

Kinetics of the formation and decomposition of chlorination by-products in surface waters

A.D. Nikolaou*, T.D. Lekkas, S.K. Golfinopoulos

Water and Air Quality Laboratory, Department of Environmental Studies, University of the Aegean, Karadoni 17, 81100 Mytilene, Greece

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Abstract

The presence of organic chlorination by-products (CBPs) in drinking waters has caused great public health concerns. One of the most important factors affecting their formation during the disinfection procedure is reaction time. The kinetics of the formation of CBPs can be different for the different categories or species of compounds, depending also on the chlorine dose, organic matter content and the presence of bromide ion. Decomposition of some CBPs also occurs due to hydrolysis or reactions with residual chlorine. Therefore, the final concentrations of individual species of CBPs reaching the consumers' tap may deviate from the predictions. The aim of the present investigation was the determination of formation or decomposition kinetics of CBPs during chlorination of natural waters. 24 CBPs were studied in chlorinated water from three different sources. Different speciation of CBPs and different formation rates were observed for different water quality regarding bromide ion presence and organic matter content. Decomposition of some CBPs occurred, specifically haloketones, BCA and DBA, after an initial formation step. The percentages of incorporation of chlorine and organic matter into CBPs indicated that other halogenated compounds not identified during the present study have also been formed during chlorination. The importance of chlorine dose for the formation of CBPs and for the incorporation of organic matter was highlighted. Moreover, linear correlations were observed between the concentrations of chloroform-MCA, chloroform-DCA and chloroform-TCA as well as between total THMs and total HAAs, in all waters studied.

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1. Introduction

Due to their potential harm to human health, organic chlorination by-products (CBPs) forming during drinking water disinfection [1–5] have caused great public health concerns. The trihalomethanes (THMs) chloroform, dichlorobromomethane and bromoform have been classified by EPA as probable human carcinogens (cancer group B2), while dibromochloromethane, chloral hydrate, dichloroacetonitrile and dibromoacetonitrile as possible human carcinogens (cancer group C) [6]. The haloacetic acids (HAAs) dichloroacetic acid and trichloroacetic acid are both harmful to human's liver and can cause neuropathy and deformity in rat embryo. Regulatory limits for the concentrations for a number of CBPs in drinking waters have already been set by the EPA, the WHO and the European

Union [7–9], in order to minimize the associated risks for the water consumers' health.

In order to achieve minimization of the formation of CBPs, while maintaining proper disinfection, the parameters affecting their formation need to be fully investigated and interpreted. This is a very complicated issue, since the behavior of these compounds can be entirely different in varying qualities of water and under different chlorination conditions. Numerous studies have been reported in the literature regarding the formation of CBPs [1–5,10]. The main parameters involved in the reactions of formation of CBPs are reaction time, chlorine dose and residual, natural organic matter, pH, temperature and bromide ion. Increase of chlorine dose has been reported to have positive influence of CBPs yield. The same is true for increased concentrations of natural organic matter and increased temperature. The presence of bromide ion shifts the speciation of CBPs to more brominated analogues, while increased pH can enhance the formation of some categories of CBPs, e.g. THM, and inhibit the formation of some others, e.g. haloacetonitriles and haloketones.

* Corresponding author. Tel.: +30-22510-36226;
fax: +30-22510-36099.

E-mail address: nnikol@aegean.gr (A.D. Nikolaou).

Reaction time is one of the most important parameters affecting the yields of CBPs in chlorinated water. A significant aspect that must be taken into account is that reaction time can have different influence on different CBPs. It has been reported that THMs concentrations increase with time, while some volatile by-products such as haloacetonitriles and halo ketones can decompose due to hydrolysis and reactions with residual chlorine [10,11]. Studies reporting formation kinetics of some CBPs have been reported, mainly for THMs [12–14]. A second-order model for the formation of THMs as a function of chlorine demand and time has been proposed [15], and the kinetics of the formation of individual THM species, based on the bromine content factor, have been studied [16]. The common observation of most researchers is a rapid initial formation of THMs during the first 30–100 min, followed by a slower rate of increase [13,14,17]. The kinetics of the formation of six congeners of HAAs has also been investigated [17–19]. Carlson and Hardy [17] reported similar behavior of HAA6 with that of THMs, i.e. rapid initial formation followed by a slower rate of increase, however pointed out that the reaction rates for THMs and HAAs were different. In another study, contradictory results have been reported, i.e. yields of DCA and TCA increased continuously after a slow initial formation rate [19], probably because the particular study regarded chlorinated fulvic acid from sediments, which seems to be a “slow former” of CBPs.

Investigation of the influence of reaction time on CBPs formation is critical in order to determine the final concentrations to which people could be exposed. Substance-by-substance analysis is needed for this purpose, because the final concentration could be lower or higher than expected, due to decomposition of some CBPs, or due to transformation of some compounds to others. During this study, surface waters were chlorinated in order to determine kinetics of the formation of different species of CBPs, including not only THMs, but also species of halo ketones, chloral hydrate and all nine congeners of HAAs. The results should be of value for the design and optimization of the chlorination conditions in water industries, so that the

chlorinated water reaching the consumers' tap contains as low concentrations of CBPs as possible.

2. Materials and methods

2.1. Glassware

Preparation of all glassware used during analysis included washing with detergent, rinsing with tap water, ultrapure water (Millipore: Milli-Ro 5 plus and Milli Q plus 185), acetone (Mallinckrodt Chemical Works, St. Louis) and placing in an oven at 150 °C for 2 h.

2.2. Reagents-standard solutions

Methanol (purge and trap grade) was purchased from Sigma–Aldrich, methyl-*tert*-butyl ether (MTBE) suprasolv grade, potassium dichromate, potassium iodide, sodium sulfite, ammonium chloride, copper(II) sulfate pentahydrate and sulfuric acid concentrated ISO for analysis from Merck, boric acid (analytical grade) from Ferak and sodium sulfate anhydrous (granular) from Mallinckrodt Chemical Works, St. Louis. Ultrapure water was from a Milli-Q water purification system (Millipore: Milli-Ro 5 plus and Milli Q plus 185). Stock solutions were prepared in 10 ml volumetric flasks containing MTBE (Merck, for organic trace analysis) by addition of high purity CBPs standards accompanied by certificate of analysis (Chemservice, purity > 99% for THMs and the other volatile CBPs and Supelco, purity > 99%). The CBPs investigated during this study are presented in Table 1.

2.3. Sample preparation

Surface water samples were collected in March 2000 from three rivers, in Mytilene, Greece. The organic matter content of these rivers is high, since the flux is low and not continuous throughout the year (in summer they are

Table 1
The CBPs investigated during this study

THMs	Other volatile CBPs	HAAs
Chloroform (CHCl ₃)	Chloral hydrate (CH)	Monochloroacetic acid (MCA)
Dichlorobromomethane (CHCl ₂ Br)	1,1-Dichloropropanone (1,1-DCP)	Dichloroacetic acid (DCA)
Dibromochloromethane (CHClBr ₂)	1,3-Dichloropropanone (1,3-DCP)	Trichloroacetic acid (TCA)
Bromoform (CHBr ₃)	1,1,1-Trichloropropanone (1,1,1-TCP)	Monobromoacetic acid (MBA)
	Monochloroacetonitrile (MCAN)	Dibromoacetic acid (DBA)
	Dichloroacetonitrile (DCAN)	Tribromoacetic acid (TBA)
	Trichloroacetonitrile (TCAN)	Bromochloroacetic acid (BCA)
	Bromochloroacetonitrile (BCAN)	Bromodichloroacetic acid (BDCA)
	Monobromoacetonitrile (MBAN)	Dibromochloroacetic acid (DBCA)
	Dibromoacetonitrile (DBAN)	
	Chloropicrin (CP)	

completely dry). Samples were stored in 1-l amber glass bottles and, kept at 4 °C, they were transported to the Water and Air Quality Laboratory of the University of Aegean. After pH measurements (using a Crison MicroPH2001 pH meter), and filtration (with Whatman GF/A glass microfibre filters 4.7 cm), samples were analyzed for chloride, bromide and nitrate ions by a modification of EPA Method 300.0 [20], using a Dionex 2000i ion chromatograph with a Dionex HPLC-AG4A column and a suppressed conductivity detector. As an indicator of organic matter content, UV absorbance was measured at 272 nm (with a Cary 1E UV-Vis spectrophotometer). UV absorbance has been reported to be an equivalent or better indicator than Total Organic Carbon (TOC) of the organic matter content of the water [21,22]. The most commonly used wavelength for UV-absorbance measurements is 254 nm, however it has been reported that especially in the case of presence of reducing agent in the water (e.g. sulfite), UV-272 nm is a more precise measurement, since at 254 nm a peak is detected due to sulfite [21,22]. During this study, sulfite was used to quench the residual chlorine in the chlorinated samples in order to cease the chlorination reaction, as described below; therefore UV-272 measurements were conducted.

Chlorination of the samples was performed according to the procedure described in Standard Methods for the Examination of Water and Wastewater (Iodometric Method I 4500B) [23]. The chlorine dosages used were 2 and 4 mg/l and the reaction times tested were 0, 1, 2, 3, 4, 8, 16, 24, 32, 40, 48, 56, 64 and 72 h.

The chlorinated samples were divided into 40 ml amber glass bottles with polypropylene screw caps and TFE-faced septa (Pierce 13075) and incubated at 21 °C for the desired contact times. Then, residual chlorine was measured according to the DPD colorimetric method [24] and the quenching agent for depletion of residual chlorine (sodium sulfite for THMs and other volatile CBPs, and ammonium chloride for HAAs, 100 mg/l of sample) was added after the required contact times were completed.

For the determination of THMs and other volatile CBPs, a modification of EPA Method 551.1, which includes liquid–liquid extraction (LLE) with MTBE was performed [25–27]. For the determination of HAAs, acidic methanol esterification [27–29] was used. Each sample was analyzed twice, and the average of the measurements was calculated.

2.4. Apparatus

A HP 5890 Series II Gas Chromatograph equipped with a ⁶³Ni Electron Capture Detector (ECD) was used for the

measurements of CBPs. The column was fused silica capillary DB-1, 30 m × 0.32 mm i.d. × 0.25 μm film thickness. The injection technique was splitless, the carrier gas helium (purity 99.999%) and the makeup gas nitrogen (purity 99.999%). A Hewlett Packard Mass Selective Detector 5971, supported by the HP G1034C system software, with a fused silica capillary HP-VOC (60 m × 0.32 mm × 1.8 μm) was used for confirmatory purposes. Percent recoveries, relative standard deviations and detection limits of the analytical methods used have been reported elsewhere [26,29].

3. Results and discussion

The general characteristics of the waters studied are given in Table 2. The highest UV-absorbance was measured in Mylopotamos river water (0.249 cm⁻¹). In Mylopotamos river, chloride and bromide concentrations were also high (138.9 and 2.4 mg/l, respectively). It must be noted that the sampling point in Mylopotamos river is located near a saltwork. Water from rivers Evergetoulas and Tsiknias showed significantly lower UV-272 and chloride concentrations than Mylopotamos river. Moreover, in water from these two rivers, bromide ion concentration was not detectable. The highest nitrate concentration was detected in Tsiknias river water.

The concentrations of residual chlorine in the chlorinated samples are given in Table 3. The consumption of chlorine was very fast, due to the high organic matter content of the waters, especially in the case of Mylopotamos river.

In non-chlorinated water samples (raw water), none of the CBPs studied were present. However, in chlorinated samples, a large number of CBPs were detected: CHCl₃, CHCl₂Br, CHClBr₂, CHBr₃, CH, 1,1-DCP, 1,1,1-TCP, MCAN, DBAN, MCA, MBA, DCA, BCA, TCA, DBA, BDCA, DBCA and TBA.

3.1. CBPs in chlorinated water from Evergetoulas river

The concentrations of the major CBPs detected in chlorinated water from Evergetoulas river as a function of time (Cl dose 2 and 4 mg/l) are shown in Fig. 1. The major species formed was CHCl₃, followed by DCA and MCA. TCA, CHCl₂Br, CH, 1,1-DCP, 1,1,1-TCP, BCA and BDCA were detected at lower concentrations.

Increase of CHCl₃ concentration over time was higher compared to the other THMs, Its concentration after 72 h reaction time became six-fold higher than the initial concentration. However, for the volatile CBPs, decreasing trends were observed, especially for 1,1,1-TCP

Table 2
General characteristics (pH, T, UV-272, Cl⁻, Br⁻, NO₃⁻) of the natural waters studied

	pH	T (°C)	UV-272 (cm ⁻¹)	Cl ⁻ (mg/l)	Br ⁻ (mg/l)	NO ₃ ⁻ (mg/l)
Evergetoulas	7.77	13	0.179	10.1	<0.06	3.7
Tsiknias	7.33	13	0.107	17.7	<0.06	10.2
Mylopotamos	7.81	13	0.249	138.9	2.4	3.5

Table 3
Concentrations of residual chlorine (mg/l) in the chlorinated samples

Time (h)	Chlorine dose 2 mg/l			Chlorine dose 4 mg/l		
	Evergetoulas	Tsiknias	Mylopotamos	Evergetoulas	Tsiknias	Mylopotamos
0	ND ^a	0.1	ND ^a	0.5	0.5	0.1
1	ND ^a	0.1	ND ^a	ND ^a	0.1	ND ^a
2	ND ^a	0.1	ND ^a	ND ^a	0.1	ND ^a
3	ND ^a	0.1	ND ^a	ND ^a	0.1	ND ^a
4	ND ^a	0.1	ND ^a	ND ^a	0.1	ND ^a
8	ND ^a	0.1	ND ^a	ND ^a	0.1	ND ^a
16	ND ^a	ND ^a	ND ^a	ND ^a	ND ^a	ND ^a
24	ND ^a	ND ^a	ND ^a	ND ^a	ND ^a	ND ^a
32	ND ^a	ND ^a	ND ^a	ND ^a	ND ^a	ND ^a
40	ND ^a	ND ^a	ND ^a	ND ^a	ND ^a	ND ^a
48	ND ^a	ND ^a	ND ^a	ND ^a	ND ^a	ND ^a
56	ND ^a	ND ^a	ND ^a	ND ^a	ND ^a	ND ^a
64	ND ^a	ND ^a	ND ^a	ND ^a	ND ^a	ND ^a
72	ND ^a	ND ^a	ND ^a	ND ^a	ND ^a	ND ^a

^a ND: not detectable concentration.

(concentration not detectable after 48 h). From HAAs, DCA was the compound showing the highest increase with time (its concentration became four-fold higher than its initial concentration within 72 h), followed by MCA and TCA.

3.2. CBPs in chlorinated water from Tsiknias river

The concentrations of the major CBPs detected in chlorinated water from Tsiknias river as a function of time (Cl dose 2 mg/l) are shown in Fig. 2.

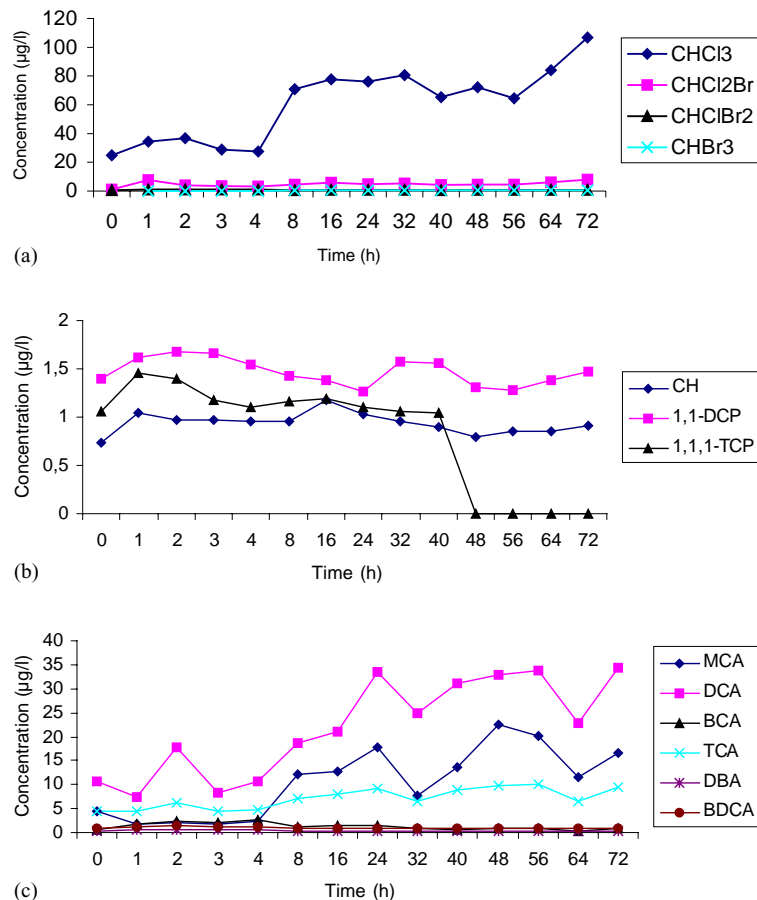


Fig. 1. Formation of (a) THMs, (b) other volatile CBPs and (c) HAAs in chlorinated water from river Evergetoulas (chlorine dose 2 mg/l).

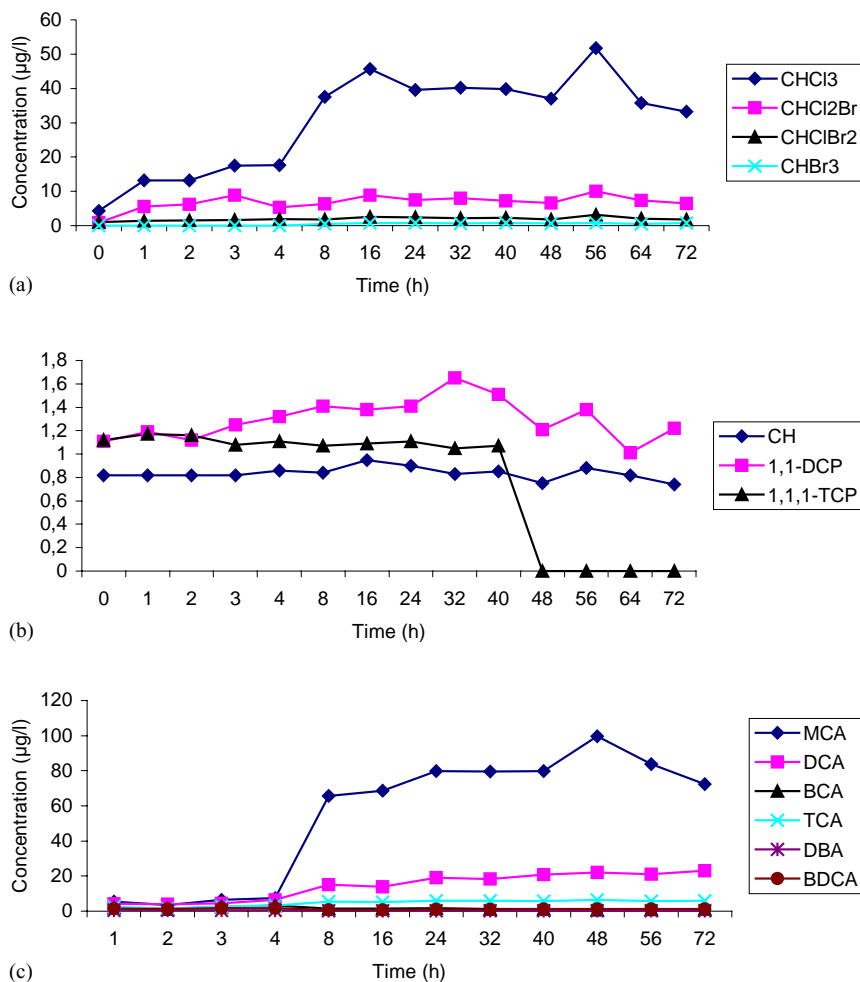


Fig. 2. Formation of (a) THMs, (b) other volatile CBPs and (c) HAAs in chlorinated water from river Tsiknias (chlorine dose 2 mg/l).

The evolution of CBPs concentrations in chlorinated water from Tsiknias river was similar to that in Evergetoulas river, with CHCl₃, MCA, DCA and TCA showing the greatest concentration increase over time. Decreasing trends were observed again for volatile CBPs, especially for 1,1,1-TCP.

3.3. CBPs in chlorinated water from Mylopotamos river

The concentrations of the major CBPs detected in chlorinated water from Mylopotamos river as a function of time (Cl dose 2 and 4 mg/l) are shown in Fig. 3.

The speciation of CBPs in chlorinated water samples from Mylopotamos river was entirely different from that in samples from Evergetoulas and Tsiknias rivers, with brominated species predominating due to intense presence of bromide ion. For the compounds CHCl₂Br and CHClBr₂, great increase of concentration over time was observed (25-fold higher concentration after 72 h compared to the initial concentration). The concentrations of CHBr₃ and CHCl₃ also increased significantly (15 and 10-fold increase, respectively after 72 h reaction time).

1,1,1-TCP was not detectable after 40 h, while the concentrations of MCAN and DBAN remained at the same levels throughout the time range studied. Formation of TCAN seems to be completed within 24 h. 1,1-DCP showed decreasing trends. Regarding HAAs, the highest concentration increase was observed for DCA (after 72 h its concentration became 5-fold higher than the initial concentration), followed by TCA, BCA, BDCA and DBA.

3.4. Kinetics of the formation of CBPs

The formation of THMs had been completed within 24 h reaction time in all chlorinated waters. Table 4 presents the average reaction rate $\Delta C/\Delta t$ for different compounds detected, where ΔC = (molar concentration at the end of the time interval Δt) – (molar concentration at the beginning of the time interval Δt), for selected time intervals. The THMs formation rates were higher than those reported by El-Dib and Ali [12], probably because of the high organic matter content of the waters used in this study. Furthermore, the type of organic matter contained in the different waters

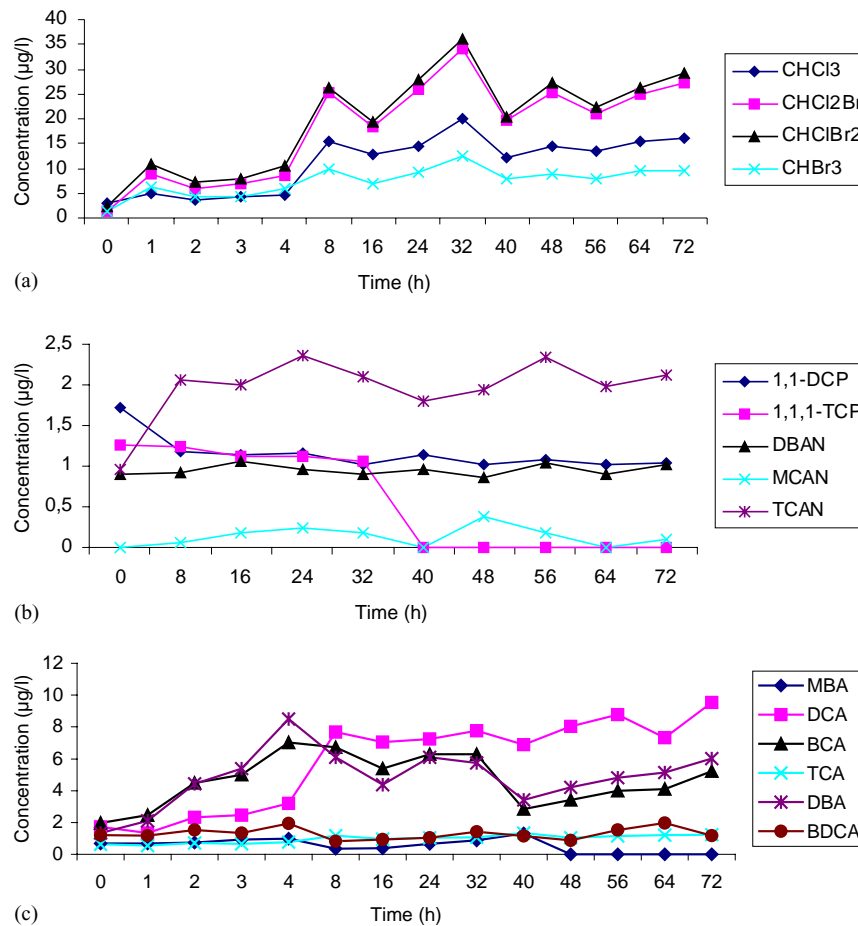


Fig. 3. Formation of (a) THMs, (b) other volatile CBPs and (c) HAAs in chlorinated water from river Mylopotamos (chlorine dose 2 mg/l for (a) and (c), 4 mg/l for (b)).

could also play a significant role. For CHCl₃, CHCl₂Br and CHClBr₂ in chlorinated water from river Evergetoulas the formation rates were highest during the first hours of the reaction and then decreased. However, for waters from rivers Mylopotamos and Tsiknias the opposite behavior was observed, with the formation rates increasing after the first hours of the reaction. Bromoform was the only compound with formation rate increasing with time in all three rivers. Increase of chlorine dose resulted in increase of the THMs formation rates, especially for CHCl₃ and CHCl₂Br in water from river Evergetoulas. Regarding the rate of formation of the different species of THMs, in chlorinated waters from river Evergetoulas and Tsiknias the order followed was CHCl₃ > CHCl₂Br > CHClBr₂ > CHBr₃, while for chlorinated water from river Mylopotamos, in significant presence bromide ion, the order was CHCl₂Br > CHClBr₂ > CHCl₃ > CHBr₃ at the low chlorine dose, and became CHClBr₂ > CHBr₃ > CHCl₂Br > CHCl₃ at the higher chlorine dose (Table 4).

The behavior of the volatile CBPs CH and 1,1-DCP generally consisted of two steps: formation and decomposition step. The duration of these steps was different for the different compounds, with the first step lasting from 2 to 16 h,

and the second from 3 to 64 h. The formation rates of the volatile CBPs CH, 1,1-DCP and 1,1,1-TCP for selected time intervals are presented in Table 4. In water from river Evergetoulas, CH formed during the first 3 h of the reaction for chlorine dose 2 mg/l and during the first 16 h for chlorine dose 4 mg/l, and decreased afterwards in both cases. In water from river Tsiknias CH formation rate after 2 h for chlorine dose 2 mg/l and after 8 h for chlorine dose 4 mg/l, was very low. CH was not formed in chlorinated water from river Mylopotamos, probably because the presence of bromide ion favors mostly the formation of brominated CBPs species. 1,1-DCP and 1,1,1-TCP concentrations, forming initially with low rates, decreased 3 h after chlorination of water from river Evergetoulas, and 8 h after chlorination of water from rivers Tsiknias and Mylopotamos.

For 1,1,1-TCP the general trend was decreasing from the beginning of the experiment until 64 h. Decomposition of this compound has been reported in the literature [10,30], also leading to the formation of chloroform. Therefore, the formation of chloroform derives not only from the direct pathway of the chlorination reaction with organic matter, but also from the indirect pathway of decomposition of 1,1,1-TCP initially formed. This could also be the case for

Table 4
Formation rates ($\Delta C/\Delta t$) of CBPs in the chlorinated waters studied ($\mu\text{mol}/(\text{lh})$) for selected time intervals

	Time interval (h)					
	0–3	3–8	8–16			
River Evergetoulas						
Chlorine dose 2 mg/l						
CHCl ₃	0.081	0.070	0.007			
CHCl ₂ Br	0.007	0.001	0.001			
CHClBr ₂	0.002	0	0			
CHBr ₃	0	0.0004	4.95×10^{-6}			
CH	0.002	<0	0			
1,1-DCP	0.004	<0	<0			
1,1,1-TCP	0.002	<0	<0			
MCA	0.006	0.021	0.00078			
DCA	0.021	0.016	0.002			
BCA	0.004	<0	<0			
TCA	0.009	0.003	0.0007			
DBA	0.0007	<0	0			
BDCA	0.002	<0	0			
	0–1	1–2	2–3	3–8	8–16	16–24
Chlorine dose 4 mg/l						
CHCl ₃	0.384	0.115	0.109	0.085	0.029	0.010
CHCl ₂ Br	0.033	0.007	0.007	0.002	0.0007	0.0008
CHClBr ₂	0.0012	0.0005	0.0003	<0	0	0
CHBr ₃	0	0	0	0.0004	4.9×10^{-6}	0
CH	0.007	0.002	0.0002	0.0003	0.0002	<0
1,1-DCP	0.011	<0	0	0	0	0
1,1,1-TCP	0.012	<0	<0	0	0	0
MCA	0.027	0.0003	0	0.087	0.004	<0
DCA	0.107	0	0	0.060	0.008	<0
BCA	0.018	0	0	0.0005	0.0001	<0
TCA	0.109	0	0	0.019	0.0009	0.0003
DBA	0.002	<0	<0	<0	<0	<0
BDCA	0.011	<0	0.0001	<0	0.0002	<0
	0–2	2–8	8–16			
River Tsiknias						
Chlorine dose 2 mg/l						
CHCl ₃	0.111	0.314	0.382			
CHCl ₂ Br	0.038	0.039	0.054			
CHClBr ₂	0.007	0.009	0.012			
CHBr ₃	0	0	0.003			
CH	0.002	2×10^{-5}	8.3×10^{-5}			
1,1-DCP	0.004	0.0004	<0			
1,1,1-TCP	0.004	<0	<0			
MCA	0.019	0.109	0.004			
DCA	0.015	0.014	<0			
BCA	0.004	0.0002	<0			
TCA	0.0044	0.0039	<0			
DBA	0.0011	<0	<0			
BDCA	0.0027	<0	<0			
	0–1	1–8	8–16	16–24		
Chlorine dose 4 mg/l						
CHCl ₃	0.193	0.583	0.874	0.958		
CHCl ₂ Br	0.035	0.079	0.106	0.113		
CHClBr ₂	0.011	0.019	0.027	0.032		
CHBr ₃	0	0.002	0.028	0.003		
CH	0.005	0.0004	7.5×10^{-6}	0.0002		
1,1-DCP	0.0102	0.0003	<0	<0		
1,1,1-TCP	0.008	7.1×10^{-5}	<0	<0		
MCA	0.119	0.195	<0	0		
DCA	0.028	0.035	<0	0		
BCA	0.011	7.4×10^{-5}	<0	0		

Table 4 (Continued)

	Time interval (h)			
	0–3	3–8	8–16	
TCA	0.003	<0	<0	0
DBA	0.009	<0	<0	0
BDCA	0	0.005	0.003	<0
	0–2	2–8		
River Mylopotamos				
Chlorine dose 2 mg/l				
CHCl ₃	0.031	0.128		
CHCl ₂ Br	0.04	0.154		
CHClBr ₂	0.034	0.125		
CHBr ₃	0.017	0.039		
1,1-DCP	0.004	0.0005		
1,1,1-TCP	0.003	6.2×10^{-5}		
MBA	0.375	<0		
DCA	0.009	0.007		
BCA	0.013	0.002		
TCA	0.002	0.0005		
DBA	0.010	0.001		
BDCA	0.004	<0		
	0–8	8–16	16–24	
Chlorine dose 4 mg/l				
CHCl ₃	0.119	0.134	0.144	
CHCl ₂ Br	0.294	0.311	0.327	
CHClBr ₂	0.483	0.500	0.520	
CHBr ₃	0.415	0.437	0.434	
1,1-DCP	0.001	<0	0	
1,1,1-TCP	7.2×10^{-6}	<0	<0	
MCAN	9.9×10^{-5}	0.0002	0.0001	
TCAN	0.002	<0	0	
MBA	0.0009	0.0011	0	
DCA	0.009	<0	0	
BCA	0.009	<0	<0	
TCA	0.001	<0	0	
DBA	0.015	<0	0	
BDCA	0.002	0.0005	0	
DBCA	0.002	0.0006	0	

the other CBPs detected, since after chlorination of natural waters many of them are simultaneously present in water.

Regarding HAAs, different observations were made for the different congeners of this group of CBPs. Particularly, for MCA, DCA and TCA, which in most cases were the major species detected, the formation rates were higher during the first hours of the reaction, decreasing significantly after 8 h, when their concentrations stabilized. On the contrary, the formation of BCA, BDCA and DBA, which were usually detected at lower concentrations, consisted of two steps: a formation step lasting for the first 1–2 h of the experiment in the case of chlorine dose 4 mg/l and for the first 2–8 h in the case of chlorine dose 2 mg/l (Table 4), and afterwards, either stabilization of their concentration or decomposition until up to 40 h. These observations imply that increased chlorine dose results in decreased duration of the formation step for the particular compounds.

In chlorinated water from rivers Evergetoulas and Tsiknias, the species MCA, DCA and TCA showed higher

formation rates than BCA, DBA and BDCA, whereas the opposite was observed in the case of Mylopotamos river, probably due to the high concentration of bromide ion.

3.5. Incorporation of chlorine, organic matter content and bromide into the CBPs

The percent incorporation of chlorine and bromide into the detected CBPs was calculated on the basis of the molecular weights of the compounds formed and their molar concentrations, the atomic masses of Cl and Br, the chlorine dose added and the initial bromide concentration.

Regarding chlorine incorporation in all CBPs detected, the highest percentage was 6.6% and was observed in chlorinated water from river Evergetoulas. The lowest total percent chlorine incorporation occurred for river Mylopotamos and was 2%. In Tsiknias river, the total percent chlorine incorporation ranged from 5.3 to 5.9%.

From the total chlorine incorporation, the largest part is divided into the two major categories of CBPs formed, i.e. THMs and HAAs. In two of the rivers studied, Evergetoulas and Mylopotamos, incorporation of chlorine into the THMs was higher than in HAAs. For river Evergetoulas it ranged from 4.1 to 4.9% for THMs and from 1.7 to 2.0% for HAAs and for river Mylopotamos from 1.7 to 1.9% for THMs and from 0.3 to 0.4% for HAAs. On the contrary, for river Tsiknias, the percentage of chlorine incorporated into THMs (2.6–2.8%) was slightly less than that incorporated into HAAs (2.7–3.2%).

The fact that water from river Tsiknias was the one with the lowest organic matter content leads to the assumption that elevated organic matter concentration in water favors chlorine incorporation into THMs over HAAs. The estimations of chlorine incorporation, taking into account the fact that the entire amount of chlorine added to the water was consumed during the formation of CBPs, shows that only a very low percentage (maximum 6.6%) of the chlorine incorporation has been characterized by the analyses performed during the present study. This means that a large amount of the chlorine added has been incorporated into not identified compounds, some of which could have an impact on environmental quality and human health. Therefore, investigation of further categories of CBPs is necessary so that chlorine incorporation is sufficiently identified and chlorinated water quality more accurately estimated.

The above assumption is further confirmed by the calculation of the incorporation of organic matter—expressed as UV-272 nm—into CBPs. It must be clarified that the percentage calculated refers to the formation of all organic compounds and not only those investigated during the present work. The incorporation of organic matter was calculated as follows:

$$\frac{[\text{UV272 initial (before chlorination)} \times \text{UV272 final}]}{[\text{UV272 initial}]} \times 100$$

The results obtained were within the range 5.3–29.8% for all waters. Therefore, it seems that during chlorination a significant part of organic matter is transformed to organic compounds other than those detected during this study. Furthermore, when chlorine dose was doubled (from 2 to 4 mg/l), the percent incorporation of organic matter was also doubled for all waters (from 16 to 29.8% for Evergetoulas, from 5.3 to 8.7% for Mylopotamos and from 12.4 to 27.7% for Tsiknias river waters), a fact that emphasizes the importance of maintaining the chlorine dose applied during water treatment at low levels in order to avoid formation of excessive amounts of CBPs. Another observation was that for water from river Mylopotamos, which was the richest one in organic matter, incorporation of organic matter into CBPs was the lowest. This could probably be attributed either (a) to the higher UV-272/chlorine ratio in this river ($0.12 \text{ cm}^{-1} \text{ l mg}^{-1}$ for chlorine dose 2 mg/l) compared to the others ($0.09 \text{ cm}^{-1} \text{ l mg}^{-1}$ for Evergetoulas and $0.05 \text{ cm}^{-1} \text{ l mg}^{-1}$ for Tsiknias rivers) which means

that chlorine could be the limiting factor for organic matter transformation to CBPs, or/and (b) to the nature of the organic matter in this river, e.g. the particular organic matter may consist from compounds not easily/preferably attacked by chlorine, therefore limiting the “consumed” amount of UV-272.

Bromide incorporation into the CBPs was calculated only for chlorinated water from Mylopotamos river, since it was the only river where bromide ion was present. The total bromide incorporation into the detected CBPs was 2.6% for chlorine dose 2 mg/l, while for chlorine dose 4 mg/l it was significantly higher, 11.5%. Since there was excess bromide ion in the water, increase of chlorine dose shifted the speciation of CBPs to brominated species, thus increasing bromide incorporation. The percentage of bromide incorporation into THMs was 2.2 and 10% for chlorine dose 2 and 4 mg/l, respectively, while the corresponding percentages of bromide incorporated into HAAs were lower, 0.4 and 1.4%.

3.6. Correlations between individual species of CBPs

Correlations between trihalomethanes and haloacetic acids with total organic halides formed during water treatment have been reported in the literature [31,32]. Based on the observations of decomposition of some CBPs during the present study, the possible existence of linear correlations between the concentrations of individual species of CBPs was investigated, especially for 1,1,1-TCP which decomposes forming chloroform. However, linear correlation existed neither between 1,1,1-TCP and chloroform nor between 1,1-DCP and chloroform. In fact, correlations did not exist in any case between individual or total volatile CBPs and THMs, or between volatile CBPs and HAAs. It must be taken into account that chloroform formation does not derive only from the decomposition of 1,1,1-TCP, but also from the chlorination of organic matter and maybe via other transformation pathways of the existing compounds. Therefore this could be the reason that the particular correlations could not be established.

On the other hand, linear correlations were observed between chloroform-MCA, chloroform-DCA and chloroform-TCA in all waters studied (Table 5). In the case of river Tsiknias, linear correlation between bromoform-DBA was also observed, but only for the low chlorine dose (2 mg/l). The most interesting correlation, which could be of practical importance, was the one between total THMs and total HAAs, which was linear for all waters and for all chlorine doses studied. This means that THMs concentration could be used as an indicator of HAAs, thus avoiding a large part of analytical work for HAAs determination. Furthermore, this correlation as well as the individual chloroform-MCA, chloroform-DCA and chloroform-TCA correlations, implies chemical relationships between THMs and HAAs species. Therefore, the formation mechanisms of these two important groups of CBPs seem to be directly related during water chlorination.

Table 5
Correlation coefficients (R^2) between trihalomethanes and haloacetic acids concentrations in the chlorinated waters

	Chlorine dose 2 mg/l	Chlorine dose 4 mg/l
Evergetoulas river		
THMs-HAAs	0.60	0.82
CHCl ₃ -MCA	0.56	0.82
CHCl ₃ -DCA	0.64	0.80
CHCl ₃ -TCA	0.57	0.78
Tsiknias river		
THMs-HAAs	0.85	0.85
CHCl ₃ -MCA	0.85	0.86
CHCl ₃ -DCA	0.79	0.79
CHCl ₃ -TCA	0.85	0.53
CHBr ₃ -DBA	0.74	— ^a
Mylopotamos river		
THMs-HAAs	0.69	0.35
CHCl ₃ -DCA	0.87	0.36
CHCl ₃ -TCA	0.71	0.35

^a Not linear correlation.

4. Conclusions

Reaction kinetics was studied for the formation of a number of CBPs detected in chlorinated surface waters from three different sources. Different speciation of CBPs and different formation rates were observed for different water quality regarding bromide ion presence and organic matter content. Decomposition of some CBPs occurred, specifically haloketones, BCA and DBA, after an initial formation step.

The percentage of chlorine incorporation in all detected CBPs ranged from 2 to 6.6%. The incorporation of organic matter into CBPs—referring to all organic compounds and not only those detected during the present work—ranged from 5.3 to 29.8%. These results imply that other halogenated compounds not identified during the present study have also been formed during chlorination, some of which could have an impact on environmental quality and human health.

When chlorine dose was doubled, the percent incorporation of organic matter was also doubled for all waters studied, therefore maintaining the chlorine dose applied during water treatment at low levels is critical in order to limit the formation of CBPs.

In the case of presence of excess bromide ion, the total bromide incorporation into the detected CBPs also increased significantly with increasing chlorine dose.

Linear correlations were observed between the concentrations of chloroform-MCA, chloroform-DCA and chloroform-TCA as well as between total THMs and total HAAs, in all waters studied, which indicate directly related formation mechanisms for these two major groups of CBPs. Moreover, THMs concentration could be used as an indicator of HAAs concentration, thus avoiding a large part of analytical work for HAAs determination.

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