Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2013.834271

52 (2014) 7598–7608
December

Taylor & Francis
Taylor & Francis Group

Linking UF reversible and irreversible fouling to the water quality of surface water and treated municipal wastewater

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Received 21 February 2013; Accepted 9 August 2013

ABSTRACT

The interdependencies between water quality parameters and ultrafiltration characteristics (reversible, and irreversible fouling) of surface water (SW) in comparison with treated domestic wastewater (TDW) were systematically investigated. A focus was set to the macromolecular dissolved fraction ("biopolymers"), accounting for about 50% of the full fouling resistance. Correlation matrices were used to point out overall differences of both waters, whereas seasonal monitoring was used to reveal different inter-annual variability. The correlation matrices show that biopolymer concentration significantly correlates with total and reversible fouling of both waters but not with irreversible fouling. The membrane rejection of SW biopolymers showed significant correlations to all parameters (biopolymer concentration, reversibility, etc.). We found significant correlations of temperature with total and reversible fouling (positive in SW but negative in TDW) and irreversible fouling (negative in SW but positive in TDW). Therefore, temperature is suggested as a very handy indicator for total/reversible fouling and especially irreversible fouling. Seasonally, the SW biopolymer concentration shows a clear development (high in summer and low in winter); no comparable trend was observed for TDW. Filtration parameters are clearly subject to seasonal variation. The irreversible amount of SW-induced fouling was maximal in winter and minimal in summer, whereas treated TDW-related variability was lacking such obvious trends.

Keywords: Biopolymers; Ultrafiltration; Irreversible fouling; Surface water; Secondary effluent; Organic fouling; Temperature

1. Introduction

Within the last 15 years, the application of low pressure membrane systems has developed rapidly for the production of drinking water, the reclamation of treated municipal treated domestic wastewater (TDW) or in TDW treatment using membrane bioreactors. Microfiltration (MF) or ultrafiltration (UF) permeates are of high quality, as they are purified and

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physically disinfected and can be used for different applications. However, the loss of productivity due to membrane fouling is still one of the major obstacles for further spreading of this technology. Fouling has been investigated in a wide range of studies. In MF and UF, particulate ($>1.2\,\mu$m) and colloidal (0.45–1.2 μm) foulants were found to be of minor concern [1,2] as larger agglomerations can be easily backwashed from the membrane surface [3–5]. However, adverse effects due to interactions between particulate, colloidal, and dissolved material have been reported [6,7]. The beneficial effect of backwashing is exploited if coagulation is applied prior to filtration. Using ferric or alumina salts, colloidal particles are bound into the flocs which build a porous cake layer on the top of the membrane that can be easily backwashed [8–10]. This kind of fouling is identified as hydraulically reversible fouling. Accordingly, the irreversible fouling is the relevant form of production loss, as this blockage of membrane surface or pores can only be removed by reactive chemical cleaning.

Soluble organic compounds that adsorb onto the membrane material are mainly responsible for the irreversible decay of water flux in surface water (SW) and TDW filtration (e.g. [5,11]). However, different concepts exist about the classification, identification, and relevance of these organic compounds. Depending on the origin of compounds and methods to detect them, recent studies differentiate them into soluble microbial products, extra-cellular polymeric substances (EPSs) (comprising both proteins and polysaccharides), effluent organic matter (EfOM), humic substances, and biopolymers. Proteins and polysaccharides, for example, are measured as EPS photo-metrically e.g. in activated sludge filtration [12,13] by UV absorption (for proteins) in SW [14] or by size-exclusion chromatography (SEC) in combination with UV 254 nm and nitrogen detection [15] or by fluorescence [16]. Another analytical approach often applied for foulant characterization is fluorescence analysis yielding excitation–emission matrices (EEMs). Peiris et al. [17] stated that for river water, colloidal/particulate matter contributes primarily to reversible fouling and humic as well as protein-like matter identified by fluorescence analysis were largely responsible for irreversible fouling. In another study, the contribution of protein-like matter identified with principal component analysis of fluorescence EEM seemed not be relevant for irreversible fouling in SW [18] and a recent study by Henderson et al. [19] found the tyrosine-like peak ($\lambda_{ex/em} = 250/304\,$nm) in a fluorescence EEM analysis relevant for total fouling resistance in TDW. Polysaccharides, accounting for a substantial part of biopolymers, mostly do not exhibit fluorescence and are not captured by EEM measurements. Even if identification made progress in recent years, a clear understanding of details and mechanisms of irreversible fouling does not yet exist, possibly also due to interactions of different types of foulants [20].

Next to the chemical properties, the size of the molecules is important for fouling behavior. Bioavailable macromolecules (so-called biopolymers) determined by liquid chromatography-organic carbon detection (LC-OCD) have been intensively investigated and showed strong correlation with total filtration resistances [1,21,16]. These biopolymers can be further characterized by parallel detection of UV 254nm absorption and organic nitrogen content (N_{BP}). This analytical approach may provide more information on the molecular composition of potential organic fouling compounds either in treated domestic wastewater (TDW) or in SW.

The present study analyzes filtration parameters such as *filterability* and *reversibility* of SW and TDW in flat-sheet membrane filtration tests. Potential fouling indicator parameters are determined by biopolymer content (DOC_{BP}) via LC-OCD and by the ratio of biopolymer carbon to biopolymer nitrogen (DOC_{BP}/N_{BP}). The study analyzes the variation of potential indicator parameters during a period of one year, comparing SW and TDW. The conduction of a fouling indicator that allows determination of irreversible fouling potential without the application of membrane pilot tests, just by simple water analysis, or even by online analysis would be a promising treatment strategy.

2. Materials and methods

2.1. Study approach

Within this study, data from a SW body and a TDW effluent for a variety of parameters over a period of one year were obtained. The first approach was to gather these annual sets of data for general analysis of pairs of parameters by correlating them using correlation matrices. In this respect, overall correlations between parameters could be revealed. The second approach was to plot the data over time to check for developments during the monitoring period. Using these two approaches, potential coincidences/correlations of parameters were covered as well as the temporal change of single parameters.

2.2. Water samples and pretreatment

SW samples were taken from the *Landwehrkanal* (Berlin, Germany), a canal water body under sporadic anthropogenic influence (combined sewage overflow in case of heavy rain showers, samples were taken in the morning of days with dry weather), behind a cascade ensuring mixture of the water. TDW was sampled from the *Berlin-Ruhleben* wastewater treatment plant (activated sludge process with nitrification/denitrification and biological P removal) in the morning of sampling days. Temperature, pH, and conductivity of the waters were measured directly at the sampling sites (online measurements of TDW conducted by the *Berliner Wasserbetriebe*). The observational periods were March 2010–February 2011 (SW) and November 2009–2010 (TDW), respectively. Table 1 gives an overview on the water characteristics of the studied waters.

Ultra pure water (electric resistivity $\geqslant 17\,\text{M}\Omega\,\text{cm}$) was produced of fully de-ionized water, using a *Maxima UF* (*ELGA LabWater*, Germany). Salt solution was made by dissolving $CaCl_2 \cdot 2H_2O$ and NaCl in ultra pure water (411 and 316 mg/L, equivalent to 2.8 and 5.4 mmol/L Ca^{2+} and Na^+, respectively (*Carl Roth GmbH + Co. KG*, Germany); with respect to Ca^{2+}, this matches the average concentrations found in the Berlin WWTP Ruhleben effluent and the Landwehrkanal SW; with respect to Na^+, this matches the average concentrations found in Berlin WWTP Ruhleben effluent and about three times the average concentration found in the Landwehrkanal SW; varying salt concentration showed little effects on the outcomes of the UF tests, as shown in Fig. 1).

Prior to lab-scale flat-sheet UF tests, all water samples were pre-filtered by 0.45 μm (cellulose nitrate, *Sartorius*, Germany, rinsed with ultra pure water prior to application); except for the identification of the contributions to fouling resistance by different fractions of foulants, where UF was conducted with differently pre-treated water samples (non-filtered SW or non-filtered TDW, respectively, and 1.2 μm-pre-filtered samples (cellulose nitrate, *Whatman GmbH*, Germany), 0.45 μm-pre-filtered samples, and UF permeate samples (corresponding to a pre-filtration by 0.026 μm, cf. Section 2.3) of the corresponding raw water), cf. Section 2.4.

2.3. Lab-scale UF tests

Flat-sheet UF tests were conducted using AMICON® stirred cells (*8,200*, *Millipore*, USA, stirring speed 120 rpm), with a volume of 200 mL and an effective membrane filtration area of $2.87 \times 10^{-3}\,\text{m}^2$, constantly pressurized by nitrogen gas at 1 bar. Hydrophilized polyethersulfone (PES, *UP 150*, *Microdyn Nadir GmbH*, Germany) was used as membrane material, with a molecular weight cut-off (MWCO) of 150 kDa (according to manufacturer, corresponding to a nominal pore diameter of 0.026 μm). Prior to feed water filtration, the membranes were rinsed with 2L (equivalent to $700\,\text{L}\,\text{m}^{-2}$) ultra pure water and subsequently the pure water flux was determined (filtration of 500 mL ultra pure water, J_{pure}). The pure water permeability of the applied membrane was $\sim$1,000 $\text{L}\,\text{m}^{-2}\,\text{h}^{-1}\,\text{bar}^{-1}$. UF tests comprised five repetitions (first to fifth cycles) of filtration of 500 mL feed water ($J_{\text{f-C1B}}$ = flux at the beginning of cycle 1, $J_{\text{f-C1E}}$ = flux at the end of cycle 1, and so on), followed by backwash (turning over the membrane) with 50 mL

Table 1
Averages, coefficients of variation (CV, unitless), and minima/maxima of water parameters; $n_{\text{SW}} = 21$, $n_{\text{TDW}} = 12$.

		SW			TDW		
		Average	CV	min, max	Average	CV	min, max
Temperature	[°C]	15.9	0.53	1.0, 28.9	11.9*	0.36*	5.1*, 21.1*
pH		7.6	0.03	6.9, 7.8	7.8*	0.02*	7.6*, 8.2*
κ	[μS/cm]	665	0.03	410, 883	1,278*	0.16*	1,050*, 1,720*
DOC-bypass or DOC*	[mg/L]	8.4	0.14	6.4, 11.3	11.9	0.2	7.8, 15.3
DOC_{BP} (by SEC)	[mg/L]	0.79	0.29	0.25, 1.12	0.88	0.15	0.58, 1.14
UV abs. at 254 nm	[1/m]	20.9	0.23	15.1, 30.7	28.2	0.14	21.5, 33.6
TN-bypass (by SEC)	[mg/L]	3.1	0.24	1.5, 4.9	17.0	0.21	9.7, 21.3
N_{BP} (by SEC)	[mg/L]	0.12	0.29	0.05, 0.19	0.19	0.19	0.12, 0.24
DOC_{BP}/N_{BP} (by SEC)		6.9	0.15	4.6, 8.7	4.8	0.11	4.1, 5.9
Total resistance (1. cycle)	[10^{11}/m]	19.4	0.31	7.5, 28.6	25.4	0.4	13.1, 41.0
Total resistance (5. cycle)	[10^{11}/m]	21.9	0.24	9.2, 29.8	29.3	0.34	17.0, 47.3
Irrev. resistance (1. cycle)	[10^{11}/m]	0.7	0.47	0.2, 1.7	0.8	0.38	0.4, 1.5
Irrev. resistance (5. cycle)	[10^{11}/m]	2.4	0.46	1.3, 6.7	2.8	0.23	1.8, 3.7

*Additional data ($n_{\text{min}} = 10$) from the lab of *Berliner Wasserbetriebe*, TN: total nitrogen, abs.: absorbance

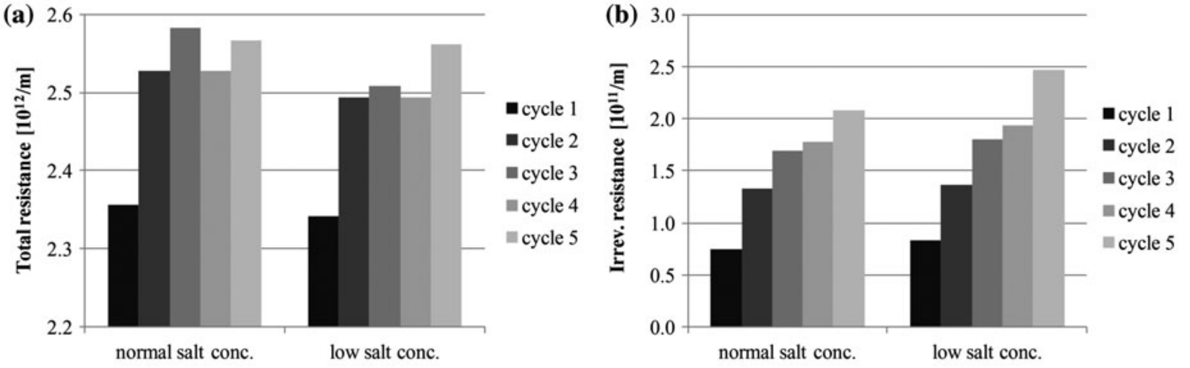

Fig. 1. Resistance at varying salt concentrations in salt solution used for backwash and flux determination; (a) total resistance and (b) irreversible resistance. "Normal salt conc.": 411 mg/L $CaCl_2 \times 2\ H_2O$, 316 mg/L NaCl; "low salt conc.": 294 mg/L $CaCl_2 \times 2\ H_2O$, 76.3 mg/L NaCl (SW).

salt solution and flux determination (with salt solution, $J_{\text{salt-C1}}$ = flux of saltwater after first cycle and backwash). Salt solution was used for backwash and flux determination, in order to reduce the impacts on the ions within the fouling layers [22,23,6], as in practical applications for backwashing, permeate which has a salt composition similar to that of the respective feed water is used. Sample water was tempered to 20°C (± 4°C) prior to UF; prior to the experiment, the temperature was measured for exact adjustment to a standard temperature (cf. Section 2.4, [24]).

2.4. Calculations

Flux data were adjusted to a standard temperature (20°C) according to Eq. (1) [24].

$$J_s = J_m \times 1.03^{(T_s - T_m)} \quad (1)$$

where J_s and J_m are standardized and measured fluxes, respectively [m s^{-1}], and T_s and T_m are standard and measured temperatures, respectively [°C].

Fouling resistance was calculated according to Eq. (2).

$$R = p/J/\eta \quad (2)$$

where R is resistance [m^{-1}], p is pressure [N m^{-2}], J is flux [m s^{-1}], and η is viscosity [N s m^{-2}]. (Henceforth, the terms total/reversible/irreversible resistances refer to total/reversible/irreversible fouling resistances, respectively.)

To calculate the *total resistance*, the relevant feed water flux ($J_{\text{f-CnE}}$ with n from 1–5) is applied in Eq. (2), whereas to calculate the *irreversible resistance*, salt solution flux ($J_{\text{salt-Cn}}$ with n from 1 to 5), measured after having backwashed the membrane, is used. *Reversible resistance* is the difference between the *total* and *irreversible resistances*. (Pure water resistance is always subtracted, as it defines the resistance of the non-fouled membrane).

The *total resistance* evoked by a specific fraction of foulants was identified by comparing resistances measured during UF of differently pre-filtered water samples (raw & 1.2 μm, 1.2 μm & 0.45 μm, 0.45 μm & 0.026 μm, and < 0.026 μm, respectively):

- R_{total} = resistance of raw water,
- $R_{>1.2\mu m}$ = difference of resistances of raw water and 1.2 μm-pre-filtered water,
- $R_{0.45\text{–}1.2\mu m}$ = difference of resistances of 1.2 μm and 0.45 μm pre-filtered waters,
- $R_{0.026\text{–}0.45\mu m}$ = difference of resistances of 0.45 μm and 0.026 μm pre-filtered waters, and
- $R_{<0.026\mu m}$ = resistance of 0.026 μm-prefiltered water.

Moreover, the following parameters were calculated: *filterability* (normalized feed water flux at the end of the first filtration cycle = $J_{\text{f-C1E}}/J_{\text{pure}}$), and *reversibility*, which is given as salt solution flux at the end of a filtration cycle, relative to pure water flux at the beginning of the experiment ($J_{\text{salt-Cn}}/J_{\text{pure}}$).

Rejection was calculated using Eq. (3).

$$r = 1 - c_p/c_f \quad (3)$$

where r is rejection, and c_p and c_f are permeate and feed concentration, respectively [mg L^{-1}].

2.5. Data evaluation

All assigned parameters were statistically evaluated using *SPSS 17* software (*SPSS*, Chicago, IL, USA). Correlation tests were carried out using the

Pearson correlation (bivariate and two-tailed). Parameters are assumed to be normally distributed and pairs of parameters are tested only for linear correlation. The terminology in this research paper refers to “not significant” if the correlation was found to range below the 95% level, and “significant” if it is above the 95% level; and “very significant” explicitly refers to a level of 99% or higher.

2.6. Analytical procedures

Dissolved organic carbon (DOC) was measured using a *Vario TOC CUBE* (*Elementar Analysensysteme GmbH*, Germany), using catalyzed-oxidized combustion. Chromatographic separation and subsequent measurement of fractionized DOC were obtained using a combined system with a liquid size-exclusion chromatography (SEC column *HW55S*, *Alltech-GROM GmbH*, Germany) and UV 254nm, organic carbon, and organic nitrogen detectors (LC-UV-OCD-OND, referred to as LC-OCD, *DOC-LABOR Dr. Huber*, Germany, [25]). The integral of the LC-OCD and LC-OND curve between retention times of 40–51 min identifies the concentration of biopolymers (measured as carbon originating from biopolymer fraction, thus referred to as DOC_{BP}) and nitrogen biopolymer concentration (measured as nitrogen stemming from the biopolymer fraction, thus referred to as N_{BP}), respectively; however, the information of the nitrogen data in the biopolymer time range is limited due to interference by the nitrate peak which can overlap with the biopolymer peak. The LC-OCD system can bypass the SEC column and determine the total DOC oxidized by UV radiation (DOC-bypass), as well as the total nitrogen (TN-bypass). A typical wastewater effluent chromatogram for carbon and nitrogen is shown in Fig. 2.

DOC data for TDW were obtained from the analytical lab of the *Berliner Wasserbetriebe*. UV absorption of water samples (0.45 µm pre-filtered) was measured at 210, 220, and 254 nm, using a UV–vis spectrometer Lambda 12 (*Perkin-Elmer*, USA), with quartz Spurasil 10 mm cuvettes (*Type No. 100-QS*, *Hellma GmbH & Co. KG*, Germany).

3. Results and discussion

3.1. Identification of major foulants in SW and TDW

The respective contribution to the *total resistance* of different fractions of water constituents (cf. Sections 2.1 and 2.4) is shown in Fig. 3, for the tested SW (a) and the TDW (b). In both water types, the dissolved substances between 0.026 and 0.45 µm contribute to about 50% of the *total resistance* observed. These sub-

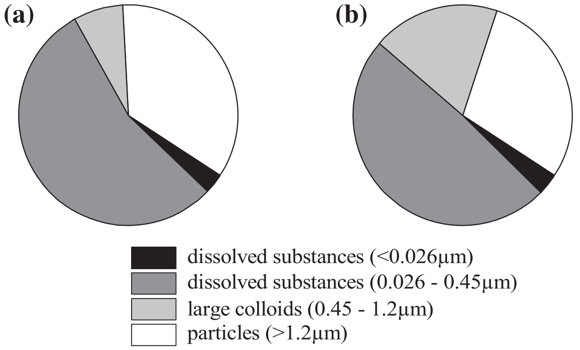

Fig. 3. Contributions to total resistance by different fractions of water constituents; (a) SW and (b) TDW.

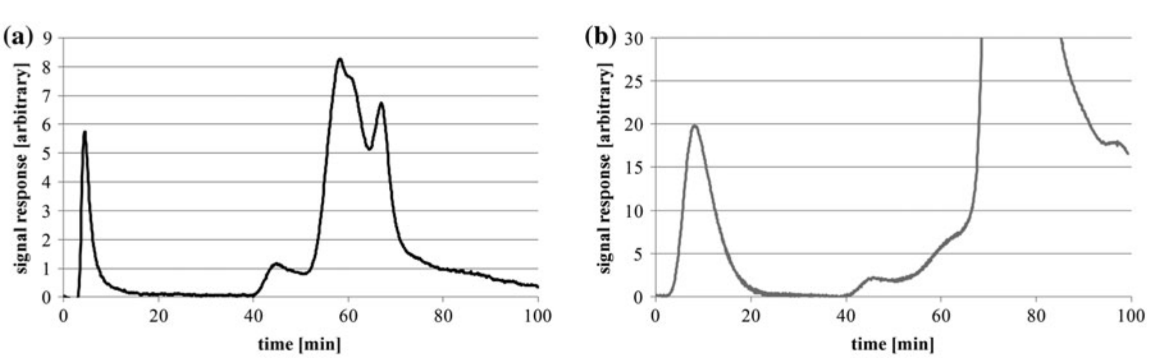

Fig. 2. Typical TDW effluent LC-OCD-OND chromatogram with bypass peak (∼1/10 of the area of the total chromatogram area, as injection volume is 100 µL for bypass and 1,000 µL for chromatogram) at the beginning; (a) signal for carbon and (b) nitrogen; the biopolymer fraction is defined as the first peak of the chromatogram, i.e. from 40 to 51 min. Note the strong interference in the nitrogen signal, starting around minute 60, which is caused by nitrate contained in the water sample.

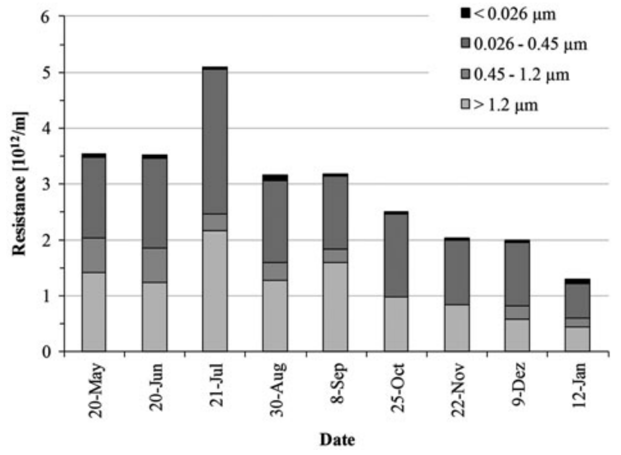

Fig. 4. Contributions to total resistance by different water constituent fractions at varying dates (SW).

stances also contain the biopolymer fraction identified by size-exclusion chromatography. For wastewater, it has been shown that biopolymer concentration correlates with fouling resistance [1]. Assuming that this correlation applies to SW, too, only filtered samples ($< 0.45\,\mu$m) were used to conduct filtration and water analysis tests, to focus on dissolved substances which comprise the organic biopolymer fraction. As shown in Section 3.2, this assumption for SW could be verified; the contribution of different fractions of SW constituents to total resistance at different dates is shown in Fig. 4.

3.2. Correlations between water quality and filtration parameters

The Pearson's correlation coefficients for pairs of relevant water quality and filtration parameters are shown in Table 2 (bottom left: SW and top right: TDW). The correlation matrices highlight overall similarities and differences between correlations of water parameters and the filtration comportments of the two waters, without accounting for seasonal variation (all data from the period of investigation are included).

The filtration behavior of both water types is similarly influenced by the respective biopolymer concentration with regard to *filterability* ($J_{\text{f-C1E}}/J_{\text{pure}}$) with slightly stronger negative correlation for the SW. Accordingly, flux decline during a filtration cycle is

Table 2
Correlation matrices with Pearson correlation coefficients of pairs of water quality and filtration parameters

	filterability	reversibility 1st cycle	total resistance 1st cycle	irreversible resistance 1st cycle	reversible resistance 1st cycle	Biopolymer concentration	DOC bypass	BP C/N	rejection	temperature	reversibility 5th cycle	total resistance 5th cycle	irreversible resistance 5th cycle	reversible resistance 5th cycle	pH
filterability		.637*	-.853**	-.586*	-.848**	-.801**	-.548	.226	-.766*	.639*	-.048	-.877**	.210	-.884**	.741*
reversibility 1st cycle	.106		-.358	-.918**	-.334	-.752**	-.748**	.280	-.370	.039	.638*	-.516	-.488	-.481	.602
total resistance 1st cycle	-.921**	-.007		.488	1.000**	.650*	.398	-.049	.521	-.711*	.332	.964**	-.214	.970**	-.656
irreversible resistance 1st cycle	.023	-.959**	-.071		.464	.810**	.810**	-.118	.219	-.014	-.490	.615*	.588*	.572	-.551
reversible resistance 1st cycle	-.918**	.040	.999**	-.119		.635*	.378	-.046	.533	-.724*	.352	.959**	-.236	.966**	-.650
Biopolymer concentration	-.873**	.124	.930**	-.186	.935**		.711**	.068	.517	-.377	-.140	.686*	.165	.670*	-.799**
DOC bypass	.262	-.234	-.249	.375	-.266	-.230		-.209	.556	.033	-.382	.473	.481	.438	-.375
BP C/N	-.481*	.159	.367	-.190	.374	.459*	-.249		-.327	.380	.024	-.169	.190	-.180	-.030
rejection	-.764**	.450*	.775**	-.513*	.795**	.802**	-.571**	.471*		-.349	-.011	.395	-.303	.438	-.369
temperature	-.845**	.237	.911**	-.294	.921**	.907**	-.329	.427*	.867**		-.699*	-.656*	.743*	-.694*	.658
reversibility 5th cycle	-.390	.577**	.366	-.623**	.395	.342	-.483*	.329	.797**	.534*		.161	-.796**	.211	-.105
total resistance 5th cycle	-.869**	-.131	.956**	.092	.947**	.914**	-.066	.326	.627**	.827**	.148		-.098	.998**	-.694*
irreversible resistance 5th cycle	.504*	-.468*	-.415	.609**	-.443*	-.375	.605**	-.356	-.782**	-.547**	-.931**	-.177		-.162	.244
reversible resistance 5th cycle	-.926**	-.029	.983**	-.036	.980**	.943**	-.185	.410	.744**	.892**	.329	.978**	-.366		-.694*
pH	.176	-.001	-.237	.020	-.234	-.002	.181	.024	-.250	-.185	-.252	-.066	.198	-.085	

Light grey: SW matrix; dark grey: TDW matrix; *: significant, **: very significant; and n_{SW}: 22, n_{TDW}: 12, unless indicated otherwise.

proportional to the biopolymer concentration of the respective water, independent of the origin of the water. *Filterability* provides information about the filtration behavior for the first cycle and therefore is not suitable to project irreversible fouling trends.

This is different with *reversibility* ($J_{\text{salt-Cn}}/J_{\text{pure}}$) as this parameter considers information on irreversibility and extended filtration performance. Increasing loads of the biopolymer foulants effect decreasing *reversibility* in early filtration ($J_{\text{salt-C1}}/J_{\text{pure}}$) of the TDW. However, these correlations are not significant at the end of filtration ($J_{\text{salt-C5}}/J_{\text{pure}}$). There is no such development of the correlation of SW biopolymer concentration and *reversibility* as it is not significant at any time.

Temperature of both of the waters correlates significantly with the respective total and reversible resistances, as well as with reversibility/irreversible resistance (fifth cycle). However, the corresponding correlations have opposite algebraic signs in the case of SW as opposed to TDW. With respect to reversibility, the correlation is positive in the case of SW but negative in that of TDW. Hence, increased temperatures come along with readily backwashable fouling in filtering SW but coincide with irreversible fouling in filtering TDW. This finding may be useful for future fouling prediction in UF of either of these waters. The results suggest that the respective water temperature can be applied as an easy-to-use indicator for the overall water quality affecting total/reversible, and particularly irreversible fouling.

The results show that irreversible fouling develops differently during ongoing filtration of both tested waters and a likely reason for this may be differences in the properties of biopolymer and DOC compounds and potential foulant interactions. With respect to the biopolymer C/N (BP C/N) ratio, we did not find significant correlations to filtration parameters (except *filterability* in the case of SW). Thus, the DOC_{BP}/N_{BP} ratio turns out to contain little information on fouling, possibly due to the limited resolution and insufficient yields of the N detection within the range of biopolymers.

Further differences in filtration behavior are highlighted by the relationship between *rejection* of biopolymers (rejection_{BP}) and determined filtration parameters for both waters such as *filterability*, *total resistance*, *reversible resistance*, *irreversible resistance* and the further differentiation of these possible indicators for proceeding filtration (first and fifth filtration cycles, with the exception of *filterability*). In TDW, a significant (negative) correlation to rejection_{BP} can only be identified for *filterability*. Accordingly, *filterability* is the lower, the stronger biopolymers are rejected at the membrane, which supports former studies [26,1,2]. For all other filtration parameters, no correlation with rejection_{BP} could be found in TDW.

In plain contrast, in filtering SW, the *rejection* of biopolymers shows significant correlation to all filtration parameters. The correlation coefficients of parameters linked to irreversible fouling (*reversibility* and *irreversible resistance*) highlight that irreversible fouling is decreased if biopolymers are well held back by the membrane. Moreover, these coefficients increase during ongoing filtration (fifth cycle compared to first cycle), indicating that the impact of *rejection* is especially crucial for long-term fouling development. This means that in filtering SW, highly strained biopolymer loads can form a compact fouling layer on the membrane and this fouling layer is more readily backwashable (increasing *reversibility*). Opposed to these findings, rejection of TDW biopolymers demonstrated overall decreased variation compared to that of the SW biopolymers and only correlated with filterability, pointing to decreased impact of biopolymer straining on irreversible fouling in the filtration of the TDW.

3.3. Seasonal variation

3.3.1. Organic water parameters

The seasonal developments of biopolymer characteristics and water temperatures are shown in Fig. 5. In the SW, the biopolymer concentration (represented by carbon content) and temperature are low in spring, increasing steeply towards summer and decreasing again during autumn and winter. A similar development is not observable in the TDW where values are coarsely spread. In the TDW, there is a trend of overall lower values in summer than in winter, possibly due to increased microbial decomposition of wastewater constituents at higher temperatures in summer [26,27]. The carbon-to-nitrogen ratio is slightly higher in summer than in winter for both waters but the seasonal variation is small; it is higher in the SW than in the TDW, suggesting a higher amount of protein-like substances in the latter [28,26].

The seasonal water quality data for the SW and the TDW point up their different origins. SW biopolymer concentration reflects the microbial activity in a eutrophic SW body which is restrained to the boundaries of seasonal change, such as temperature and sunlight radiation [29]. In contrast, the TDW lacks a distinct seasonal development as of the comparatively constant quality of its origin. Seasonal patterns for the total DOC of the studied waters are shown in Fig. 6.

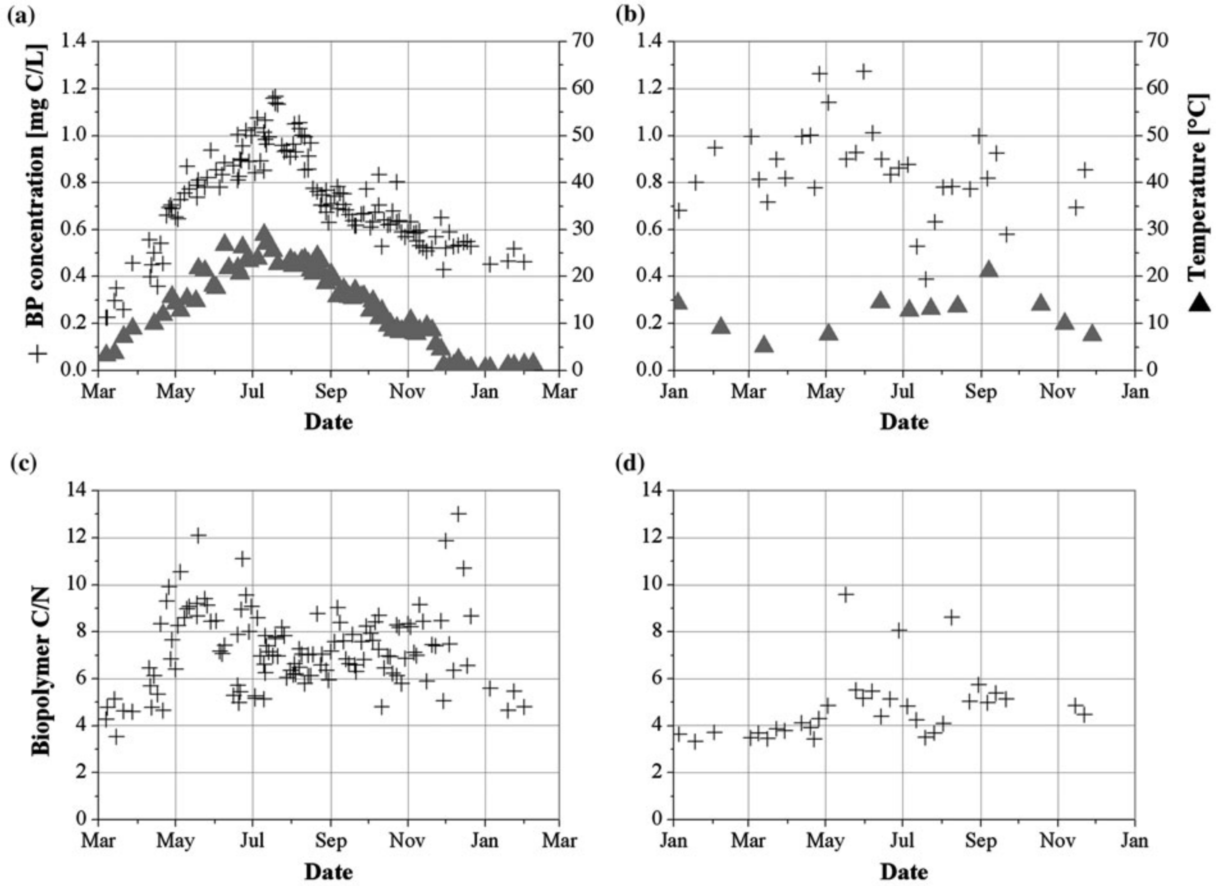

Fig. 5. Seasonal development of biopolymer concentration and temperature, and biopolymer carbon-to-nitrogen ratio (DOC_{BP}/N_{BP} ratio), ((a) and (c)): SW, ((b) and (d)): TDW).

3.3.2. Filterability and total resistance

As shown in Fig. 7, *total resistance* (either at first or fifth cycle) inclines until mid-summer and declines thereafter in the filtration of the SW, whereas for the TDW, *total resistance* is overall higher during the first half of the year but misses a smooth development similar to that in the filtration of the SW. The increase of *total resistance* from first to fifth filtration cycles is comparatively small in summer but larger in winter for the SW; for the TDW, the opposite is the case.

3.3.3. Ratio of irreversible to total resistance

The *ratio of irreversible to total resistance* is shown in Fig. 8, for the experiments conducted during the monitoring period of both of the tested waters. As for other parameters in filtering the SW, the *ratio of irreversible to total resistance* shows a seasonal dependency, however, the development is opposite to that of *total resistance* which peaks in summer and hits the bottom in winter/spring. Moreover, the development of the *ratio of irreversible to total resistance* is in general opposite to that of the biopolymer concentration (compare Fig. 5). However, a detailed view into Fig. 8 shows that at the end of the year when biopolymer concentration in SW is constant, the *ratio of irreversible to total resistance* is strongly increasing, even more pronounced for the fifth filtration cycle (November–February). The data clearly reveal that irreversible fouling is not only depending on biopolymer concentration but also on foulant properties which appear to be shifting during the investigated period, as indicated by a decline of the biopolymer C/N ratio during winter/spring (see Fig. 5(c)).

Biopolymer loads to the membrane in filtering SW are maximal in summer, favoring pronounced cake layers being formed during filtration. Thus, foulants arriving at the membrane surface can be easily hindered from attaching to it and accordingly, are better removable during backwash, leading to highly reversible fouling [30]. During the cold season, the concentration of biopolymers as well as the foulant properties change.

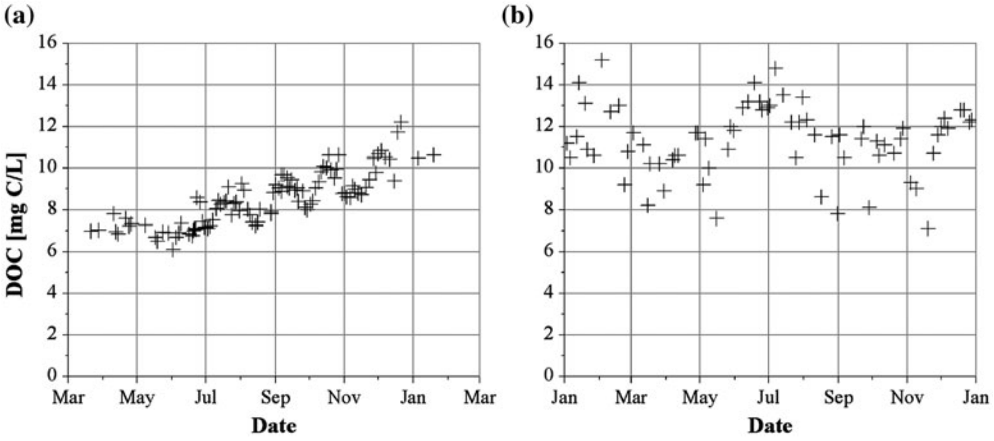

Fig. 6. Dissolved organic carbon (DOC) during the respective monitoring periods, (a) SW, (b) TDW (data from the lab of *Berliner Wasserbetriebe*).

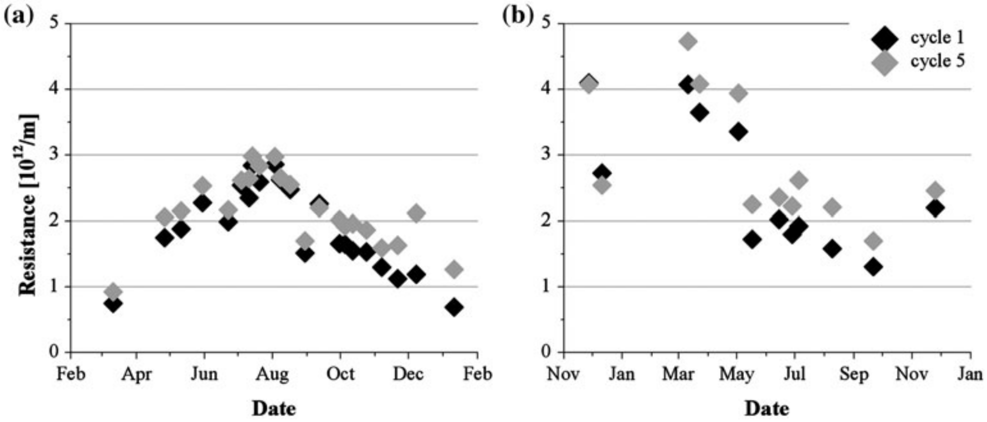

Fig. 7. Total resistance during the period of observation; (a) SW, and (b) TDW.

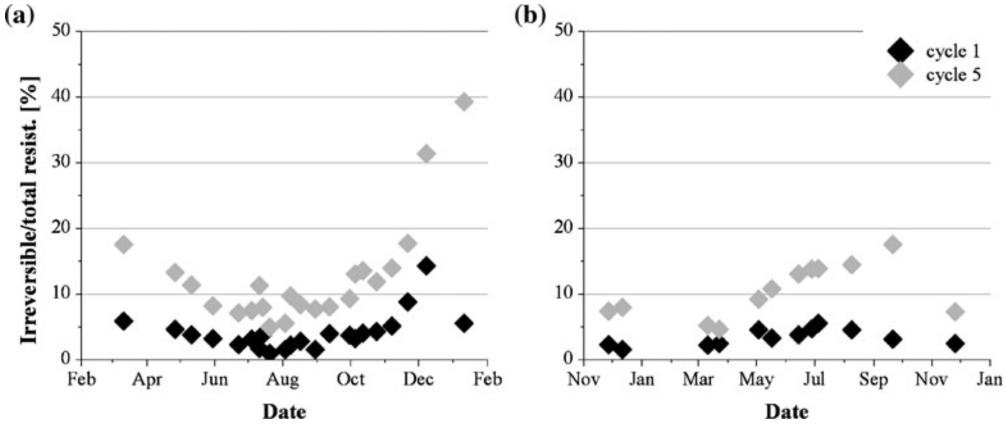

Fig. 8. Ratio of irreversible to total resistance: (a) SW and (b) TDW.

The TDW shows some seasonality as the *ratio of irreversible to total resistance* is increased during summer and autumn compared to that in winter and spring, at least for the fifth cycle. The curve in Fig. 8 (b)) is roughly opposite to that observed in SW filtration. The percentage of irreversible fouling is clearly larger for SW than for TDW in the winter season, at least in the fifth filtration cycle.

4. Conclusions

In the present study, water quality parameters and UF filtration behavior of SW and TDW were correlated, and monitored seasonally. The filtration procedure comprised five cycles, to account for initial and proceeded filtration behavior.

The concentration of biopolymers (DOC_{BP}) correlates significantly with *filterability,* as well as *total* and *reversible resistances* in both waters, which confirms earlier studies [26], [1], [2]; and similar DOC_{BP} in SW and TDW effectuate comparable *total* and *reversible resistances*. However, no connection between biopolymer concentration and irreversible fouling parameters could be established. Therefore, irreversible fouling must be accountable on other water characteristics such as organic foulant properties and foulant interactions; at similar DOC_{BP}, TDW exhibits higher irreversible fouling than SW while biopolymer C/N-ratio is overall lower in TDW than in SW, indicating that higher protein contents in TDW may be the reason. Combinations of LC-OCD and techniques which aim more precisely at protein-like compounds should be employed for foulant characterization in the future. Furthermore, the rejection of biopolymers relates to *reversibility* in SW, indicating that fouling layers that are well held back at the membrane contain more reversible biopolymers.

Temperature of both waters has clear correlations with the filtration parameters but the effects are completely adverse in SW and TDW. Total and reversible resistances relate positively to temperature in SW but negatively in TDW, whereas irreversible fouling relates negatively to temperature in SW but positively in TDW. We suggest that water temperature does *not directly* affect filtration but rather indicates different water composition and/or quality which affect filtration. Nevertheless, and despite the adverse correlations in SW and TDW, the potential of water temperature to indicate total/reversible fouling, and especially irreversible fouling, is shown here. The use of temperature as an indicator for reversible/irreversible fouling needs to be tested for other membrane types (material, molecular weight-cutoff, etc.).

The extension of the observations to a seasonal scale demonstrates that inter-annual change affects the water/filtration parameters and accordingly underlines that one-time/random UF experiments may only have little informative value. In the SW, the biopolymer concentration shows a strong seasonal dependency, this is not the case for the TDW. Similar to the seasonality of water quality parameters, the inter-annual change of filtration characteristics is more pronounced in the SW than in the TDW. In the SW, total resistance depicts a curve similar to that of the biopolymers. In contrast, the irreversible amount in total resistance is overall low in summer and high in the winter months but varies at similar biopolymer concentrations and also develops unequal during ongoing filtration in different UF experiments. These findings further point to the importance and the seasonal change of the properties of and interactions between irreversible foulants.

The outcomes of the multi-cycle filtration tests show clearly that both of the waters tested exhibit different filtration comportment during proceeding filtration, indicating that fouling develops differently. Some parameters exhibited significant correlations only at the beginning or at the end of the experiments, but not throughout the entire five-cycle procedure, highlighting the importance of multi-cycle tests to increase the significance of results, especially with regard to irreversible fouling.

Acknowledgments

This study was performed within the BMBF (German Federal Ministry of Education and Research) research projects "Membranbiofouling" (contract number 02WT1046) and "Sustainable water concept and its application for the Olympic Games 2008—Phase II" (Contract no.: 02WA1016). Funding of BMBF is greatly acknowledged. The authors also like to thank the Berliner Wasserbetriebe (BWB) for continuous support and access to their treatment facilities. The laboratory support of Ulrike Förster, Katrin Noack, Christopher Gabler (Chair of Water Quality Control, TU-Berlin), and Stephan Plume (DVGW-Technologiezentrum Wasser, Außenstelle Dresden, Germany) is greatly acknowledged.

List of symbols

c_f	—	foulant concentration in feed	$[mg\,L^{-1}]$
c_p	—	foulant concentration in permeate	$[mg\,L^{-1}]$
J	—	flux	$[m\,S^{-1}]$
J_S	—	standardized flux	$[m\,S^{-1}]$
J_M	—	measured flux	$[m\,S^{-1}]$
p	—	pressure	$[N\,m^{-2}]$
r	—	rejection	[–]
R	—	resistance	$[m^{-1}]$
η	—	dynamic viscosity	$[N\,S\,m^{-2}]$
T_S	—	standard temperature	[°C]
T_M	—	measured temperature	[°C]

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