

The influence of temperature on chlorine bulk-decay rates in drinking water

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Introduction

Chlorine is used worldwide to assure the microbiological safety of drinking water in transport and distribution systems. There, its concentration is usually kept within the range of 0.2 mg L⁻¹ to 1 mg L⁻¹, in order to protect public health (WHO, 2011). However, chlorine concentration decays as the water travels through the transport and distribution systems. Such decay is mainly due to chemical reactions of chlorine with the water natural organic matter (NOM) and, generally to a minor extent, with the pipes' wall material. The former, the so-called bulk decay (k_b), is a key parameter in the modelling of chlorine behaviour in drinking water systems.

In addition to water NOM contents and reactivity (Hua *et al.*, 1999), k_b is mainly affected by the water temperature (Powell *et al.*, 2000). Powell *et al.* (2000) found that 10°C raises in water temperature may lead to 2.5 fold increases in k_b values. However, increments as small as 5°C may double the rates of bulk chlorine decay (Kastl *et al.*, 1999).

Such phenomenon is particularly important in Continental countries where the water temperature spans from close to freezing to very high. Ongoing climate changes, including global warming and higher frequency and severity of extremes, such as

heat and cold waves, are likely to aggravate such conditions and to extend them to other areas including the Mediterranean regions like Algarve (Portugal). There the distribution systems water temperature may range from 13°C in winter to ca. 21°C in summer (Pina *et al.*, 2010).

In this study the effect of temperature on k_b was investigated for raw and clarified waters of surface origin. The latter had undergone ozonation and coagulation/flocculation/sedimentation. The waters were from Alcantarilha and Tavira drinking water treatment plants (DWTP), located in Algarve.

Methods

Chlorine decay was studied in Winkler bottles with 100 mL of membrane filtered (0.45 µm, Pall) water samples. The bottles were previously treated with 10 mg/L free chlorine in Milli-Q water to remove any chlorine demand. Concentrated sodium hypochlorite (Panreac, 5% w/v) was added to each bottle to give an initial concentration of free chlorine of 1.0 mg L⁻¹. Bottles were kept in the dark at 5°C, 12°C, 20°C or 30°C, till the chlorine concentration had decayed to ca. 0.1 mg L⁻¹. For each testing temperature two duplicate bottles were outdrawn at intervals and analysed for chlorine by using the DPD (N,N-diethyl-p-phenylenediamine)

colorimetric method (APHA, 2005). The first order model

$$C = C_0 e^{(-k_b t)}$$

was used to estimate k_b (Powell *et al.*, 2000; Rossman *et al.*, 1994). To evaluate the effect of temperature on k_b , experimental results were fitted to the Arrhenius equation:

$$\ln(k) = \ln(A) - E_a/(RT)$$

Where k is the rate constant of the chemical reaction (*i.e.*, k_b), A is the pre-exponential factor, E_a is the activation energy, R is the ideal gas constant and T is the temperature.

The waters' pH and conductivity were determined potentiometrically. Dissolved organic carbon (DOC) was determined with a TOC analyser (Teledyne TOC Fusion). A UV/VIS spectrophotometer (Jasco V-630) was used for measuring UV absorbance at 254 nm.

Results

As expected, NOM contents were higher in raw water than in the clarified ones, as observed DOC values indicate (Table 1). In what concerns the NOM quality, observed SUVA values indicated similar contents in aromatic compounds in both clarified waters. The raw water NOM had higher aromaticity, which highest intensity was observed for Tavira raw water. While comparable in pH, Alcantarilha and Tavira waters had different ionic composition, as their dissimilarity in conductivity depicts.

Table 1. Tested waters characteristics.

	Water samples			
	Raw		Clarified	
	Alcantarilha	Tavira	Alcantarilha	Tavira
DOC (mg L ⁻¹)	2.4	2.8	1.4	1.7
SUVA (L mg ⁻¹ m ⁻¹)	1.42	2.17	0.94	0.83
pH	7.6	7.2	7.3	7.4
Conductivity (µS cm ⁻¹)	370	120	375	81

As described in Table 2, chlorine decay in all tested waters was satisfactorily described by the first order model.

Table 2. Computed k_b values (day⁻¹), number of chlorine measurements over time (n) and R^2 of first order model fitting.

T (°C)	Raw water					
	Alcantarilha			Tavira		
	k_b	n	R^2	k_b	n	R^2
5	0.79	9	0.87	2.82	8	0.84
12	1.83	10	0.89	2.25	9	0.92
20	5.02	10	0.78	7.46	9	0.96
30	7.41	9	0.93	14.2	8	0.95
T (°C)	Clarified water					
	Alcantarilha			Tavira		
	k_b	n	R^2	k_b	n	R^2
5	1.27	8	0.84	0.20	9	0.86
12	1.44	7	0.84	0.42	9	0.95
20	1.43	11	0.83	2.34	11	0.97
30	5.84	9	0.85	2.85	10	0.89

On the whole, chlorine decayed faster in both raw waters than in the clarified ones, as expected, owing to the higher NOM contents of the former (Hua *et al.*, 1999; Hallam *et al.*, 2003). Unexplicable exceptions for this finding were Alcantarilha waters at 5°C, which clarified one exhibited higher k_b than the raw one.

In general, experimental k_b increased with temperature, although results show very similar decay constants for some assays (e.g., Tavira raw water at 5°C and 12°C). In any case, as Figure 1 shows, the influence of the water temperature on k_b in all tested waters approached the Arrhenius law.

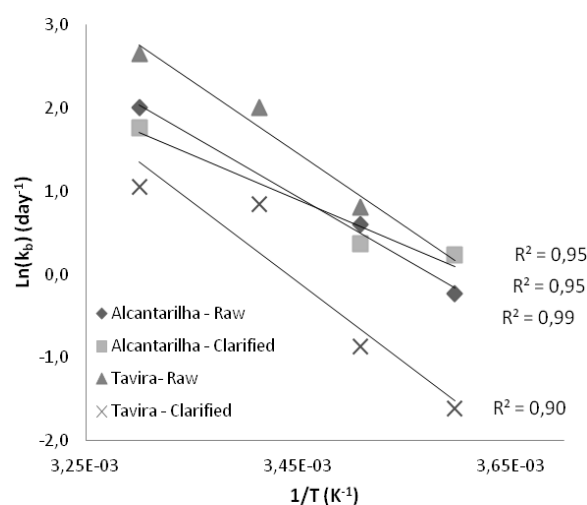


Figure 1. Arrhenius equation fitting to experimental data.

Arrhenius equation linear fittings of the results allowed estimations of k_b for 20°C and 10°C. Ratios of estimated $k_b(20^\circ\text{C}) / k_b(10^\circ\text{C})$ and Arrhenius coefficient E_a/R presented in Table 3 show that the temperature influence on k_b differed among the tested waters.

Table 3. E_a/R and $k_b(20^\circ\text{C}) / k_b(10^\circ\text{C})$ ratio.

	Water Samples			
	Raw		Clarified	
	Alcantarilha	Tavira	Alcantarilha	Tavira
E_a/R (°C)	7393	8748	5424	9701
$k_b(20^\circ\text{C}) / k_b(10^\circ\text{C})$	2.44	2.87	1.92	3.22

According to these results, a temperature raise of 10°C will lead to a 1.92

(Alcantarilha clarified water) to 3.22 (Tavira clarified water) fold increase in k_b values.

Discussion and Conclusions

Temperature effects on k_b were observed and could be modelled with the Arrhenius equation. Observed E_a/R values, as well as $k_b(20^\circ\text{C}) / k_b(10^\circ\text{C})$ ratios, are comparable to those reported by Powell *et al.* (2000) and AWWARF (1996). However, the observed dissimilarity in E_a/R values suggest that temperature impact on k_b is different amongst tested waters. Therefore, in estimating the effect of temperature on k_b , care must be taken in using published E_a values, as these may differ significantly among waters.

Differences in temperature effects on k_b could not apparently be ascribed to NOM contents and quality, as DOC and SUVA values were quite similar (Table 1) in the samples that exhibited the highest and lowest $k_b(20^\circ\text{C}) / k_b(10^\circ\text{C})$ ratios. Possibly, SUVA values do not reflect all the NOM properties associated with its reactivity towards chlorine. Also, different water inorganic matrix characteristics (e.g., ionic strength) may have influenced dissimilarly the kinetics of NOM reactions with chlorine. Research is being undertaken with focus on these issues.

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Disclosures

Authors have nothing to disclose.