Removal of polar organic micropollutants by pilot-scale reverse osmosis drinking water treatment

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ABSTRACT

The robustness of reverse osmosis (RO) against polar organic micropollutants (MPs) was investigated in pilot-scale drinking water treatment. Experiments were carried in hypoxic conditions to treat a raw anaerobic riverbank filtrate spiked with a mixture of thirty model compounds. The chemicals were selected from scientific literature data based on their relevance for the quality of freshwater systems, RO permeate and drinking water. MPs passage and the influence of permeate flux were evaluated with a typical low-pressure RO membrane and quantified by liquid chromatography coupled to high-resolution mass spectrometry. A strong inverse correlation between size and passage of neutral hydrophilic compounds was observed. This correlation was weaker for moderately hydrophobic MPs. Anionic MPs displayed nearly no passage due to electrostatic repulsion with the negatively charged membrane surface, whereas breakthrough of small cationic MPs could be observed. The passage figures observed for the investigated set of MPs ranged from less than 1%–25%. Statistical analysis was performed to evaluate the relationship between physicochemical properties and passage. The effects of permeate flux were more pronounced for small neutral MPs, which displayed a higher passage after a pressure drop.

1. Introduction

The occurrence of organic micropollutants (MPs) in natural drinking water sources is regarded as a high-priority environmental issue (Loos et al., 2013; Luo et al., 2014; Schwarzenbach et al., 2006). In particular, polar MPs can be highly water-soluble and mobile (Reemtsma et al., 2016), potentially reaching source waters and even finished drinking water (Benotti et al., 2009; Eschauzier et al., 2012; Reemtsma et al., 2016). There is concern over the potential effects of human exposure to trace concentrations of individual compounds or chemical mixtures via drinking water (Brack et al., 2015; Schriks et al., 2010). Drinking water utilities tend to (i) use the cleanest sources available and (ii) implement advanced treatments to remove unwanted chemicals. Riverbank filtration is an efficient natural pre-treatment used by several drinking water utilities across Europe, capable of lowering biological and chemical impurities as a result of mechanical retention, adsorption and (bio)chemical degradation taking place during infiltration of surface water through the riverbank and the subsurface (Tufenkji et al., 2002). Not all MPs are eliminated by riverbank filtration (Bertelkamp et al., 2014; Huntscha et al., 2013) and therefore additional treatment might still be necessary. In this article we focus on reverse osmosis (RO) drinking water treatment applied to raw bank filtrate. RO filtration *per se* doesn't involve chemical reactions, so that by-products are not expected in the treated water (RO permeate) unless membrane integrity is compromised, e.g. by pre-treatment with disinfection agents such

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as chlorine or by biofouling (Agus and Sedlak, 2010; Misdan et al., 2012). RO is a physical separation process in which the passage of organic solutes through osmotic membranes is assumed to follow the solution-diffusion model (Wang et al., 2014; Wijmans and Baker, 1995). Complex solute-membrane interactions can promote or hinder the solution-diffusion mechanism. These interactions are steric hindrance (Kimura et al., 2003b; Ozaki and Li, 2002), electrostatic interactions (Nghiem et al., 2006; Verliefde et al., 2008) and hydrophobic-hydrophobic interactions (Kimura et al., 2003b; Verliefde et al., 2009). Solute-membrane interactions are in turn influenced by solute and membrane physicochemical properties, feed water composition and operating conditions (Bellona et al., 2004).

The aim of this study was to quantify the removal of MPs from a raw riverbank filtrate in pilot-scale RO drinking water treatment and assess whether stand-alone RO step can be considered for further implementation in lieu of the conventional production chain. We also aimed to elucidate the transport of organic solutes through RO membranes by relating solute physicochemical properties to passage rates and by assessing the influence of the permeate flux. A series of experiments were performed at the research facility of a drinking water utility in the Dutch province of Zuid-Holland so that an actual source water, i.e. raw anaerobic riverbank filtrate, could be used as RO feed water. We studied the removal of thirty model polar MPs relevant for the water cycle such as herbicides, industrial chemicals, pharmaceuticals, personal care products and metabolites formed under environmental conditions. The effects of the permeate flux were also investigated. We introduce a RO pilot system capable of keeping hypoxic conditions while being operated in recirculation mode. Such system is novel and ensured that the precipitation of the dissolved iron naturally occurring in the bank filtrate used as RO feed water would not take place, *de facto* preventing membrane fouling. With this paper we report and aim to understand the removal efficiencies of known and emerging MPs, some of which have not been investigated either in bank filtrate or in RO filtration at all, e.g. the polycyclic aromatic hydrocarbons metabolite 2-hydroxyquinoline and its isomer 4-hydroxyquinoline, the industrial chemicals 2-(methyl-amino)pyridine, phenylurea, tetrapropylammonium and tetrabutylammonium.

2. Materials and methods

2.1. Standards and chemicals

All chemicals used in this study were of analytical grade. More details are provided in section S-1 of the Supplementary material.

2.2. MPs selection

Scientific literature data were reviewed to select 30 model MPs based on their detection in natural freshwater, RO permeates, and finished drinking water (Table 1). The compounds were amenable for analysis by liquid chromatography coupled to high-resolution mass spectrometry (LC-HRMS). The MPs were assigned to four physicochemical properties categories based on their charge and hydrophobicity. The pH-dependent octanol-water distribution coefficient expressed as log D_{ow} was used as a measure of hydrophobicity due to the inclusion of ionisable MPs amongst the model compounds. The log D values were calculated at pH 7 to match the pH of the natural water fed to the RO pilot (more details in section 2.4). A cut-off value of 2 was used to distinguish between hydrophilic and moderately hydrophobic MPs, in line with previous literature (Fujioka et al., 2015a; Verliefde et al., 2007a). The chemicals were categorised as (i) neutral and moderately

hydrophobic (log $D_{(pH7)} > 2$), (ii) neutral hydrophilic (log $D_{(pH7)} < 2$), (iii) anionic, and (iv) cationic. The selection ensured that a broad range of physicochemical properties were covered to support the elucidation of the removal mechanisms. The molecular weight (MW) distribution ranged evenly from approximately 100 Da—300 Da, with perfluorooctanoic acid (PFOA) being the only outlier (413.97 Da). The log $D_{(pH7)}$ ranged from -1.5 (acesulfame) to 4.6 (triclosan). A variety of chemical structures were represented.

2.3. MPs stock solutions

Stock solutions with a volume of 2 L were prepared by dissolving MPs with Na_2SO_3 in anaerobic ultrapure water to obtain a concentration of 14 and 28 mg/L of positive and negative MS ionisation MPs, respectively, and 17.5 g/L Na_2SO_3. For each experiment one stock solution was diluted in 698 L feed water to obtain concentrations of approximately 10 and 20 μg/L per MPs and 50 mg/L Na_2SO_3 as oxygen scavenger. These concentrations guaranteed the quantification of 99% removal, i.e. 1% passage, based on the analytical method's detection limits.

2.4. RO feed water

Raw anaerobic riverbank filtrate was freshly abstracted from a well field in the premises of the drinking water treatment plant (DWTP) where the experiments were conducted. This bank filtrate is also used as source water by the DWTP where conventional treatment is applied. The feed was kept in hypoxic conditions throughout filtration. Quality parameters are reported in table S-2.1 of the Supplementary material.

2.5. Hypoxic RO pilot-scale installation

A pilot-scale RO system was built and operated in recirculation mode to treat anaerobic riverbank filtrate under hypoxic conditions. Such a system was not commercially available or reported elsewhere. The pilot was a closed system consisting of a 720-L stainless steel feed reservoir, a high-pressure pump and one 4-inch membrane pressure vessel. Permeate and concentrate lines were recirculated to the feed reservoir via airtight connections. A detailed description and a picture of the RO pilot are provided in the Supplementary material Section S-3 and Figure S-3.1, respectively, whereas a diagram displaying the essential features of the system is provided in Fig. 1.

The low pressure RO (LPRO) membrane chosen for this study was an ESPA2-LD-4040 (Hydranautics, Oceanside, CA). This membrane is a typical thin-film composite (TFC) with an active layer of cross-linked aromatic polyamide, designed for low-pressure filtration and employed in a variety of water recycling applications (Fujioka et al., 2012a). The properties of the ESPA2 membrane are summarized in Table 2.

2.6. RO filtration protocol

The 720-L feed reservoir was filled with 698 L of anaerobic riverbank filtrate while being flushed with nitrogen. The MPs were dosed to the feed water with a SMART Digital pump from Grundfos B.V. (Almere, The Netherlands). Filtration was carried at a constant 15% recovery and 25 L m^{-2} h^{-1} permeate flux. The temperature was kept at 20 °C. Filtration was conducted for 4 d before taking feed and permeate samples at t = 5d to minimize the influence of hydrophobic interactions on the passage of moderate hydrophobic MPs (Verliefde et al., 2007b). During sampling the feed reservoir was supplied with nitrogen. Feed water and permeate samples (V = 200 mL; n = 2) were collected in 250 mL polypropylene bottles

Table 1
List of model MPs with physicochemical properties and selection criteria-matched references.

Compound	Molecular weight (Da)	[a]pK_a(pK_b)	[a]Log $D_{(pH7)}$	Chemical classification	[b]Properties category	Detected in freshwater sources	Detected in RO permeate	Detected in drinking water
2,6-dichlorobenzamide	188.97	12.1	2	Biodegradation product	I	(Björklund et al., 2011; Malaguerra et al., 2012; Ruff et al., 2015)	(Madsen et al., 2015)	
2-hydroxyquinoline	145.05	13.9	2.4	Biodegradation product	I	(Johansen et al., 1997; Mundt and Hollender, 2005)		
Atrazine	215.09	15.8	2.2	Herbicide	I	(Benotti et al., 2009; Bohn et al., 2011; Loos et al., 2010; Ruff et al., 2015; Verliefde et al., 2007a)		(Benotti et al., 2009; Bohn et al., 2011; Verliefde et al., 2007a)
Bisphenol A	228.29	9.8	4	Personal care product	I	(Benotti et al., 2009; Loos et al., 2009; Luo et al., 2014; Verliefde et al., 2007a)	(Al-Rifai et al., 2011; Huang et al., 2011; Kimura et al., 2004; Yangali-Quintanilla et al., 2010)	(Benotti et al., 2009; Kleywegt et al., 2011; Verliefde et al., 2007a)
Carbamazepine	236.27	16	2.8	Pharmaceutical	I	(Benotti et al., 2009; Loos et al., 2009; Luo et al., 2014; Verliefde et al., 2007a)	(Cartagena et al., 2013; Pisarenko et al., 2012)	(Benotti et al., 2009; Kleywegt et al., 2011; Verliefde et al., 2007a)
DEET	191.13	(-0.9)	2.5	Herbicide	I	(Loos et al., 2010; ter Laak et al., 2012)	(Huang et al., 2011)	(Benotti et al., 2009)
Diuron	233.09	13.2	2.5	Herbicide	I	(Loos et al., 2009; Ruff et al., 2015)	(Fujioka et al., 2015a)	
Triclosan	287.95	7.6	4.6	Personal care product	I	(Benotti et al., 2009; Loos et al., 2010; Luo et al., 2014)	(Cartagena et al., 2013; Huang et al., 2011)	(Benotti et al., 2009)
1H-benzotriazole	119.05	8.6	1.3	Industrial chemical	II	(Buerge et al., 2009; Giger et al., 2006; Loos et al., 2009; Ruff et al., 2015)	(Busetti et al., 2015; Loi et al., 2013)	(Wang et al., 2016)
4-hydroxyquinoline[c]	145.06	10.6	1.8	Biodegradation product	II			
Barbital	184.19	7.5	0.6	Pharmaceutical	II	(van der Aa et al., 2009)		
Caffeine	194.19	(-1.2)	-0.5	Stimulant	II	(Loos et al., 2009; Luo et al., 2014; Ruff et al., 2015)	(Boleda et al., 2011; Comerton et al., 2008; Sui et al., 2010)	
Chloridazon	221.04	(-1.8)	1.1	Herbicide	II	(Ruff et al., 2015)		
Paracetamol	151.16	0.4	1.2	Pharmaceutical	II		(Comerton et al., 2008; Fujioka et al., 2015a; Radjenović et al., 2008)	
Phenazone	188.22	-0.5	0.9	Pharmaceutical	II	(ter Laak et al., 2012)		
Phenylurea	136.06	13.8	0.9	Industrial chemical	II	(European Chemical Agency, 2016)		
Tolyltriazole	133.15	8.8	1.8	Industrial chemical	II	(Giger et al., 2006; Loos et al., 2009; Ruff et al., 2015)	(Busetti et al., 2015; Loi et al., 2013)	(Wang et al., 2016)
Triethyl phosphate	182.15	n/a	1.2	Industrial chemical	II	(Bollmann et al., 2012; ter Laak et al., 2012)	(Busetti et al., 2015)	
Acesulfame	162.39	3	-1.5	Sweetener	III	(Lange et al., 2012; Ruff et al., 2015)	(Busetti et al., 2015)	(Lange et al., 2012; Scheurer et al., 2010)
Bentazon	240.28	3.7	-0.2	Herbicide	III	(Loos et al., 2009; Ruff et al., 2015; ter Laak et al., 2012)		
Diclofenac	295.02	4	1.4	Pharmaceutical	III	(Benotti et al., 2009; Loos et al., 2009; Luo et al., 2014; Ruff et al., 2015)	(Cartagena et al., 2013)	(Benotti et al., 2009)
Ibuprofen	206.13	4.8	1.7	Pharmaceutical	III	(Loos et al., 2009; Luo et al., 2014; Ruff et al., 2015; Verliefde et al., 2007a)	(Garcia et al., 2013)	(Kleywegt et al., 2011; Verliefde et al., 2007a)
PFBA	213.99	1.2	-1.2	Industrial chemical	III	(Eschauzier et al., 2013, 2012)		(Eschauzier et al., 2012)
PFBS	299.95	-3.3	0.2	Industrial chemical	III	(Eschauzier et al., 2013, 2012; 2010; So et al., 2007)		(Eschauzier et al., 2012)
PFOA	413.97	-4.2	1.6	Industrial chemical	III	(Eschauzier et al., 2013, 2012; 2010; Loos et al., 2009; So et al., 2007)		(Eschauzier et al., 2012)
Sulfamethazine	278.08	7	0.4	Pharmaceutical	III	(Loos et al., 2009)		
Sulfamethoxazole	253.05	6.2	0.1	Pharmaceutical	III	(Benotti et al., 2009; Loos et al., 2010, 2009; Ruff et al., 2015)		(Benotti et al., 2009)

Table 1 (*continued*)

Compound	Molecular weight (Da)	[a]pK_a(pK_b)	[a]Log $D_{(pH7)}$	Chemical classification	[b]Properties category	Detected in freshwater sources	Detected in RO permeate	Detected in drinking water
2-(methylamino)pyridine	108.07	-6.6	0.7	Industrial chemical	IV	(European Chemical Agency, 2016)		
Tetrabutylammonium[d]	242.46	n/a	1.3	Industrial chemical	IV			
Tetrapropylammonium	186.35	n/a	-0.4	Industrial chemical	IV			(Kolkman and Vughs, 2014)

[a] pK_a, pK_b and Log D calculated with Chemaxon (http://www.chemicalize.com).
[b] Properties Category I: neutral and moderate hydrophobic MPs (log$D_{(pH7)}$ > 2); Category II: neutral hydrophilic MPs (log$D_{(pH7)}$ < 2); Category III: anionic MPs; Category IV: cationic MPs.
[c] No published data available, compound is isomer of target MP.
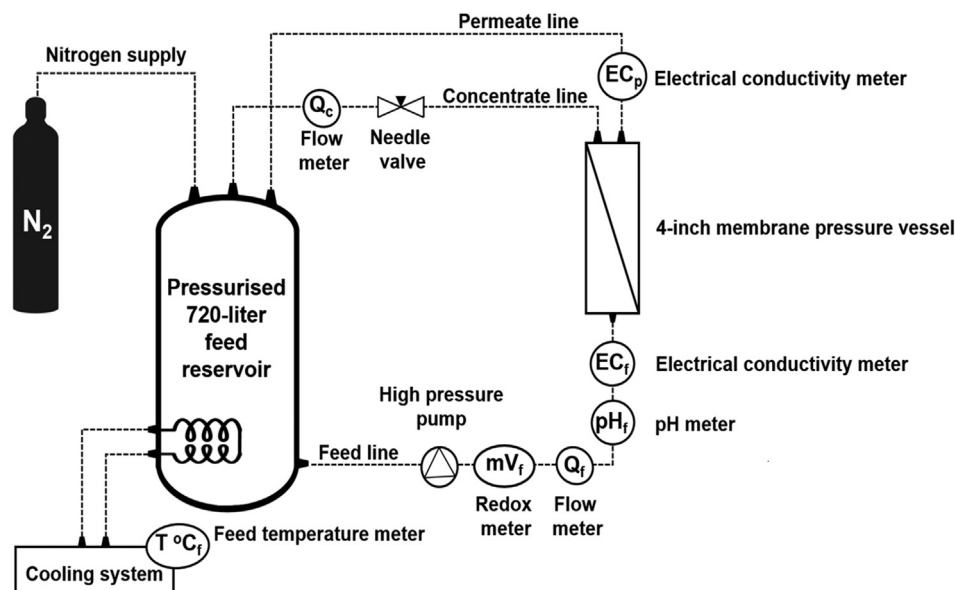[d] No published data available, compound structurally related to tetrapropylammonium.

Fig. 1. Schematic diagram of the hypoxic RO-pilot system.

Table 2
Performance characteristics and properties of a virgin ESPA2 membrane.

Performance		Properties					
Salt rejection[a]	Permeate flux[a]	Surface area	Surface roughness[b]	Contact angle[b]	Zeta-potential[c]	MWCO[d]
(%)	(m³/day)	(m²)	(nm)	(o)	(mV)	(Da)
99.4	5.57	7.4	89	25–40	< −20	<200

[a] Manufacturer data.
[b] Fujioka and Nghiem, 2013
[c] Tu et al. (2015).
[d] MWCO: Molecular weight cut-off. Source: Yangali-Quintanilla et al. (2010).

and frozen immediately. The second part of the study was conducted in a different season and focussed on the effects of operating conditions on the removal of a sub-set of 18 MPs. We assessed the permeate flux as the quality of temperature and pH of the riverbank filtrate at the DWTP location has proven to be very stable in time. We started RO filtration by applying the protocol used for the 30-analyte set. The only difference was the feed temperature, which this time was kept at 13° (see Table S-2). After the fourth day of filtration, the permeate flux was kept constant at $10 \, \text{L m}^{-2} \, \text{h}^{-1}$. Samples were then taken at $t = 2 \, \text{h}$, $t = 5 \, \text{h}$, and $t = 24 \, \text{h}$ before returning the permeate flux to $25 \, \text{L m}^{-2} \, \text{h}^{-1}$ and repeating the sampling at $t = 2 \, \text{h}$, $5 \, \text{h}$ and $24 \, \text{h}$.

2.7. Assessment of solute passage

The rejection equation can be used to quantify the removal of solutes by RO membranes:

$$R(\%) = \left(1 - \frac{C_{ROP}}{C_{ROF}}\right) \times 100 \tag{1}$$

Where C_{ROP} and C_{ROF} are the permeate and the bulk feed concentrations, respectively. Similarly, the passage can be defined as:

$$P(\%) = \left(\frac{C_{ROP}}{C_{ROF}}\right) \times 100 \tag{2}$$

In principle rejection and passage can be used to describe the same phenomenon, i.e. the removal of a solute by membrane filtration. However, the observed rejection equation (Eq. (1)) quantifies the percentage of solute that has been removed by RO filtration, whereas the passage (Eq. (2)) quantifies the percentage of solute in the permeate.

Finally, the EC passage was calculated by adapting Eq. (2):

$$ECP(\%) = \left(\frac{EC_{ROP}}{EC_{ROF}} \right) \times 100 \qquad (3)$$

where EC_{ROP} and EC_{ROF} are the electrical conductivity (in μS/cm) in the permeate and the in the bulk feed solution, respectively. Chemical passage was calculated by using Eq. (2) and the values reported in this manuscript are the averages and ranges obtained from experimental duplicates.

Statistical analysis was performed within the R statistical environment (R Core Team, 2017). The analysis was limited to Category I (7 neutral moderate hydrophobic MPs), Category II (10 neutral hydrophilic MPs) and Category III (9 anionic MPs) as only three cationic MPs populated Category IV. One-way analysis of variance (ANOVA) was performed to reject the null hypothesis that the physicochemical properties categories were the same in terms of passage mean. Pairwise comparisons between categories were conducted with post-hoc Tukey Honestly Significant Difference (HSD) test (Ruxton and Beauchamp, 2008). Both ANOVA and Tukey's HSD test were calculated with 95% confidence intervals (CI). In addition, the Spearman correlation coefficient (r) was calculated to assess the correlation between passage, molecular weight and hydrophobicity of all model MPs including cationic compounds.

2.8. Sample preparation

A sample preparation method validated in our laboratories was adapted to this study (Albergamo et al., 2018). The feed water samples (V = 1 mL; n = 2) were enriched with 2 μg/L of internal standards and filtered over 0.22 μm PP filters (Filter-Bio, Jiangsu, China) before direct injection analysis. The RO permeate samples (V = 200 mL; n = 2) were spiked with 100 ng/L of internal standards and concentrated by solid-phase extraction (SPE) with Oasis HLB (150 mg) from Waters (Etten-Leur, The Netherlands). The cartridges were conditioned with 5 mL of methanol and equilibrated with 5 mL ultrapure water. The samples were loaded, the cartridges were washed with 1 mL of ultrapure water and dried under vacuum for 15 min. The cartridges were eluted 4 times with 2.5 mL of methanol and the extracts evaporated to 1 mL, filtered with 0.22 μm PP filters and diluted ten times in ultrapure water before analysis. Aliquots of permeate samples were also collected before sample preparation for direct injection analysis.

2.9. Chemical analysis

The analyses of selected inorganic compounds in the feed water, i.e. ammonium, bicarbonate, calcium, chloride, iron, magnesium, manganese, potassium, and sulphate were performed by Vitens Laboratory Utrecht (Utrecht, The Netherlands) via standard methods conforming to (inter)national standards. The MPs were analysed by applying a LC-HRMS method validated in our laboratories (Albergamo et al., 2018). Feed water samples were analysed by direct injection, whereas RO permeate was enriched with SPE prior analysis. Aliquots of 1 mL RO permeate were collected prior SPE and directly injected to quantify acesulfame and hepta-fluorobutyric acid (PFBA). An ultrahigh-performance LC system (Nexera, Shimadzu, Den Bosch, The Netherlands) equipped with a core-shell Kinetex 2.6 μm biphenyl 100 Å column (Phenomenex, Utrecht, The Netherlands) was used for chromatographic separation. The mobile phase consisted of deionised water 0.05% acetic acid (A) and methanol (B). A maXis 4G quadrupole time-of-flight high-resolution mass spectrometer equipped with an electrospray ionisation source (ESI-Q-TOF) was operated in positive and negative mode to achieve MS detection (Bruker Daltonics, Wormer, The Netherlands). Full-scan MS and MSMS spectra acquired in broadband collision induced dissociation mode (bbCID) were screened for the accurate masses, retention time (t_R), mass accuracy, isotopic fit and MSMS for unambiguous identification of the target analytes. Detailed screening parameters for analytes identification are given in the Supplementary material (Table S-4.1). Quantification with internal standards was achieved for all the analytes except acesulfame and PFBA, for which an external standard calibration was used instead. The calibration series used for quantification were prepared in ultrapure water spiked with 32 μg/L and serially diluted to obtain ten concentration factors, with 31.25 ng/L being the lowest concentration. All calibration standards had a final volume of 1 mL and a concentration of isotope-labelled standards equal to 2 μg/L. Calibration curves were obtained from at least six calibration levels and displayed r-squared values greater than 0.99. The evaluation of the direct injection method is described in section S-5 of the Supplementary material. The method detection limits (LODs), quantification limits (LOQ) and recoveries are provided in Table S-5.1. Details about the evaluation of the performance of the SPE method are given in section S-6 of the supplementary material. LODs, LOQs and recoveries of the SPE procedure are provided in Table S-6.1.

3. Results and discussion

3.1. Removal of neutral and moderate hydrophobic MPs

Neutral and moderate hydrophobic MPs (log $D_{(pH7)}$>2) were substantially removed. With the exception of 2-hydroxyquinoline all target analytes displayed a passage lower than 5% (Fig. 2). The
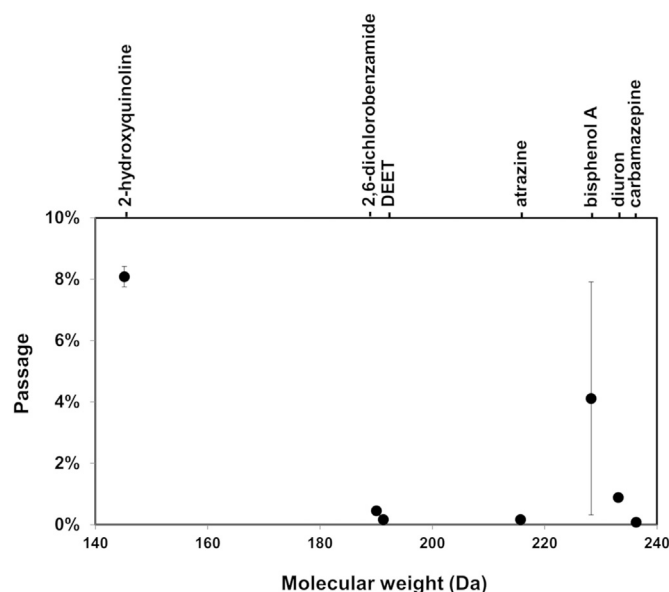
Fig. 2. Passage of neutral and moderate hydrophobic MPs as a function of their MW. The reported passage values are averages and ranges of experimental duplicate results. Ranges are shown when larger than the data point symbol. Conditions: average permeate flux 25 L m^{-2} h^{-1}, recovery 15%, feed pH 6.8 ± 0.1, feed conductivity 830 μS/cm, feed T 20 ± 1 °C.

results of triclosan are not reported due to the large deviation between the measurements.

The hydroxyquinoline isomers selected as target MPs are mid-small organics (145.05 Da) with almost identical physicochemical properties except for the log $D_{(pH7)}$, which is 2.4 and 1.8 for 2- and 4-hydroxyquinoline, respectively. Due to our log $D_{(pH7)} = 2$ cut-off, the two isomers were assigned to different categories: 2-hydroxyquinoline was regarded as moderate hydrophobic (log $D_{(pH7)} > 2$), whereas 4-hydroxyquinoline as neutral hydrophilic (log $D_{(pH7)} < 2$). After 4d, the passage of 2-hydroxyquinoline was $8.1 \pm 0.3\%$ (Fig. 2), whereas that of 4-hydroxyquinoline was $3.5 \pm 0.1\%$ (Fig. 3). While size exclusion represents the main removal mechanism for neutral MPs, the rejection of (moderate) hydrophobic MPs is also influenced by solute-membrane affinity interactions. These MPs can adsorb onto RO membranes due to the affinity between hydrophobic moieties such as aromatic rings and hydrocarbon chains and the active layer of RO membranes (Kimura et al., 2003a; Nghiem et al., 2002). Once membrane saturation is reached the adsorbed MPs can partition through the membrane and diffuse to the permeate side in a process influenced by solute-membrane affinity, i.e. hydrophobic-hydrophobic interactions and hydrogen bonding (Verliefde et al., 2009). Consequently, a higher rejection of moderate hydrophobic MPs can be observed in the early filtration stages due to the combined effect of adsorption and size exclusion (Kimura et al., 2003a). For this reason, the correlation between passage and size of hydrophobic MPs appears to be weaker than that of neutral hydrophilic MPs. When plotting the passage of moderate hydrophobic MPs as a function of their log D no clear correlation between these variables could be observed (data not shown). The passage differences between the hydroxyquinoline isomers could be explained by the lower hydrophilicity of 2-hydroxyquinoline and therefore its higher affinity for the

active layer of the ESPA2 membrane, which consisted of aromatic polyamide. Thus, the removal of 2-hydroxyquinoline could also be influenced by solute-membrane affinity interactions in addition to the size exclusion mechanism. The higher hydrophobicity of 2-hydroxyquinoline could be confirmed by its chromatographic behaviour. In a 7-min analysis run with reversed-phase chromatography 2-hydroxyquinoline had a retention time (t_R) of 5.03 min, whereas the t_R of 4-hydroxyquinoline was 4.03 min. This is also in agreement with earlier work published by our group (Brulik et al., 2013). The second least-well removed moderate hydrophobic MP was bisphenol A, for which we observed up to 4% passage. The result is in accordance with the removal efficiency from spiked raw lake water in a bench-scale RO filtration study (Comerton et al., 2008). In a recent pilot–scale investigation bisphenol A was rejected by approximately 75% by a cellulose triacetate (CTA) RO membrane (Fujioka et al., 2015a).

3.2. Removal of neutral hydrophilic MPs

The transport of neutral hydrophilic MPs is mainly hindered by a sieving mechanism (cf. introduction), thus the larger the molecule the lower its passage (Bellona et al., 2004; Fujioka et al., 2012a; Kiso et al., 1992; Ozaki and Li, 2002). The MPs selection included 10 uncharged hydrophilic compounds covering a MW range from approximately 100 Da–300 Da. The overall removal of these MPs was very high with observed passages lower than 5% for almost all compounds. All neutral hydrophilic MPs larger than 180 Da were almost completely removed (passage < 1%). In accordance with scientific literature a strong correlation between MW and MPs removal by RO membranes was found (Fig. 3). By adapting a method proposed by López-Muñoz et al. (2009) it was estimated that the cut-off value (MWCO) of the ESPA2 membrane in our
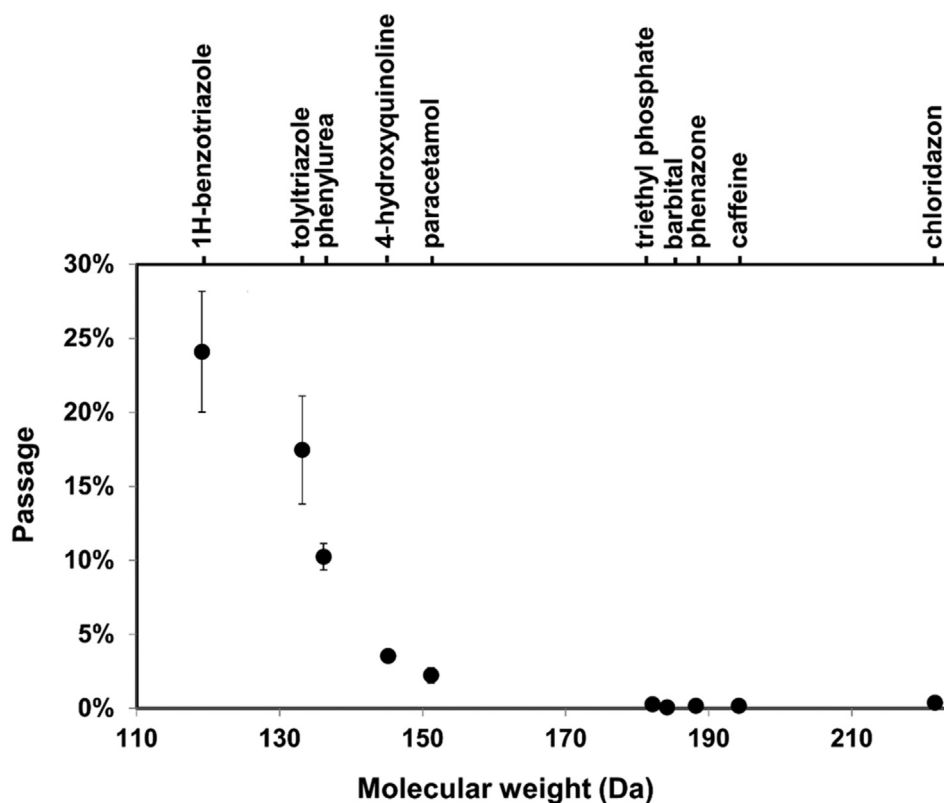

Fig. 3. Passage of neutral hydrophilic MPs as a function of their MW. The reported passage values are averages and ranges of experimental duplicate results. Ranges are shown when larger than the data point symbol. Conditions reported in Fig. 2.

operating conditions corresponded to approximately 140 Da, which is in accordance with findings from Yangali-Quintanilla et al. (2010). However, the MWCO of RO membranes is not an absolute value and should be used for semi-qualitative prediction only.

As expected the smallest MPs displayed the lowest removal efficiencies. 1H-benzotriazole (119.05 Da) and tolyltriazole (133.15 Da) showed $25 \pm 4\%$ and $17 \pm 4\%$ passage, respectively. The third least-well removed neutral hydrophilic MP was phenylurea (136.06 Da), for which we quantified $10 \pm 1\%$ passage. To the best of our knowledge, this compound has not been investigated in membrane filtration before. The addition of a methyl group to 1H-benzotriazole resulted in a decreased passage of the methylated derivative (tolyltriazole), which supports size exclusion as main removal mechanism. This is in accordance with previous research, where a correlation between removal and number of methyl groups was observed (Steinle-Darling et al., 2007). The removal efficiencies of benzotriazoles quantified in this study were in close agreement with observations from a full-scale advanced water recycling plant where RO was applied to treat secondary waste-water treatment effluents, where 70% and 85% rejection were observed for 1H-benzotriazole and methyl-1H-benzotriazole, respectively (Loi et al., 2013). In a separate study on advanced water recycling where RO permeate was used for groundwater replenishment the average removal efficiencies were 51% and 53% for 1H-benzotriazole and its methylated derivatives, respectively (Busetti et al., 2015). It is challenging to explain the lower removal efficiencies reported in the latter study since no details about feed water characteristics and RO operational parameters were given by the authors whose goal was the validation of an analytical method. Nevertheless, the lower removal might be attributed to a different feed water composition, higher feed water temperature or to the employment of a more open RO membrane. The benzotriazoles are small emerging contaminants which are frequently and globally detected in the water cycle in the high ng/L to low μg/L range due to their incomplete removal by conventional wastewater treatment (Giger et al., 2006; Loos et al., 2013; van Leerdam et al., 2009). In general, small neutral MPs like the benzotriazoles are not fully retained by LPRO membranes. Observations from a DTWP in which the production chain consisted of riverbank filtration, aeration, a split stream treatment with RO, and full stream active-carbon filtration suggest that the combined treatments are only partially effective on small neutral MPs (Kegel et al., 2010). Observation from a full-scale municipal wastewater treatment plant upgraded with post-ozonation followed by sand filtration (Hollender et al., 2009) showed that a medium ozone dose ($0.6 \, g \, O_3 \, g^{-1}$ DOC) led to 70% removal of 1H-benzotriazole. Where necessary, the passage of small neutral MPs such as the benzotriazoles could be lowered by employing tighter RO membranes. In general, the removal efficiencies of RO drinking water treatment can be maximised following combination with other treatments. However, the smallest neutral polar MPs might still be detectable in the permeate (Boleda et al., 2011).

3.3. Removal of ionic MPs

As expected, excellent removal of anionic MPs was observed (passage<1%). The ESPA2 has its isoelectric point at pH 4 (Tu, Chivas & Nghiem, 2015) and a zeta-potential of - 40 mV at pH 7 (Fujioka et al., 2013). Consequently, it displayed a net negative charge at the operating feed pH. The electrostatic repulsion between anionic solutes and negatively charged membranes represents an additional mechanism that leads to low passage (Ozaki and Li, 2002). The results are shown in Fig. 4. Considering the behaviour of neutral polar compounds in RO filtration and the MW of the anionic MPs investigated, steric hindrance should be considered in addition

to electrostatic repulsion when interpreting the low passage values of negatively charged MPs observed in this study.

Two quaternary ammonium ions were selected as cationic MPs along with 2-(methylamino)pyridine. We observed passage of $2.5 \pm 0.1\%$ and $0.3 \pm 0.1\%$ for tetrapropylammonium and tetrabutylammonium, respectively, whereas the passage of 2-(methylamino) pyridine, the smallest cation, was $8.8 \pm 0.1\%$. These values, although limited to three compounds only, suggest a decreasing passage trend with increasing MW and a higher transport of cationic MPs compared to anionic MPs of comparable size. Passage of positively charged MPs during RO filtration can be expected due to charge concentration polarization, i.e. a localized increase in concentration of cations onto the negatively charged active layer due to electrostatic attractions, leading to lower rejection (Fujioka et al., 2015b; Verliefde et al., 2008).

3.4. Statistical analysis

The passage values of the MPs in Category I, II and III were log-transformed and visualised in a box-and-whisker plot. This highlighted the overall lower passage of anionic MPs compared to neutral compounds (Fig. 5).

The ANOVA test run on this dataset returned a p-value of 0.00297 with 95% CI, indicating significant difference in the mean passage amongst the three categories. The Tukey's test showed modest difference between Category I and III ($p = 0.04077$), significant difference between Category II and III ($p = 0.00264$), whereas the differences between Category I and II were not significant ($p = 0.66295$). These results indicate a significant relationship between passage and compound physicochemical properties as categorised in this study and highlight the role of electrostatic repulsion in preventing transport of anionic MPs through TFC RO membranes. However, the additional effects of size should not be excluded when interpreting the low passage of anionic MPs as commented in the previous section (3.3). Hydrophobicity expressed as log D had no significant impact on the passage of neutral polar organics. To gain more insights, data of all MPs excluding triclosan (29 compounds) were pulled together and the Spearman correlations between MW, log D and passage were assessed. Passage and MW showed good correlation ($r = -0.77$, $p \leq 0.01$), contrary to the log D ($r = 0.20$, $p = 0.31$). This highlights (i) the overall relevance of compound size in hindering transport of polar organics through TFC RO membranes and (ii) the lack of relationship between passage and hydrophobicity, which is in line with the results obtained from the ANOVA and the Tukey's test.

The results of the statistical analysis pointed to compound MW as a prominent physicochemical property and in part to charge to explain the passage of polar MPs through RO membranes. The clear trend between passage and MW can be used to qualitatively predict the passage, especially in RO systems equipped with TFC membranes of known MWCO. For MPs which deprotonate at operating feed water pH, even lower passage figures could be expected. Despite the lack of significance between Category I and Category II, the impact of solute-membrane affinity interactions on the passage of uncharged organics needs further assessment. Caution should be exercised when predicting the passage of neutral compounds exhibiting high log D values as seen for bisphenol A, which displayed 4% passage despite its size of 228.29 Da.

3.5. Influence of permeate flux

The overall removal efficiencies of the investigated MPs at $t = 5$ d (data not shown) were comparable to those presented in sections 3.1, 3.2 and 3.3 and therefore the results and discussion in this section are limited to the compounds for which we quantified
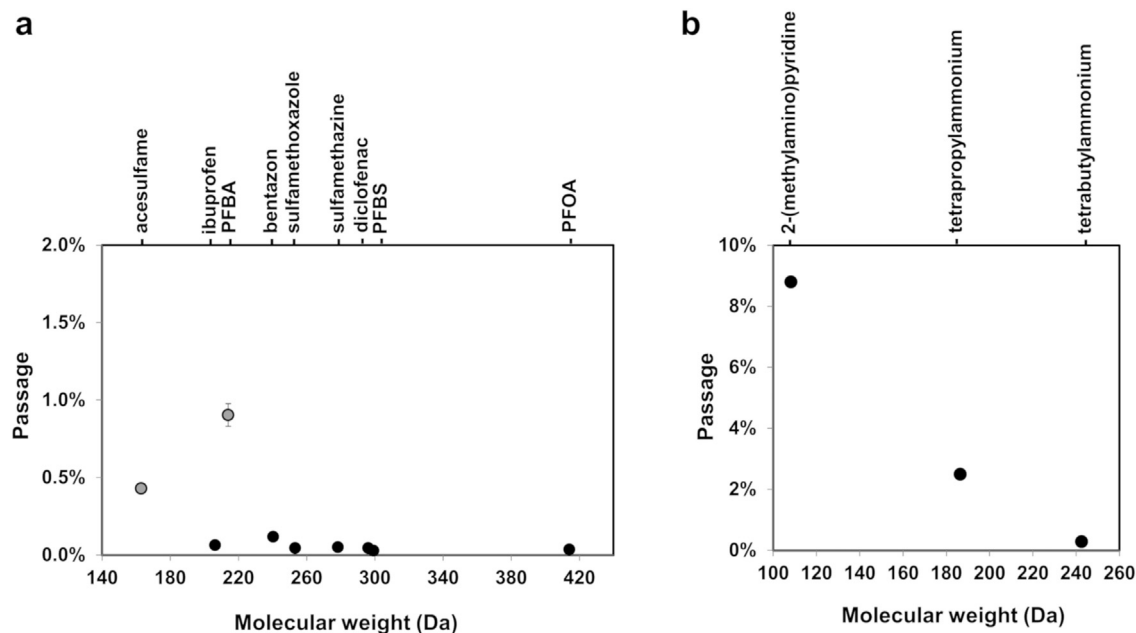
Fig. 4. Passage of anionic MPs (a) and cationic MPs (b) as a function of their MW. The reported passage values are averages and ranges of experimental duplicate results. Ranges are shown when larger than the data point symbol. Grey dots represent removal below detection limits. Conditions reported in Fig. 2.
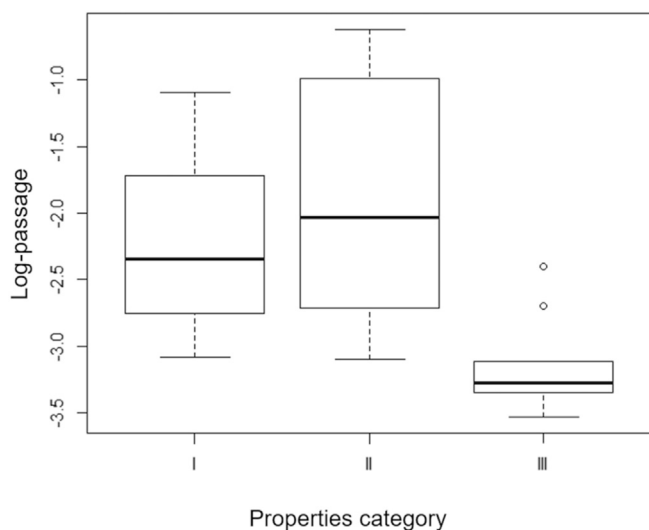

Fig. 5. Box-and-whisker plot illustrating the log-passage range observed for each physicochemical property category, i.e. Category I (neutral and moderate hydrophobic), Category II (neutral hydrophilic), Category III (anionic).

more than 1% passage, i.e. 1H-benzotriazole, tolyltriazole, 2-hydroxyquinoline, and paracetamol. With the exception of 2-hydroxyquinoline, the highest passages were observed for neutral hydrophilic MPs. In accordance with scientific literature, the effects of the permeate flux were more prominent on the smallest MPs (Fujioka et al., 2012b) and an inverse correlation between passage and permeate flux could be observed (Verliefde et al., 2009). After 2 h of filtration at a permeate flux of $10 \, L \, m^{-2} \, h^{-1}$ no relevant passage variations could be observed with the exception of 2-hydroxyquinoline which increased from 9% to 15%. After 5 h the passage of the four target MPs was almost doubled compared to the previous measurements, whereas after 24 h the passage decreased to values which were higher than those observed at a permeate flux

of $25 \, L \, m^{-2} \, h^{-1}$: 1H-benzotriazole passage increased from $22 \pm 2\%$ to $30 \pm 2\%$, tolyltriazole from $15 \pm 2\%$ to $18 \pm 2\%$, 2-hydroxyquinoline from $8.7 \pm 0.2\%$ to $14 \pm 4\%$, and paracetamol from $3.2 \pm 0.6\%$ to $4 \pm 0.4\%$ for $25 \, L \, m^{-2} \, h^{-1}$ after 2 h and $10 \, L \, m^{-2} \, h^{-1}$ after 24 h respectively. When the flux was set back to $25 \, L \, m^{-2} \, h^{-1}$ the MPs passage after 24 h was comparable to that observed after 4 d of filtration, suggesting repeatability of the methodology and reversibility of the membrane structure. From these measurements we could obtain four different MPs passage profiles as a function of filtration time (Fig. 6).

The behavior of polar MPs deviated from that of the EC passage, which increased at the lower permeate flux, but remained stable throughout filtration at a given permeate flux (Fig. 6 - bottom). Based on the EC data, these variations in MPs passage cannot be attributed to changes in membrane properties, e.g. enlargement of intramolecular spaces within the active layer, or membrane charge. The results suggest that the transport of small hydrophilic MPs is enhanced within at least the first 5 h following a pressure drop, possibly due to accumulation onto or within the membrane and subsequent permeation. Unknown matrix effects leading to higher passage cannot be excluded. To the best of our knowledge, the passage profiles obtained from the results of this study have not been reported before and can provide information worth considering when designing MPs rejection experiments from an untreated water matrix by RO in recirculation mode. Based on our results and depending on the quality of the feed water it can be advised to discharge the permeate produced within at least 5 h following a pressure drop and to monitor the permeate quality during the subsequent 24 h.

4. Conclusions

RO proved to be a robust barrier against most polar MPs. Overall, the passage figures observed for the investigated set of compounds ranged from less than 1%—25% in standard conditions. Statistical analysis showed significant influence of physicochemical properties on compound passage. Compound size and passage were highly correlated for neutral MPs, and charge for anionic MPs.
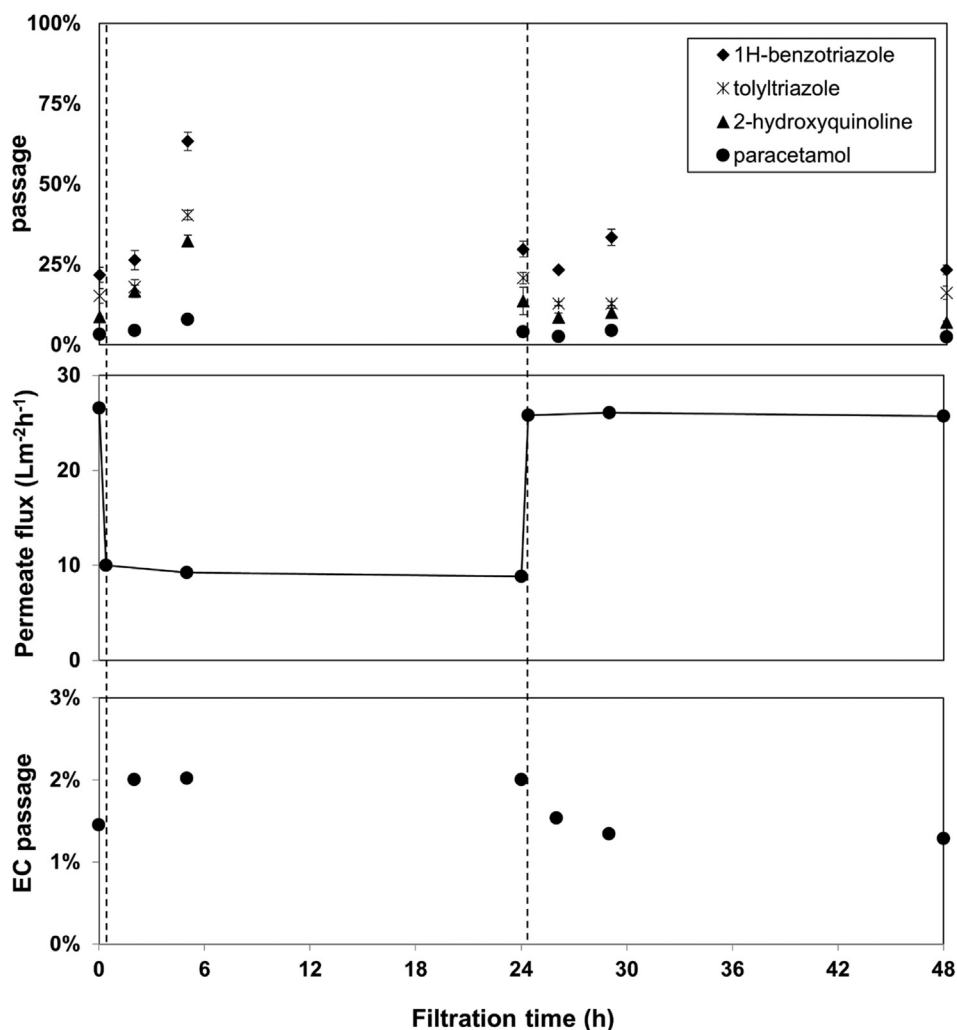
Fig. 6. Influence of permeate flux on MPs passage. Passage of MPs (top), permeate flux (middle), and EC passage (bottom) are shown as a function of the RO filtration time. The reported passage values are averages and ranges of experimental duplicate results. Ranges are shown when larger than the data point symbol. Dashed lines represent the point in time in which the permeate flux was set to a different value. Starting conditions: average permeate flux 25 L m^{-2} h^{-1}, recovery 15%, feed pH 7.0 $\pm$ 0.1, feed conductivity 880 μS/cm, feed T 13 $\pm$ 1 °C.

Determining key factors were also membrane chemistry and feed water properties.

- Neutral and moderate hydrophobic MPs showed a weak inverse correlation between size and passage. However, in some cases passage values higher than those of a hydrophilic compound of comparable size were observed
- Neutral hydrophilic MPs showed a strong inverse correlation between size and passage. When larger than 180 Da, nearly no passage was observed. The smaller uncharged hydrophilic MP, 1H-benzotriazole (119.05 Da), displayed up to 25 $\pm$ 5% passage
- Anionic MPs displayed almost no passage, whereas minor breakthrough of cationic MPs of comparable size was observed
- RO carried at a low permeate flux resulted in higher MPs passage, particularly for small neutral hydrophilic MPs. For at least 5 h following a pressure drop strong passage fluctuations were observed

In summary, the passage-size correlation can be used to qualitatively predict the behavior of neutral MPs in RO system equipped with TFC membranes of known MWCO. For anionic MPs even lower passage figures could be expected. For neutral MPs the influence of solute-membrane affinity (H-bonding or non-polar interactions) should be taken into account when predicting passage. This study encourages further investigation of RO applied to bank filtrate. Higher removal efficiencies could be achieved by using tighter membranes, larger membrane elements or multi stage RO.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.watres.2018.09.029.

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