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Characterisation of organic foulants on full-scale UF membranes during filtration, backwash and chemical cleaning episodes

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ABSTRACT

Understanding organic fouling on ultrafiltration (UF) membranes during water filtration and cleaning episodes has become one of the major factors driving UF technology forward. The aim of this study was to quantify and characterise the organic foulants on an UF membrane at a full-scale drinking water treatment plant when it is fed with surface water and groundwater with different dissolved organic carbon (DOC) contents. DOC characterisation was performed by high-performance size-exclusion chromatography and fluorescence excitation–emission matrix (FEEM). The masses of DOC (and its fractions) retained by the membrane over a whole filtration period (and detached during cleaning episodes) were calculated through mass balances. Under river water feeding conditions, DOC was retained by 22%, being biopolymers the most retained DOC fraction (59%), followed by humic substances (17%) and other minor organic fractions. Routine backwashing resulted in the detachment of only 8% of the total mass of DOC retained, with biopolymers as the most detached fraction (27%). Within biopolymers, proteins appeared to contribute more to hydraulically irreversible fouling than polysaccharides. Under groundwater feeding conditions, no apparent retention of DOC was observed. FEEM analyses showed neither significant removal of fluorescent components during filtration nor detachment from the UF membrane during routine backwashing.

Keywords: DOC characterisation; Drinking water; Fouling reversibility; Organic fouling; Ultrafiltration

1. Introduction

The two major topics in the use of ultrafiltration (UF) in drinking water treatment plants (DWTPs) are quality of the permeate, which is related to the rejection of solutes from feed water, and membrane fouling, which is related to the accumulation of solutes on the membrane. With regard to the latter, considerable effort has been devoted to control this fouling, since it leads to a decrease in membrane permeability and in the efficiency of the filtration process [1]. This effort has particularly been oriented to better understand fouling formation, composition and detachment when a physical cleaning such as

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backwashing (BW) or a chemical cleaning such as cleaning-in-place (CIP) are applied.

Fouling formation and detachment from UF membranes have been widely researched, but mostly in terms of changes in membrane permeability during filtration and cleaning [2–7]. Although membrane permeability is a widely accepted index of fouling extent, it is also true that it does not always correlate with foulant amounts accumulated on the UF membrane [8]. Studies quantifying the total mass of foulants on a membrane through a mass balance are scarce and, to our best knowledge, they are limited to lab-scale tests [9–11] whilst no published studies exist on a full-scale basis.

Fouling composition, and in particular with regard to organic matter, since it is acknowledged to most contribute to UF membrane fouling in DWTPs [1,2,12], has traditionally been studied by monitoring bulk parameters such as dissolved organic carbon (DOC) or total organic carbon (TOC). However, it is well known that DOC is comprised by a complex and heterogeneous mixture of compounds that can largely differ in their behaviour and treatability. For this reason, analytical techniques such as high-performance size-exclusion chromatography (HPSEC) and fluorescence excitation–emission matrix (FEEM) are increasingly employed to fractionate and characterise DOC. By applying these techniques, fouling composition has been inferred from differences in concentration of fractions between feed and permeate streams [13,14], but rarely quantified through mass-balance calculations [11,15]. The difference between such approaches can explain, for instance, why some published studies report that the main UF membrane foulants consist of humic substances (HS; which constitute the main part of DOC in surface water but are removed at moderate percentages) [6,11,16] whilst some others of biopolymers (BP; which account for a small part of DOC but are removed at high percentages) [1,17–19]. Other studies have obtained information on fouling composition by undertaking autopsies of fouled membranes by Fourier-transform infrared spectroscopy (FTIR), scanning electron microscopy and atomic force microscopy [3]. However, these techniques require sacrificing membranes, which is rarely possible at full-scale DWTPs.

At full-scale DWTPs cleaning is generally performed using trial-and-error methods, whereby empirical sequences involving a variety of cleaning solutions are applied based on membrane manufacturer's recommendations. Identifying which organic fractions mostly contributed to membrane fouling and which are preferentially detached when BWs and CIPs are applied, which would undoubtedly allow refined BW and CIPs strategies, is a matter of ongoing research.

A large body of this research has been performed on lab-scale systems with configurations (e.g., flat-sheet membranes) and under operational conditions (e.g., filtration under constant transmembrane pressure [TMP]) that differ from those in full-scale DWTPs [1,9,10], providing results that are not always comparable with practical situations. Moreover, most of these studies are based on short-term experiments run for only one filtration cycle with no BWs or CIPs [19,20], and when studies include BWs, these are applied for a limited number of filtration cycles (rarely more than 10, and usually not more than half a dozen) [1,2,13,15,21,22] and/or are different from those in DWTPs (e.g., are not air-assisted) [2,13,14,17]. Furthermore, some studies apply cleaning protocols that are impractical in DWTP (e.g., manual wiping of a fouled membrane with a lab sponge, or manual shaking of a beaker containing fouled membrane modules submerged in MilliQ water) [3,7,15]. Finally, other studies use synthetic solutions containing organic model compounds (e.g., bovine serum albumin [BSA], dextran and sodium alginate) often at very high concentrations (up to 100 mg/L) compared with those in real surface waters [5,12,13,23], making difficult a reliable translation of results to full DWTPs. Therefore, whilst lab-scale studies provide very useful information on UF membrane fouling, their results cannot automatically be extrapolated to full-scale DWTPs, making necessary further research on full-scale systems.

The aim of this study was to assess the organic fouling on an UF membrane of a full-scale DWTP fed with two raw waters (surface water and groundwater) with different qualities. More specifically, the study aimed at quantifying the mass of foulants accumulated on the UF membrane during filtration and detached when BWs and CIPs are applied. DOC was characterised by means of HPSEC and FEEM coupled with PARallel FACtor (PARAFAC).

2. Materials and methods

2.1. Plant description

The DWTP of this study is located in Sant Joan Despí (Barcelona, Spain) and has a nominal capacity of 5.3 m^3/s. The raw water used by the DWTP comes from the Llobregat river and, when required, its aquifer. Llobregat river presents high TOC concentrations (2–14 mg/L), high turbidity (5 up to >1,000 FNU) and high conductivity (1,160–1,939 μS/cm), whilst groundwater exhibits lower TOC concentrations (1.1–1.5 mg/L) and turbidity (0.2–0.5 FNU), but slightly higher conductivity (1,970–2,012 μS/cm). It is when river water quality deteriorates due to unusual events (e.g., peaks in TOC and/or turbidity caused by intense rainfall events) that groundwater is fed into the DWTP in substitution to (or together with) river water.

The whole treatment process of the DWTP is displayed in Fig. 1. It includes a conventional treatment comprised of preliminary screening, pre-chlorination with ClO_2, coagulation/flocculation by the addition of aluminium sulphate, subsequent sedimentation and sand filtration. It is at this stage where groundwater, when required, is incorporated. From this point on, water flow is split into two halves: one undergoes ozonation and granular activated carbon filtration, whilst the other undergoes inline coagulation with $FeCl_3$, UF, UV irradiation, reverse osmosis filtration and remineralisation. Both treated streams are blended and the resulting stream is post-chlorinated prior to distribution.

2.2. UF description stage

UF is performed through 0.02-μm pore size submerged polyvinylidene difluoride hollow fibre UF membranes (ZeeWeed 1000, GE Water & Process Technologies-ZENON, USA) operating under an outside-in mode. The whole UF stage consists of 9 in-ground concrete tanks (hereafter referred to as trains) each holding 9 cassettes with 57 modules each, totalling 4,104 modules (with a total membrane surface area

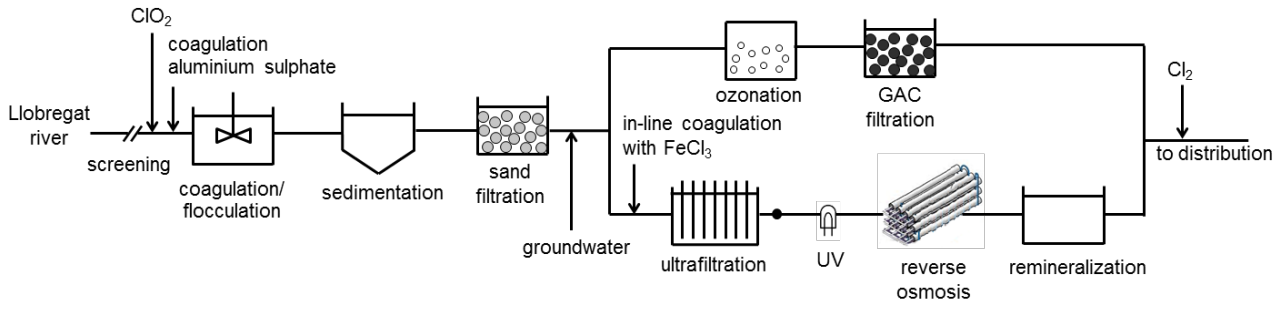

Fig. 1. Schematic representation of the DWTP of Sant Joan Despí.

of 228,575 m^2). At the base of the membrane modules, bubble aerators allow aeration during BW. All trains, run open to the atmosphere, are identical and are operated in parallel under the same conditions. All experimental work in this study was performed on a train basis, and the trains sampled were trains #3 and #4. It must be pointed out that UF feed exhibits substantial fluctuation in DOC content depending on the type of raw water sourced into the DWTP.

2.3. UF train operation

Each UF train is operated as a simple semi-batch process where filtration and BW alternate in sequence with durations of approximately 45 and 4 min, respectively. Periodically, after approximately 65,000–70,000 m^3 of permeate production (which corresponds to every 5–6 d) a four-step maintenance cleaning (MC) with a duration of 3–4 h is applied. Additionally, only when required (a few times per year), a recovery cleaning is undertaken similar to an MC but with higher doses and more prolonged exposure times. The objective of this study was to investigate the behaviour of DOC over a filtration period between two consecutive MCs and when an MC is applied.

2.3.1. Filtration

During filtration, water enters into the train and completely submerges the membrane modules. The volume of water in the train (V_{tank}) is ~42 m^3. Water permeates through the UF membrane in an outside-in mode by applying a gentle suction (TMP = 0.3 bar), leaving behind in the tank all particulate materials, bacteria and certain DOC constituents rejected by the membrane. The permeated water is continuously replaced with new feed water to maintain a constant level in the tank at ca. 4.10 m.

2.3.2. Backwashing

Routine BWs are applied when TMP reaches a predetermined limit or on a pre-set timeframe (usually about 45 min). Such BWs proceeds as follows: first, ~17.5 m^3 of the total 42 m^3 are drained (i.e., the water level in the tank is decreased to a pre-set level of 3.45 m). Then, the BW is carried out with air bubbling (at a 600 L/s) and UF permeate in an inside-out mode. The amount of UF permeate injected is 6 m^3, and therefore the tank is filled to a total volume of ca. 30.5 m^3 (i.e., the water level in the tank rises to a level of ca. 3.65 m). Bubbling air creates a scouring effect that loosens and dislodges foulants from the membrane. Finally, the train is emptied completely, refilled with new feed water and filtration resumes. The duration of a whole BW is 4 min. Because the BW is air-assisted, the routine BW in this study will be referred to as BW(+air).

2.3.3. Maintenance cleaning

An MC involves the following steps:

- The train is completely emptied and refilled with 42 m^3 of a solution of NaClO (150 ppm). Membranes are soaked in this solution for 45 min. ClO^- is used to oxidise organic foulants thereby favouring their detachment from the UF membrane.
- The train is emptied and membranes are backwashed with UF permeate in an inside-out mode for ca. 80 s. This step is repeated twice. These BWs are carried out without air bubbling, and therefore they will be referred to as BW-A1 and BW-A2.
- The train is put in a filtration mode for 2 h, and then it is completely emptied again and refilled with 42 m^3 of a solution of H_3PO_4 (1,000 ppm, pH = 2.2). Membranes are soaked in this solution for 30 min. H_3PO_4 is used to dissolve any scaling present on the membrane.
- Finally, the train is emptied and two consecutive BWs similar to those in the second step are applied (referred to as BW-B1 and BW-B2).

2.4. Sampling program and calculations

2.4.1. Mass retained by an UF train over a filtration period between two MCs

A first campaign was carried out in train #3 to get insight into the treatability of DOC and its fractions. The filtration period treated a total volume of water (V_{period}) of 72,000 m^3 and lasted 5 d before the following MC was applied. During this period, samples of feed and permeate were collected at three different days. These samples were analysed for DOC concentration and fractionation through HPSEC. Because composition of each stream was found to be fairly constant, average concentrations for each constituent "i" (i.e., DOC or any of its fractions) were considered for both feed (c_i^{feed}) and permeate ($c_i^{permeate}$) streams. The total mass retained by the membrane over the whole filtration period ($m_i^{retained}$) was calculated through a simple mass balance:

$$m_i^{\text{retained}} = V_{\text{period}} \cdot (C_i^{\text{feed}} - C_i^{\text{permeate}}) \quad (1)$$

Additionally, DOC was characterised by FEEM to provide additional information on the character of DOC and its fractions. In this case, feed and permeate samples were periodically collected beyond a simple filtration period. Samples were collected on a bimonthly basis over 1 year (i.e., six campaigns).

2.4.2. Mass detached by routine BW(+air) over a filtration period between two MCs

Backwash solution (containing the detached foulants from the membrane) was sampled immediatlely after the application of a BW(+air) and before the train was completely drained. In order to gain in representativity, samples from three different locations within the train were combined to create a composite sample. Again, samples were analysed for DOC concentration and fractionation through HPSEC. The concentration of "i" in such sample is referred to as $C_i^{\text{post-BW(+air)}}$. A total of four backwash solutions were sampled at four distinct BW(+air) episodes over the filtration period. Again, HPSEC analysis showed little variability in the composition and then average concentrations were used. The mass of "i" detached by all BW(+air) applied over the whole filtration period ($m_i^{\text{BW(+air)}}$ was calculated from the mass of "i" detached by a single BW(+air) multiplied by the total number of routine BW(+air) ($N_{\text{BW(+air)}}$) performed during the whole filtration period as shown in the following equation:

$$m_i^{\text{BW(+air)}} = V_{\text{train,BW}} \cdot \left(C_i^{\text{post-BW(+air)}} - C_i^{\text{pre-BW(+air)}} \right) \cdot N_{\text{BW(+air)}} \quad (2)$$

where $C_i^{\text{pre-BW(+air)}}$ is the concentration of "i" in the tank just before the BW(+air). As explained in section 2.3.2, before any BW(+air) the train initially filled with 42 m^3 of feed water was emptied by 17.5 m^3 and filled with additional 6 m^3 of UF permeate (yielding a $V_{\text{train,BW}}$ of 30.5 m^3). Then, $C_i^{\text{pre-BW(+air)}}$ could be calculated as:

$$C_i^{\text{pre-BW(+air)}} = \frac{24.5}{30.5} \cdot C_i^{\text{feed}} + \frac{6}{30.5} \cdot C_i^{\text{permeate}} \quad (3)$$

2.4.3. Mass detached by an MC

A second campaign was conducted in train #4 to validate the above findings but also to quantify the masses of "i" detached by each step of an MC. In this case, the filtration period treated a total volume of water of 60,000 m^3 and lasted 7 d. During filtration, feed and permeate were sampled at two different days. Similar to previous calculations, the detached masses at each step (i.e., backwashing BW-A1, soaking with ClO^-, backwashing BW-A2 and soaking with H_3PO_4) were calculated through a mass balance considering the volume of each cleaning solution and its composition before and after applying it, yielding the amounts $m_i^{\text{ClO}^-}$, m_i^{BWA1}, $m_i^{\text{H}_3\text{PO}_4}$ and m_i^{BWA2}, respectively. Again, samples were also analysed for characterisation through HPSEC and FEEM.

2.5. Analysis

All samples were collected in 500 mL amber glass bottles and stored at 4°C until analyses, which were performed within 1 week for HPSEC and within 24 h for FEEM. Prior to any analysis, samples were filtered through 0.45 μm filters.

HPSEC analysis was performed by DOC-Labor Laboratory (Karlsruhe, Germany) using a Toyopearl TSK HW-50S column coupled to online ultraviolet (UV_{254}), organic carbon and organic nitrogen detectors. Such system separates DOC fractions according to their hydrodynamic molecular size. Table 1 gives details on the molecular weight (MW) and constituents of each fraction [24]. The International Humic Substances Society (IHSS) Suwannee River reference materials, humic acid and fulvic acid, were used as reference samples for the system calibration for molar masses, whilst potassium hydrogen phthalate and potassium nitrate were used for the calibration of TOC and total organic nitrogen, respectively. Because proteins and polysaccharides in fraction BP differ in their composition and properties (the former contain N and UV-active components whilst the later do not), the technique can provide (under the presumption that all organic N in the BP fraction originates from proteins) an estimation of protein content within the BP fraction.

Three-dimensional FEEM spectra were performed by Aigües de Barcelona's laboratory on a LS55 PerkinElmer fluorescence spectrophotometer with a xenon lamp as excitation source using a 1 cm path length quartz cuvette. Fluorescence intensities were measured at excitation wavelengths of 225–515 nm in 10 nm increments and emission wavelengths of 230–650 nm in 10 nm increments, using a scan speed of 600 nm/s. The slit widths on excitation and emission modes were both set at 5 nm. The photomultiplier

Table 1
Chromatographic fractions of DOC as determined by HPSEC

DOC fraction	Abbreviation	MW (g/mol)	Constituents within fraction
Biopolymers	BP	>20,000	Polysaccharides, proteins
Humic substances	HS	≈1,000	Fulvic and humic acids
Building blocks	BB	300–500	Hydrolysates of humic substances
Low molecular weight neutrals	LMWN	<350	Alcohols, aldehydes, ketones,
Low molecular weight acids	LMWA	<350	monoprotic organic acids

tube voltage was set to 750 V. MilliQ water was run as blank and its FEEM was subtracted from the sample FEEM in order to reduce the influence of Raman scattering. The sample FEEM spectra were then normalised by dividing the fluorescence intensity by the Raman scatter peaks of the blank, yielding fluorescence results as Raman Units (R.U.). FEEMs were plotted in MATLAB 2009 using the contour function and in-house routines. FEEM spectra were divided into five regions (Region I to Region V) according to Chen et al. [25]. The wavelength boundaries for this division were selected by Chen et al. [25] based on the characterisation of DOC fractions (acids, bases and neutrals) and model organic compounds by a number of different techniques (fluorescence, ultraviolet-visible absorption, solid state ^{13}C NMR spectroscopy and FTIR spectroscopy). The fluorescent DOC within each region in a given sample can then be quantified as normalised regions-specific FEEM volume, following the fluorescence regional integration described by Chen et al. [25]. Table 2 gives details on the excitation and emission ranges and constituents of each region.

Because fluorescence from different organic molecules may overlap, using simple excitation–emission wavelength pair(s) of each fluorescence peak may not be sufficient. In such a case, decomposing the FEEM into their underlying chemical components is desired. This can be accomplished by mathematical tools such as the PARAFAC analysis, which is able to decompose trilinear multiway data arrays and facilitate the identification and quantification of independent underlying signals, termed "components". PARAFAC analysis was performed using the N-way v.3.00 Toolbox for MATLAB following published procedures [26]. The number of fluorescence components was identified by a validation method including variance explained, core consistency diagnostic and split-half analysis. Component spectra were also compared against the online repository of published fluorescence spectra OpenFluor (www.openfluor.org) to evaluate spectral matching and component identification [27].

Table 2
FEEM fractions of DOC as determined by FEEM spectroscopy

DOC region	Excitation range (nm)	Emission range (nm)	DOC character
Region I	0–250	180–320	Aromatic protein-like DOC-I
Region II	0–250	320–370	Aromatic protein-like DOC-II
Region III	0–250	370–570	Fulvic acid-like DOC
Region IV	250–350	180–370	Microbial by-product-like DOC
Region V	250–420	370–400	Humic acid-like DOC

3. Results and discussion

3.1. Filtration cycle of an UF train between two consecutive MCs

As described in section 2.4.1, a first campaign was carried out to monitor a filtration period in train #3, which treated a total volume of water (V_{period}) of 72,000 m^3 and lasted 5 d before the following MC was applied. The origin of raw water feeding the DWTP during this filtration cycle was mostly the Llobregat river (>95%), which is more loaded with DOC than groundwater and for which higher DOC removals are expected, as found in a previous study [28].

Fig. 2 shows the operational conditions during the filtration period. The above graph in the figure shows the operation status of the UF train over the whole period (filtration, BW(+air), MC or stand-by), whilst the below graph shows the permeability and TMP values (the permeability is positive and TMP negative when the UF unit is in production). As it can be seen, the total number of routine BW(+air) ($N_{BW(+air)}$) over the studied period was 32.

3.2. DOC treatability under river water feeding conditions

3.2.1. Mass retained over the filtration period

During the 5-d filtration period, samples of UF feed and permeate were collected at three different days for HPSEC analysis. The composition of both streams is shown in Table 3. The relatively high content of DOC (3,570 ppb) in UF feed is typical when the DWTP is fed with river water, in opposition to when it is fed with groundwater (in the order of 1,000 ppb or less). With regard to DOC composition, HS clearly predominated (with average percentages of 45% of total DOC), followed by low molecular weight neutrals (LMWN; 22%), building block (BB; 16%) and BP (8%), whilst low molecular weight acids (LMWA) was detected at <1%.

As shown in Table 3, the average removal percentages removed by UF for DOC, BP, HS, BB and LMWN were 22%, 59%, 17%, 15% and 15%, respectively. These values were consistent with other researchers treating water by UF [2,7,17]. For instance, removal percentages for BP are reported in the range of 63%–93% [7], 40%–90% [29], 57% [30] and 42% [28]; for HS in the range of 20%–40% [17], 0%–33% [7] and 0%–12% [29]; for BB in the range of 8%–15% [7] and <10% [28]; and for LMWN <10% [7,28]. The differences in percentage removal between organic fractions can be attributed to size-exclusion effects, whereby fractions with larger MW are better retained than those with lower MW [11].

Proteins within BP, as analysed by HPSEC, were removed at a similar percentage (65%) as for BP (59%), indicating that proteins and polysaccharides (the main constituents of BP) were similarly retained by the UF membrane. Preferential removal of proteins (and protein-like substances) over polysaccharides is in agreement with previous studies [1,3], but in disagreement with others [2,7,17]. The disagreement might come, at least partially, from differences in methods employed in determining proteins (FEEM against Lowry method) and polysaccharides (HPSEC against phenol–sulphuric acid method), since it is acknowledged that Lowry and phenol–sulphuric acid methods can present critical limitations in the analysis of proteins and polysaccharides [13,17].

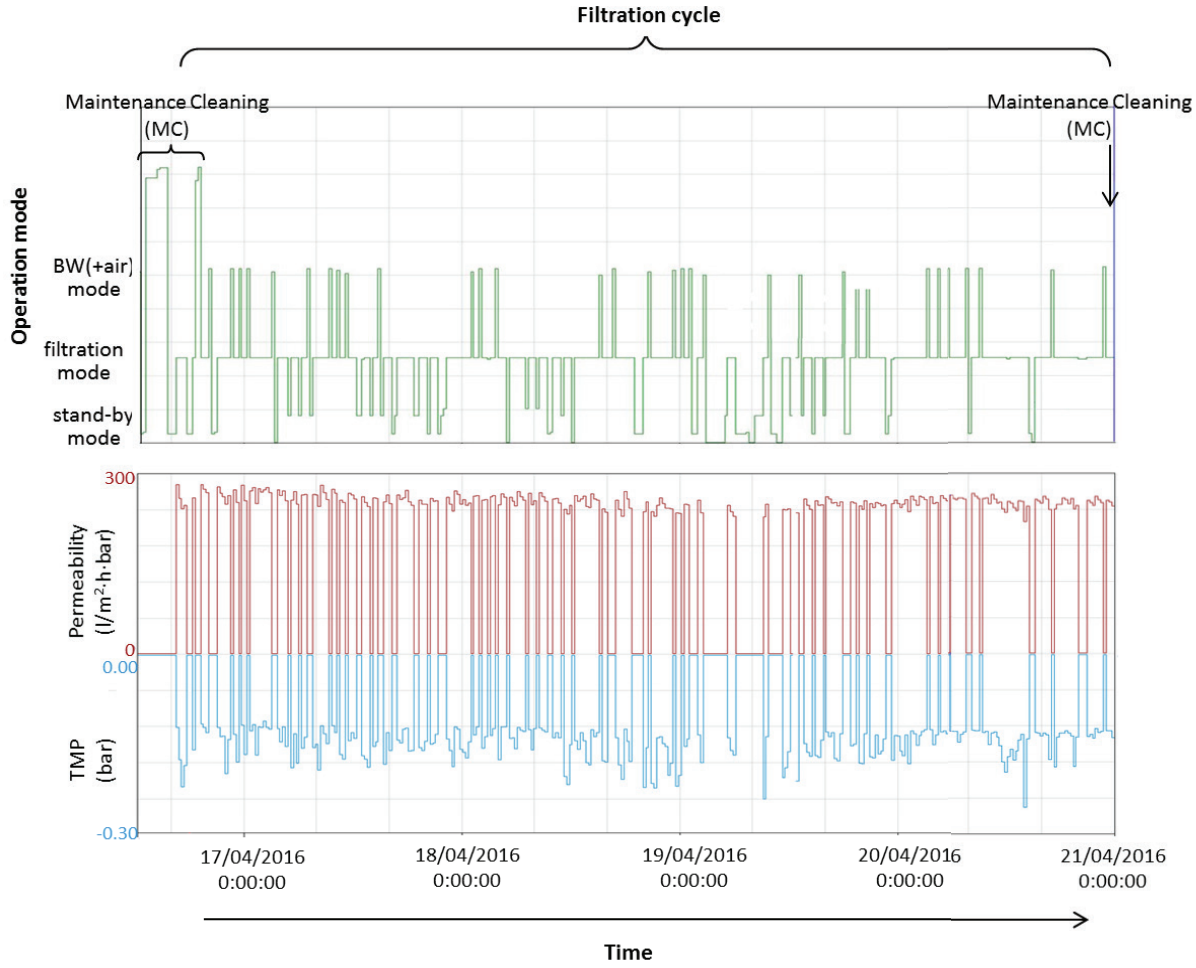

Fig. 2. Operational conditions of the monitored UF train over the whole filtration period between two consecutive maintenance cleanings (MCs).

Table 3
Removal percentage during filtration and detachment during BW(+air) over a filtration period between two consecutive MCs as analysed by HPSEC when the DWTP was fed with Llobregat river water

			DOC	BP	Protein in BP	HS	BB	LMWN	LMWA
Removal During filtration	c_i^{feed}	ppb	3,570 ± 141	280 ± 8	113 ± 30	1,590 ± 49	569 ± 15	773 ± 96	<10
	$c_i^{permeate}$	ppb	2,801 ± 875	116 ± 49	39 ± 27	1,318 ± 377	483 ± 116	661 ± 154	<10
	Removal (%)		22%	59%	65%	17%	15%	15%	n.q.
	$m_i^{retained\ a}$	kg	55	12	5	20	6	8	n.q.
Detachment During BW(+air)	$C_i^{pre-BW(+air)}$	ppb	3,419	248	98	1,536	552	751	<10
	$C_i^{post-BW(+air)}$	ppb	7,976 ± 699	3,566 ± 411	1,428 ± 232	1,914 ± 119	756 ± 41	1,157 ± 121	<10
	Enrichment (%)		133%	1,338%	1,357%	25%	37%	54%	n.q.
	$m_i^{BW(+air)b}$	kg	4.4	3.2	1.3	0.4	0.2	0.4	n.q.
	Percentage detached by BW(+air)		8%	27%	25%	2%	3%	5%	n.q.

Confidence intervals correspond to a confidence level of 90% for all cases where replicates were performed (N = 3 or 4); n.q.: not quantifiable.
[a]Taking into account that V_{period} was 72,000 m^3.
[b]Taking into account that $V_{train,BW}$ was 30.5 m^3 and that $N_{BW(+air)}$ was 32.

The total mass retained by the UF train over the whole filtration period for each constituent "i" (m_i^{retained}) was calculated according to Eq. (1). As it can be seen in Table 3, $m_{\text{DOC}}^{\text{retained}}$ was 55 kg. With regard to fractions, m_i^{retained} were 12 kg (BP; of which 5 kg corresponded to proteins), 20 kg (HS), 6 kg (BB) and 8 kg (LMWN). In terms of amount accumulated, thus, the main foulant potentially most affecting filterability was HS.

3.2.2. Mass detached by routine BW(+air)

The masses of "i" detached from the membrane by routine BW ($m_i^{\text{BW(+air)}}$) were calculated according to Eq. (2). These masses, which constitute the so-called hydraulically reversible fouling, are also reported in Table 3.

All BW(+air) applied during a filtration period (N = 32) resulted in the detachment of ca. 4.4 kg (which represented 8% of the total $m_{\text{DOC}}^{\text{retained}}$), indicating that most organic foulants were well adhered on/in the membrane. BP was clearly most detached the fraction (27%), whilst the detachment percentages of the other fractions were ≤5%. This finding indicated that HS, together with BB and LMWN, remained bound on the membrane, contributing to the hydraulically irreversible fouling.

The preferential washing out of the BP fraction has been observed in previous lab-scale studies and is likely due to the size of BP relative to that of the membrane pores. Organic substances much larger than the membrane pores lead to the formation of a cake weakly bound to the membrane that is more readily washed out [4,7,31], whilst lighter fractions such as HS, BB and LMWN can cause pore blocking or build-up a denser and tight cake layer more closely adhered to the membrane surface that is less readily detached from it by BW [5,15]. This trend has also been observed by previous studies, mostly at lab-scale systems, by comparison of foulant amounts detached from a membrane [7,11,21,28].

It is of note that proteins in this study were detached by 25%, revealing that proteins contributed to both reversible and irreversible fouling (though more to the latter). The finding suggests that proteins contribute to both reversible and irreversible fouling whilst HS only to the irreversible is consistent with previous studies [3,21,22] and partially in agreement with Chen et al. [32] and Peldszus et al. [18], who stated that HS does not contribute to the irreversible fouling either. As pointed out by Peldszus et al. [18], their finding with regard to HS "may be different for other e.g. tighter UF membranes than the one used in [their] study".

BP and proteins were detached at similar percentages (27% and 25%, respectively), suggesting that, under river feeding conditions, proteins and polysaccharides contributed at comparable levels to the hydraulically irreversible fouling. How proteins and polysaccharides affect the reversibility of membrane fouling is a matter of ongoing research. By using BSA and dextran as representatives of proteins and polysaccharides, respectively, Tian et al. [19] found that the former contributed more than the latter to the hydraulically irreversible fouling, but also that the irreversibility extent of BSA was affected by the presence of Na and Ca ions. The reason for the larger contribution of proteins to the irreversible fouling might be that protein molecules are more compact than long-chain polysaccharides and, hence, can enter more easily to the membrane pores and be more tightly bound to the membrane material [17]. This is in contrast with Hwang and Sz [23], who observed that BSA aggregated onto the membrane surface whilst dextran molecules adsorbed onto the wall of the membrane pores, contributing more to membrane internal fouling, which tended to be more hydraulically irreversible than that caused by cake formation. Undoubtedly, more research is needed to elucidate which BP components and under which conditions contribute more to reversible and irreversible fouling.

Fig. 3 shows the evolution of the inverse of the normalised permeate flux (i.e., the flux at any given time divided by the initial flux; $1/J_s^{'}$) with cumulative permeate specific volume during a filtration period under (a) river water feeding conditions and (b) groundwater feeding conditions. It can be seen in Fig. 3(a) that, as expected, the retention of DOC and its fractions discussed above resulted in an increase of $1/J_s^{'}$ (or, equivalently, of the fouled membrane resistance) and that the application of BWs partially restored the membrane permeability.

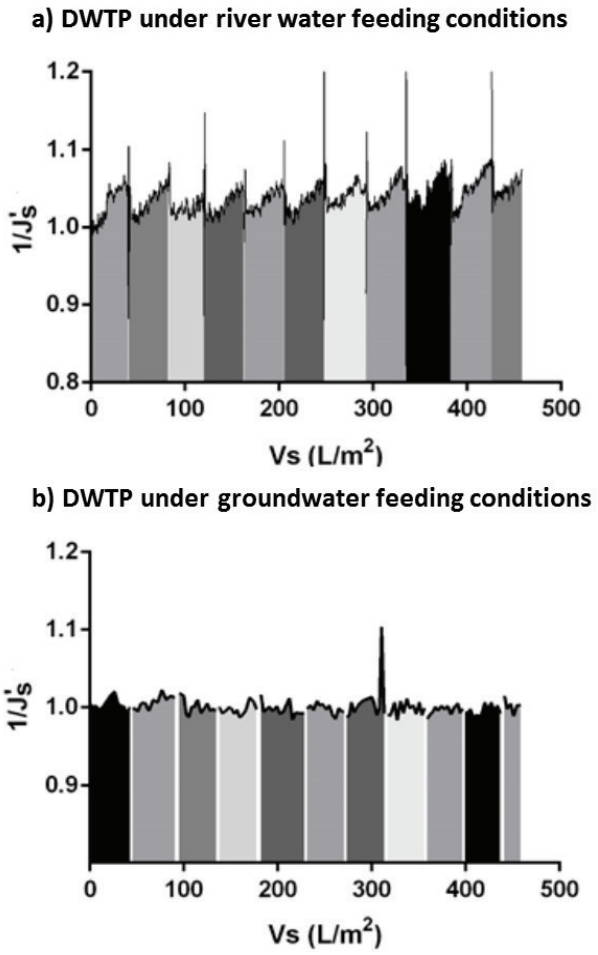

Fig. 3. Variation of the inverse of the normalised flux ($1/J_s^{'}$) with cumulative permeate specific volume during a filtration period between two consecutive maintenance cleanings (MCs) under (a) river water feeding conditions and (b) groundwater feeding conditions.

3.3. DOC treatability under groundwater feeding conditions

3.3.1. Mass retained over the filtration period

A second campaign was carried out to monitor not only a filtration period but also the subsequent MC episode. In this case, the monitoring included sampling and analysis of feed, permeate and BW(+air) solution but also of each of the cleaning solutions (before and after its application).

It is worth noting that, unlike the previous campaign, the DWTP was fed mainly with groundwater and, therefore, lower removals of DOC (in the order of 5%–10%) were anticipated from previous studies [28]. Feeding the DWTP with groundwater was due to a seasonal increase in turbidity and to a punctual peak in dioxanes in the Llobregat river.

The results are given in Table 4. The most noticeable difference in comparison with Table 3 was that the organic content in feed water and permeate were lower and also very similar to each other. Such small differences even gave negative removal percentages and, therefore, removal in terms of concentrations and m_i^{retained} were not quantifiable.

3.3.2. Mass detached by routine BW(+air)

Whilst the extent of DOC removed was not large enough to be measured reliably, it was likely that, though at very low rates, DOC would slowly accumulate on the membrane. Analysis of BW(+air) solution revealed an enrichment percentage of 3% in DOC, indicating that DOC accumulated on the membrane and that it was (at least partially) detached by routine BW(+air).

Table 4 shows the masses of "i" detached by routine BW(+air), which were approximately 28 g for DOC, 16 g for BP (of which proteins not quantifiable), 1 g for HS, 9 g for BB and 1 g for LMWN. Although these amounts were much lower as compared with those detached when the DWTP was fed with river water, the pattern was similar in that the fraction preferably extracted was BP, followed by HS, whilst the BW(+air) solution was barely enriched in BB and LMWN. In this campaign, the percentage removed could not be quantified because m_i^{retained} could not be determined.

The undetectable removal of DOC was in accordance with the irrelevant increase of $1/J_s^{'}$ (or of the fouled membrane resistance) during a filtration period (Fig. 3(b)). Under such conditions, BW(+air) could be applied at a lower frequency than the one currently used in the DWTP of Sant Joan Despí. By comparing Figs. 3(a) and (b), it is clear that, in agreement with the masses of DOC retained, the rate of membrane fouling under river water feeding conditions was much higher than under groundwater feeding conditions (a paper on the application of fouling indices to quantify the fouling phenomena under different water qualities is under preparation). Temperature of river and groundwater during the campaigns of this study were 18.8°C and 17.4°C, respectively. Given the similarity between these values, observed differences in $1/J_s^{'}$ were attributed to differences in composition of the raw waters rather than in temperature.

3.3.3. Mass detached by an MC

The campaign included also the monitoring of the entire sequence of the MC performed after the filtration period. For each stage of the MC, aliquots of cleaning (NaClO and H_3PO_4) and backwash (BW-A and BW-B) solutions were collected and analysed before and after their application. Table 5 reports the concentration of each constituent "i" in each stream, which allowed to calculate enrichment factors as indicators of the ability of the cleaning solution to extract foulants from the membrane. A quantification of the amount extracted (i.e., chemically reversible fouling) and remaining (i.e., chemically irreversible fouling) was not possible because m_i^{retained} was not quantifiable. Table 5 shows the analysis of each cleaning solution.

The application of NaClO did not yield clear-cut results. First, it appeared that the NaClO solution used for the MC already contained a high DOC concentration (>9,000 ppb) probably coming from previous MCs.

Table 4
Removal percentage during filtration and detachment during BW(+air) over a filtration period between two consecutive MCs as analysed by HPSEC when the DWTP was fed with groundwater

			DOC	BP	Protein in BP	HS	BB	LMWN	LMWA
Removal	c_i^{feed}	Ppb	864 ± 148	<10	<10	348 ± 6	166 ± 13	183 ± 16	<10
During filtration	c_i^{permeate}	Ppb	892 ± 4	<10	<10	364 ± 1	175 ± 2	220 ± 47	<10
	Removal (%)		n.q.	n.q.	n.q.	n.q.	n.q.	n.q.	n.q.
	m_i^{retained} [a]	Kg	n.q.	n.q.	n.q.	n.q.	n.q.	n.q.	n.q.
Detachment	$C_i^{\text{pre-BW(+air)}}$	Ppb	870	<10	<10	358	168	189	<10
During BW(+air)	$C_i^{\text{post-BW(+air)}}$	Ppb	896	16	<10	352	176	190	<10
	Enrichment (%)		3%	>60%	n.q.	–2%	5%	<1%	n.q.
	$m_i^{\text{BW(+air)}}$ [b]	G	28	16	n.q.	1	9	1	<1
	Percentage detached by BW(+air)		n.q.	n.q.	n.q.	n.q.	n.q.	n.q.	n.q.

Confidence intervals correspond to a confidence level of 90% for all cases where replicates were performed (N = 3); n.q.: not quantifiable.
[a]Taking into account that V_{period} was 60,000 m^3.
[b]Taking into account that $V_{\text{train,BW}}$ was 30.5 m^3 and that $N_{\text{BW(+air)}}$ was 35.

Table 5
Enrichment percentages of DOC and its fractions as analysed by HPSEC in each step of a maintenance cleaning (MC)

		DOC	BP	Protein in BP	HS	BB	LMWN	LMWA
Cleaning solution		Concentration (ppb)						
NaClO	Before	>9,000	179	68	640	4,893	>9,000	53
	After	>9,000	127	50	614	79	>9,000	10
	Enrichment (%)	n.q.	–29%	–26%	–4%	–22%	n.q.	–81%
BW-A	Before (UF permeate)	892	<10	<10	364	175	220	<10
	Post-BW-A1	1,304	43	15	468	229	332	13
	Post-BW-A2	1,199	12	n.q.	421	234	452	67
	Enrichment A1 (%)	48%	>330%	>50%	28%	33%	45%	>30%
	Enrichment A2 (%)	36%	>20%	n.q.	15%	36%	97%	>85%
H_3PO_4	Before	1,530	26	n.q.	411	590	418	<10
	After	1,255	19	n.q.	406	245	519	<10
	Enrichment (%)	–18%	–27%	n.q.	–1%	–58%	24%	n.q.
BW-B	Before (UF permeate)	892	<10	n.q.	364	175	220	<10
	Post-BW-B1	985	13	n.q.	367	193	293	<10
	Post-BW-B2	934	13	n.q.	393	191	264	<10
	Enrichment B1 (%)	11%	>30%	n.q.	1%	12%	28%	n.q.
	Enrichment B2 (%)	6%	>30%	n.q.	8%	11%	15%	n.q.

These high concentrations might hinder the detection of any DOC detached from the membrane because, in such a case, it would likely be overwhelmed in the HPSEC chromatograms by the very high concentration of initial DOC present in the NaClO solution. Second, the NaClO extracted samples did not show higher concentrations (with the exception of DOC and LMWN). This is explained by the fact that the strong oxidation ability of NaClO generates more oxygen containing functional groups such as ketone, aldehyde and carboxylic acids (categorised as LMWN), favouring a transformation of BP, HS, BB into LMWN and thus altering the proportion between organic fractions [10,33]. The high concentration in LMWN (>9,000 ppb) might corroborate this hypothesis. Difficulties in characterising DOC by HPSEC in samples treated with NaClO have been reported by previous researchers [10,21].

The application of BW-A showed that the BW solution was enriched in DOC and its fractions, demonstrating clearly the importance of the BW step on the whole MC. The rate of DOC extraction was higher for the first BW (BW-A1) (enrichment percentage in DOC of 48%) than for the second BW (BW-A2) (enrichment percentage in DOC of 36%).

The application of H_3PO_4 did not seem to detach any organic foulant from the membrane. More research is needed to identify the reason lying behind the negative detachments observed for DOC and some fractions. However, it is well known that acid cleaning is effective at dissolving precipitated salts but not organic foulants [10].

Finally, the application of BW-B led to a further detachment of DOC. Again, the most detached fraction was BP and enrichment factors were generally higher for BW-B1 becoming lower afterwards for BW-B2.

3.4. Mass treatability as analysed by FEEM

DOC was characterised by FEEM to provide additional information on the character of DOC and its fractions. In this case, feed and permeate samples were periodically collected beyond a simple filtration period. Samples were collected on a bimonthly basis over 1 year (i.e., six campaigns). The raw water treated in the DWTP during this year consisted of blends of river and groundwater, with the latter clearly predominating (>90%). Therefore, low DOC removals were obtained again.

The FEEM spectra for the six campaigns exhibited a rather similar pattern. FEEM spectra of UF feed water, UF permeate and BW(+air) solution for a representative campaign are depicted in Fig. 4, showing labelled areas for each region (from I to V) described in section 2. It can be seen that fluorescence of feed water was dominated by Regions II and III (aromatic- and humic-like substances, respectively). It must be stated that the values of the fluorescence intensity of each peak (F_{max}; in arbitrary fluorescence units) depend on the concentration of the fluorophore, the molar absorptivity and the quantum yield. Because the two latter are unknown, F_{max} signals cannot be converted to concentrations, and therefore, F_{max} give only estimates of the relative concentrations of each fluorophore. Using F_{max} values, removal percentages during filtration and enrichment percentages during BW(+air) could be calculated for each region (Table 6).

Removal percentages for all regions exhibited confidence intervals overlapping zero, making evident that no significant removal was observed for any of the fluorophores categorised by Chen et al. [25]. This undetectable removal of fluorescent DOC (likely due to the low concentration in DOC) was also consistent with the undetectable removal of DOC as analysed by HPSEC (Table 3). This finding concurred with other researchers who visually compared raw FEEMs of UF feed and permeate (by subtraction of the latter from the former) in a DWTP plant and found negligible differences between the two FEEM spectra [2,34].

It must be underlined that the treatability of total DOC (as analysed by HPSEC) does not necessarily parallel to that

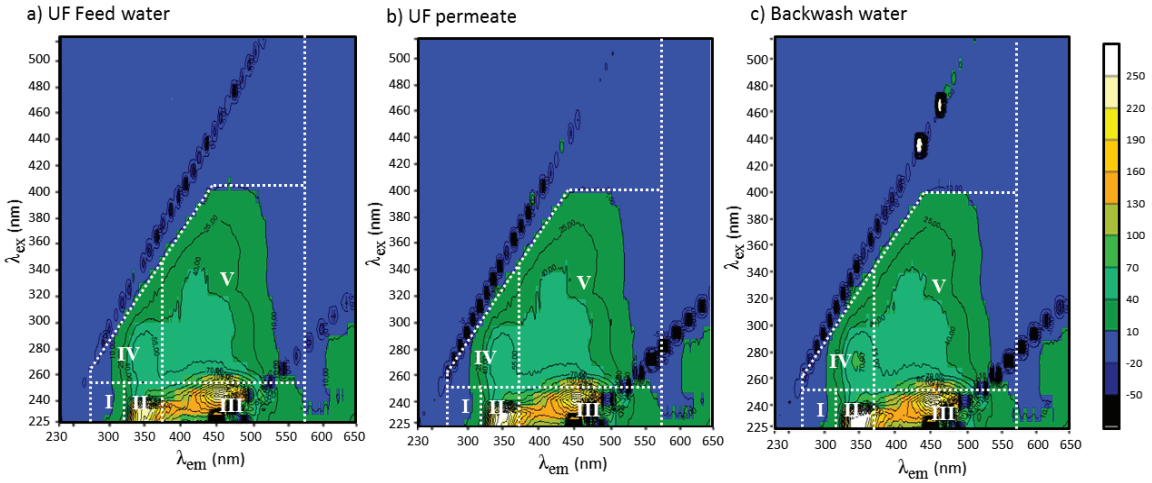

Fig. 4. FEEM contour plots for (a) UF feed water, (b) UF permeate and (c) backwash water.

Table 6
Removal percentage during filtration and enrichment percentage during BW(+air) for each constituent type as categorised by Chen et al. [25] and as categorised by the six components PARAFAC model

	Region	$\lambda_{ex}/\lambda_{em\ (nm)}$	Constituent	Removal (%) during filtration	Enrichment (%) during BW(+air)
As Categorised by Chen et al. [25]	Region II	225/345	Aromatic protein-like DOC-II	1.6% ± 1.8%	2%
	Region III	245/450	Fulvic acid-like DOC	1.7% ± 1.5%	–2%
	Region IV	275/343	Microbial by-product-like DOC	0.7% ± 0.8%	n.d.
	Region V	335/430	Humic acid-like DOC	0.9% ± 1.3%	n.d.
As categorised by PARAFAC	Component C1	275/343	Protein-like (tryptophan)	–0.2% ± 2.9%	–7%
	Component C2	255/391	Humic-like	0.7% ± 1.7%	–4%
	Component C3	345/430	Humic-like	2.0% ± 1.4%	–1%
	Component C4	255/463	Non-identified	–0.2% ± 2.9%	–2%
	Component C5	265/318	Protein-like (tyrosine)	0.2% ± 1.8%	3%
	Component C6	265/486	Humic-like	–0.5% ± 1.8%	2%

Confidence intervals correspond to a confidence level of 90% for all cases ($N = 6$).

of fluorescent DOC (as analysed by FEEM), as not all DOC gives fluorescent signal. Rather than quantifying concentrations, the FEEM technique rapidly provides insight into the character of the DOC, thus complementing the information obtained by HPSEC. In this study, whilst neither HPSEC nor FEEM techniques did not detect any DOC removal, the former could detect DOC detached by BW(+air) (mainly BP, with an enrichment factor in the BW(+air) solution >60%; Table 4) whilst the latter could not. The fact that this BP fraction did not contain proteins as analysed by HPSEC (Table 4) nor hardly aromatic protein-like (Region II) as analysed by FEEM (Table 6) suggested that BP detached by BW(+air) might be made of polysaccharides rather than proteins, indicating that polysaccharides were more associated to hydraulically reversible fouling whereas proteins to hydraulically irreversible fouling. This finding agreed with previous studies [3,7,17,18]. As stated above, this finding can be explained by the fact that, according to some of these studies, proteins are more compact and can better penetrate through the membrane pores causing more irreversible fouling [17]. This complementarity between HPSEC and FEEM with regard to BP and proteins must be regarded with caution, because characterisation based on MW and fluorescence do not lead to fractions that can be unequivocally allocated to each other. For example, it is acknowledged that protein-like substances mostly have indeed a MW >20,000 g/mol (as shown in Table 1) but can also have smaller MW in the range corresponding to LMWN [7,17].

Correlations between other HPSEC fractions (HS, BB and LMWN) and FEEM regions (III, IV and V) were not possible as they were not removed during filtration nor detached during BW(+air).

3.4.1. PARAFAC components

PARAFAC analysis was applied to FEEMs of 50 water samples to get further insight into the fluorescent substances. A six-component model best fitted the FEEMs obtained in this study (99% explained variation and 99% split-half validation) and matched FEEMs contained in the OpenFluor database (www.openfluor.org), and therefore, it was the one

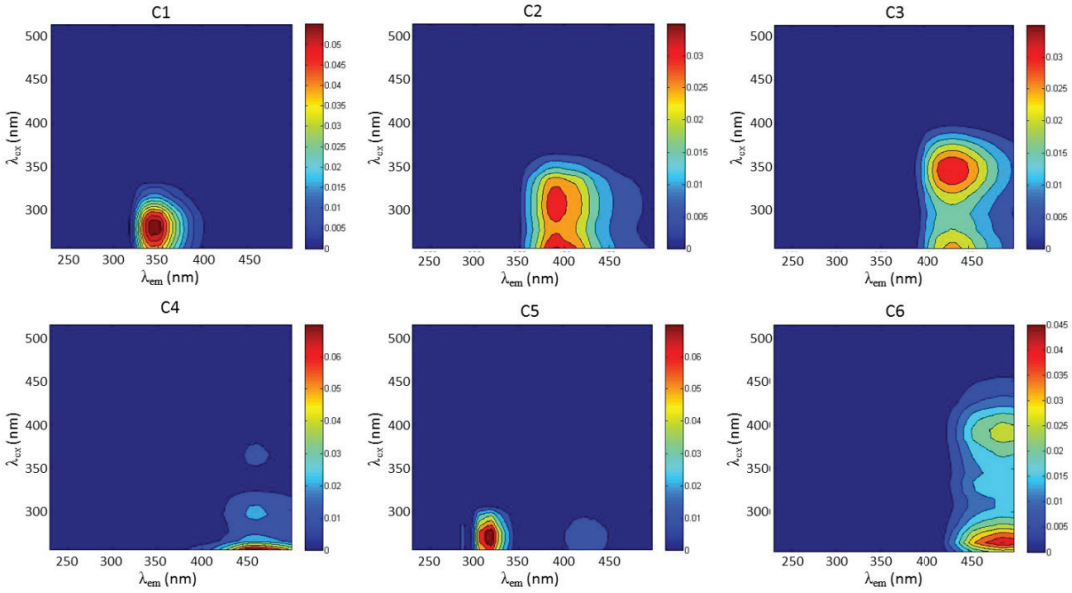

Fig. 5. Output from the PARAFAC modelling showing the contour plots of the six PARAFAC fluorescent components.

considered for further analysis. Fig. 5 shows the fluorescence contour plots of the six components.

Components C1, C2, C3 and C6 have been commonly reported in the literature (33 matchings with a minimum similarity score of 0.95 in the OpenFluor database) and they are associated to protein-like substances (similar to the amino acid tryptophan; C1) and humic-like substances (C2, C3 and C6) [25,35–37]. Component C5 can be attributed to fluorescent protein-like compounds, particularly simple aromatic proteins such as tyrosine [14,35,36]. Component C4 did not resemble any of the components reported in the OpenFluor database.

The removal and enrichment percentages during filtration and BW(+air), respectively, for each individual PARAFAC component is also given in Table 6. Their values were low or very low for all components, with a maximum variation of –7% for C1 for the enrichment percentage. Due to these low values with relatively high confidence intervals, correlation between components and other parameters analysed was not conducted. PARAFAC analysis, thus, did not seem to add new and relevant interpretability to the FEEM analysis.

4. Conclusions

The present study attempted to quantify through mass-balances the amount of DOC (and its fractions) accumulated onto an UF membrane at a full-scale DWTP, and detached from it when routine BW(+air) and MC are applied. The percentage removal of DOC by UF depended upon whether the DWTP was fed with river water (3.6 mg/L DOC) or groundwater (0.9 mg/L DOC).

Under river water feeding conditions the DOC removal was 22%, and the retention sequence of its fractions was BP >> HS ≈ BB ≈ LMWN (in terms of concentration) and HS > BP > LMWN ≈ BB (in terms of masses). BW(+air) resulted in the detachment of only 8% of the total mass of DOC retained. BP was clearly the most detached fraction (27%), indicating that hydraulically reversible fouling mainly consisted of BP. Therefore, results showed that increasing the frequency of BW(+air) would easily help to reduce fouling on the UF membrane. From an analytical point of view, HPSEC proved to be a successful technique in determining concentrations of DOC (and its fractions) that allow the application of mass balances over the UF train.

Under groundwater feeding conditions, no apparent removal of DOC was observed. This finding suggested that, with regard to organic fouling, BW(+air) can be applied at a lower frequency when the DWTP is fed with river water, thus helping save operation costs. During an MC, the application of H_3PO_4 did not seem to detach any organic foulant from the membrane and, therefore, unless inorganic foulants are present (e.g., as coagulant residuals), the H_3PO_4 step seems to be unnecessary.

FEEM analysis was applied under groundwater feeding conditions and results showed that neither significant removal of fluorescent components by the UF membrane during filtration nor detachment from the UF membrane during BW(+air) occurred. PARAFAC analysis did not seem to add new and relevant interpretability to the FEEM analysis. The fact that BP washed out by BW(+air) as analysed by HPSEC was not detected by FEEM suggested that polysaccharides might be associated to hydraulically reversible fouling, whilst proteins to hydraulically irreversible fouling. Therefore, future efforts should be oriented towards improving MC to detach more efficiently protein-like material from UF membranes.

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