The relationship between chlorine consumption and trihalomethane formation from hydrophobic and transphilic fractions: a comparative study between two dams of east Algeria

Dhaouadi Mellahi, Ridha Zerdoumi, Nacer Rebbani and Abdelhak Gheid

ABSTRACT

In Algeria, the use of chlorine in drinking water treatment is a widespread practice. When chlorine combines with natural organic matter (NOM), it forms various chlorine by-products such as trihalomethanes (THMs). In this work, we studied the relationship between chlorine consumption and THM formation, by chlorination of hydrophobic and transphilic (TRS) fractions. We compared the kinetic behavior and the THM formation potential of two major dams in east Algeria. A nonlinear regression modeling study showed a good correlation of the specific chlorine consumption and the specific THM formation. In the case of Ain Zeda dam and at pH = 7, the specific THM yield coefficients α_S were: 6.57 and 10.22 μg-THM/mg-Cl$_2$.mg-C.L^{-1} for hydrophobic and TRS fractions, respectively, while at the same pH, they were 12.07 and 23.66 μg-THM/mg-Cl$_2$.mg-C.L^{-1} for Ain Dalia dam. Although the NOM concentration of Ain Zeda dam was higher than that of Ain Dalia dam, the THM formation potential of Ain Dalia dam was greater than that of Ain Zeda dam. It seems clear that the water source origin and characteristics play a key role in this case. They affect the THM formation due to the complex composition of humic substances which differs from one source to another.

Key words | chlorine consumption, hydrophobic fraction, transphilic fraction, trihalomethanes

Dhaouadi Mellahi (corresponding author)
Ridha Zerdoumi
Laboratory of Chemistry and Environmental
    Chemistry (LCCE),
Hadj Lakhdar University,
Batna,
Algeria
E-mail: *mellahipg@yahoo.fr*

Nacer Rebbani
Laboratory of Water Treatment and Revalorization
    of Industrial Waste,
Badji Mokhtar University,
Annaba,
Algeria

Abdelhak Gheid
Laboratory of Water and Environmental Sciences,
Messadia MedCherif University,
Souk Ahras,
Algeria

INTRODUCTION

In recent years, the drinking water supply in Algeria has increasingly been provided by surface water. The drinking water treatment company (ADE: Algérienne Des Eaux), is still using chlorine as a primary disinfectant. Although this product has played a key role in the fight against waterborne diseases, it can cause other potential risks. In fact, surface water is known by its richness of natural organic matter (NOM). Since the first studies by Rook (1974), the formation of disinfection by-products (DBPs) has been confirmed by combination of chlorine and NOM. The dissolved NOM is the main precursor of the formation of trihalomethanes (THMs) and other chlorinated by-products such as haloacetic acids and halogenated acetonitriles (Chang *et al.* 2001; Gang *et al.* 2003). The chlorinated by-products are mainly formed during the chlorination treatment by combination with the NOM in the

presence of bromide ions. The combination of chlorine with the active sites of humic substances, including 3,5-dihydroxybenzoic acid, resorcinol, and 1,3-dihydroxybenzene forms high rates of THMs (Boyce & Hornig 1983). There are four chlorinated and/or brominated THMs: chloroform (CHCl$_3$), bromodichloromethane (CHBrCl$_2$), dibromochloromethane (CHBr$_2$Cl) and bromoform (CHBr$_3$). Their formation depends on several factors, such as the dissolved organic carbon (DOC) concentration and nature, pH, chlorine dose and residual, reaction time, bromine concentration, and temperature.

THMs and haloacetic acids are the main DBPs recognized as harmful to human health (Bellar *et al.* 1974; Richardson *et al.* 2007). In addition, those types of DBPs were associated with the hydrophobic and transphilic (TRS) NOM fractions (Roccaro *et al.* 2014). The International

Agency for Research on Cancer (IARC 1991) has determined that chloroform is possibly carcinogenic to humans (2B). The Environmental Protection Agency (EPA) has determined that chloroform is a probable human carcinogen. The Carcinogenic Risk Assessment Verification Endeavor group of the United States Environmental Protection Agency assigned bromodichloromethane and bromoform to Group B2, probable human carcinogen, and dibromochloromethane to Group C, possible human carcinogen (USEPA 2005).

The objective of this work is to study and to compare the THM formation kinetics of two NOM fractions from two dams.

The studied sources were two large dams: Ain Dalia (Souk Ahras) and Ain Zeda (Setif), located in eastern Algeria. Together, they ensure the drinking water supply for more than two million people.

To obtain reproducible and meaningful results, the control of such variables as temperature, reaction time, residual chlorine, and pH is a necessary condition. Therefore, the use of a standard set of chlorination conditions is a requirement. Standardized conditions facilitate the comparison of data from different studies and allow the evaluation of precursor characteristics of different types of water sources. To compare between different sources or organic fractions at different pHs, it is essential to take into account the chlorine demand, which can provide information on the dose that should be added in order to have, at the end of all kinetics, an amount of residual chlorine close to a constant value.

MATERIALS AND METHODS

Concentration and fractionation of humic substances

The fractionation of humic substances was performed on two columns of macroporous resins, XAD-7 and XAD-4HP, giving the hydrophobic (HPO) and the TRS fractions, respectively (Leenheer & Croué 2003). The TRS fraction is defined as the fraction isolated from the XAD-4 resin. It is a complex mixture of aromatic and aliphatic hydrocarbon structures with attached amide, carboxyl, hydroxyl, ketone, and various minor functional groups.

The TRS structure is similar to humic substance fraction (fulvic and humic acids), with an intermediate polarity between that of hydrophobic and hydrophilic fractions and a molecular weight lower than that of humic acids.

Figure 1 explains the main steps of humic substance concentration and fractionation, where the XAD-7 plays the same role as the XAD-8 (APHA 2005; Chuang *et al.* 2013).

First step: Fifty liters of each sample were taken from the raw water used to supply the treatment plant (Dams: Ain Zeda and Ain Dalia). The samples were immediately filtered through a filtration membrane pilot of 05, 01 and 0.45 μm pore size (polymer filter water quality member).

Second step: After a softening on cationic resin (amberlite IR-120(Na) BDH Chemicals Ltd, Poole, UK), the organic
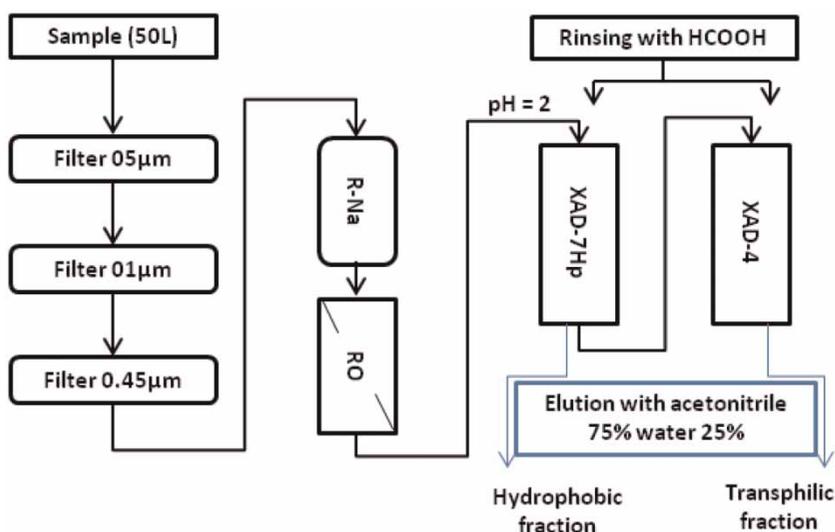

Figure 1 │ Extraction and fractionation protocol of the hydrophobic and the TRS fractions.

matter was concentrated on a reverse osmosis unit (Film TEC Model No. 30-1812-50 TW, USA). The retained organic matter on the reverse osmosis membrane was desorbed by a solution of 0.05 M NaOH. Sodium eluate was mixed with the concentrate.

Third step: The resulting mixture was acidified with a concentrated HCl solution (Riedel-de Haën 37% Germany) until pH = 2. Then, samples were passed successively through cartridges of XAD-7HP and XAD-4 macroporous resin (Acros Organics, New Jersey, USA). After elution, the columns were rinsed with a formic acid solution of pH = 2 (Paneac, Spain). The hydrophobic and the TRS fractions were desorbed with a mixture of acetonitrile 75% (Sigma-Aldrich) and water 25%. Then, a vacuum rotary evaporator was used for the efficient removal of eluting solvents and formic acid traces.

Kinetics of chlorine consumption and THM formation

The stock sodium hypochlorite solution was dosed with a solution of sodium thiosulfate using 5710B of the American *Standard Methods* (APHA 2005). The concentration of residual chlorine was measured using spectrophotometry (HI 96711, Hanna Instruments Deutschland GmbH) and recommended reagents DPD (N,N-diethyl-p-phenylenediamine). The solution used in the kinetics of chlorine consumption and THM formation has a concentration of 140 mg/L. The chlorine demand was determined using 5710B of the American *Standard Methods* (APHA 2005). Samples of different fractions were placed in amber glass bottles of 250 mL, chlorinated with 10 mL of stock solution and sealed with Teflon-lined caps. The pH was fixed by two buffer solutions: pH 7 (a mixture of potassium dihydrogen phosphate and sodium hydroxide) and pH 9.2 (a mixture of boric acid and sodium hydroxide).

THM analysis

THM analysis was performed with liquid–liquid extraction gas chromatography (LLE-GC-ECD) following the USEPA method 551.1 (USEPA 1995) modified by Nikolaou *et al.* (2002). The detection limit of this method is 0.8–1 μg/L.

Liquid–liquid extraction conditions

Thirty-five mL of samples were used for the THM extraction with 1×2 mL of 2 mL of n-Pentane (Merk Class GC, Germany) plus 6 g of anhydrous Na_2SO_4 (Riedel-de Haën, Germany). The neutral salt (Na_2SO_4) was added to the aqueous phase in order to reduce the solubility of THM. Each mixture was shaken for 1 min.

GC-ECD analysis conditions

Separation and identification of individual THMs were carried out on a GC 17-A class VP fitted to a ^{63}Ni radioactive detector (ECD), using nitrogen as a carrier gas.

05 μL of the extract was injected into a capillary column (25 m × 0.25 mm fused-silica id, 0.25 μm film thickness, OV17). The temperature was programed from an initial temperature held at 35 °C for 5 min, and then increased by 10 °C/min until 70 °C, and from 70 °C by 20 °C/min until 200 °C, with a final time of 14 min. The split/splitless injector was held at 280 °C and operated in the splitless mode. The split flow was set at 32 mL/min, and the radioactive detector (ECD) was maintained at 300 °C.

The stock standard solution of THMs was prepared in methanol (Riedel-de Haën Class GC, Germany).

Organic carbon analysis

Organic carbon analysis was conducted by two devices: analysis of total organic carbon was carried out on a TOC analyzer (Formacs SKALAR Total Organic Carbon); and UV/Vis (UV PHARMASPEC 1700 Shimadzu with a 1-cm quartz cell).

Analysis method: high temperature combustion

The sample was injected into a heated reaction chamber. The water was vaporized and the organic carbon was oxidized at high temperature to CO_2. The CO_2 was transported in the carrier-gas stream and measured by means of a NDIR (non-dispersive infrared gas analyzer).

Chlorine consumption kinetics and THM formation model

The model used to study the chlorine consumption was that already used by Gang *et al.* (2003) and Chang *et al.* (2006). Two reaction rates (fast and slow) were attributed to the chlorine consumption reaction

$$C(t) = C_R(t) + C_S(t) \tag{1}$$

We define

$$f = \frac{C_{R0}}{C_0} \tag{2}$$

with

$$C_0 = C_{R0} + C_{S0} \tag{3}$$

$$C(t) = \left[(C_0.f)^{1-n} - (1-n).K_R.t \right]^{1/1-n}$$
$$+ \left[(C_0.(1-f))^{1-m} - (1-m).K_S.t \right]^{1/1-m} (n, m \# 1) \tag{4}$$

The first-order model for chlorine consumption kinetics has been proposed by Gang *et al.* (2003) and Chang *et al.* (2006)

$$C(t) = C_0[f.\text{Exp}(-K_R.t) + (1-f).\text{Exp}(-K_S.t)] \tag{5}$$

Factors K_R, K_S, and f were determined by a nonlinear regression method using XLStat-pro-7.5 software. The model used to link THM formation to chlorine consumption is

$$\text{THM} = \alpha.[C_0 - C(t)]$$
$$= \alpha.C_0[1 - f.\text{Exp}(-K_R.t) - (1-f).\text{Exp}(-K_S.t)] \tag{6}$$

Since the concentration of dissolved organic carbon is proportional to THM formation and in order to generalize the model, we preferred to use the specific THMs where

$$\text{Specific THM} = \frac{\text{THM}}{[\text{DOC}]} \tag{7}$$

$$\text{Specific THM} = \frac{\alpha.C_0}{[\text{DOC}]}$$
$$[1 - f.\text{Exp}(-K_R.t) - (1-f).\text{Exp}(-K_S.t)] \tag{8}$$

where

$$\alpha_S = \frac{\alpha}{[\text{DOC}]} \tag{9}$$

$$\text{Specific THM} = \alpha_S.C_0[1 - f.\text{Exp}(-K_R.t) - (1-f).\text{Exp}(-K_S.t)] \tag{10}$$

The new parameter α_S allows the comparison between various obtained results, where

α, THM yield coefficient, defined as the ratio of the formed THMs concentration to the concentration of consumed chlorine (μg-THM/mg-Cl$_2$). α_S, specific THMs yield coefficient, defined as the ratio of the formed THM concentration to the consumed chlorine concentration by DOC (μg-THM/mg-Cl$_2$.mg-C.L^{-1}). C_0, the initial chlorine concentration (mg-Cl$_2$/L). $C(t)$, the residual chlorine concentration (mg-Cl$_2$/L). K_R, the first-order rate constant for rapid reactions (h^{-1}). K_S, the first-order rate constant for slow reactions (h^{-1}). C_{R0}, the initial chlorine concentration participating in the rapid reaction (mg/L). C_{S0}, the initial chlorine concentration participating in the slow reaction (mg/L). $C_R(t)$, the hypothetical residual chlorine concentration separate rapid reaction (mg-Cl$_2$/L). $C_S(t)$, the hypothetical residual chlorine concentration separate slow reaction (mg-Cl$_2$/L). n, m, the order of the rapid reactions and the slow reactions, respectively (dimensionless). f, the fraction of the chlorine demand attributed to rapid reactions (dimensionless).

RESULTS AND DISCUSSION

The raw water and the fractions quality

The main physicochemical properties and the distribution of humic substances are summarized in Table 1.

Chlorine demand

The chlorine demand was determined as follows: the HPO and TRS fractions were chlorinated with different concentrations of chlorine and left for a 7-day incubation period.

Table 1 | Distribution of humic substances and main parameters of raw water

Parameters	Ain Zeda	Ain Dalia
DOC mg-C/L raw water	12.73	3.54
UV^{254} cm^{-1} raw water	0.105	0.047
SUVA m^{-1}.mgC^{-1}.L	0.824	1.327
Hydrophobic compound HPO%	46.5	34
TRS compound TRS%	22	18
pH	7.75	8.42
Conductivity μS/cm	1,379	665
NH_4^+ mg/L	0.49	0.03
Organic nitrogen mg/L	0.78	0.18
Temperature °C	16	15

SUVA: specific ultraviolet absorption.

The Cl_2/DOC ratios are: 0.5, 1, 1.5, 2, and 3 at a temperature of 20 °C and a pH of 7.0 ± 0.2 (phosphate buffer) where

$$\text{(Chlorine demand)} = \text{(starting chlorine dose)} - \text{(residual chlorine)}$$

The obtained results show a linear relationship between the starting specific chlorine dose (SSCD) and the residual chlorine C_R

$$\left(\text{SSCD} = \frac{C_0}{[\text{DOC}]} \right) \qquad (11)$$

$$C_R = K \frac{C_0}{[\text{DOC}]} = K.\text{SSCD} \qquad (12)$$

The proportionality constant K is shown in Table 2.

To obtain the desired concentration of residual chlorine (2.5 to 3 mg/L) at the end of a 7-day reaction period, the residual chlorine concentration and the starting chlorine dose were fixed as follows: $C_R = 3$ mg/L and $C_0 = 5.46$ mg/L. Then, the DOC concentrations preparing for the kinetic

monitoring of chlorine consumption and the THM formation were determined according to Equation (12). The results are summarized in Table 3.

Modeling of chlorine consumption kinetics

The model constants of chlorine consumption kinetics at different pHs were determined from Equation (5). The obtained results are shown in Table 4.

The reaction mechanisms that may occur in the reaction between humic substances and free chlorine are addition, substitution, and oxidation. Hypochlorous acid (HOCl) and hypobromous acid (HOBr) are the sources of electrophilic species (halogens). They react mainly with the aromatic rings of humic substances and with the resorcinol-like structure of fulvic acids (Rook 1976).

The chlorine consumption according to the obtained model depends on three parameters: K_R, K_S, and f. Therefore, we have to consider the three parameters to compare between different fractions. Figure 2 shows that during the first 2 hours, the chlorine consumption was very fast and then decreased after this period (Urano *et al.* 1983); it is valid for different fractions at different pHs.

At pH 7, the factor f, which represents the percentage of consumed chlorine attributed to the fast speed, was 31.2 and 32.7% for the hydrophobic fraction of Ain Zeda and Ain Dalia dam, respectively. Under the same conditions, for TRS fraction, the percentage of the consumed chlorine during the rapid phase was 17.9 and 22.2% for Ain Zeda dam and Ain Dalia dam, respectively. When we increased the pH, the chlorine consumption increased with irregular variation of the three constants K_R, K_S, and f.
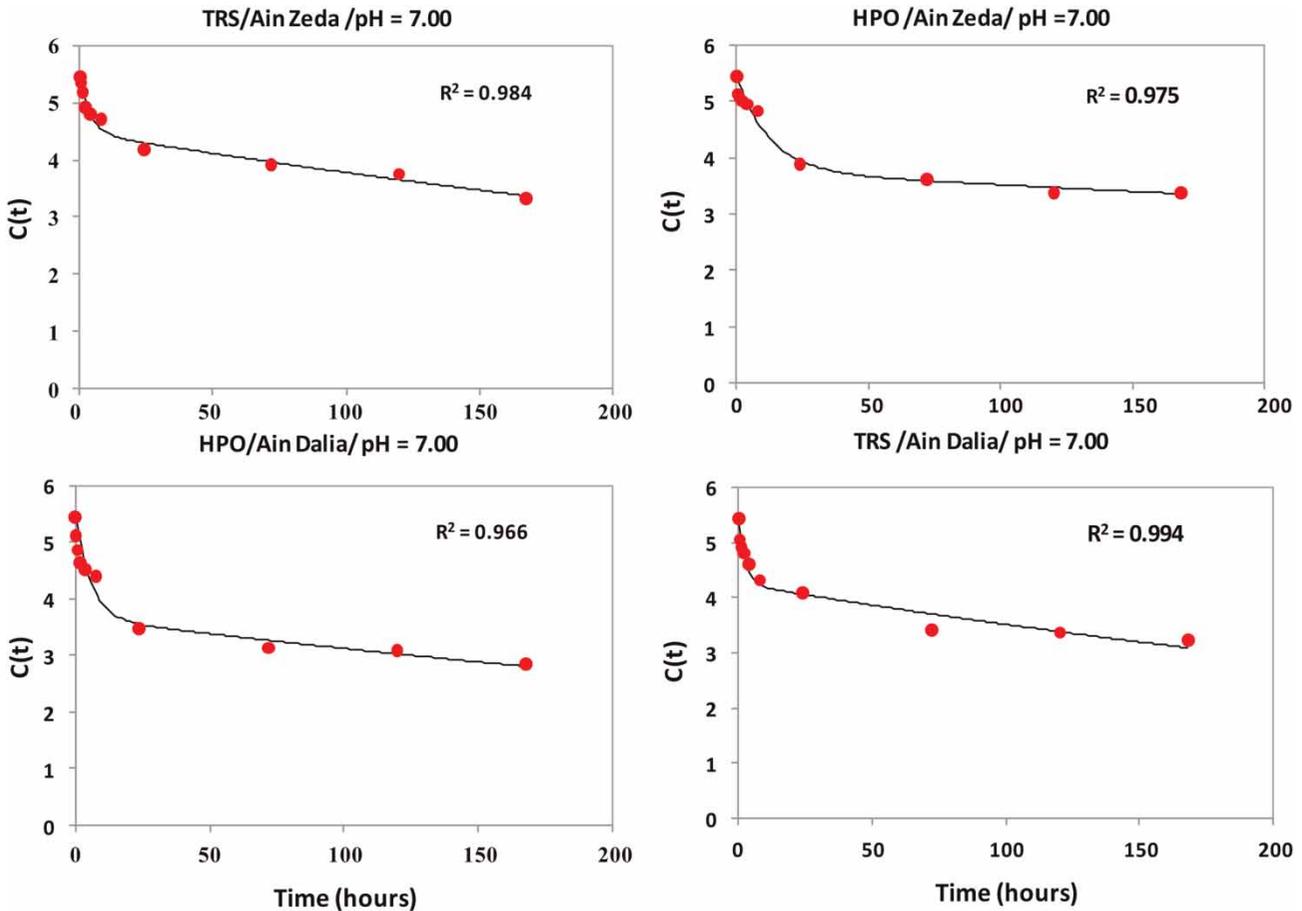
To compare the chlorine consumption kinetics between different fractions and at different pH, we calculated the specific consumption of chlorine expressed in mg-Cl_2/mg-C, as shown in Figure 3.

Table 2 | Constant K linking the starting SSCD and chlorine residual concentration

Fractions	Ain Zeda		Ain Dalia	
	HPO	TRS	HPO	TRS
K	3.39	2.09	1.67	1.43
R^2	0.970	0.981	0.931	0.922

Table 3 | Concentrations of COD used in the THM formation model and chlorine consumption

Dams	Ain Zeda		Ain Dalia	
	HPO	TRS	HPO	TRS
DOC mg-C/L	6.17	3.81	3.05	2.6
C_0 mg-Cl_2/L	5.46	5.46	5.46	5.46

Table 4 | Comparison of chlorine consumption kinetics of different fractions at different pHs

Source pH	Model constants	Ain Zeda		Ain Dalia	
		HPO	TRS	HPO	TRS
pH = 7	f	0.312	0.179	0.327	0.344
	K_R	0.080	0.259	0.179	0.053
	K_S	10^{-3}	2×10^{-3}	2×10^{-3}	10^{-3}
	R^2	0.975	0.984	0.966	0.994
pH = 7.73	f	0.338	0.113	0.220	0.233
	K_R	0.074	0.577	0.389	0.158
	K_S	10^{-3}	2×10^{-3}	3×10^{-3}	3×10^{-3}
	R^2	0.978	0.997	0.98	0.992
pH = 8.2	f	0.259	0.285	0.229	0.282
	K_R	0.542	0.561	1.658	0.634
	K_S	2×10^{-3}	2×10^{-3}	4×10^{-3}	3×10^{-3}
	R^2	0.988	0.993	0.975	0.982

Figure 2 | Chlorine consumption kinetic of the two fractions at pH = 7.00 determined by nonlinear regression using XLStat-pro-7.5 software.
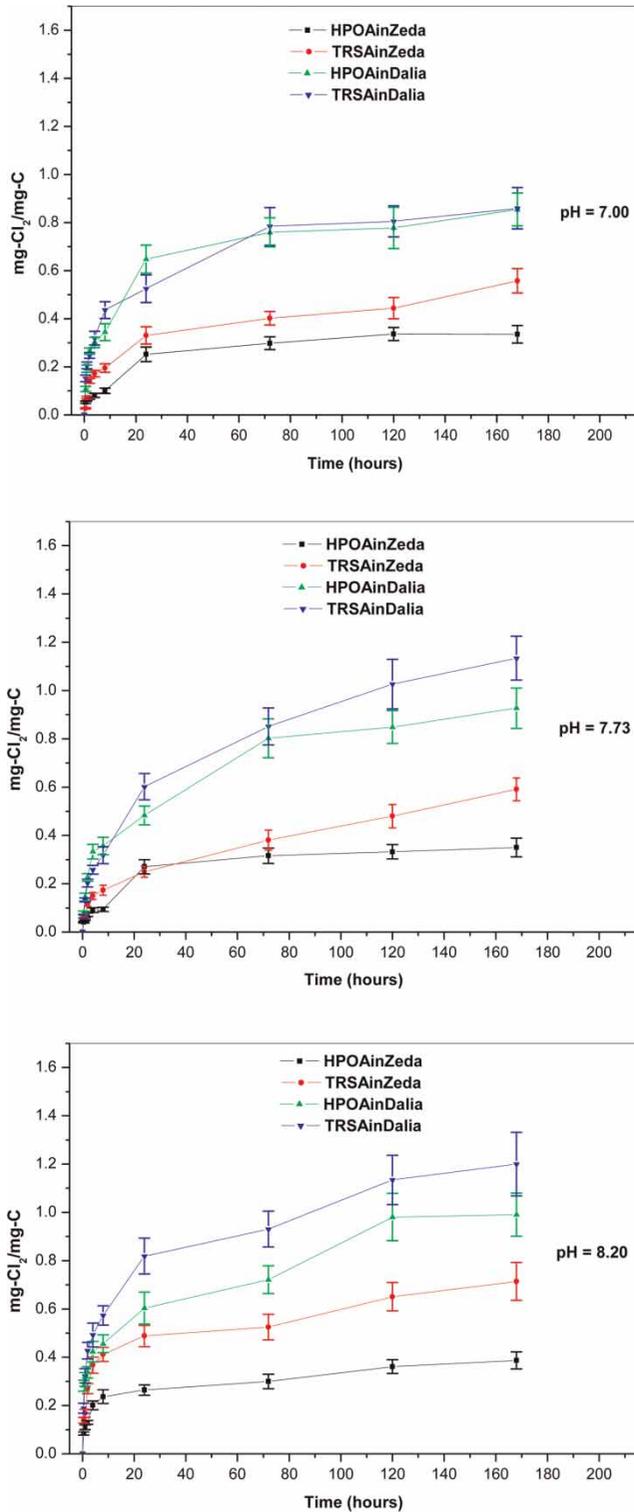
Figure 3 │ Comparison between specific consumption kinetics of chlorine for different fractions at different pHs.

The chlorine consumption of different fractions increases with pH. The TRS fractions consume more chlorine than the hydrophobic fractions. Comparing the two sources, the chlorine consumption of Ain Dalia dam is higher than that of Ain Zeda dam.

Relationship between chlorine consumption and THM formation

THM kinetics formation

We noted that the THM formation has virtually the same chlorine consumption kinetics. To compare THM formation kinetics of the different fractions, we show in Figure 4 the formation kinetics of specific THMs expressed in μg-THM/mg-C.

From Figure 4, we distinguish two speeds: a fast speed (from 0 to 2 hours) and then a low speed. During the fast speed, the THM formation is related to the most reactive precursors, mainly with aromatic structures of resorcinol-type and other compounds of β-diketones or β-ketoacides family (Gallard & von Gunten 2002) while during the slow speed it is related to the least reactive precursors.

Bond et al. (2009) found that the resorcinol compounds are the most reactive activated-aromatic THM precursors. The reaction mechanism of chlorine with resorcinol compounds is shown in Figure 5 (Rook 1974; Adin et al. 1991). The process involves an initial fast reaction of the ortho-carbon atom chlorination, activated by hydroxyl substitution (compound I), which produces chlorinated intermediates (compound II). According to the reaction conditions (protonation or halogenation), there are several possible pathways to produce many by-products. THMs will be formed when a cleavage of compound IV occurs at the position 'a'.

The majority of the least reactive compounds are in the NOM; these precursors are phenol compounds and methyl carbonyl. They play an important role in chlorine demand and in the formation of the majority of THMs. According to Figure 4, the specific THM formation kinetics of TRS fractions are greater than those of
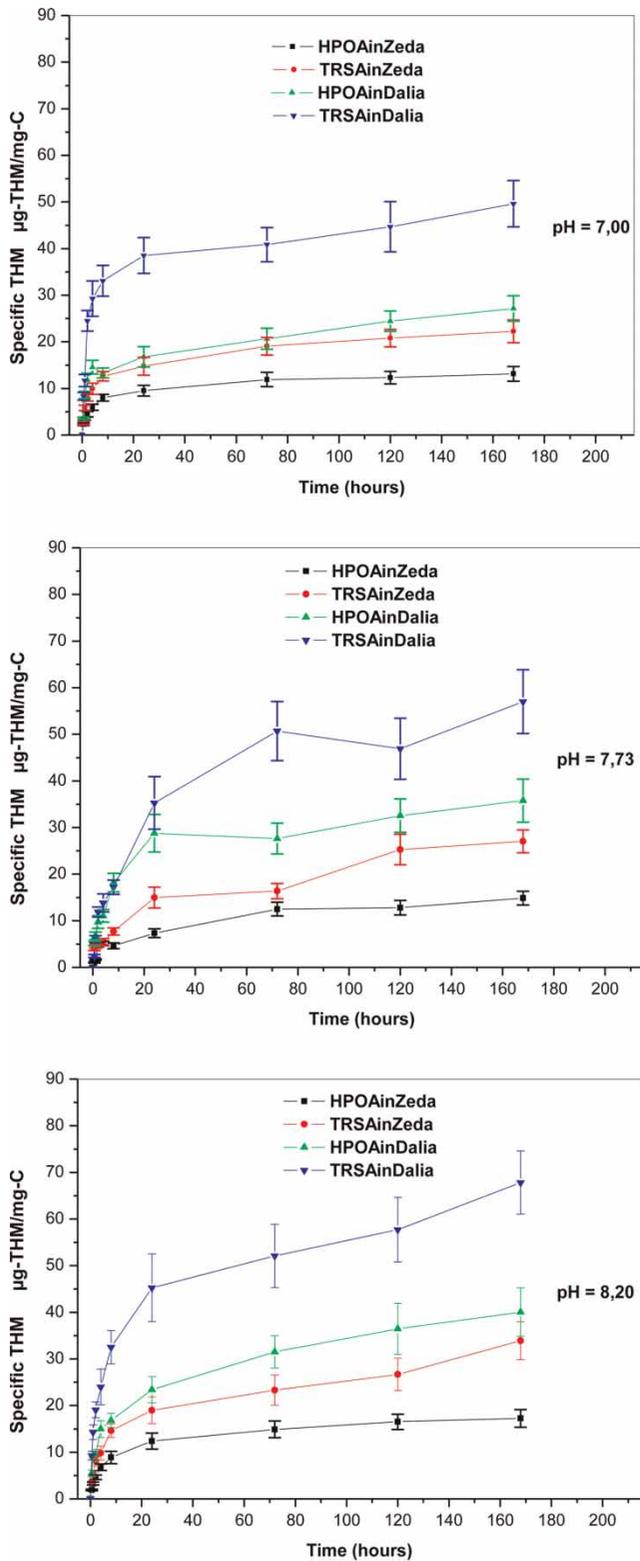
Figure 4 │ Comparison of the specific THM formation for different fractions at different pHs.

hydrophobic fractions. This result is consistent with previous studies (Marhaba *et al.* 2006; Platikanov *et al.* 2010).

The TRS and the hydrophobic fractions have the same functional groups, but with different proportions. Thus, the TRS fraction is probably richer in phenol compounds and methyl carbonyl than the hydrophobic fraction is. Although it is less reactive (slow kinetic) it could lead to the formation of more than 70% of THMs.

It has also been found that the formation of THMs is strongly affected by pH. The increase of pH enhances the THM formation reaction (Hansen *et al.* 2012). At pH = 8.2, Ain Dalia Dam has a specific THMFP of 67.8 µg-THM/mg-C for the TRS fraction and 40.04 µg-THM/mg-C for the hydrophobic fraction, while for Ain Zeda dam they are 33.9 µg-THM/mg-C and 17.24 µg/mg-C, respectively, which is lower than those of Ain Dalia dam.

$$HOCl \rightarrow H^+ + OCl^- \quad K_a = 10^{-7.54}$$

The pH is responsible for the distribution of hypochlorite and hypochlorous species. The effect of pH on the chlorination process should be simultaneously explained by the deprotonation of hypochlorite and/or organic compounds that can change the reaction kinetics (Peters *et al.* 1980; Platikanov *et al.* 2010). According to this equilibrium, the hypochlorite ion concentration increases with increasing pH. Another probable reason is that humic acids have many functional groups, particularly acetyl groups that are active at high pH and react with chlorine (Fooladvand *et al.* 2011).

On the other hand, pH can affect chlorination reactions in many ways. The reaction responsible for the formation of THMs occurs in two steps: the kinetic of the first step is favored by the presence of the non-ionized form of HOCl at low pH. The second step could be favored by the base-catalyzed hydrolysis mechanism that has the greatest overall effect. The THM formation increases at high pH values because many of the hydrolysis reactions actually lead to THM formation. Ultimately, the second THM formation step is the key-enabling one in this case and it is favored at high pH values (Edzwald 2010).
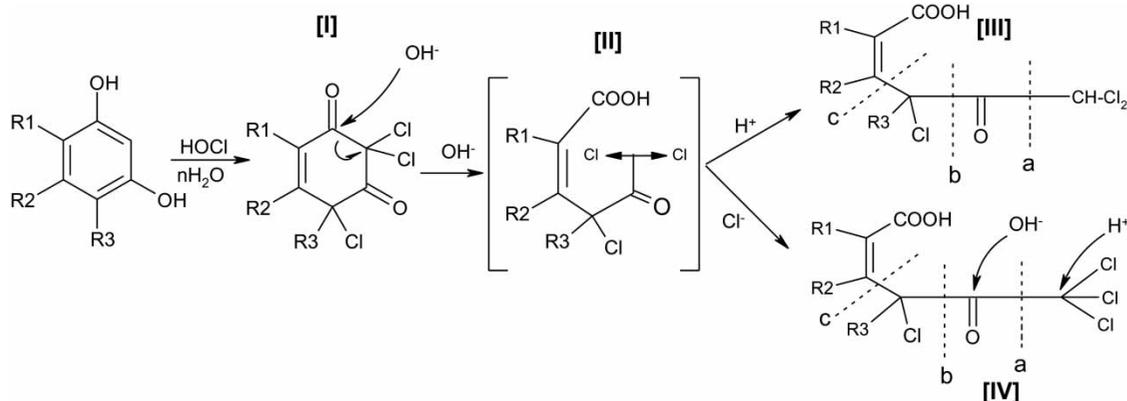
Figure 5 | By-product formation mechanism.

The studied THM formation model described by Equation (6) links the THM formation to chlorine consumption. In order to generalize this model, new parameters called specific THM and specific THMs yield coefficient (α_S) have been introduced in Equations (7), (9) and (10).

The values of α and α_S were determined by linear regression. The results are summarized in Table 5.

Specific THM yield coefficient α_S (μg-THM/mg-Cl$_2$.mg-C.L^{-1}) is more expressive than the coefficient α. It can really compare between the formation rate of different specific THMs fractions. Despite the fact that the comparison between the different fractions depends simultaneously on four model parameters, Table 5 shows that the values of α_S for the TRS fractions are always higher than those of hydrophobic fractions.

Furthermore, similar studies have been carried out on various sources. The study carried out by Lu *et al.* (2009)

on the chlorination of the hydrophobic acid fraction of Songhua River showed that the specific THM yields were relatively high compared to those obtained in this study. Roccaro *et al.* (2014) show that the formation of THMs and other chlorinated by-products from hydrophobic, TRS, and hydrophilic fractions depends on the water source. Therefore, the specific THM yields vary quite strongly for selected water samples.

CONCLUSION

In the present work, the relationship between chlorine consumption and THM formation from hydrophobic and TRS fractions was investigated. The obtained results could lead to the following main conclusions:

- The studied model, which links chlorine consumption to THM formation kinetics, gave satisfactory results with a good linearity. It could be used to predict the THM concentrations at different times.
- Comparing the two studied sources, it appears that Ain Dalia dam has a kinetic and a THM formation potential higher than those of Ain Zeda dam. This difference could be attributed to the complex composition of humic substances which changes from one source to another.
- The standardization of the starting chlorine dose is a necessary condition in such studies. In fact, the starting chlorine dose could be the limiting factor of THM

Table 5 | Determination of specific THM yield coefficient α_S at different pHs

Fractions		HPO Ain Zeda	TRS Ain Zeda	HPO Ain Dalia	TRS Ain Dalia
pH = 7	α	40.574	45.983	31.164	61.519
	α_S	6.576	12.069	10.217	23.66
	R^2	0.8174	0.9293	0.838	0.9013
pH = 7.73	α	38.824	48	40.057	51.751
	α_S	6.292	12.598	13.133	19.904
	R^2	0.90	0.95	0.92	0.96
pH = 8.20	α	43.68	40.8	38.18	53.73
	α_S	7.079	10.708	12.518	20.665
	R^2	0.95	0.93	0.94	0.97

formation. In order to obtain comparable results, the final residual chlorine concentrations have to be almost the same in all samples.

• Many worthwhile studies have been conducted with solution of model compounds, but it is difficult to render a judgment on the likely concentration level expected in tap water based on such studies. Also, the chlorination study of isolated humic substance fractions has several advantages: in the case of direct chlorination of raw water, the chlorine consumption kinetics and THM formation should be attributed to the other organic and/or inorganic compounds such as Fe^{2+}, Mn^{2+}, Br^-, NH_4^+ and organic pollutants.

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