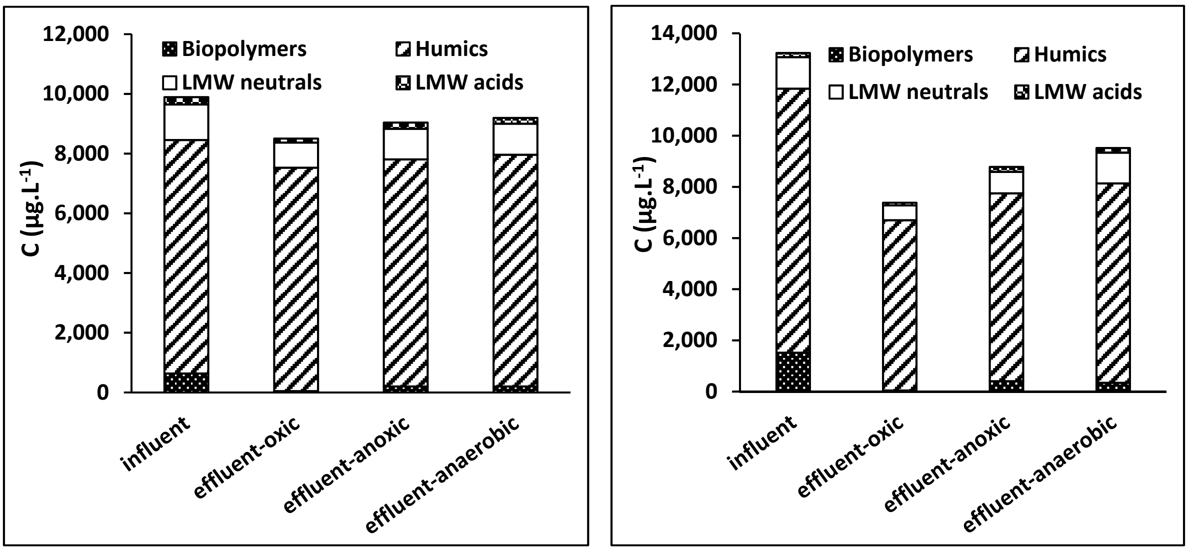


Figure 5. Changes of ATP concentrations (µg·g^{-1}) in a function of redox conditions during the column experiment for DC and WEOM influent.

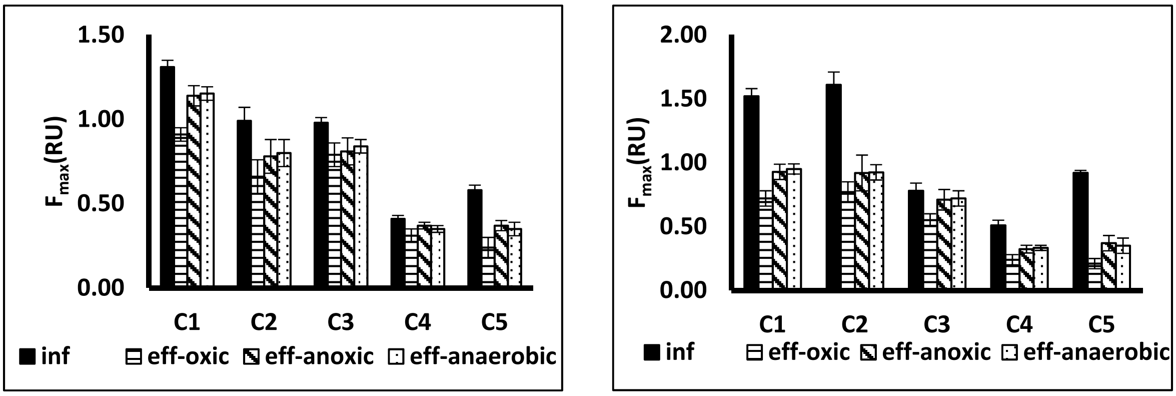


(a) **(b)**

Figure 6. Changes of LC-OCDND fractions in batch reactors under different redox conditions: (**a**) DC and (**b**) WEOM (temperature = 30 °C, column study).

3.3.4. PARAFAC-EEM Analysis

The fate of PARAFAC components under different redox conditions was examined using their maximum fluorescence intensity (F_{max}). The results reveal that the redox environment plays a substantial role in the removal efficiency of fluorescence components during soil passage (Figure 7). The removal of protein-like components was decreased by 15–22% under sub-oxic conditions. In the same manner, the microbial humic component (C3) displayed redox-dependent behaviour, with higher reduction under oxic conditions. The removal of microbial humics was reduced by 20–22% for WEOM and 2–5% for DC influent under sub-oxic conditions. Similar to protein-like components, terrestrial-derived humic components showed a higher removal under oxic conditions; the removals of C1, C2, and C4 were reduced by 14–19%, 9–14%, and 10–18%, respectively, during sub-oxic filtration.



(a) **(b)**

Figure 7. Changes of PARAFAC components (F_{max}) under different redox conditions: (**a**) DC and (**b**) WEOM (temperature = 30 °C) (column study) (influent = inf and effluent = eff).

4. Discussion

4.1. Impact of Temperature and Influent Organic Composition on DOM Behaviour

DOM removal during BF is principally due to a combination of DOM sorption to the sand media and biodegradation through bacteria in biofilms associated with the media. In this study, DOC decreased during the filtration process, showing a high dependence on the feed water DOC composition, which is highly correlated with the biomass activity associated with the sand. This is in agreement with Li et al. [47], who reported a positive correlation between biofilm density and influent DOC concentration. However, the results infer that there is no effect of the temperature on the biomass activity associated with the sand and thus the impact of temperature on DOC biodegradation is low. On the other hand, the abiotic results indicate preferential DOM adsorption at a lower temperature. Thus, it can be concluded that the relatively higher removal of DOM at lower temperatures in the range of 20–30 °C during the BF process is mainly ascribed to adsorption. These results are inconsistent with Massmann et al. [48], who reported DOM attenuation independent of 0–24 °C temperature, based on a field study conducted at an operational artificial recharge site over Tegel Lake in Germany. In contrast, Abel et al. [49] found a positive relationship between DOC removal and temperature (5–25 °C) during the filtration process. Alidina et al. [50], on the other hand, reported a minor temperature (10–30 °C) effect on DOM removal during a column filtration process, with higher removal at lower temperatures. These contradictions in DOM behaviour during infiltration at different temperatures could be attributed to different feed water DOM characteristics. This goes in line with the conclusion of Chen et al. [51] who reported that the organic composition of the raw water determines its behaviour during filtration. Thus, it is important to assess the behaviour of DOM fractions individually during filtration.

BPs (Molecular weight MW > 20,000 Da) are the most readily biodegradable DOM fraction, thus they are preferentially removed during the filtration process [52]. According to So et al. [53], the BP was reported to be highly degraded at higher temperatures; however, in this research, there is no significant effect of temperature (20–30 °C) on BP removal observed during filtration. The removal of BP reached >80% at all temperatures during filtration, and this is mainly attributed to the prolonged filtration period. Moreover, the high ratio between organic nitrogen BP and DOC in the feed water indicated that they are principally composed of proteinaceous matter that is highly degraded during filtration. This is in consonance with the PARAFAC-EEM results, where labile compounds (i.e., protein-like compounds) exhibited independent behaviour upon temperature variation. However, the results demonstrated that protein-like component removal is more sensitive to temperature variation when the protein content of the feed water is low. This specifies the vital role of co-metabolism in the removal of this biodegradable matter. These results are consistent with Maeng et al. [23], who reported the total removal of BP during bank filtration over Tegel Lake (Germany). Likewise, other biogenic organic matter fractions (LMWn and LMWa) exhibited temperature-independent behaviour during the filtration process.

In contrast, the removal of humic compounds was highly dependent on the temperature of the feed water, with a favourable reduction at a lower temperature (20–25 °C). This reduction is mainly ascribed to the high ability of these refractory compounds to adsorb onto sand grains at a lower temperature. On the contrary, an increase in the concentration of HS was observed at a higher temperature (30 °C) for DC, DCWW, and WW influent. The HS concentration enrichment may be attributed to microorganisms and enzymes that are able to: (I) transform microbial matter to more refractory and conjugated matter (i.e., microbial humification process), that was reported in several laboratory-scale and field studies [54–56]; and (II) leach soil humic compounds into filtrate water [57]. In contrast, the humic of WEOM influent exhibited a unique behaviour, and its concentration decreased at all three temperatures. This may be due to: (I) the absence of microorganisms to transform labile matter or leach organics from soil, as mentioned above; and (II) the inability of these organic compounds to bio-transform into refractory compounds, which may be attributed to their higher aromaticity ($SUVA_{254} = 2.9\ L \cdot mg^{-1} \cdot m^{-1}$) compared to other influents. PARAFAC-EEM results revealed that the condensed structure humic compounds are the most impacted by changing temperature during the filtration process. These results are compatible with those of Abel et al. [49], who illustrated that the optimum temperature for the removal of these refractory compounds is 15 °C. The ratios between the PARAFAC components were used in many studies [10,45] to assess treatment efficacy. In this research, only the ratios between the F_{max} of terrestrial humic components (C1, C2, and C4) and the protein-like component (C5) exhibited a clear increasing trend with rising temperature. These results also confirm the preferential removal of terrestrial humic components at lower temperatures.

4.2. Impact of Redox Conditions on DOM Behaviour

This research specifies the preferential removal of DOM under oxic conditions during the BF process, which is mainly attributed to oxygen as an electron acceptor for microorganism respiration to degrade the organic matter. Slower biodegradation of organic matter under sub-oxic conditions was also reported in previous studies [49,58]. Moreover, $SUVA_{254}$ values exhibited a lower increase during sub-oxic conditions, which refers to the preferential removal of aliphatic compounds during oxic filtration.

LC-OCD data revealed that BP is the most impacted DOM fraction by the alteration in the redox environment, with favourable removal under oxic conditions. In the same regard, the ratio between nitrogen and carbon BP exhibited higher values under oxic conditions, which infers lower biodegradation of protein compounds under sub-oxic conditions. This finding was confirmed with PARAFAC-EEM results, where F_{max} of the protein-like component (C5) exhibited higher reduction (relative to influent F_{max}) under oxic conditions than other redox conditions. This reduction is mainly ascribed to the degradation of high molecular weight biodegradable organic matter into non-fluorescing material. This is in agreement with field data collected at the Tegel Lake (Berlin, Germany) BF site, where the partial removal of biopolymers was detected under sub-oxic conditions [58]. Furthermore, previous studies [19,49] also emphasized the superior removal of protein-like components under oxic environmental conditions by conducting laboratory-scale experiments. Likewise, LMW (acids and neutrals) exhibited a lower removal efficiency under sub-oxic conditions. An exception was the LMW acid of WEOM, which increased under sub-oxic conditions, likely due to the breakdown of larger molecular weight humic matter into lower molecular weight compounds under these conditions [59].

HS removal followed the same trend as BP (with less removal efficiency), in that higher removal was obtained under oxic than other redox conditions. Nonetheless, the HS removal efficiency is much lower for DC influent than WEOM influent, presumably attributed to the nature and molecular weight of the humic present. PARAFAC-EEM humic components (C1–C4) also exhibited higher reduction under oxic conditions. Terrestrial humic-like components (C1 and C2) exhibited the highest reduction of F_{max} among other humic components, followed by lower aromatic-humic, such as component (C4). According to Gerlach et al. [60], humic compounds with a higher molecular weight are preferentially removed during aerobic soil passage.

5. Conclusions

Based on the results of laboratory-scale batch and column studies, the following conclusions can be drawn:

- A positive correlation was found between DOM biodegradation and raw water concentration, which was likely due to the higher microbial activity associated with sand, as determined by ATP measurements of the biomass attached to the sand grains.
- The removal of DOM during filtration is significantly impacted by temperature variation, with higher removal at lower temperatures.
- LC-OCD results revealed that the labile compounds (i.e., biopolymers) are highly removed (>80%) under oxic filtration, regardless of the temperature and organic matter composition of the feed water. Likewise, the PARAFAC protein-like component exhibited the highest reduction at all temperatures studied.
- Humic compound removal exhibited a significant dependence on temperature, with higher removal at a lower temperature. PARAFAC analysis indicated that terrestrial humic components are the least persistent humic type adsorbed at a lower temperature. The contradictory behaviour of protein and humic compounds explains the positive relationship between SUVA and temperature.
- DOM was preferentially removed under oxic conditions; its removal decreased by 5–10% under anoxic, and by 7–15% under anaerobic conditions. LC-OCD results reveal that biopolymers are the most impacted fraction by altering the redox conditions. Humic compounds also exhibited a lower removal efficiency (with less extent) under sub-oxic conditions. Therefore, post-treatment steps should be considered in case of sub-oxic filtration.
- In general, this study revealed that the BF removal efficiency for DOM components under arid conditions (high temperature) is determined by the feed water organic composition and redox conditions in the infiltration area.
- Finally, this study shows that PARAFAC-EEM and LC-OCD can be promising tools to provide further insight into BF processes and for determining the treatment efficiency for DOM components.

Supplementary Materials: The following are available online at http://www.mdpi.com/2073-4441/10/12/1730/s1, Figure S1: The contour plots and the corresponding excitation (solid curves) and emission (dotted curves) loadings of the fluorescent components C1–C5; Table S1: The spectral slopes of the identified components and their corresponding components in previous studies from the OpenFluor database; Table S2: $SUVA_{254}$ ($L \cdot mg^{-1} \cdot m^{-1}$) values of the batch effluents at different temperatures (20, 25, 30 °C) and biotic/abiotic conditions under oxic conditions; Table S3: Changes in the LC-OCD fractions concentration in batch reactors at different temperatures under oxic conditions using different water types (DC, DCWW, WW, and WEOM).

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