Desalination and Water Treatment
www.deswater.com

36 (2011) 344–353
December

1944-3994/1944-3986 © 2011 Desalination Publications. All rights reserved
doi: 10.5004/dwt.2011.2524

The impact of natural organic matter seasonal variations in drinking water quality

Margarida Ribau Teixeira[a*], Luís Miguel Nunes[b]

[a]*CENSE, Center for Environmental and Sustainability Research, University of Algarve, Faculty of Sciences and Technology, building 7, Campus de Gambelas, 8005-139 Faro, Portugal. Tel.: +351289800900ext7235; email: mribau@ualg.pt*
[b]*CVRM, Geo-Systems Center, University of Algarve, Faculty of Sciences and Technology, Campus de Gambelas, 8005-139 Faro, Portugal*

ABSTRACT

Seasonal variations imply new challenges in operational control and engineering design for water treatment plants. The purpose of this study is to measure and compare the molecular weight (MW) of natural organic matter (NOM) in different seasons and drinking water stages by high-performance size-exclusion chromatography to better understand the impact of organic matter removal on the trihalomethanes present in drinking water. Ultraviolet absorbance at 254 nm, dissolved organic carbon and inorganic parameters are measured between June 2008 to July 2009 to provide additional information of MW and NOM in different water treatment stages. Results demonstrated that summer and spring are the seasons when waters have organic compounds of highest MW, when the highest removals of these compounds are obtained with the water treatment, but also with the highest concentrations of trihalomethanes in drinking water. Furthermore, waters from spring and especially summer are considered to exhibit predominantly organic character, whereas fall and winter waters are more influenced by their physical and chemical signature. Results also showed that trihalomethanes in drinking water are influenced by the quantity and also by the composition of NOM, which resulted in the proposal of a model relating the two. UV_{254} and organic matter molecular weight are considered as very good indicator parameters to measure overall water treatment efficiency.

Keywords: Natural organic matter; Molecular weight; Trihalomethanes; Seasonal variation; Water treatment

---

1. Introduction

Natural organic matter (NOM) has become of significant relevance to the water treatment managers since its relation to public health was recognised. NOM is a complex mixture of organic materials present in natural waters, the structure and physicochemical properties of which depends mainly of climate, source and season [1,2]. NOM plays an important role in water treatment because it causes colour, taste and odour, acts as precursor of disinfection by-products (DBP) and promotes microbial regrowth in distribution systems [3,4]. In addition, NOM affects significantly the treatment operation – controls coagulant and disinfectant demand [5], blocks activated carbon pores and competes with taste and odour compounds for available adsorption sites [6], and is one of the major membrane foulants [7]. Therefore, the changes in NOM composition and concentration over time should be properly controlled by water treatment operators. Also, some authors [8–11] referred recently an increase of NOM concentration in natural waters on the last decade,

---

*Corresponding author

as a result of the global warning, intense rain events, and declining acid deposition and rising temperatures.

Molecular weight (MW) is a key factor in behaviour of NOM reactivity and has been used as an important tool in recent years to understand NOM in drinking water operation and optimization [12–15]. Typically high MW NOM is more amenable to removal by coagulation than low MW compounds [14,16] and tend to be more hydrophobic-aromatic (ArOH) and with higher electrostatic potential [17]. Matilainen et al. [14] observed that after coagulation, flotation is more efficient than conventional sedimentation for higher removal of MW compounds. Ozonation oxidizes high MW compounds to low MW and decreases UV-absorbing organic fractions [13]. Low MW NOM is better removed with activated carbon [12,14] but these compounds can block pores [6] due to their smaller radii. They tend to be more soluble and hydrophilic-aliphatic (COOH) [17]. Charged low MW NOM is efficiently retained by nanofiltration while neutrals of low MW pass to a relatively large extent through the membranes (10–20% DOC reduction) [18].

High performance size exclusion chromatography (HPSEC) has become a useful technique for organic characterisation in water treatment processes, because it is a rapid and reproducible method for characterising MW [12–15]. This technique separates NOM fractions by MW through differential permeation of molecules into a porous solid phase. Molecules larger than the gel pores move rapidly through the column, while the smallest molecules penetrate into the gel pores and are eluted last [19]. According with Allpike et al. [15] and Chow et al. [20], nonideal interactions between column stationary phase and solute take place and the use of known MW standards that may not be representative of the true hydrodynamic size of NOM molecules, make the term ''apparent'' MW more adequate. This was the definition used.

This study intended to evaluate the effectiveness of the conventional drinking water treatment on the removal of different molecular size fractions of NOM, and understand the seasonal variations of molecular NOM size in relation with the processes and the formation of trihalomethanes (THM). Seasonal characterization of physicochemical properties of NOM may provide detailed information to understand, check and optimise drinking water treatment.

2. Materials and methods

2.1. Water treatment processes and water samples

Water samples were collected at four locations within the Alcantarilha water treatment process once a month, and twice a month in summer and winter for one year, between 2008 July and June 2009. The four samples collected were: (i) *raw water* (RW); (ii) after ozonation, *ozonated water* (OW); (iii) after coagulation (C)/ flocculation (F)/ sedimentation (S), *decanted water* (DW); and (iv) after disinfection, treated water (TW). This water treatment plant pumps surface water from Funcho reservoir (2 km^2 and 43.4×10^6 m^3) in Algarve, southern Portugal. Due to seasonal variations in surface water quality and strong water demand (ca. 650,000 people in summer; 180,000 people in winter) Funcho surface water is mixed with groundwater from the large Querença-Silves carbonate aquifer.

2.2. HPSEC analysis

The operating HPSEC system consisted of a Dionex Summit high-pressure gradient pump, an autosampler (Dionex ASI-100), a column thermostat (Dionex STH-585) and a photo diode-array detector (Dionex PDA-100). NOM was separated with a TSK-G3000SW$_{XL}$ column (30 cm × 7.8 mm ID) protected by a TSK-SW$_{XL}$ guard column (4.0 cm × 6.0 mm ID) (Tosoh Biosciences, GmbH). TSK gel packing is silica-modified with hydrophilic diol groups and separation range is between 1 and 35 kDa (polyethylene glycol). Sodium acetate 0.01 M at pH 7 (pH adjusted using acetic acid, VWR) was used as eluent. The flow rate was 1 mL/min, injection volume 100 μL and analysis time 17 min with UV detection at 254 nm. This solution was vacuum-filtered through a 0.2 μm hydrophilic polypropylene membrane filter (Pall Corporation). The system was calibrated with sodium polystyrene sulfonates (PSS) standards of the following MWs: 17,000, 6,800 and 4,300 Da (Fluka) and acetone 58 Da (VWR International). All standards were dissolved in chromatographic eluent at a concentration of 1 mg/L. The calibration equation used was: $\log M_{Wi} = -0.312\mathrm{Rt}_i + 6.194$ ($n = 4$, $R^2 = 0.991$): where M_{Wi} is the MW and Rt_i the retention time of some solute at *i*th point (peak position calibration). The column void (V_o, 7.5 mL) and permeation (V_p, 18 mL) volumes were determined using Blue Dextran (2000 kDa, Sigma) and acetone (58 Da). All water samples were filtered through a pre-rinsed 0.45 μm polycarbonate membrane filter (Aquatron CA, 30 mm) and analysed in the same day or the day after collection (4°C cooled).

The number-averaged (M_n) and weight-averaged (M_w) MWs were determined using equations proposed by Yau et al. [21]. Polydispersivity (ration between M_w/M_n) was also calculated and is a measure of the sample heterogeneity [22].

2.3. Analytical methods

All samples were analysed based on procedures described in Standard Methods [23]. Identical samples of HPSEC were used for dissolved organic carbon (DOC) measurement and spectroscopic analysis. The concentration of DOC was measured using Shimadzu TOC-5000A analyzer, which was calibrated with potassium hydrogen phthalate standards at concentrations ranged 1–10 mg C/L. UV absorption was acquired at 254 nm with a Beckman DU 640B spectrophotometer. The specific UV absorbance at 254 nm (SUVA), the ratio of UV 254 nm absorbance and DOC, was determined and is an indicator of the relative aromaticity of DOC. THM were determined using gas chromatography-mass spectrometry (GC-MS) method 6232C [23]. The analyses were made by a certified laboratory.

3. Results and discussion

3.1. Water quality

Table 1 summarizes source water quality for the period of one year (July 2008 to June 2009), as well as water quality from different treatment stages (RW, OW, DW, TW).

Source water (RW) was hard [24] during the studied period and conductivity was higher than 500 μS/cm (Table 1). These characteristics were due to the mixture of groundwater/surface water in consequence of seasonal variations in water quality, strong water demand in summer and low rainfall observed during the period. Groundwater from Querença-Silves aquifer is of very good quality water in terms of organic matter, containing concentrations of DOC and total organic carbon (TOC) always below the quantification limit of 0.5 mg/L, and 0.004 ± 0.002 1/cm of UV_{254}. As a consequence, the resolution of the HPSEC peaks results was very poor. Therefore, organic matter present in the blended RW must have come almost exclusively from surface water. Results also showed that the highest UV_{254} absorbance and SUVA values were obtained during the hot period (summer and spring, Table 1). As SUVA is related to the carbon aromaticity content in NOM and in consequence with DBP formation [25], from these results hot periods should have higher DBP potential formation than cold periods (fall and winter). In addition, SUVA values were always lower than 3 L/(m.mg), implying that RW NOM was mainly composed of nonhumic substances, hydrophilic, less aromatic and of lower MW compared to waters of higher SUVA values [26]. For DOC, concentrations were low (ca. ≤ 2 mg/L), with the lowest values observed in winter, and high, but similar concentrations, during the remaining seasons (Table 1).

As ozone oxidizes organic compounds present in water, especially UV-absorbing organic fractions, OW presented lower UV_{254} values than RW, and as a result the SUVA of the former also decreased in all seasons (Table 1). However, fall and winter showed again lower values of UV_{254} and SUVA than the other two seasons. DOC slightly decreased or remained equal to RW DOC, as organic matter became more fragmented, with lower MW, when ozonation takes place [5].

C/F/S reduced the amount of organic material present in water, as shown by the decrease in the values of DOC, UV_{254}, SUVA and turbidity, for all seasons, from OW (and RW) to DW (Table 1). However, as DOC from RW was relatively low (Table 1) and as C/F/S was designed and optimised to reduce target parameters such as turbidity, DW DOC showed an average reduction of only ca. 26% in the hot period and ca. 14% in the cold period after C/F/S.

TW results were quite similar to those of DW especially for UV_{254} absorbance and SUVA (Table 1). DOC and turbidity decreased due to chlorination because chlorine oxidizes both dissolved and particulate organic matter. Seasonally, waters had similar values after coagulation indicating the presence of the same remaining organic compounds after treatment. However, an increase in RW NOM induced an increase in TW NOM (Table 1).

For inorganic parameters like Ca^{2+}, Mg^{2+} and Br^{-}, no significant differences were observed during hot and cold periods and along treatment (Table 1).

3.2. Changes in MW during water treatment process and seasons

Generally, the chromatograms of the studied waters showed an MW distribution between ca. 2,400 and 200 Da (Fig. 1). The chromatograms represent the average MW for each season. These fractions may comprise medium-low MW humic substances and fulvic acids conjugated with unsaturated acids [15]. Fig. 1 also shows different chromatograms between seasons. Summer and spring presented similar chromatogram shapes, whereas similar shapes are also observed between fall and winter. The main differences between hot and cold periods are in fractions I and VI. During hot periods fraction I is much better defined and fraction VI practically does not exist (Fig. 1a and 1d). During the cold period, fraction I is not well defined being fractions V and VI the most representative (Fig. 1b and 1c). This indicates that higher MW compounds were more present during hot periods, while during cold periods the most relevant compounds were of lower MW classes. These results are in accordance with results obtained for SUVA (Table 1) which

Table 1
Water quality at different treatment stages during one year (confidence interval for the mean value with $\alpha = 0.05$, n = 4)

	Summer (21 Jul–1 Sep)				Fall (6 Oct–22 Dec)				Winter (5 Jan–2 Mar)				Spring (6 Apr–2 Jun)			
	RW	OW	DW	TW	RW	OW	DW	TW	RW	OW	DW	TW	RW	OW	**DW**	**TW**
pH	7.19 ± 0.13	7.18 ± 0.14	7.17 ± 0.10	7.26 ± 0.10	7.44 ± 0.06	7.42 ± 0.08	7.50 ± 0.12	7.68 ± 0.06	7.40 ± 0.11	7.44 ± 0.09	7.41 ± 0.04	7.57 ± 0.08	7.41 ± 0.10	7.37 ± 0.07	7.40 ± 0.10	7.52 ± 0.08
Conductivity (μS/cm)	513 ± 11	482 ± 21	400 ± 153	464 ± 94	627 ± 46	638 ± 63	654 ± 30	672 ± 30	657 ± 37	657 ± 38	661 ± 51	665 ± 40	585 ± 33	557 ± 67	600 ± 17	613 ± 19
Hardness (mg/L $CaCO_3$)	197 ± 11	193 ± 12	190 ± 10	190 ± 8	286 ± 22	279 ± 32	287 ± 31	294 ± 20	269 ± 26	271 ± 24	279 ± 22	279 ± 26	256 ± 25	239 ± 3	236 ± 3	243 ± 5
Br^- (μg/L)	158 ± 9	155 ± 6	–	–	163 ± 5	158 ± 12	–	–	163 ± 5	168 ± 5	–	–	–	165 ± 24	–	–
Ca^{2+} (mg/L)	41 ± 3	40 ± 3	39 ± 3	39 ± 2	66 ± 6	64 ± 9	66 ± 9	68 ± 6	62 ± 6	62 ± 5	64 ± 5	64 ± 6	57 ± 5	54 ± 1	53 ± 0	54 ± 2
Mg^{2+} (mg/L)	23 ± 1	23 ± 1	23 ± 1	22 ± 0	30 ± 1	29 ± 2	30 ± 1	30 ± 1	28 ± 3	28 ± 3	29 ± 3	29 ± 3	28 ± 2	26 ± 0	25 ± 0	26 ± 0
Turbidity (NTU)	1.47 ± 0.57	2.00 ± 0.82	0.73 ± 0.54	0.09 ± 0.03	0.60 ± 0.21	0.80 ± 0.41	0.16 ± 0.12	0.12 ± 0.07	1.15 ± 0.49	1.35 ± 0.41	0.42 ± 0.11	0.17 ± 0.05	10.1 ± 4.04	9.89 ± 4.77	1.91 ± 0.89	0.14 ± 0.04
DOC (mg/L)	2.12 ± 0.22	2.04 ± 0.27	1.55 ± 0.29	1.55 ± 0.25	1.77 ± 0.05	1.81 ± 0.41	1.55 ± 0.30	1.37 ± 0.29	0.95 ± 0.14	0.99 ± 0.12	0.78 ± 0.16	0.73 ± 0.08	1.76 ± 0.22	1.59 ± 0.20	1.32 ± 0.38	1.07 ± 0.14
UV_{245} (1/cm x 100)	3.6 ± 0.4	2.0 ± 0.3	1.0 ± .0.3	1.0 ± 0.3	1.7 ± 0.6	1.0 ± 0.4	0.6 ± 0.4	0.7 ± 0.5	1.5 ± 0.3	0.6 ± 0.2	0.3 ± 0.2	0.3 ± 0.1	3.3 ± 1.4	1.9 ± 0.6	0.9 ± 0.4	0.9 ± 0.6
SUVA (L/ m.mg)	1.91 ± 0.11	1.01 ± 0.24	0.67 ± 0.14	0.64 ± 0.20	0.96 ± 0.21	0.56 ± 0.17	0.36 ± 0.25	0.42 ± 0.14	1.52 ± 0.31	0.62 ± 0.21	0.26 ± 0.07	0.25 ± 0.04	2.24 ± 0.8	1.19 ± 0.31	0.68 ± 0.29	0.80 ± 0.43

RW – Raw Water; OW – Ozonated Water; DW – Decanted Water; TW – Treated Water.

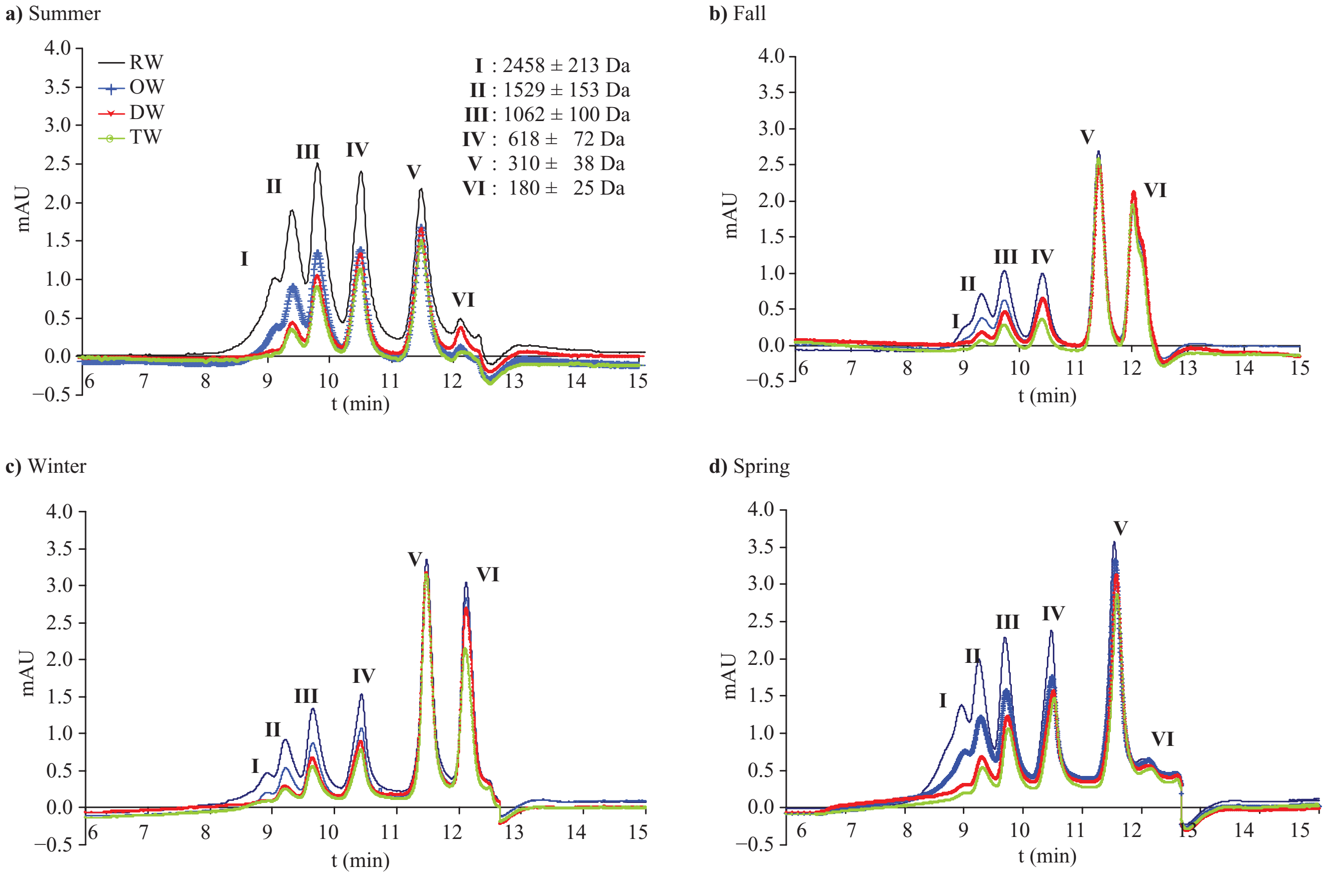

Fig. 1. HSPEC chromatogram for water samples collected in stages along the water treatment process in different seasons.

were also higher during the hot periods. However, the aggregated SUVA parameter is not sufficiently detailed, as reported by Allpike et al. [15], to explain the seasonal differences observed in MWs.

In addition, the amount of natural organic matter decreased along the treatment process (Fig. 1) from RW to TW, in all fractions and seasons, since the height of the peak in the HPSEC chromatogram refers to the amount of NOM in specific molecular size fraction [14]. The MW of RW was the highest and MW always decreased along the treatment process (Figs. 1 and 2). Higher decreases in MW were observed during seasons when waters presented higher MW (hot period) (Fig. 2). However, this higher decrease was not sufficient to bring NOM concentrations in TW to values lower than those of raw source water during fall and winter (Table 1 and Fig. 2). In addition, compounds present in winter are more difficult to remove as a whole as indicated by the lowest DOC concentration and quantity of compounds with low MW (Table 1 and Fig. 1c and 2). Compounds with the highest MW (fractions I and II) were primarily removed while a limited reduction of the lowest MW compounds was observed (Figs. 1 and 2). These results are related with the water treatment since pre-ozonation oxidizes organic matter present in water to lower MW compounds and more polar species, therefore decreasing the sum of the HPSEC peaks height and shifting the MW towards smaller weights. Similar results were obtained by Vuorio et al. [12] and Nissinen et al. [13]. C/F/S process decreases effectively the NOM content [2,5], leading to the elimination of the first fraction, i.e., the largest MW fraction (Figs. 1 and 2c). As reported by Amy et al. [27] and Owen et al. [28], coagulation better removes larger molecular size, hydrophobic, acidic molecules than the smaller molecules. The lowest MW compounds are more difficult to remove by conventional water treatment process, which justifies the insignificant removal of these compounds observed in all seasons (fractions V and VI, Figs. 1 and 2). These results were corroborated by the change in polydispersivity ($\triangle\rho$) after treatment, determined according with Fabris et al. [2], as indicated by a large reduction in polydispersivity observed throughout the year ($-0.167 > \triangle\rho > -0.174$, $\alpha = 0.05$, $n = 14$).

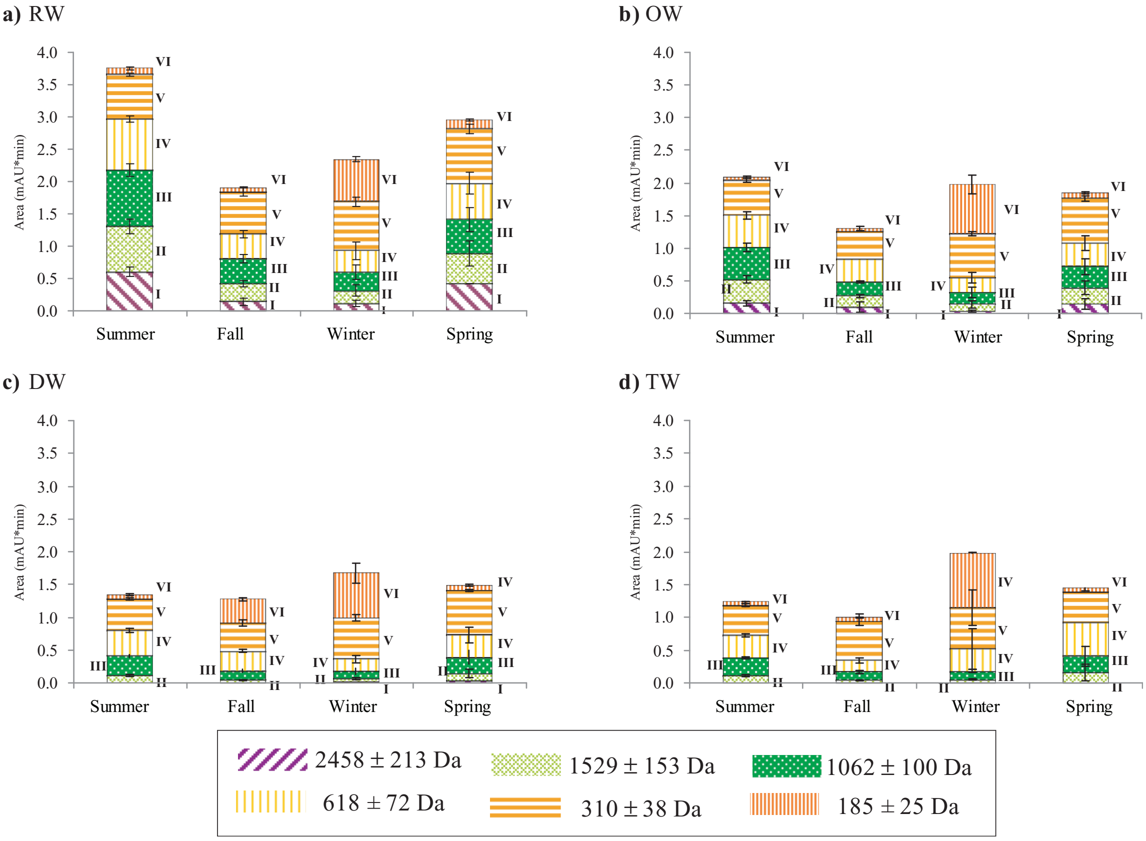

Fig. 2. Seasonal variation in MW distribution for waters collected in stages along water treatment process (confidence interval for the mean value with $\alpha = 0.05$, $n = 4$).

Principal component analysis (PCA) was used to better interpret water quality data, namely as to the effect of seasonality and treatment processes in water quality. ACP was made including all variables from Table 1. Two components (axis) were considered enough for the intended evaluation as they represented together a total of over 81% of data variance. Component 1 identifies seasonal variation, allowing clear distinction between hotter periods and colder ones (Fig. 3b). The former are associated with higher concentrations of organic matter with high MW. Fall and winter project on the negative side of the component together with all inorganic parameters, indicating that the water ‘‘chemical signature’’ is physical-chemical (Fig. 3a and 3b). Spring and especially summer have in opposition ‘‘organic signature’’.

Fig. 3b also shows a very clear distinction between the chemical signatures of water along the treatment processes. As the treatment process evolves the chemical signature progresses from waters containing more organic matter of higher MW to waters with lower, but still maintaining a relatively constant value of DOC and physical-chemical parameters, whereas UV_{254} and organic matter molecular weight decreased between ca. 3 and ca 5 times. UV_{254} and organic matter molecular weight were considered, therefore, as very good indicator parameters to measure overall water treatment efficiency and progression. UV_{254} and fractions II to IV clearly define the progression from RW to TW (Fig. 3).

3.3. Organic matter and its contribution to THM

Seasonal variation of THM in TW is presented in Fig. 4. THM showed significant seasonal variability (one way ANOVA, $F(3,11) = 10.8$, $p = 0.0013$), being the hot period statistically different from the cold one (t-test, $p < 0.05$). The highest concentrations of THM were observed in summer and spring, which could be attributed to a higher organic matter concentration [29] as a result of reactions between chlorine and organic matter. Uyak et al. [30] concluded that seasonal variations in DBP were associated to changes in NOM quantities and characteristics of water sources. These authors also referred that a higher DOC level is likely to produce more THM. However, during fall and spring DOC concentrations were similar while THM was higher in spring (Fig. 4). In this season, a higher amount of compounds with high MW were present

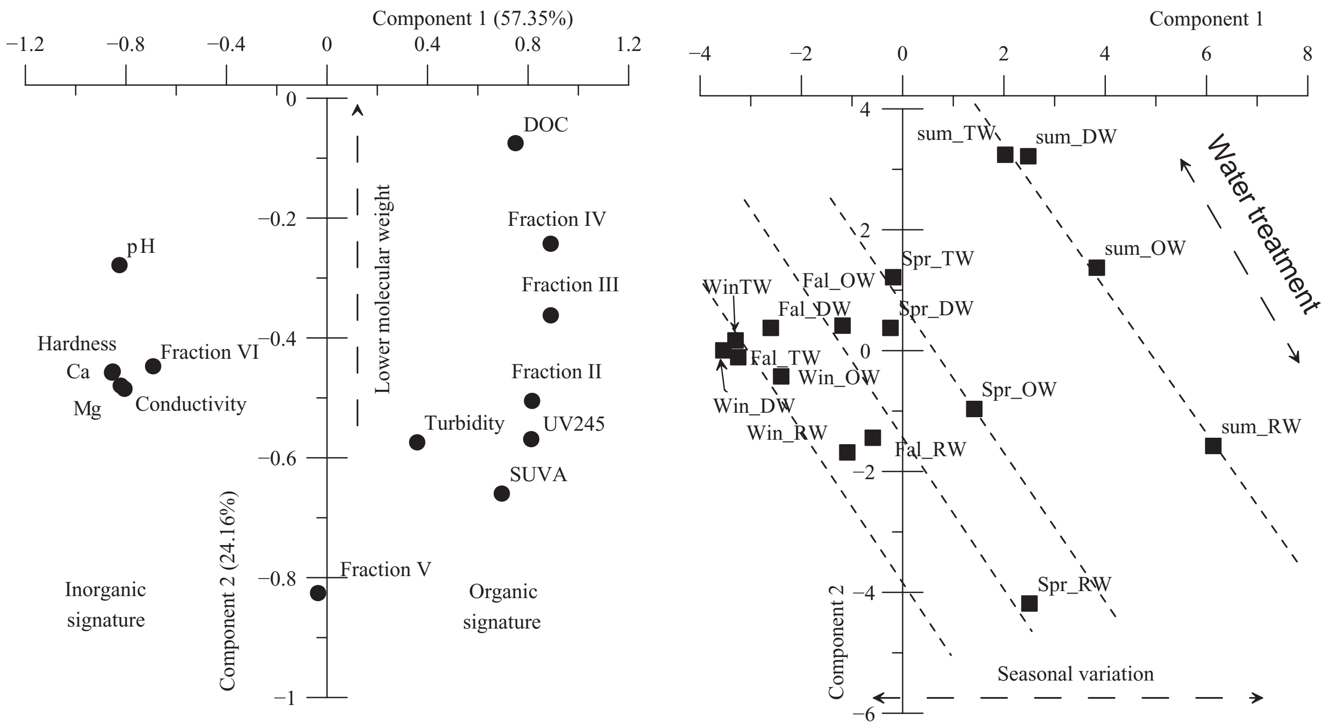

Fig. 3. (a) Projection of parameters on component-plane 1 vs. 2 and (b) Projection of cases on component-plane 1 vs. 2.

than in fall (Fig. 2a). These observations indicate that not only the quantity but also the composition of NOM influences the production of THM. Other authors [31] discussed the potential of using total organic carbon (TOC) as a surrogate for THM and concluded that there is no consistent relationship between RW TOC and THM formation, showing the influence of the other independent parameters.

Other factors affect the THM formation like chlorine dosage, contact time, temperature, pH and bromide concentration. Generally, disinfection efficiency (*Ct*) increases when increasing the concentration of residual disinfectant and the contact time. For a specific contact time, higher chlorine doses are required in winter than in summer, since lower *Ct* values are required in warm water than in cold water for inactivating microorganisms [32,33]. However, as disinfectant residual deplete rapidly at high temperatures, to maintain a minimum residual concentration in distribution systems, higher disinfectant doses are usually applied in summer [32,33]. Chlorine is more effective against microorganisms and THM formation is lower at acidic conditions [34]. Some authors indicate that an increase of bromide concentration in water leads to an increased of brominated THM in the total THM [35,36]. Chowdhury et al. [37] referred that brominated THM may not be adequately characterised by low SUVA or UV$_{254}$ values, in hydrophilic waters with Br$^-$, and hydrophilic fractions of NOM can favour the formation of brominated THM. Table 1 presents the results of Br$^-$ in raw and OWs and the pH values of DWs (before disinfection). These results showed no significant inter-seasonal differences for Br$^-$ (*t*-test; $p > 0.05$). During the hot period Br$^-$ varied between 155 ± 6 μg/L and 165 ± 24 μg/L and in the cold period between 158 ± 12 μg /L and 168 ± 6 μg/L (Table 1). pH varied between 7.17 ± 0.10 and 7.50 ± 0.12 (Table 1) (note that no correction to pH is made in the WTP before disinfection). According with Uyak and Toroz [38] the increase in

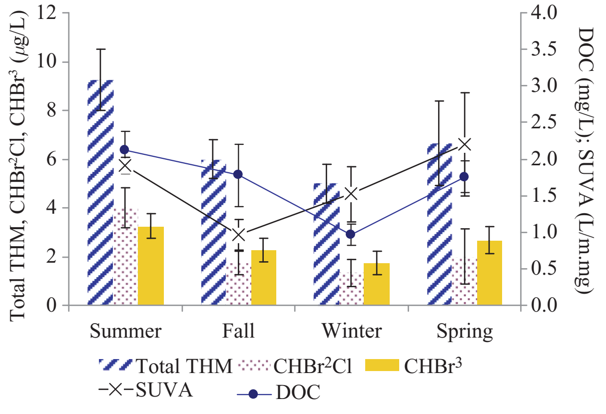

Fig. 4. Total THM in treated water, and SUVA and DOC in raw water (confidence interval for the mean value with $\alpha = 0.05$, $n = 4$)

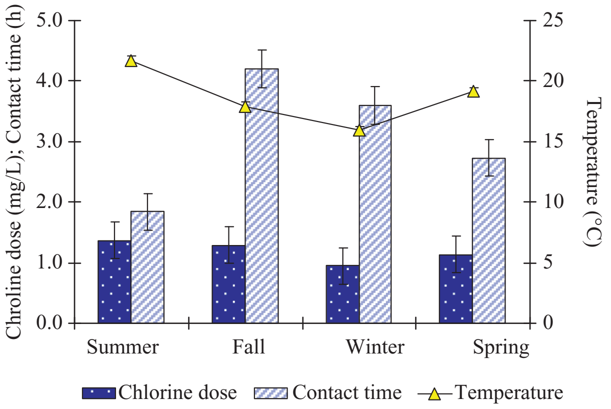

Fig. 5. Disinfectant dose, contact time and temperature of water during disinfection (confidence interval for the mean value with $\alpha = 0.05$, $n = 4$).

bromide concentration gradually shifts THM speciation from chlorinated species to the mixed bromochloro species during chlorination, even at low bromide concentration, as obtained in the present study (Fig. 4). In addition, these authors also concluded that Br^- forms HOBr in chlorinated water, which is approximately 20 times more reactive with NOM than HOCl [38]. Contact time of the chlorine, disinfectant dose and temperature of water are presented in Fig. 5. Results show no significant differences between seasons for chlorine doses applied to water (chlorine dose is statistically constant over the year: ANOVA test, $F(3,14) = 2.47$, $p = 0.105$; contact time is statistically lower during summer (t-test $p < 0.05$). Therefore, it is possible to conclude that the seasonal differences obtained in THM concentrations were due to quantity and composition of NOM present in water, as mentioned.

The low THM concentrations are due to the treatment. Ozonation oxidized the organic matter to compounds with low MW (Fig. 1), which resulted in a decrease of organic matter during C/F/S processes (Figs. 1 and 2) and therefore in THM concentration in TW.

Taking these results and the results of PCA (Section 3.2) into consideration several mathematical models relating these parameters and THM were studied due to their well known relationship. There are several published works on the modelling of disinfection by-products (DBP) formation in drinking water. Chowdhury et al. [37] reviewed 118 DBP predictive models, analysing model variables and assessing the advantages and limitations of each model. Sohn et al. [39] analysed and developed several empirical models for predicting disinfectant decay and DBP formation and showed a strong correlation between measured and predicted THM and haloacetic acid formation for RWs by an empirical model. In addition, Brown et al. [31] developed a simple tool to model chlorine decay and THM formation in water treatment works and distribution systems, and to provide an initial assessment of the risks of total THM formation at different sites. Therefore, two models presented high correlation coefficient and overall good adjustment parameters (see Table 2). Significant mathematical multilinear relations were only found between THM in TW and fractions II, III and IV together for all waters. No significant linear or log linear models could be found between THM and any of the organic parameters, nor between THM and individual treatment waters. The models correlate well for waters from all treatment phases as no data point stands beyond the 2σ interval. These models clearly show the relation between the NOM MW and THM in the final water and, therefore, the importance of the MW determination by water treatment operators. These models should in the future be validated using different datasets.

4. Conclusion

This study shows the importance of the MW determination in waters, along water treatment and seasonally and its relation with the THM in the final water, even in water with low concentrations of NOM and THM. Seasonally, summer and spring presented compounds with higher MW compounds, whereas in cold seasons the most relevant compounds were of lower MW classes. This resulted in waters with ‘‘physical-chemical signature’’ in fall and winter and in opposition with an ‘‘organic signature’’ in spring and especially summer. A decrease in the amount of natural organic matter from raw to TWs in all fractions and seasons was also observed. However, higher decrease in MW was observed in seasons where waters presented higher MW, i.e., summer and spring. Results also indicated that the conventional water treatment process can remove effectively compounds with high MW, but is ineffective for removing low MW compounds.

As a final conclusion, the concentration of THM in TW is influenced not only by the quantity but also by the composition of the NOM. This resulted in the proposal of two mathematical multilinear relations between THM in TW and fractions II, III and IV. These models clearly show the importance of MW determination for water treatment operators and the relationship between NOM MW and THM formation potential and presence in TW. In addition, it was demonstrated that UV_{254} and organic matter MW are very good indicator parameters to measure overall water treatment efficiency and progression.

Table 2
Bilinear models between THM and organic matter molecular weight (mAU)

Model name	Equation (THM=)	R	$F(2,11)$	p
Model 1	$2.4 - 41.2$ fraction II $+ 41.8$ fraction III	0.87	16.85	<0.00045
Model 2	$3.1 + 36.1$ fraction III $- 10.6$ fraction IV	0.89	20.17	<0.00021

Acknowledgements

The authors would like to thank the Portuguese Science and Technology Foundation (Project no PTDC/ECM/68323/2006-NFPilotCYANO) for funding this project and Águas do Algarve, SA for their participation in the project.

References

[1] S. McDonald, J.M. Pringle, A.G. Bishop, P.D. Prenzler and K. Robards, Isolation and seasonal effects on characteristics of fulvic acid isolated from an Australian floodplain river and billabong, J. Chromatogr. A 1153 (2007) 203–213.

[2] R. Fabris, C.W.K. Chow, M. Drikas and B. Eikebrokk, Comparison of NOM character in selected Australian and Norwegian drinking waters, Water Res., 42 (2008) 4188–4196.

[3] S.D. Richardson, Drinking Water Disinfection By-products, John Wiley & Sons, Inc., New York, 1998.

[4] L. Hem and H. Efraimsen, Assimilable carbon in molecular weight fractions of natural organic matter, Water Res., 35 (2001) 1106–1110.

[5] AWWA,Water Quality and Treatment. A Handbook of Community Water Supplies, 5th ed. McGraw-Hill, USA, 2000.

[6] G. Newcombe, M. Drikas, S. Assemi and R. Beckett, Influence of characterised natural organic material on activated carbon adsorption: I. Characterisation of concentrated reservoir water, Water Res., 31 (1997) 965–972.

[7] A.E. Childress and S.S. Deshmukh, Effect of humic substances and anionic surfactants on the surface charge and performance of reverse osmosis membranes, Desalination, 118 (1998) 167–174.

[8] F. Worrall, R. Harriman, C.D. Evans, C. Watts, J. Adamson, C. Neal, E. Tipping, T.P. Burt, I. Grieve, D. Montieth, P.S. Naden, T. Nisbet, B. Reynolds and P. Stevens, Trends in dissolved organic carbon in UK rivers and lakes, Biogeochemistry, 70 (2004) 369–402.

[9] A. Korth, C. Fiebiger, K. Bornmann and W. Schmidt, NOM increase in drinking water reservoirs – relevance for drinking water production, Water Sci. Technol.: Water Supply, 4 (2004) 55–60.

[10] C.D. Evans, D.T. Monteith and D.M. Cooper, Long-term increases in surface water dissolved organic carbon: observations, possible causes and environmental impacts, Environ. Pollut., 137 (2005) 55–71.

[11] C. Freeman, C.D. Evans, D.T. Monteith, B. Reynolds and N. Fenner, Export of organic carbon from peat soils, Nature, 412 (2001) 785–785.

[12] E. Vuorio, R. Vahala, J. Rintala and R. Laukkanen, The evaluation of drinking water treatment performed with HPSEC, Environ. Int., 24 (1998) 617–623.

[13] T.K. Nissinen, I.T. Miettinen, P.J. Martikainen and T. Vartiainen, Molecular size distribution of natural organic matter in raw and drinking waters, Chemosphere, 45 (2001) 865–873.

[14] A. Matilainen, N. Lindqvist, S. Korhonen and T. Tuhkanen, Removal of NOM in the different stages of the water treatment process, Environ. Int., 28 (2002) 457–465.

[15] B.P. Allpike, A. Heitz, C.A. Joll, R.I. Kagi, G. Abbt-Braun, F.H. Frimmel, T. Brinkmann, N. Her and G. Amy, Size exclusion chromatography to characterize DOC removal in drinking water treatment, Environ. Sci. Technol., 39 (2005) 2334–2342.

[16] E.L. Sharp, S.A. Parsons and B. Jefferson, The impact of seasonal variations in DOC arising from a moorland peat catchment on coagulation with iron and aluminium salts, Environ. Pollut., 140 (2006) 436–443.

[17] Q. Zhou, S. Cabaniss and P. Maurice, Considerations in the use of high-pressure size exclusion chromatography (HPSEC) for determining molecular weights of aquatic humic substances, Water Res., 34 (2000) 3505–3514.

[18] E.K. Lee, V. Chen and A.G. Fane. Natural organic matter (NOM) fouling in low pressure membrane filtration – effect of membrane and operation modes, Desalination, 218 (2008) 257–270.

[19] M. Potschka, Mechanism of size-exclusion chromatography, J. Chromatogr. A 648 (1993) 41–69.

[20] C.W.K. Chow, R. Fabris, J.V. Leeuwen, D. Wang and M. Drikas, Assessing natural organic matter treatability using high performance size exclusion chromatography, Environ. Sci. Technol., 42 (2008) 6683–6689.

[21] W.W. Yau, J.J. Kirkland and D.D. Bly, Modern Size Exclusion Liquid Chromatography. John Wiley and Sons, New York, 1979.

[22] C. Pelekani, G. Newcombe, V.L. Snoeyink, C. Hepplewhite, S. Assemi and R. Beckett, Characterization of natural organic matter using high performance size exclusion chromatography, Environ. Sci. Technol., 33 (1999) 2807–2813.

[23] APHA, AWWA, WEF, Standard Methods for the Examination of Water and Wastewater. APHA, American Public Health Association; AWWA, American Water Works Association; WEF, Water Environment Federation, USA, 2005.

[24] C.N. Sawyer, P.L. McCarty and G.F. Parkin, Chemistry for Environmental Engineering and Science, 5th ed., McGraw-Hill, 2003.

[25] D.A. Reckhow, P.C. Singer and R.L. Malcolm, Chlorination of humic materials: byproduct formation and chemical interpretations, Environ. Sci. Technol., 24 (1990) 1655–1664.

[26] J.K. Edzwald and J.B. Van Benschoten, H.H. Hahn and R. Klute (Eds.), Aluminium Coagulation of Natural Organic Matter, Springer-Verlag, Berlin, 1990.

[27] G. Amy, R.A. Sierka, J. Bedessem, D. Price and L. Tan, Molecular size distributions of dissolved organic matter, J. Am. Water Works Assoc., 84 (1992) 67–75.

[28] D.M. Owen, G. Amy, Z.K. Chowdhury, R. Paode, G. McCoy and K. Viscosil, NOM characterization and treatability, J. Am. Water Works Assoc., 87 (1995) 46–63.

[29] C. Chen, X.-J. Zhang, L.-X. Zhu, J. Liu, W.-J. He and H. Han, Disinfection by-products precursors in a water treatment plant in North China: Seasonal changes and fraction analysis, Sci. Total Environ., 397 (2008) 140–147.

[30] V. Uyak, K. Ozdemir and I. Toroz, Seasonal variations of disinfection by-product precursors profile and their removal through surface water treatment plants, Sci. Total Environ., 390 (2008) 417–424.

[31] D. Brown, J.R. West, B.J. Courtis and J. Bridgeman, Modelling THMs in water treatment and distribution systems, Proceedings of the Institution of Civil Engineers - Water Management, 2010, pp 165–174.

[32] R. Sadiq and M.J. Rodriguez, Disinfection by-products (DBPs) in drinking water and predictive models for their occurrence: a review, Sci. Total Environ., 321 (2004) 21–46.

[33] D. Brown, J. Bridgeman and J.W. West, Predicting chlorine decay and THM formation in water supply systems, Rev. Environ. Sci. Biotechnol., 10 (2011) 79–99.

[34] A. Adin, J. Katzhendler, D. Alkaslassy and C. Rav-Acha, Trihalomethane formation in chlorinated drinking water: A kinetic model, Water Res., 25 (1991) 797–805.

[35] C.J. Nokes, E. Fenton and C.J. Randall, Modelling the formation of brominated thrihalomethanes in chlorinated drinking waters, Water Res., 33 (1999) 3557–3568.

[36] E.E. Chang, Y.P. Lin and P.C. Chiang, Effect of the bromide on the formation of THMs and HAAs, Chemosphere, 43 (2001) 1029–1034.

[37] S. Chowdhury and P.J.M. Champagne, Models for predicting disinfection byproduct (DBP) formation in drinking waters: A chronological review, Sci. Total Environ., 407 (2009) 4189–4206.

[38] V. Uyak and I. Toroz, Investigation of bromide ion effects on disinfection by-products formation and speciation in an Istanbul water supply, J. Hazard. Mater., 149 (2007) 445–451.

[39] J. Sohn, G. Amy, J. Cho, Y. Lee and Y. Yoon, Disinfectant decay and disinfection by-products formation model development: chlorination and ozonation by-products, Water Res., 38 (2004) 2461–2478.