CHARACTERISATION OF ORGANIC FOULANTS ON FULL-SCALE UF MEMBRANES DURING FILTRATION, BACKWASH AND CHEMICAL CLEANING EPISODES

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ABSTRACT

Understanding the formation of organic fouling on ultrafiltration (UF) membranes during water filtration (and its detachment during 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 a UF train at a full- scale drinking water treatment plant when it is fed with surface- and groundwater with different dissolved organic carbon (DOC) contents. DOC characterisation was performed by high-performance size-exclusion chromatography and fluorescence excitation-emission matrices (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 backwashes.

Keywords: DOC characterisation, drinking water, fouling reversibility, organic fouling, ultrafiltration.

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, fouling composition and fouling detachment when a physical cleaning such as a backwash (BW) or a chemical cleaning such as a cleaning-in-place (CIP) are applied.

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. Optimisation of BWs and CIPs would then entail first identifying the treatability of the major membrane foulants, i.e. identifying how they are accumulated on the membrane during filtration and how they are detached when BWs and CIPs are applied. Such identification, which would undoubtedly allow refined BW and CIPs strategies, is a matter of ongoing research.

Fouling formation on UF membrane has been widely researched, but mostly in terms of losses of membrane permeability during filtration [1-4]. 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. Studies quantifying the total mass of foulants accumulated on the membrane through a mass balance are scarce and, to our best knowledge, they are limited to lab-scale tests [5-7] while no published studies exist on a full-scale basis.

Fouling composition, and in particular that of organic fouling because organic substances are acknowledged to most contribute to UF membrane in DWTPs [1,2], 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 behavior and treatability. For this reason, innovative analytical techniques such as high-performance size-exclusion chromatography (HPSEC) and fluorescence excitation-emission matrix (FEEM) are increasingly being employed to characterize DOC. By applying these techniques, fouling composition has sometimes been inferred from differences in concentration of fractions between feed and permeate streams [8,9], but rarely quantified through mass-balance calculations [6,10]. The difference between such approaches can explain, for instance, why some published studies report that the main UF membrane foulants consist of humic substances (which constitute the main part of DOC in surface water but are removed at moderate percentages) [6,11,12] while some others of biopolymers (which account for a small part of DOC but are removed at high percentages) [1,13-15]. Other studies have obtained information on fouling composition by undertaking autopsies of fouled membranes by techniques such as FTIR, SEM and AFM [3], but this requires sacrificing a membrane which is rarely possible at full-scale DWTP.

Fouling detachment by BW, and particularly by CIP, has been less studied. Again, the cleanliness of the membrane after a BW and/or a CIP has almost always been deduced in terms of permeability recovery [1,4,12,16,17] but rarely in terms of detached mass of foulant. But, as it has been pointed out, permeability recovery alone is itself insufficient to characterize changes in membrane fouling after a BW and/or a CIP [18]. In best cases, the preference in detaching some foulants over others has been estimated by comparing foulant concentration in the cleaning solution prior and after application, which has served to infer the composition of hydraulically reversible and irreversible fouling [3,4,8,19]. Again, quantification of the mass extracted through a mass-balance

after a BW and/or a CIP is applied has rarely been reported and always for lab-scale studies [5,6,10].

Regardless the approach for monitoring fouling (i.e. from hydraulic or mass detachment perspectives), it must be underlined that the large body of research existing on UF fouling formation, composition and detachment has been mostly performed on a lab-scale with configurations and operation conditions that may differ from full-scale DWTPs. For instance, some lab-scale studies are based on short-term experiments run for one filtration cycle with no BWs nor CIPs [15,20], although it has been acknowledged that fouling reversibility may differ under short- and long-term operations [11]. Some studies do include BWs, but only applied for a limited number of filtration cycles (rarely more than ten, and usually not more than half a dozen) [1,2,8,10,19,21]. Moreover, BWs in lab-scale tests are not always air-assisted [2,8,9,13], while BW in DWTP commonly are. Furthermore, some studies apply cleaning protocols that differ too much from those applied 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) [3,10,16].

Another common limitation of some published lab-scale studies is that, with the purpose of ensuring constant and homogeneous feed water, they use synthetic solutions containing organic model compounds (e.g. bovine serum albumin, dextran and sodium alginate) often at very high concentrations (up to 100 mg/L) compared to those in real surface waters, providing results that are not always comparable to practical situations [8,17,22,23]. Furthermore, and focusing on studies in a drinking water context, some lab-scale UF configurations and operations are impractical in full-scale DWTPs (e.g. flat-sheet membranes or filtration under constant TMP) [1,5,7] and, when they are not (e.g. lab-systems based on submerged hollow fiber configuration), devices scale is too

small for a reliable translation of results to full DWTPs [2,3,14,21,24]. To sum up, while lab-scale studies provide very useful information on fouling, their results cannot automatically be extrapolated to full-scale DWTPs, making necessary further research on full-scale systems.

Within this framework, the objective of this study was to quantify the organic fouling on a UF membrane of a full-scale DWTP fed with two raw waters (surface water and groundwater) with different qualities. The specific objectives were (1) to quantify the mass of foulants accumulated on the UF membrane during filtration; (2) to quantify the mass of foulants detached when a BW is applied (i.e. to determine the hydraulically reversible and irreversible fouling); (3) to quantify the mass of foulants detached when a CIP is applied (i.e. to determine the chemically reversible and irreversible fouling); and (4) to assess such treatability of DOC by means of HPSEC and FEEM coupled to PARAFAC.

2. MATERIALS AND METHODS

2.1. Plant description

The DWTP of 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 total organic carbon (TOC) (2-14 mg/L), high turbidity (5 up to >1000 FNU) and high conductivity (1160-1939 µS/cm), while groundwater exhibits lower TOC concentrations (1.1-1.5 mg/L) and turbidity (0.2-0.5 FNU), but slightly higher conductivities (1970-

2012 μS/cm). It is when river water 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 Figure 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 (GAC) filtration, while the other undergoes in-line coagulation with $FeCl_3$, ultrafiltration (UF), UV irradiation, reverse osmosis (RO) filtration and remineralisation. Both treated streams are blended and the resulting stream is post-chlorinated prior to distribution.

2.2. UF description stage

Ultrafiltration is performed through 0.02 μm-pore size submerged PVDF hollow fiber 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 4104 modules (with a total membrane surface area of 228575 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 approx. 45 min and 4 min, respectively. After approx. 65000-70000 m^3 of permeate production (which corresponds to every 5–6 d) a 4-step maintenance cleaning (MC) with a duration of 3-4 hr is applied. Additionally, only when required (a few times per year), a recovery cleaning is undertaken similar to a 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 a 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 approx. 42 m^3. Water permeates through the UF membrane in an out-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 the TMP reaches a predetermined limit or on a pre-set timeframe (usually about 45 min). Such BWs proceeds as follows: first, approx. 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 in-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 pre-set 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 thereafter to as BW(+air).

2.3.3. Maintenance cleaning

A maintenance cleaning (MC) involves the following steps:

1) 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.
2) the train is emptied and membranes are backwashed with UF permeate in an in-out mode for ca. 80 s. This step is repeated twice. Unlike routine BW(+air) applied during the filtration period, these ones are carried out with no air

bubbling. To distinguish these two types of BWs applied in the MC, they will be referred to as BW-A1 and BW-A2.

3) the train is put in a filtration mode for 2 hr, and then it is completely emptied again and refilled with 42 m^3 of a solution of H_3PO_4 solution (1000 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.

4) finally, the train is emptied and two consecutive backwashes like 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 a UF train over a filtration period between two consecutive 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 72000 m^3 and lasted 5 days before the following MC was applied. During this period, samples of feed and permeate streams 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, averaged 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 ($m_i^{retained}$) could be calculated through a simple mass balance:

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

Additionally, DOC was characterised by FEEM to provide additional information on the characteristics 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. 6 campaigns).

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

Backwash extracted 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 $C_i^{post-BW(+air)}$. A total of four backwash extracted solutions were sampled at four distinct BW(+air) episodes over the filtration period. Again, analyses showed little variability in the composition and then averaged concentrations were used. The mass of constituent "i" detached by all BW(+air) applied over the whole filtration period ($m_i^{BW(+air)}$) was calculated from the mass of "i" detached by a single BW(+air) episode multiplied by the total number of routine BW(+air) ($N_{BW(+air)}$) performed during the whole filtration period as shown in the following equation:

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

where $C_i^{pre-BW(+air)}$ is the concentration of "i" in the tank just prior 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 $V_{train,BW}$ of 30.5 m^3). Then, $C_i^{pre-BW(+air)}$ can be calculated as:

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

2.4.3. Mass detached by a Maintenance Cleaning (MC)

A second campaign was conducted in train #4 with the purpose of validating the findings above but also quantifiying the masses of "i" detached by each step of a MC. In this case, the filtration period treated a total volume of water of 60000 m^3 and lasted 7 days before the following MC was applied. During filtration, feed and permeate streams were sampled at two different days. Similarly 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^{ClO-}, m_i^{BWA1}, m_i^{H3PO4} 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 ambered glass bottles and stored at 4ºC until analyses, which were performed within one week for HPSEC and within 24 hr 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 on-line ultraviolet (UV_{254}), organic carbon (OC) and organic nitrogen (ON) 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 [25]. 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 fluorescence excitation-emission matrix (FEEM) spectra were performed by Aigües de Barcelona's laboratory on a LS55 Perkin Elmer 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 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.

The FEEMs were divided into five regions (Region I to Region V) according to Chen et al. [26]. 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 PARallel FACtor (PARAFAC) analysis, which is able to decompose trilinear multi-way 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 [27]. The number of fluorescence components was identified by a validation method including variance explained, core consistency diagnostic, and half split analysis. Component spectra were also compared against the on-line repository of published fluorescence spectra OpenFluor (www.openfluor.org) to evaluate spectral matching and component identification [28].

3. RESULTS AND DISCUSSION

3.1. Filtration cycle of a 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 72000 m^3 and lasted 5 days 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 [29].

Figure 2 shows the operation conditions during the filtration period. The graph above shows the operation status of the UF train over the whole period (filtration, BW(+air), MC or stand-by), while the graph below 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-day 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 (3570 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 1000 ppb or less). With regard to DOC composition, HS clearly predominated (with averaged percentages of 45% of total DOC), followed by LMWN (22%), BB (16%) and BP (8%), while LMWA was detected at <1%.

As shown in Table 3, the averaged 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 [2,13,16]. 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 [6].

Proteins within BP, as analysed by HPSEC, were removed at a similar percentage (65%) as for BP itself (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 has been reported in previous studies [1,3], which is however in disagreement with others [2,13,16]. The disagreement with the latter might come, at least partially, from differences in methods employed in determining proteins (FEEM against Lowry method) and polysaccharides (HPSEC against phenol-sulfuric acid method), since it is acknowledged that Lowry and phenol-sulfuric acid methods can present critical limitations in the analysis of proteins and polysaccharides [8,13].

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, $m_{DOC}^{retained}$ was 55 kg. With regard to fractions, $m_i^{retained}$ were 12 kg (BP) (of which 5 kg corresponded to protein), 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 aerated backwashes BW(+air)

The masses of "i" detached from the membrane by a BW ($m_i^{BW(+air)}$) 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 $m_{DOC}^{retained}$), indicating that most organic foulants were well adhered on/in the membrane. BP was clearly the fraction most detached (27%), while 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 and thus more readily washed out [4,16,30], while 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 and thus less readily detached from it by BW [10,17]. This trend has also been observed by previous studies, mostly at lab-scale systems, by comparison of masses of foulants detached from the membrane, comparison of concentrations of foulants in the BW extracted solution, or visual comparison of FEEM spectra of the BW extracted solution [6,16,21,29].

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 that proteins contribute to both reversible and irreversible fouling

while HS only to the irreversible is consistent with previous studies [3,19,21] and partially in agreement with Chen et al. [24] and Peldszus et al. [14], who stated that HS does not contribute to the irreversible fouling either. As pointed out by Peldszus et al. [14], their finding with regards 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 seemed to contribute with 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 bovine serum albumin (BSA) and dextran as representatives of proteins and polysaccharides, respectively, Tian et al. [22] found that the former contributed more than the latter to the hydraulically irreversible fouling, but also that the irreversibility extent of BSA can be affected by the presence of Na and Ca ions. The reason of 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 the membrane pores and be more tightly bound to the membrane material [13]. This is in contrast with Hwang et al. [23], who observed that BSA aggregated onto the membrane surface while dextran molecules adsorbed onto the wall of the membrane pores, contributing more to membrane internal fouling, which tends 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.

Figure 3 shows the variation of the inverse of the normalised flux (1/J) during a filtration period between two consecutive Maintenance Cleanings (MCs) under a) river water feeding conditions and b) groundwater feeding conditions. It can be seen in

Figure 3a that, as expected, the retention of DOC and its fractions discussed above resulted in an increase of 1/J (or, equivalently, of the fouled membrane resistance) and that the application of BWs partially restored the membrane permeability.

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) extracted solution but also of each of the cleaning solution (prior and after its application).

It is worth noting that, unlike the previous campaign, the DWTP was fed now mainly with groundwater and therefore lower removals of DOC (in the order of 5-10%) were anticipated from previous studies [29]. Feeding the DWTP with groundwater was due to a seasonal increase in turbidity and to a punctual peak in dioxanes in the Llobregat river, which made its water not suitable as feed water for the DWTP.

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

3.3.2. Mass detached by routine aerated backwashes 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) extracted solution revealed an enrichment percentage of 3% in DOC, indicating that DOC did accumulate on the membrane and that it was (at least partially) detached by the routine BW(+air).

Table 4 shows the masses of "i" detached by the routine BW(+air), which were approximately 28 g for DOC, 16 g for BP (of which protein not quantifiable), 1 g for HS, 9 g for BB and 1 g for LMWN. Although these amounts were much lower as compared to 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, while the BW(+air) extracted 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 the fouled membrane resistance during a filtration period (Figure 3b) Under such conditions, then, BW(+air) can likely be applied at a lower frequency than the one currently used. By comparing Figure 3a 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).

3.3.3. Mass detached by a 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 each cleaning solution (NaClO, H_3PO_4) and backwash extracted solutions (BW-A and BW-B) were collected and analysed prior 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 availability 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 $m_i^{retained}$ had not been 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 (>9000 ppb) probably coming from previous MCs. These high concentration 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 altering, thus, the proportion between organic fractions [7,31]. The high concentration in LMWN (>9000 ppb) might corroborate this hypothesis. Difficulties in characterising DOC by HPSEC in samples subjected to NaClO have been

reported by previous researchers [7,21. It has been demonstrated from a permeability recovery approach that NaClO is effective at detaching organic foulants from membranes [7].

The application of BW-A showed that the BW extracted 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 detaching scales and metal oxides but not organic foulants [7].

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

Moreover, DOC was characterised by FEEM to provide additional information on the characteristics 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. 6 campaigns). The raw water treated in the DWTP during this monitored 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 6 campaigns exhibited a rather similar pattern. FEEM spectra of UF feed water, UF permeate and BW(+air) extracted solution for a representative campaign are depicted in Figure 4 showing labelled areas for each region (from I to VI) described in the Methods section. It can be seen that the fluorescence of the UF 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. [26]. This undetectable removal of fluorescent DOC (likely due to the low concentration in DOC) was consistent with the also 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 in a DWTP plant and found negligible differences between the two FEEMs [2,32].

While 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) extracted solution >60% (Table 4)) while 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 [3,13,14,16]. 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 [13]. 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 >20000 g/mol (as shown in Table 1) but can also have smaller MW in the range corresponding to LMWN [13,16].

Correlations between other HPSEC fractions (HS, BB, LMWN) and FEEM regions (III, IV, V) were not possible as they were not found to be 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 6-components model best fitted the FEEMs obtained in this study (99% explained variation, 99% split-half validation) and matched FEEMs contained in the Openfluor database (www.openfluor.org), and therefore it was the one considered for further analysis. Figure 5 shows the fluorescence contour plots of the six components.

Components C1, C2, C3 and C6 have been commonly reported in the literature of DOC fluorescence (33 matchings with a minimum similarity score of 0.95 in the

database Openfluor) and they are associated to protein-like substances (similar to the amino acid tryptophan) (C1) and humic-like substances (C2, C3 and C6) [26,33-35]. Component C5 can be attributed to fluorescent protein-like compounds, particularly simple aromatic proteins such as tyrosine [9,33,34]. Component C4 did not resemble any of the components reported in the database Openfluor.

The removal and enrichment percentages during filtration and BW(+air), respectively, for each individual PARAFAC component is given also 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 this low F_{max} 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 amounts of organic foulants accumulated onto an UF membrane at a full-scale DWTP, and detached from it when routine BW(+air) and CIPs are applied.

The percentage removal of DOC by UF depended upon whether the DWTP was fed with river water or groundwater. With river water (3.6 mg/L DOC) the DOC removal was 22%, while it was undetectable with groundwater (0.9 mg/L DOC).

Under river water feeding conditions, the retention sequence of DOC 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. 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 improvement in the quality of the produced water in terms of DOC was observed. This finding suggested that, with regard to organic fouling and under groundwater feeding conditions, BW(+air) can be applied at a lower frequency than when the DWTP is fed with river water. During a MC, detachments of DOC and its fractions by the application of NaClO could not be quantified due to the alterations on DOC fractions caused by NaClO itself. On the other hand, H_3PO_4 did not seem to detach any organic foulant from the membrane. Therefore, unless inorganic foulants are present (e.g. as coagulant residuals), the H_3PO_4 step seems to be unnecessary.

FEEM analyses, either by examining raw FEEM spectra or by applying PARAFAC, showed neither significant removal of fluorescent components by the UF membrane during filtration nor detachment from the UF membrane during BW(+air). The treatability of total DOC (as analysed by HPSEC) did not necessarily parallel that 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, complementing thus the information obtained by HPSEC. For instance, under groundwater feeding conditions, the fact that BP washed out by BW(+air) was not detected by FEEM indicated that polysaccharides might be associated to hydraulically reversible fouling, while proteins to hydraulically irreversible fouling.

Research ongoing into lab-scale undoubtedly contributes to a better understanding on fouling formation, composition and reversibility, but it is only through accumulated experience at full-scale DWTP that cleaning procedures can be tailored to site-specific conditions of a given DWTP for optimisation.

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FIGURES AND TABLES

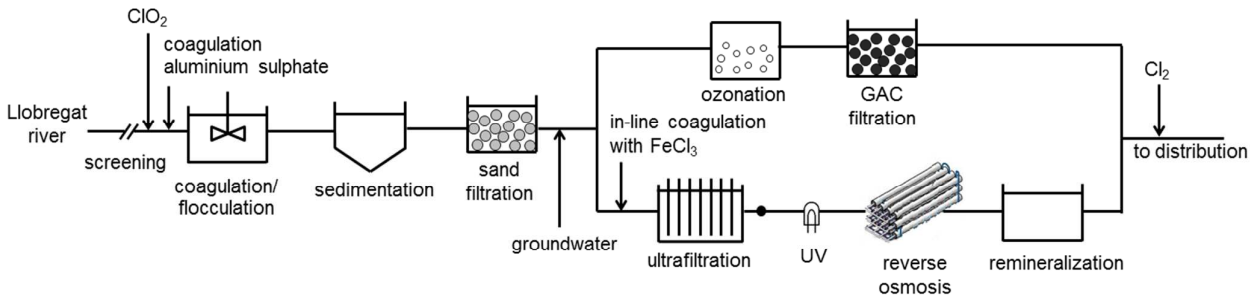

Figure 1: Schematic representation of the DWTP of Sand Joan Despí

Table 1: Chromatographic fractions of DOC as determined by the HPSEC technique.

DOC fraction	Abbreviation	MW (g/mol)	Constituents within fraction
Biopolymers	BP	>20000	Polysaccharides, proteins
Humic substances	HS	≈1000	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

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

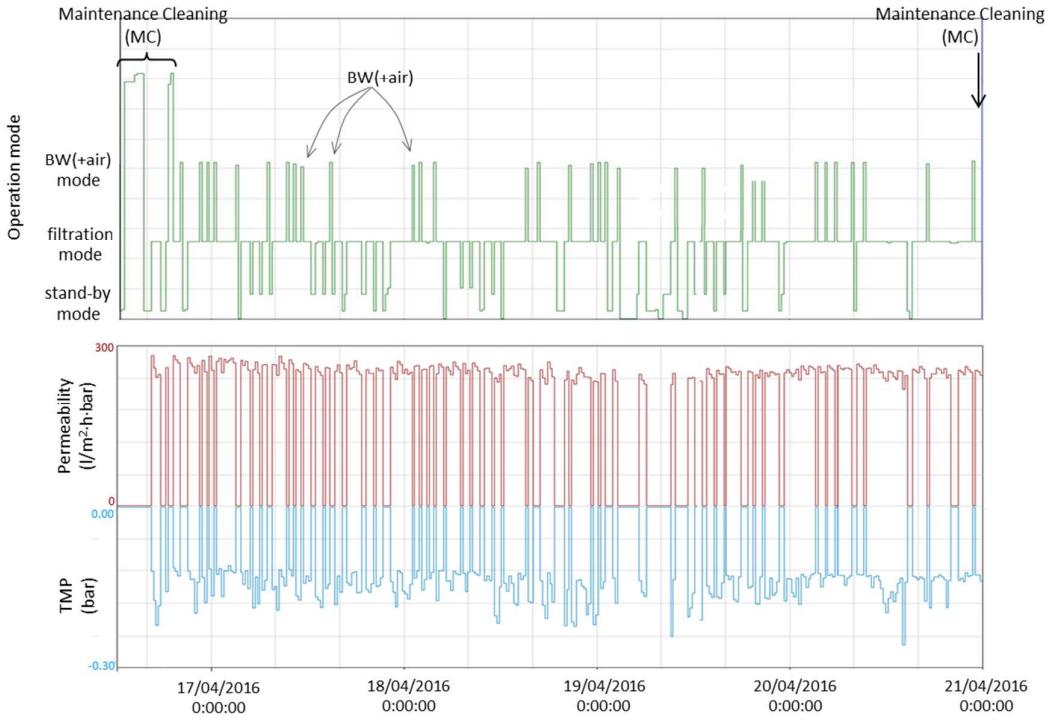

Figure 2: Operation conditions of the monitored UF train over the whole filtration period between two consecutive Maintenance Cleanings (MCs).

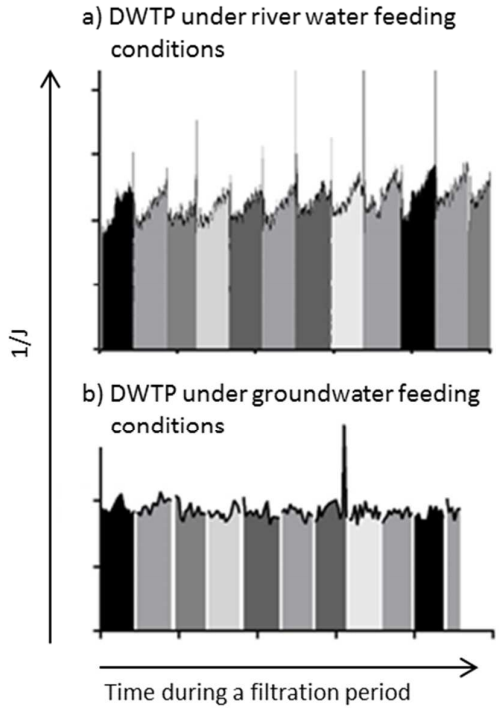

Figure 3: variation of the inverse of the normalised flux (1/J) during a filtration period between two consecutive Maintenance Cleanings (MCs) under a) river water feeding conditions and b) groundwater feeding conditions.

Table 3: Removal percentage during filtration and detachment during BW(+air) over a filtration period between two consecutive MC as analysed by HPSEC when the DWTP was fed with Llobregat river water. Confidence intervals correspond to a confidence level of 90% for all cases where replicates were performed (N=3 or 4).

			DOC	BP	Protein in BP	HS	BB	LMWN	LMWA
Removal during filtration	C_i^{feed}	ppb	3570±141	280±8	113±30	1590±49	569±15	773±96	<10
	$C_i^{permeate}$	ppb	2801±875	116±49	39±27	1318±377	483±116	661±154	<10
	Removal (%)		22%	59%	65%	17%	15%	15%	n.q.
	$m_i^{retained}$ (1)	kg	55	12	5	20	6	8	n.q.
Detachment during BW(+air)	$C_i^{pre-BW(+air)}$	ppb	3419	248	98	1536	552	751	<10
	$C_i^{post-BW(+air)}$	ppb	7976±699	3566±411	1428±232	1914±119	756±41	1157±121	<10
	Enrichment (%)		133%	1338%	1357%	25%	37%	54%	n.q.
	$m_i^{BW(+air)}$ (2)	kg	4.4	3.2	1.3	0.4	0.2	0.4	n.q.
	% detached by BW(+air)		8%	27%	25%	2%	3%	5%	n.q.

(1) taking into account that V_{period} was 72000 m^3

(2) taking into account that $V_{train,BW}$ was 30.5 m^3 and that $N_{BW(+air)}$ was 32

n.q.: not quantifiable

Table 4: Removal percentage during filtration and detachment during BW(+air) over a filtration period between two consecutive MC as analysed by HPSEC when the DWTP was fed with groundwater. Confidence intervals correspond to a confidence level of 90% for all cases where replicates were performed (N=3).

			DOC	BP	Protein in BP	HS	BB	LMWN	LMWA
Removal during filtration	C_i^{feed}	ppb	864±148	<10	<10	348±6	166±13	183±16	<10
	$C_i^{permeate}$	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.
	$m_i^{retained}$ (1)	kg	n.q.	n.q.	n.q.	n.q.	n.q.	n.q.	n.q.
Detachment during BW(+air)	$C_i^{pre-BW(+air)}$	ppb	870	<10	<10	358	168	189	<10
	$C_i^{post-BW(+air)}$	ppb	896	16	<10	352	176	190	<10
	Enrichment (%)		3%	>60%	n.q.	-2%	5%	<1%	n.q.
	$m_i^{BW(+air)}$ (2)	g	28	16	n.q.	1	9	1	<1
	% detached by BW(+air)		n.q.	n.q.	n.q.	n.q.	n.q.	n.q.	n.q.

(1) taking into account that V_{period} was 60000 m^3

(2) taking into account that $V_{train,BW}$ was 30.5 m^3 and that $N_{BW(+air)}$ was 35

n.q.: not quantifiable

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					Conc (ppb)			
NaClO	Before	>9000	179	68	640	4893	>9000	53
	After	>9000	127	50	614	79	>9000	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	1304	43	15	468	229	332	13
	Post-BW-A2	1199	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	1530	26	n.q.	411	590	418	<10
	After	1255	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.

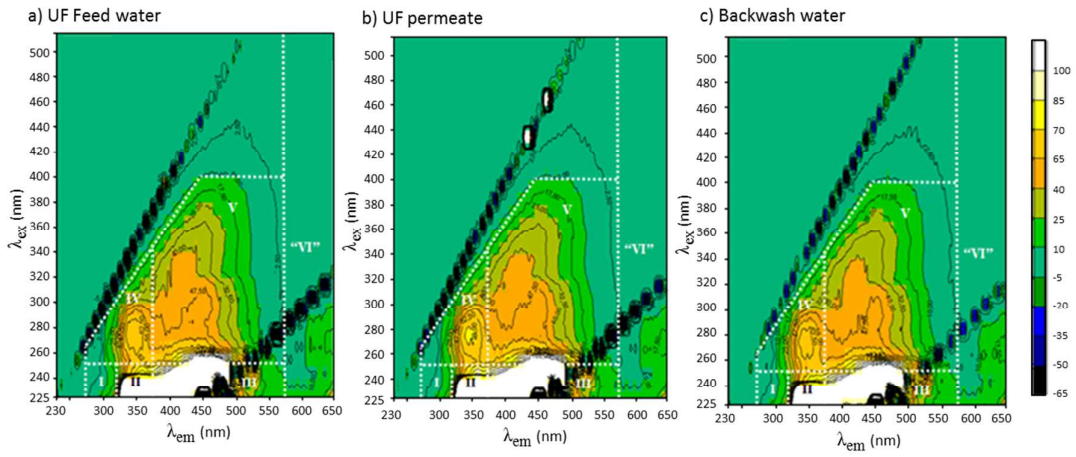

Figure 4: FEEM contour plots for a) UF feed water, b) UF permeate and c) backwash water.

Table 6: Removal percentage during filtration and enrichment percentage during BW(+air) for each constituent type as categorised by Chen et al. [26] and as categorised by the 6-components PARAFAC model. Confidence intervals correspond to a confidence level of 90% for all cases (N=6).

	Region	$\lambda_{ex}/\lambda_{em}$ (nm)	Constituent	Removal (%) during filtration	Enrichment (%) during BW(+air)
As categorised by Chen et al. (2013)	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%

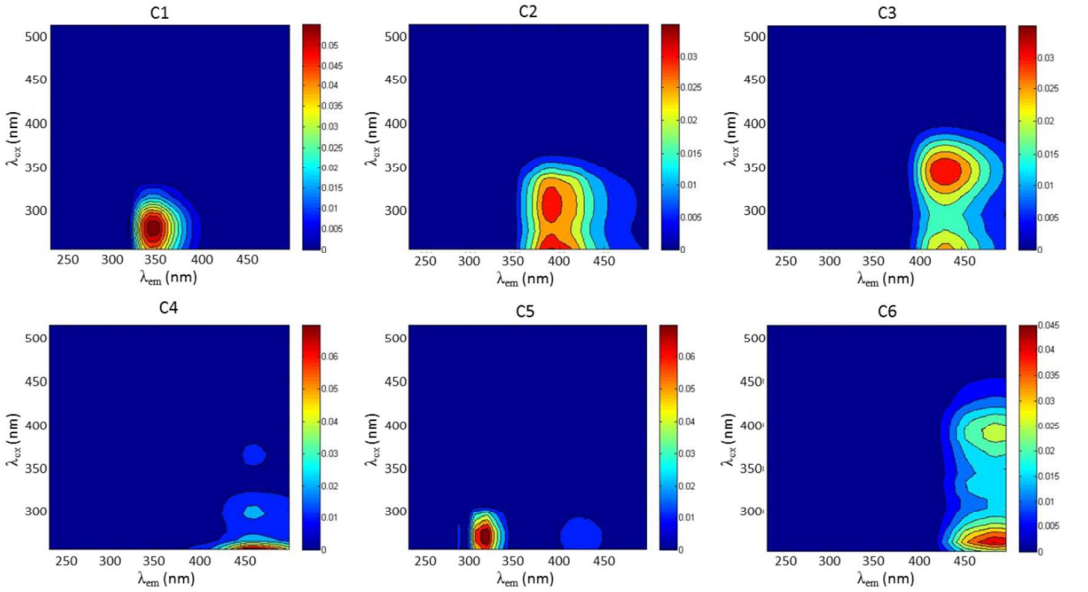

Figure 5: Output from the PARAFAC modeling showing the contour plots of the six PARAFAC fluorescent components.