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Organic foulants in estuarine and bay sources for seawater reverse osmosis – Comparing pre-treatment processes with respect to foulant reductions

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ABSTRACT

Membrane fouling in sea water RO systems is a major operational problem. Not much is known about the role of natural organic matter in fouling of RO membranes.

This study tries to characterize NOM for estuarine water and seawater sources, to present NOM analytical signatures of seawater from four different facilities at various locations, and to evaluate the effectiveness of pre-reatment in NOM removal. Focusing on organic (NOM) fouling, the analytical tools that have used in this research include: (i) liquid chromatography with on-line dissolved organic carbon detection (LC-OCD) and (ii) fluorescence excitation-emission matrix (F-EEM).

Results showed in the case of seawater that humic substances represent ~50%, biopolymers ~10%, and building blocks and neutrals the remaining 40% of the DOC. In case of estuarine water, humic substances are ~65%, biopolymers ~10%, and building blocks and neutrals the remaining 25%. The evaluation of pre-treatment efficiencies revealed for the site A (seawater) that, DMF combined with inline coagulation is more effective than MF without coagulant addition in DOC removal (35% and 26% respectively); been the biopolymers removed by 47% and 36% respectively. For the site B (seawater), the beach wells removed 21% DOC, with the biopolymer fraction removed by ~70%. This is significant reduction in organic matter with size larger than 20 kDa. For site C (estuarine water), coagulation + continous sand filtration removed 12% DOC and 17% biopolymers. The UF units removed nearly 70% of the biopolymers that were fed to the membranes. For site D (seawater), coagulation + single stage media filtration removed 12% DOC and 32% biopolymers. The deposition rates and deposition factors revealed that some organic matter is deposited on the RO membranes and large part of biopolymers are deposited on the membranes for site C and all organic matter fractions for site D.

Keywords: Natural organic matter; Seawater; Estuarine water; Pretreatment; Reverse osmosis; Deposition

1. Introduction

Due to increasing demands an increasing number of countries suffer or will suffer soon from water scarcity. These countries are looking for alternative water sources to satisfy these demands. An attractive alternative for drinking, industrial and agricultural water purposes is the use of estuarine and seawater after treatment by distillation or reverse osmosis. Reverse osmosis is increasingly applied due to lower investment and energy cost. Currently the global production of desalinated water is about 50 Mm^3/d and it is projected to double in the coming 7 years [1].

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Fouling of membranes in brackish and sea water reverse osmosis a operational problem. Several types of fouling are observed in practice. This study focuses on organic fouling due to natural organic matter (NOM).

Natural organic matter is a heterogeneous mixture of structurally complex compounds. These compounds are derived from chemical and biological degradation of animals and plants, and is a complex mixture of organic material such as humic substances, hydrophobic acids, carbohydrates, amino acids, carboxylic acids, proteins, hydrocarbons, present in natural fresh water [2].

NOM in seawater has mainly been studied by oceanographers, whose main interest is the role of DOC in ocean ecosystems. However, to understand membrane fouling in reverse osmosis (RO) a better characterization of the organic carbon found in estuarine and seawater is required.

Traditionally, the NOM fouling potential of RO feed water has been assessed in terms of DOC, UV absorbance, and colour; however, NOM fouling rates appear not to correlate with these traditional water quality parameters. A problem is that DOC only indicates the amount but not the character of the NOM. More recently, specific UV absorbance (SUVA) has been used to indicate the aromatic character of NOM but SUVA is a direct measure of humic substances which, in relation to non-humic materials, which are less problematic as foulants.

The objectives of this paper are:

1. To characterize NOM and to present NOM "signatures" in seawater and estuarine water RO systems. These signatures are derived from liquid chromatography and fluorescence excitation emission matrix analyses.
2. To evaluate the effectiveness of NOM removal by pretreatment processes used for RO systems.
3. To link LC-OCD and F-EEM results.

2. Material and methods

Focusing on organic (NOM) fouling, the analytical tools that are used in this research include: (i) liquid chromatography with on-line dissolved organic carbon detection (LC-OCD) and (ii) fluorescence excitation-emission matrix (F-EEM). While there is much experience in applying these techniques to freshwater sources with moderate amounts of DOC, this work evaluates their applicability to seawater with lower amounts of DOC (~0.5 mg/L) and much higher levels of salinity.

2.1. Source waters and NOM samples

Consensus reference materials (CRM) are available to the international community of dissolved organic carbon (DOC) analysts. The CRM's are used to reference results against the international community of DOC analysts. Deep seawater reference (DSR, Sargasso Sea at 2600 m and Florida Strait at 700 m) are provided by RSMAS/MAC from University of Miami. In this research, Batch 6 FS–2006 (Florida Strait at 700 m, 44–46 µM DOC and 32.8 µM TN) and Sargasso seawater 0504 (2600 m depth, DOC = 0.54–0.56 ppm, TN = 0.297 µM) were used for "signature" identification of seawater.

Sampling campaigns for the study were performed along the coast of the Mediteranean Sea and the North Sea over the period of July 2007 – July 2008. The total of samples was 77.

2.2. LC-OCD

LC-OCD (also called size exclusion chromatography, SEC-DOC) can be used to effectively monitor polar NOM components with a lower SUVA. LC-OCD has been successfully applied to monitoring changes in NOM associated with water treatment [3]. It has also been used to identify problematic NOM components in membrane fouling [4, 5]. LC-OCD separates NOM according size/molecular weight (MW) classes ranging from higher to lower MW: biopolymers (BP), humic substances (HS), and low MW acids (LMA). The magnitude of the BP peak has been linked with fouling potential in UF membranes [6].

A typical chromatogram of NOM contained in surface water is shown in Fig. 1. The first fraction identified after approximately 25–45 min (first peak – largest molecular size) is the biopolymer peak with significant response by organic carbon detection (OCD) only. The organic colloids and proteins present in this fraction provide response in OCD and UV detection. The second and third fraction responses in OCD and UVD are attributed to humic substances and building blocks, respectively. Building blocks are a weathering product of humic substances.

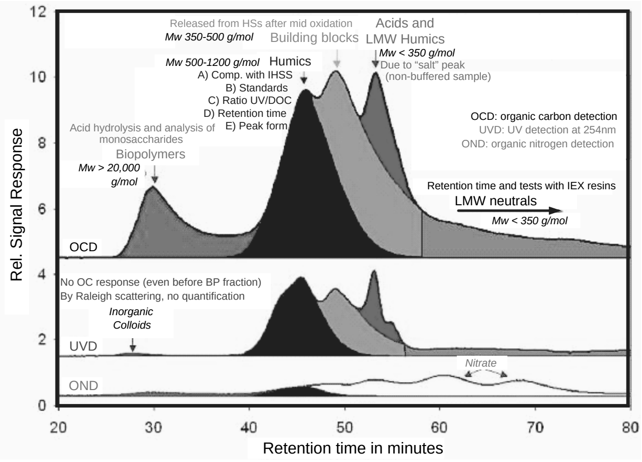

Fig. 1. Typical NOM chromatogram of a fresh water sample [Adapted from [7]].

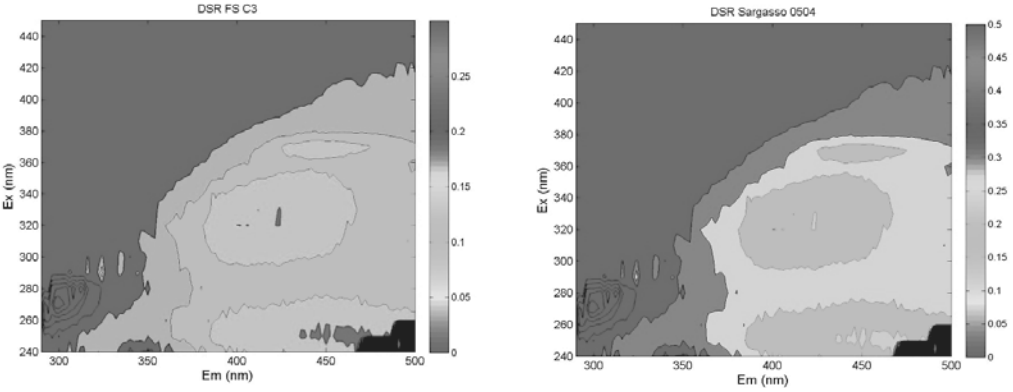

Fig. 2. F-EEMs DSR Florida strait and DSR Sargasso seawater – LC-OCD DSR Florida strait C3.

The fourth response to OCD and UV detection is attributed to low MW organics (acids and neutrals).

2.3. Fluorescence excitation emission matrix

Before performing the F-EEM measurement, the DOC of all samples was measured (Shimadzu TOC-V analyzer, Japan) and was adjusted to ~ 1.0 mg/L (as C) by diluting samples with milli-Q water having a pH of 2.8 which is the blank sample. Fluorescence EEMs measurement was performed at 240–450 nm (10 nm increments) of excitation wavelength and 290–500 nm (2 nm increments) of emission wavelength using a FluoroMax-3 spectrofluorometer (Horiba Jobin Yvon Inc., USA). The correction steps include a blank subtraction of each EEM, excitation and emission spectra correction using correction factors provided by the manufacturer, and fluorescence intensity normalization with the area of the water Raman peak at excitation wavelength 350 nm.

Protein-like organic matter, *hypothesized to be a principal membrane foulant (polysaccharides are potential foulants as well)*, exhibits a dominant peak at lower excitation/emission wavelengths while humic/fulvic substances show dominant primary and secondary peaks at higher excitation/emission wavelengths.

Data processing. In order to further remove the Rayleigh scattering effects, emission measurement data made in the region of the excitation wavelength + 20 nm were deleted, and a set of zeros were inserted in a triangular-shaped region where the emission wavelength is less than excitation wavelength (upper corner of left side of EEM).

3. Results

This section is comprised of three sections. The first one is related to characterize NOM for estuarine and seawater representative samples; the second deals with the effectiveness of pretreatment in NOM removal; and the third links LC-OCD and F-EEM results.

3.1. Water samples

Organic matter characterization for representative waters from different locations (estuarine and seawater) and of different organic matter concentrations are presented in this section.

Firstly, reference materials were considered. These reference materials can be considered without anthropoghenic pollution. Fig. 2 shows the F-EEM spectra for DSR Florida strait C3 (700 m depth) and DSR Sargasso 0504 (2500 m depth). Both spectra match in the response; they present mainly three regions described by Coble (1996) as peak A for humic-like II, peak C for humic-like I and peak M for marine-like humic substances.

The F-EEM spectrum shows response in areas corresponding typically to humic-like primary (C) and humic-like secondary (A). In the same way, typical marine humic-like response can be observed (M). Assigned nomenclature corresponds to that commonly used in fluorescence [8]. In the LC-OCD chromatogram, the effect of salinity can be observed as a negative response by the DOC and UV_{254} detectors. The humic substances

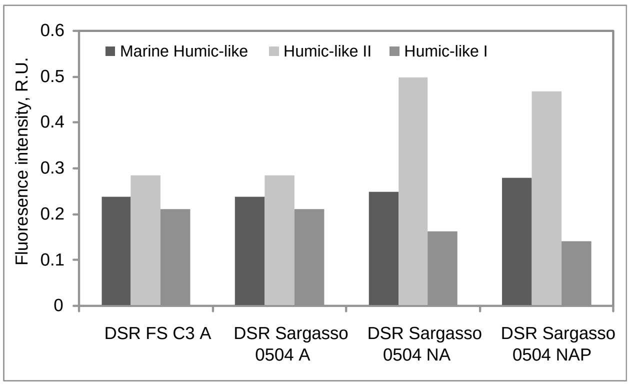

Fig. 3. Fluorescence intensity – DSR (acidified (A), not acidified (NA) and not acidified pasteurized (NAP)).

Table 1
Typical EEM peak values.

Description	Fluorescence range	
	Ex	Em
Humic-Like Primary Peak	330–350	420–480
Humic-Like Secondary Peak	250–260	380–480
Protein-Like (Tyrosine) Peak	270–280	300–320
Protein-Like (Tryptophan) Peak	270–280	320–350
Protein-Like (Albumin) Peak	280	320

are the main fraction with a concentration of 244 ppb and the biopolymer fraction is not detected by F-EEM but LC-OCD shows a concentration of 50 ppb. This indicates that the two tests are complimentary.

Fig. 3 shows the intensities at chosen typical-locations (see Table 1) in the F-EEM spectra. Acidified samples DSR FS C3 and DSR Sargasso 0504 matched in their responses.

The non acidified sample (DSR Sargasso 0504 NA) produced a higher intensity response for humic-like II (secondary peak) compared to the acidified samples. In the case of marine humic-like, in all cases the response is similar (average 0.251 ± 0.02 stdev). In the case of humic-like I (primary peak) the variation is higher (average 0.1820 ± 0.036 stdev).

The results of the characterization by F-EEM and by LC-OCD for "raw water" are shown in Fig. 4. For the three "seawater-representative" locations the DOC content is on average 1 mg/L where the humic substances represent about 50% of the DOC content. In all cases the fraction with size larger than 20 kDa (Biopolymers) represents about 7%. In the case of estuarine water, the DOC content is around 5 mg/L (see Table 2).

The samples from site A and site B are from the Western Mediterranean Sea while sample D comes from the Eastern Mediterranean Sea. Site C samples come from an estuarine of the North Sea (EC between 1 and 9 mS/cm). The DOC and SUVA values for the plants are shown in Table 2.

Fig. 5 shows the average values for all analyzed samples. Variation represents the maximum and minimum values of the samples. Higher variation is present in humic substances and building blocks in comparison with neutrals and biopolymers.

LC-OCD and F-EEM results show that humic substances are the more important fraction in seawater and estuarine water. Typically, humic substances (0.5–5 kDa in size) represent ~50% of the DOC content while the biopolymer fraction (> 20 kDa) is less than 8% of the

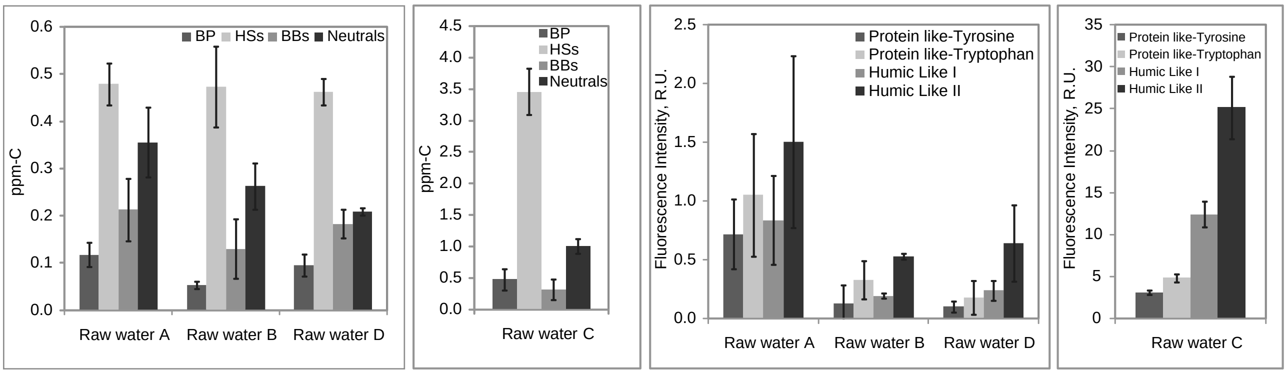

Fig. 4. Raw seawater from different locations: LC-OCD (left two) and F-EEM intensities (right two).

Table 2
Raw water DOC (ppm-C) and SUVA values (L/mg.m).

	Site A (seawater)	Site B (seawater)	Site C (estuarine water)	Site D (seawater)
SUVA	1.14 ± 0.59	0.70 ± 0.05	3.03 ± 0.54	0.89 ± 0.22
DOC	1.16 ± 0.16	0.92 ± 0.09	5.26 ± 0.56	0.95 ± 0.03

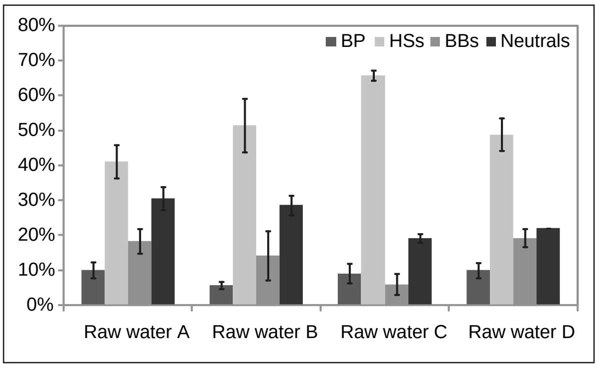

Fig. 5. Typical seawater organic matter fractions (%) for the samples received (Mediterranean Sea).

total DOC. In the case of estuarine water, the humic substances represent ~65% of the total DOC and biopolymers ~10%. F-EEM is a good tool to characterize protein-like, humic-like compounds and recent advances with PARAFAC (Parallel factor analysis, a multi-way analysis technique) forecast a major application of fluorescence for water treatment applications. LC-OCD presents a fair resolution in terms of chromatograms due to salt effects; however, it still remains the best option to quantify organic matter fractions in seawater.

3.2. Pretreatment efficiency

Three different pretreatments—beach wells, media filtration and ultrafiltration—for estuarine and seawater RO systems are studied, evaluated and compared in terms of organic matter removal and fouling potential.

3.2.1. Site A – dual media filtration versus microfiltration – Seawater

Site A plant has two parallel treatment trains. The first treatment lane consists of pH correction (6.8 with sulfuric acid), coagulation with ferric chloride + polymer addition and dual media filtration (anthracite and sand). The second treatment train consists of pH correction and microfiltration (0.1 µm PVDF membranes operating at 50 L/m^2.h).

Table shows that the DOC concentration is around 1.2 mg/L at the intake of the plant. SUVA values are in all cases less than 2, which suggest that NOM is mostly non humics with low-hydrophobicity and low-molecular weight [9].

As can be seen in Fig. 6, the pH correction with sulfuric acid breaks down slightly the humic fraction and the neutrals increase in the same ratio. In the second train (pH correction and MF) was observed some NOM removal such as humic substances (12%) and building blocks (25%).

Table 3
Studied plants/locations.

Site	Location	Water type	Pretreatment
A	W. Mediterranean Sea	Seawater	Coagulation + Dual media filtration; Microfiltration
B	W. Mediterranean Sea	Seawater	Beach well
C	North Sea	Estuarine water	Coagulation + Rapid sand filtration + Ultrafiltration
D	E. Mediterranean Sea	Seawater	Coagulation + Single stage granular filtration

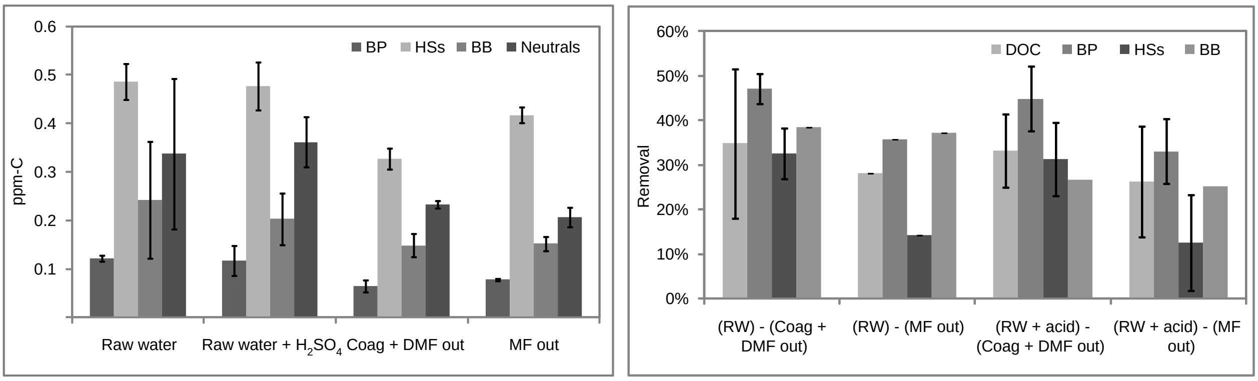

Fig. 6. Site A results: LC-OCD (left) and Removal effectiveness (right).

Table 4
Site A - Raw water DOC (ppm-C) and SUVA values (L/mg.m).

	Raw water wo/acid	Coag + DMF out	MF out
SUVA	0.78 ± 0.12	0.69 ± 0.12	0.59 ± 0.16
DOC	1.19 ± 0.32	0.77 ± 0.03	0.85 ± 0.04

Comparing coagulation + DMF and MF can be seen that the former is more effective in removing organic matter, 35% DOC removal for Coag + DMF compared with 28% DOC removal for MF. In both treatment trains, the biopolymers are significantly removed (47% Coag + DMF and 36% MF). So DMF combined with inline coagulation is more effective than MF without coagulant addition.

3.2.2. Site B – beachwells – seawater

The main beachwells' characteristics are: sand depth 0.80–1 m and filtration rate 0.4 m/h. The DOC content at site B is on average 0.94 mg/L with a SUVA value around 0.70 L/mg-m. After passage through the beach wells the DOC is reduced to 0.74 mg/L (see Table 5).

In Fig. 7 (left) are the results of LC-OCD analysis. Humic substances are the main fraction for the raw water and for the beach well effluent.

The removal effectiveness of beach wells shows that the DOC removal is around 21%, with the biopolymer fraction removed by ~70 %. This is significant reduction in organic matter with size larger than 20 kDa.

Table 5
Site B - Raw water DOC (ppm-C) and SUVA values (L/mg.m).

	Raw water	After sand filtration, Beachwell SW
SUVA	0.70 ± 0.05	0.61 ± 0.28
DOC	0.94 ± 0.09	0.74 ± 0.06

3.2.3. Site C – sand filtration and ultrafiltration – estuarine water

Inside site C plant, the water is first dosed with ferric chloride and flows through a continuous sand filter. The filtrate is then fed to the UF system. Normal backwashing of UF is done every 15 min and backwashing with NaOCl after 6 hours. A phosphonate based anti-scalant is added to the filtrate before feeding to the RO.

The RO system composed of Filmtec BW30LE-440 polyamide thin-film composite membranes. Recovery of the plant is about 75% while salt rejection is 99%. The RO is chemically cleaned (CIP) thrice a month in summer while only once during non-summer months. See Fig. 8 for a schematic of the plant.

On average the raw water DOC for the period considered is around 5 mg/L, turbidity between 5 and 20 NTU, EC between 1 and 9 mS/cm.

From the LC-OCD results it was observed that the UF backwash produces higher DOC concentration than the UF feed showing its effectiveness (1.25 times higher DOC and 2.9 times higher biopolymers concentration). The RO permeate has a DOC close to 0 mg/L, while the RO concentrate, is 3.75 times the RO feed concentration.

From the LC-OCD results it can be observed that humic substances (64%) are the main component of the water samples. The main biopolymer removal occurs after passing through UF membranes (70% removal). The RO membranes removed ~95% DOC of the influent, removing a similar ratio for most of the fractions. The coagulation + sand filtration step removed ~12% DOC, 17% biopolymers and 14% humic substances.

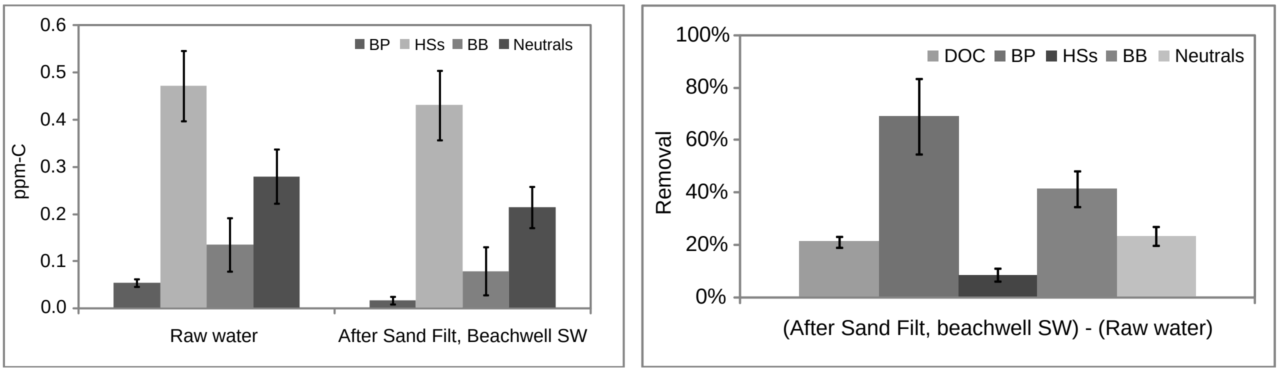

Fig. 7. Site B samples: LC-OCD (left) and NOM Removal effectiveness.

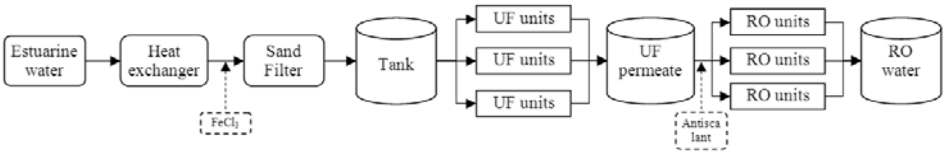

Fig. 8. Scheme of Site C plant.

In the case of the UF backwash, the main fraction removed by this process is biopolymers (66%) and humic substances (7%).

A mass balance for the first RO pass was performed. From these calculations, the deposition rate in mg/m^2.hr and the deposition factor were obtained for DOC and for the following NOM fractions: biopolymers, humic substances, building blocks and neutrals.

Particle transport in a cross-flow reverse osmosis membrane involves three process streams: the feed, the permeate and the concentrate. Unlike dead-end filtration, cake formation in cross-flow filtration is limited by back diffusion since most of the rejected particles remain in suspension flowing towards the concentrate stream. A simple mass balance was drawn base on this principle to estimate the deposition of colloidal particles in RO membranes ($dm/dt = Cf{*}Qf - Cp{*}Qp - Cc{*}Qc$). For this, it was assumed that depletion or deposition of particles is uniform for all RO elements. Subsequently, the deposition rates (DR) in terms of mg-C/m^2.h were computed by dividing dm/dt with the total membrane area (A_m) of the RO units. Therefore, the deposition rate is: $DR = (dm/dt) / (Am)$.

The deposition factor represents the ratio of the particles deposited on the RO membrane to that in the feed water [10]. Experimentally, the deposition factor is calculated as suggested by Schippers et al. (1981) from the relation between the DOC concentration of the concentrate at recovery R of the RO system and the DOC concentration of the feed water as follows: $DF = (1 / R) + (Cc / Cf) * (1 - (1 / R))$ being the concentration factor $CF = [1 - R^*(1 - f)] / (1 - R)$. For DF equal to 100 %, the NOM concentrate concentration is equal to the NOM feed concentration, this mean that there is no rejection of NOM by the membranes. For deposition factor equal to 0%, the concentrate concentration is the feed concentration times the concentration factor; in this case NOM is rejected by the membranes. It was assumed that the membranes DOC rejection is 98%, this is f = 0.98 as this influences the recovery factor. A *positive* deposition factor indicates particles are being deposited as they pass through the system while a *negative* factor indicates the number of particles in the concentrate exceeds the incoming flux (taking into account the concentration factor) [11].

The results of the deposition rate and deposition factor are presented in Table 6 corresponding to the plant recovery (R = 75%). These results suggest that some organic matter deposits on the membranes and large part of the biopolymers are deposited on the membranes. Negative deposition factors for the fractions smaller than 300 Da suggest that these organic fractions may scour from the surface of the membranes or are being formed.

Deviations may occur in the results due to accuracy of LC-OCD, accuracy of the flow meters and readings. These inaccuracies translate in deviations in conversion and ultimately in inaccuracy in deposition factor. To consider these possible inaccuracies on the deposition factor and deposition rate, the effect of 5% deviation in recovery (see Table 8) and the effect of 5% deviation in feed and concentrate concentrations (see Table 7) were calculated.

The results for the 5% deviation in concentrations showed for the deposition factor that at least 55% of biopolymers that are going through the RO system deposited on the membranes with a minimum 1.9 mg/m^2.h deposition rate. The results for 5% deviation in recovery

Table 6
Site C - Deposition rate and deposition factor analysis for 5% deviation in recovery.

	Deposition rate (mg/m^2.hr)			Deposition factor (f = 0.98)		
	70%	75%	80%	70%	75%	80%
DOC	-31.0	6.7	36.0	-20%	7%	30%
BP	1.3	2.4	2.1	51%	62%	72%
HSs	-19.1	8.1	27.5	-22%	5%	29%
BBs	-4.4	-2.8	0.1	-55%	-21%	9%
Neutrals	-18.1	-13.5	-2.0	-55%	-21%	9%

Table 7
Site C - Deposition rate and deposition factor analysis for 5% deviation in concentrations at R = 75%.

	Deposition rate (mg/m^2.h)		Deposition factor (f = 0.98)	
	0.95*Cc, 1.05*Cf	1.05*Cc, 0.95*Cf	0.95*Cc, 1.05*Cf	1.05*Cc, 0.95*Cf
DOC	31.7	-18.3	1%	-7%
BP	3.0	1.9	69%	55%
HSs	25.4	-9.1	17%	-9%
BBs	-1.4	-4.3	-6%	-37%
Neutrals	-8.3	-18.6	-6%	-37%

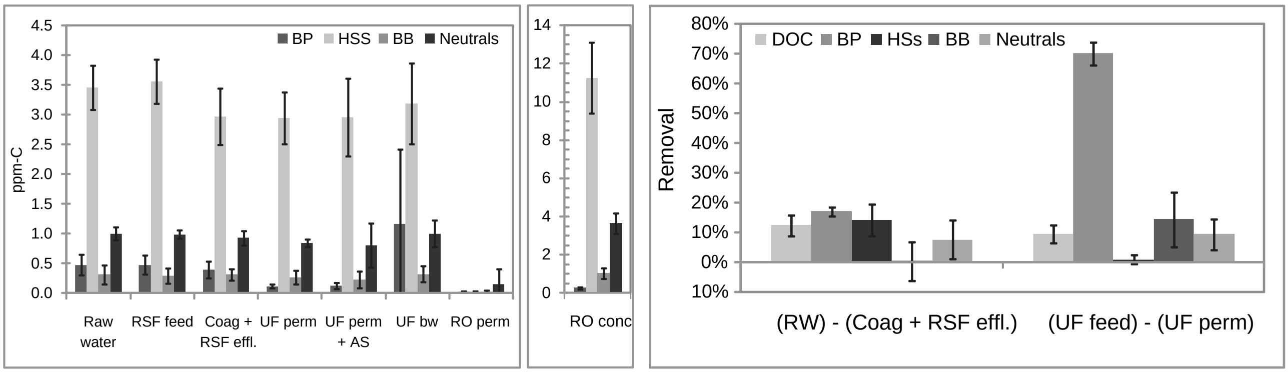

Fig. 9. Site C samples: LC-OCD (left) and NOM Removal effectiveness (right).

(Table 6. Table , R = 70% and 80%) confirm that biopolymers are deposited on the membranes.

3.2.2. Site D – dual media filtration – seawater

The raw water turbidity ranges from 0.5 to 5 NTU, TOC between 0.7 and 1.5 mg/L, and EC is around 56.5 mS/cm. The pretreatment of the plant consists of coagulation with ferric sulphate + single stage granular filtration, with the effluent of this step fed to the RO units after cartridge filtration.

The LC-OCD results show that the raw water is mainly composed of humic substances ~50%, biopolymers ~10%, and building blocks and neutrals around 20% each.

In terms of organic matter, coagulation + single stage media filtration removes 12% of DOC where the major removed fraction is the biopolymers (~32%). The passage of the water through the RO membranes (FILMTEC SW30HR) removes more than 98% of the organic carbon.

As explained for the site C, the deposition rate and the deposition factor were calculated for the first pass of the RO plant in site D. These calculated values are presented in Table 8 corresponding to the plant recovery (R = 48%). The results suggest organic matter is depositing on the membrane surface. Among the organic matter fractions, the neutrals (DF = 88%) have a higher deposition factor compared with biopolymers (65 %), humics substances (42%) and building blocks (59%).

Table 8
Site D - Deposition rate and deposition factor including analysis for 5% deviation in recovery.

	Deposition rate (mg/m^2.h)			Deposition factor (f = 0.98)		
	43%	48%	53%	43%	48%	53%
DOC	9.8	14.2	17.8	30%	43%	53%
BP	0.9	1.0	1.1	58%	65%	72%
HSs	5.0	7.2	9.0	29%	42%	52%
BBs	4.0	4.7	5.3	50%	59%	67%
Neutrals	9.9	10.2	10.4	85%	88%	90%

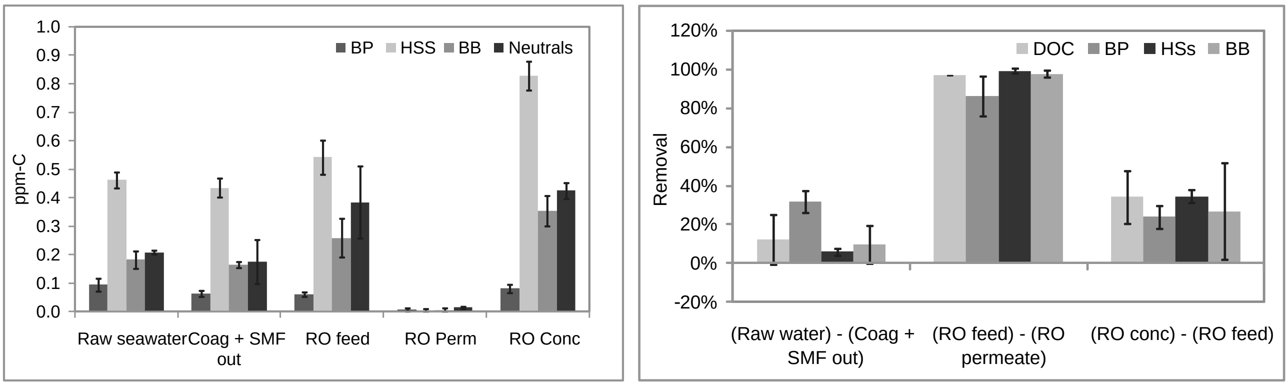

Fig. 10. Site D: LC-OCD (left) and F- NOM Removal effectiveness (right).

Table 9
Site D - Deposition rate and deposition factor analysis for 5% deviation in concentrations at R = 48%.

	Deposition rate (mg/m².h)		Deposition factor (f = 0.98)	
	0.95*Cc, 1.05*Cf	1.05*Cc, 0.95*Cf	0.95*Cc, 1.05*Cf	1.05*Cc, 0.95*Cf
DOC	20.7	7.7	59%	25%
BP	1.4	0.7	79%	50%
HSs	10.4	4.0	58%	24%
BBs	6.2	3.3	74%	43%
Neutrals	12.2	8.2	100%	75%

The effect of 5% deviation in recovery (see Table 8) and the effect of 5% deviation in feed and concentrate concentrations (see Table 9) were calculated.

The results for the 5% deviation in concentrations showed for the deposition factor that at least 50% of biopolymers and 75% of neutrals that are going through the RO system deposited on the membranes with a minimum 0.7 mg/m².h and 8.2 mg/m².h deposition rate, respectively. The results for 5% deviation in recovery (Table 6, R = 43% and 53 %) confirm that biopolymers are deposited on the membranes.

In all cases, a positive deposition factor and a positive deposition rate were obtained confirming deposition on the membranes.

3.2. Fluorescence and LC-OCDs

Both LC-OCD and F-EEM provide results for humic substances. LC-OCD gives concentrations while F-EEM provides intensity in Raman units (R.U.).

Fig. 11 shows humic substances concentrations on the horizontal axis versus fluorescence intensity (Raman

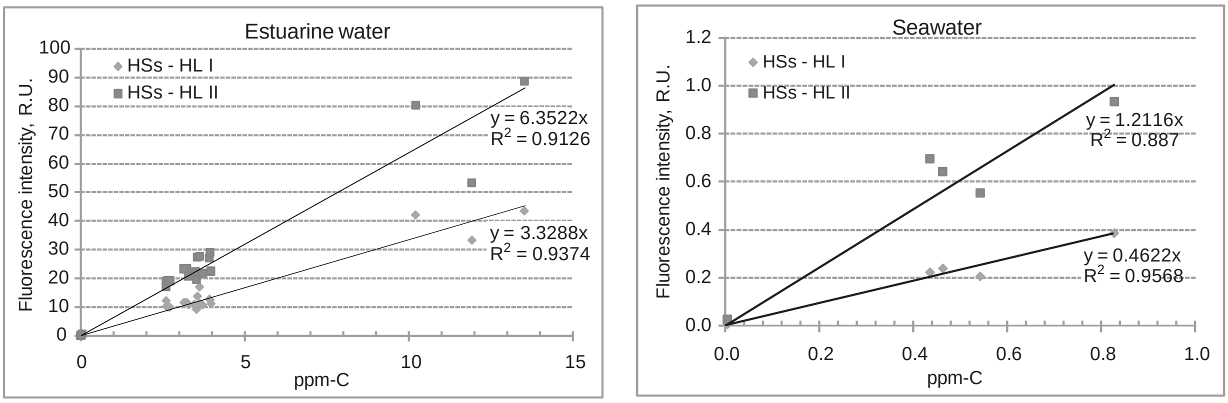

Fig. 11. Fluorescence vs. LC-OCD - estuarine and seawater results.

units, R.U.) on the vertical axis for estuarine water (left) as for seawater (right). From F-EEMs it is possible to obtain two different peaks representative of humic substances (Humic-like I and humic-like II, see Table 1); both peaks are plotted below.

The vertical and horizontal scale for estuarine water is much higher than for seawater due to higher organic matter presence in water. For *estuarine water* as for *seawater* linear relations ($r^2 > 0.88 – 0.95$) were found as shown in Fig.. *"y"* represents the fluorescence intensity in Raman units and *"x"* is the humic substances concentration in mg/L.

These relations could be used to estimate concentrations by making use of F-EEM results, which are less time consuming and less expensive to obtain.

4. Conclusions

Seawater and estuarine water were analytically characterized. In the case of seawater, in average 1 mg-C/L, humic substances represent ~50%, biopolymers ~10%, and building blocks and neutrals the remaining 40%. In case of estuarine water, in average 5.2 mg-C/L, humic substances consisted of ~65%, biopolymers ~10%, and building blocks and neutrals the remaining 25%.

The evaluation of pre-treatment efficiencies revealed for the site A (seawater) that, DMF combined with inline coagulation is more effective than MF without coagulant addition in DOC removal (35% and 26% respectively); been the biopolymers removed by 47% and 36%, respectively.

For the site B (seawater), the beach wells removed 21% DOC, with the biopolymer fraction removed by ~70%. This is significant reduction in organic matter with size larger than 20 kDa.

For site C (estuarine water), coagulation + continous sand filtration removed 12% DOC and 17% biopolymers. The UF units removed nearly 70% of the biopolymers that were fed to the membranes.

For site D (seawater), coagulation + single stage media filtration removed 12% DOC and 32% biopolymers.

The deposition factors and deposition rates revealed that some organic matter is deposited on the RO membranes. After considering deviations in concentrations and deviations in recovery, for the site C, biopolymers were calculated to deposit on the membranes (DF = 55% and DR = 1.9 mg-C/m^2.h); while for site D, all organic matter fractions were calculated to precipitate (For instance for the biopolymers the DF is 50% and DR is 0.7 mg/m^2.h).

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