

FACTORS AFFECTING THE FORMATION OF ORGANIC BY-PRODUCTS DURING WATER CHLORINATION: A BENCH-SCALE STUDY

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Abstract. The formation of chlorination by-products (CBPs) was investigated through bench-scale chlorination experiments with river water. The compounds selected for analysis belonged to the groups of trihalomethanes, haloacetic acids, haloketones and haloacetonitriles. Trihalomethanes and haloacetic acids were the major species formed during chlorination, while haloketones and haloacetonitriles occurred at lower levels. The factors affecting the formation of these compounds were examined by two sets of experiments; the first with varying pH and reaction time, and the second with varying chlorine dose and temperature. Different effects of these factors were observed for different categories of CBPs, and in many cases, these effects were compound-specific, as confirmed by statistical analysis. Optimization of chlorination conditions in water treatment plants is a critical issue that should take into account the influence of chlorination parameters on the formation of individual CBPs.

Keywords: chlorination by-products, gas chromatography, haloacetic acids, haloketones, trihalomethanes, water

1. Introduction

A large number of organic by-products have been reported to result from the use of chlorine for drinking water disinfection (Richardson, 2002). The presence of these compounds in water reaching the consumers' tap is an issue of particular importance, since many of them have been classified into carcinogenic groups (probable [B2] or possible [C] human or animal carcinogens) (Premazzi *et al.*, 1997; USEPA, 1998) and their concentrations in drinking water have been regulated by the USEPA, the WHO and the EU (Table I) (USEPA, 1998; WHO, 1995; EEC, 1998).

The major categories of chlorination by-products (CBPs) are trihalomethanes (THMs) (Rook, 1974; Alawi *et al.*, 1994; Golfinopoulos and Nikolaou, 2001), haloacetic acids (HAAs) (Nikolaou and Lekkass, 2001; Christman *et al.*, 1983;



TABLE I

Carcinogenic group classification and qualitative target levels set by the WHO and the European Union for chlorination by-products

Compound	Carcinogenic group (EPA) ^a	WHO guidelines ($\mu\text{g/L}$)
Chloroform ^b	B2	200
Dichlorobromomethane ^b	B2	60
Dibromochloromethane ^b	C	100
Bromoform ^b	B2	100
Dichloroacetonitrile ^c	C	90
Dibromoacetonitrile ^c	C	100
Chloral hydrate ^c	C	Not regulated

^aGroup B2: probable human carcinogen (sufficient data from animal studies), group C: possible human carcinogen.

^bEuropean Union guidelines: total THMs concentration 150 $\mu\text{g/L}$ until 2008 and 100 $\mu\text{g/L}$ after 2008.

^cEuropean Union guidelines: not regulated.

Miller and Uden, 1983; Reckhow and Singer, 1990), haloacetonitriles (HANs), haloketones (HKs) and chloropicrin (Krasner *et al.*, 1989; Oliver, 1983; Lekkas, 1996; Williams *et al.*, 1997; Nikolaou *et al.*, 1999). The formation of these by-products occurs due to reactions of chlorine, added to the water for inactivation of pathogen microorganisms, with natural organic matter already present in surface waters. According to the literature, the factors that were found to influence the formation of CBPs are chlorine dose and residual, natural organic matter and bromide concentration, contact time, pH and temperature.

Results from studies using different water properties, chlorination conditions and studying different compounds often lead to controversial conclusions, because the chlorination reactions and products are complicated and not fully documented. The general up-to-date findings are the following: Higher chlorine dose and natural organic matter concentration enhance the formation of CBPs (Singer, 1994). The presence of bromide ion shifts the products to brominated species (Krasner *et al.*, 1989; Pourmoghaddas and Stevens, 1995; Peters *et al.*, 1991; Heller-Grossman *et al.*, 1993; Cowman and Singer, 1996). The case with contact time, pH and temperature is more complex, since the effect of these three factors can be different for the formation of different categories or species of CBPs, as it will be described below.

Contact time has been reported to have positive effect on trihalomethanes (THMs) and some haloacetic acids (HAAs) concentrations and negative effect on the concentrations of haloacetonitriles, haloketones, and some other species of HAAs, possibly due to hydrolysis, reactions with residual chlorine (Singer, 1994) or bacterial decomposition (Williams *et al.*, 1997).

Increased pH values have positive effect on THMs formation, but negative effect on the formation of some other volatile by-products such as halo ketones, which decrease due to hydrolysis (Singer, 1994). HAAs have been reported to increase at low pH (Krasner *et al.*, 1989; Pourmoghaddas and Stevens, 1995; Summers *et al.*, 1996). According to another study, for DCA not significant changes were observed with pH change, while for TCA a concentration increase was observed during pH increase from 2 to 5, maximum concentration at pH 5 and decrease afterwards (Stevens *et al.*, 1989).

Temperature affects reaction kinetics. A general observation is that elevated temperatures have positive effect on CBPs formation, due to faster formation reactions (Krasner *et al.*, 1989; Williams *et al.*, 1997; Singer, 1994). However, it must be noted that this could not be the case for all the compounds, since a temperature increase will have as a result not only faster formation kinetics, but also faster decomposition kinetics, as it was found for example for haloacetonitriles and halo ketones (Nikolaou *et al.*, 2000, 2001).

During the present study, bench-scale chlorination experiments were conducted using river water, in order to investigate the influence of different factors on the formation of chlorination by-products. Emphasis was given on the factors reported to have different effects according to the category or species of CBPs. The factors studied were contact time, pH, temperature and chlorine dose. Statistical analysis of the results included multifactor analysis of variance to confirm the statistical significance for the observed effects. Towards the objective of minimization of the concentrations of CBPs in drinking water, optimization of the chlorination conditions requires knowledge of their influence on the different compounds concentrations. Although a combination of factors that results in simultaneous minimization of all CBPs species is very difficult to be obtained, the results of this study should be of value to the water industry especially for the cases of increased concentrations of specific CBPs in the treated water.

2. Materials and Methods

2.1. GLASSWARE

The glassware used during analysis was washed with detergent, rinsed with tap water, ultrapure water (Millipore: Milli-Ro 5 plus and Milli Q plus 185), acetone (Mallinckrodt Chemical Works St. Louis) and dried 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, sodium sulfate, copper (II) sulfate pentahydrate

and sulfuric acid concentrated ISO for analysis from Merck and boric acid (analytical grade) from Ferak. 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 monochloroacetonitrile (MCAN), dichloroacetonitrile (DCAN), bromochloroacetonitrile (BCAN), monobromoacetonitrile (MBAN), dibromoacetonitrile (DBAN), 1,1-dichloropropanone (1,1-DCP), 1,3-dichloropropanone (1,3-DCP), 1,1,1-trichloropropanone (1,1,1-TCP), chloral hydrate (CH) and chloropicrin (CP) (Chemservice, purity >99%). The concentrations of the stock solutions were calculated by flask weight change. For THMs certified commercial mix solutions (Chemservice, purity >99%) of known concentration were used. HAAs and their methyl esters as well as commercial mix solutions of HAAs and their methyl esters in MTBE were purchased from Supelco and were also accompanied with certificates of analysis (purity >99%). The nine HAAs were monochloroacetic acid (MCA), monobromoacetic acid (MBA), dichloroacetic acid (DCA), bromochloroacetic acid (BCA), trichloroacetic acid (TCA), dibromoacetic acid (DBA), bromodichloroacetic acid (BDCA), dibromochloroacetic acid (DBCA) and tribromoacetic acid (TBA). From these stock solutions, a solution of chlorination by-products at 100 mg/L in MTBE was prepared, known volumes of which were injected into ultrapure water, giving standard solutions for system calibration.

2.3. SAMPLE PREPARATION

Natural water samples were collected in March 2000 from Tsiknias river in Lesbos Island, Greece. 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. pH measurements were performed with a Crison MicropH2001 pH meter, and sample 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 (O'Dell *et al.*, 1984). A Dionex 2000i ion chromatograph was used, with a Dionex HPIC-AG4A column and a suppressed conductivity detector. The analytical conditions were as follows: eluant NaHCO₃ 0.75 mM – Na₂CO₃ 2.2 mM (flow 1.3 mL/min), regenerant H₂SO₄ 25 mN (flow 3 mL/min).

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) (APHA, 1992a). The chlorine dosages applied ranged from 2 to 30 mg/L, and the pH values tested (adjusted by addition of NaOH or HCL solution) ranged from 4 to 11. The chlorinated samples were divided into 40-mL amber glass bottles with polypropylene screw caps and TFE-faced septa (Pierce 13075). The vials were carefully filled so that trapping of air bubbles inside was prevented. Depending on the experiment, they were incubated at 21 °C, 35 °C or 4 °C for the desired contact times. Then, residual chlorine was measured according to the

DPD colorimetric method (APHA, 1992b) and the quenching agent for depletion of residual chlorine was added. The times tested ranged from 0 to 120 h. Sodium sulfite was used for the samples analyzed for THMs and other volatile chlorination by-products and ammonium chloride for the samples analyzed for HAAs (100 mg/L of sample in both cases).

2.4. SAMPLE ANALYSIS

For THMs and other volatile chlorination by-products, a modification of EPA Method 551.1, which includes liquid–liquid extraction (LLE) with MTBE was performed (EPA, 1998; Nikolaou *et al.*, 2002a). For HAAs, acidic methanol esterification (Cancho *et al.*, 1999) was used, as described elsewhere (Nikolaou *et al.*, 2002b).

The DBPs determination was carried out by use of a HP 5890 Series II Gas Chromatograph equipped with a ^{63}Ni Electron Capture Detector (ECD). A capillary fused silica DB-1 column 30 m \times 0.32 mm i.d. \times 0.25 μm film thickness was used. Injections were made in splitless mode, with helium as carrier gas and nitrogen as makeup gas. A Hewlett Packard Mass Selective Detector 5971, with a fused silica capillary HP-VOC (60 m \times 0.32 mm \times 1.8 μm) was used for confirmatory purposes. The analytical conditions have been previously described (Nikolaou *et al.*, 2002a,b).

UV absorbance measurements were carried out for raw water as well as for chlorinated water samples at 254, 272 and 280 nm by use of a Cary 1E UV-visible spectrophotometer with 1-cm quartz cells.

3. Results and Discussion

The raw water characteristics were the following: pH 7.07, UV absorbance 0.048 cm^{-1} and chloride concentration 15.5 mg/L. Bromide ion concentrations were below detectable levels. The results of the chlorinated samples analyses are presented below. For convenience, they are divided into two parts: influence of pH and reaction time and influence of chlorine dose and temperature, even though different levels of chlorine dose and reaction time were tested during both sets of experiments.

3.1. pH AND TIME

In the chlorinated water, the residual chlorine consumption was rapid, due to the high organic matter content. Chlorine dose 2 mg/L resulted in depletion of residual chlorine after 8-h reaction time and chlorine dose 4 mg/L resulted in residual chlorine concentrations of 0.4–0.8 mg/L after 24-h reaction time. It must be noted that the water flow in river Tsiknias is not constant throughout the year (in the

summer there is no water in this river), which explains the high organic matter content in the samples.

None of the CBPs studied was detected in the raw water samples. In the chlorinated samples a large number of CBPs were formed, with MCA, chloroform, dibromochloromethane and dichlorobromomethane consisting the major species, and BCA, TCA, DCA, BDCA, bromoform, MBA, DBA and 1,1,1-TCP occurring at lower concentrations. The CBPs concentrations detected in chlorinated water from Tsiknias river at various pH values (Chlorine dose 4 mg/L, reaction time 4 h) are shown in Figure 1.

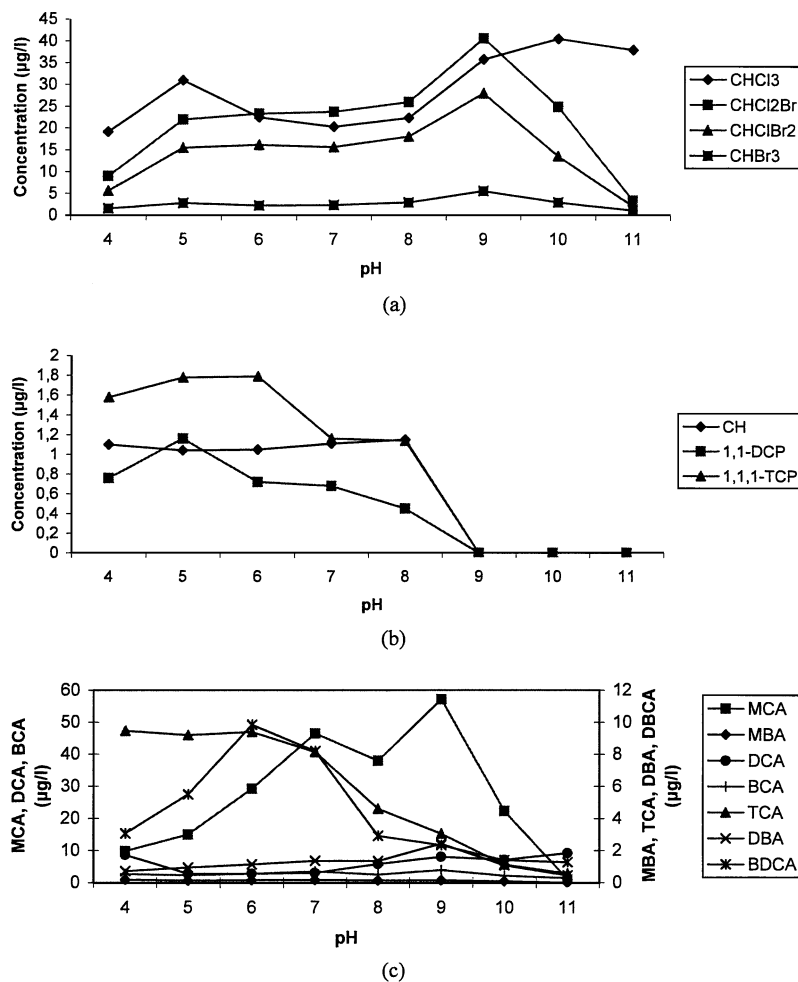


Figure 1. CBPs concentrations of detected in chlorinated water from Tsiknias river at various pH values (Chlorine dose 4 mg/L, reaction time 4 h) (a) THMs, (b) Other volatile CBPs, (c) HAAs.

The THMs concentrations increase with increasing pH, as it has been reported in the literature (Miller and Uden, 1983; Stevens *et al.*, 1989; El-Dib and Ali, 1995). In contrast, the volatile CBPs CH, 1,1-DCP, 1,1,1-TCP were only formed at pH values lower than 8 and their formation was particularly favored at low pH. For HAAs, the influence of pH was different for the individual species; MCA and DCA formation is enhanced from high pH, but TCA formation is favored at pH values lower than 7. For BDCA, the optimum pH values are 6 and 7.

Multifactor analysis of variance of the above results was applied (Statgraphics 4.0), in order to determine whether the influence of pH, reaction time and chlorine dose on the CBPs levels is statistically significant, as well as the existence of statistically significant combinations of factors' levels (interaction effects) for CBPs formation (Zar, 1999). The results for the CBPs characterized by statistically significant differences are shown in Table II.

Chloroform formation is affected from pH, reaction time and chlorine dose, with statistically significant interactions between pH-reaction time and chlorine dose-reaction time. Higher concentrations are formed at high pH values, high chlorine dose and longer reaction time.

Dichlorobromomethane formation is also affected from pH, reaction time and chlorine dose, with significant interaction effects between time-chlorine dose. Higher concentrations are formed at higher chlorine dose and the optimum pH value for its formation is 8. Dibromochloromethane shows similar behavior, with significant interactions between pH-time and time-chlorine dose. Dibromochloromethane formation increases with increasing chlorine dose and reaction time and also increases with increasing pH, with optimum values 8 and 9. The same observations are valid for bromoform.

CH formation is affected from pH, reaction time and chlorine dose, with significant interactions between time and chlorine dose. Higher CH concentrations are formed at high chlorine dose and at low pH values, probably due to hydrolysis at high pH (Singer, 1994). CH formation initially increases over time, but lower CH concentrations are observed for longer reaction times, which probably indicates decomposition of this compound over time.

1,1-DCP formation is significantly affected from pH and shows higher concentrations at low pH values. 1,1,1-TCP formation is affected from all studied factors, with significant interaction effects between time-chlorine dose. Higher concentrations are observed after long reaction times, at high chlorine doses and at low pH values.

DCAN formation is also affected from all studied factors, with significant pH-chlorine dose and time-chlorine dose interactions. Higher concentrations are formed at high chlorine doses and low pH values. TCAN formation is also affected from pH, chlorine dose and time, with significant pH-time and time-chlorine dose interactions, but unlike DCAN, it is favored from high pH values, with optimum value 8. TCAN concentrations increase over time within the first two hours and then decrease, probably due to decomposition.

TABLE II
Multifactor analysis of variance results for the CBPs concentrations as a function of pH, reaction time and chlorine dose

CBPs	Factors						Interactions between factors						Degrees of freedom (total)
	pH		Time		Chlorine dose		pH × time		pH × Cl dose		Time × Cl dose		
	F-ratio	s. l.	F-ratio	s. l.	F-ratio	s. l.	F-ratio	s. l.	F-ratio	s. l.	F-ratio	s. l.	
CHCl ₃	27.546	0.0000 ^a	66.160	0.0000 ^a	5.366	0.0265 ^a	2.770	0.0017 ^a	1.348	0.2580	4.257	0.0040 ^a	95
CHCl ₂ Br	11.949	0.0000 ^a	22.632	0.0000 ^a	30.398	0.0000 ^a	1.753	0.0507	0.933	0.4940	4.890	0.0017 ^a	95
CHClBr ₂	27.816	0.0000 ^a	30.706	0.0000 ^a	11.796	0.0015 ^a	2.282	0.0084 ^a	0.748	0.6335	2.663	0.0384 ^a	95
CHBr ₃	19.855	0.0000 ^a	18.044	0.0000 ^a	51.346	0.0000 ^a	1.479	0.1282	1.564	0.1799	12.174	0.0000 ^a	94
CH	2.988	0.0144 ^a	7.000	0.0001 ^a	9.924	0.0033 ^a	0.719	0.8331	0.795	0.5966	11.145	0.0000 ^a	95
1,1-DCP	5.886	0.0001 ^a	2.065	0.0934	3.198	0.0824	0.750	0.8010	0.745	0.6356	0.760	0.5845	95
1,1,1-TCP	17.448	0.0000 ^a	6.347	0.0003 ^a	8.294	0.0068 ^a	1.318	0.2114	1.038	0.4233	6.412	0.0003 ^a	94
DCAN	2.330	0.0462 ^a	11.259	0.0000 ^a	26.786	0.0000 ^a	1.000	0.5000	2.330	0.0462 ^a	11.259	0.0000 ^a	95
TCAN	12.283	0.0000 ^a	29.646	0.0000 ^a	29.773	0.0000 ^a	2.218	0.0104 ^a	1.953	0.0904	4.763	0.0020 ^a	95
MCA	18.013	0.0000 ^a	46.286	0.0000 ^a	2.877	0.0995	2.620	0.0036 ^a	2.731	0.0243 ^a	4.977	0.0018 ^a	92
MBA	6.212	0.0001 ^a	1.686	0.1673	0.498	0.4932	1.395	0.1750	0.317	0.9406	2.316	0.0673	91
DCA	9.366	0.0000 ^a	35.431	0.0000 ^a	0.000	0.9996	1.571	0.1001	0.941	0.4895	2.921	0.0278 ^a	92
BCA	3.722	0.0047 ^a	77.625	0.0000 ^a	8.047	0.0078 ^a	0.644	0.8976	1.341	0.2636	19.024	0.0000 ^a	92
TCA	7.224	0.0000 ^a	15.106	0.0000 ^a	0.005	0.9454	1.344	0.2006	0.420	0.8824	14.001	0.0000 ^a	92
DBA	2.341	0.0485 ^a	3.593	0.0112 ^a	0.259	0.6197	1.129	0.3680	1.251	0.3063	1.766	0.1492	91
BDCA	3.864	0.0037 ^a	3.267	0.0170 ^a	3.470	0.0717	0.557	0.9535	0.471	0.8480	6.843	0.0002 ^a	92
DBCA	2.122	0.0697	59.661	0.0000 ^a	99.437	0.0000 ^a	1.031	0.4669	1.227	0.3171	42.288	0.0000 ^a	92

s. l.: significance level.

^aStatistically significant difference (s. l. < 0.05).

The statistically significant factors for MCA formation are pH and time and their interaction effects. MCA concentration increases over time and higher values are observed at pH 7,8 and 9. MBA formation is significantly affected from pH, with optimum pH values between 6 and 8. DCA formation is affected from pH and time. DCA concentration increases over time and is higher at pH >8, with maximum value at pH 11.

BCA formation is affected from pH, time and chlorine dose, with significant interactions between time-chlorine dose. BCA increases over time and is favored from low and medium pH values. However, significantly lower BCA concentrations are formed at higher chlorine doses. A possible explanation for this observation is that at high chlorine doses, formation of other CBPs is favored over BCA.

TCA formation is significantly affected from pH and time. It is favored at low pH values (maximum concentration at pH 4) and increases over time. DBA is also affected from pH and time. At pH 10 and 11, lower concentrations are observed. DBA concentrations are significantly higher after 24-h reaction time, which indicates low formation rates for this compound.

For BDCA, pH and time are the statistically significant factors. The optimum pH values are 6 and 7. BDCA concentration increases over time, but the difference between the concentrations formed after 4 and 24 h is not statistically significant. This fact indicates fast BDCA formation rate. DBCA formation is affected from time and chlorine dose, with higher concentrations formed at higher chlorine doses.

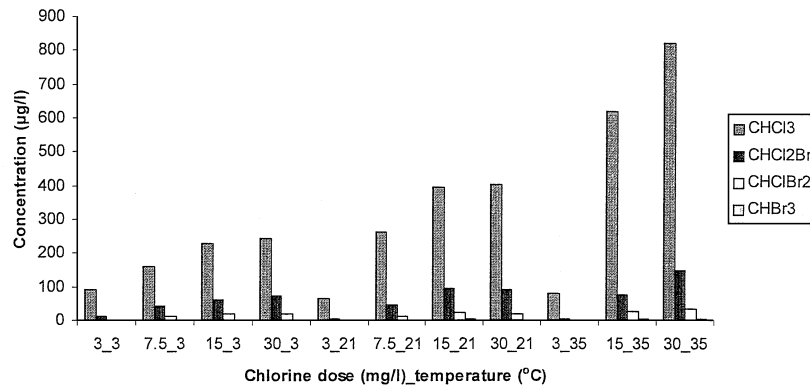
The BCAN, DBAN, MCAN, CP, MBAN and TBA compounds did not show statistically significant differences regarding the studied factors.

3.2. CHLORINE DOSE AND TEMPERATURE

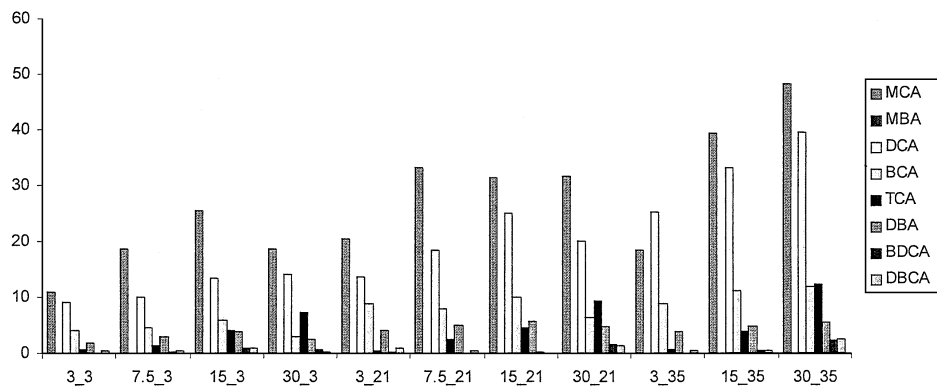
At 35 °C for chlorine dosages 3, 7.5 and 15 mg/L, residual chlorine consumption was rapid (not detectable concentrations), due to the high organic matter content and the increased CBPs formation reaction rates. Residual chlorine was present only for chlorine dose 30 mg/L (1.4–6 mg/L). At 21 °C and at 4 °C, due to slower reaction rates, residual chlorine concentration was detectable only for chlorine doses 15 and 30 mg/L (3–6 mg/L).

None of the CBPs studied was detected in the raw water samples. In the chlorinated samples a large number of CBPs were formed, with chloroform, MCA and DCA being the major species, and dibromochloromethane, dichlorobromomethane BCA, TCA, DCA, BDCA, bromoform, MBA, DBA, 1,1-DCP and 1,1,1-TCP occurring at lower concentrations. The CBPs concentrations detected in chlorinated water from Tsiknias river as a function of temperature and chlorine dose are presented in Figure 2.

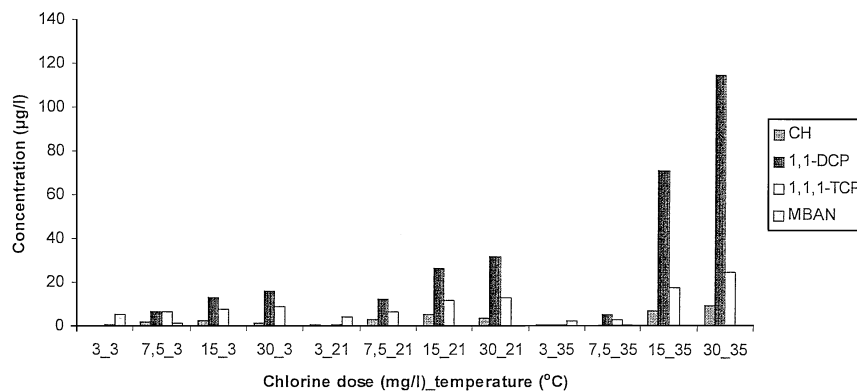
Increased concentrations were observed with increasing chlorine dose and temperature. Chloroform was the THM compound mostly favored from temperature



(a)



(b)



(c)

Figure 2. CBPs concentrations detected in chlorinated water from Tsiknias river as function of temperature and chlorine dose (a) THMs (pH 10), (b) HAAs (pH 10), (c) other volatile CBPs (pH 4).

and chlorine dose increase. When chlorine dose increased from 3 mg/L to 30 mg/L, chloroform concentration became 6-fold higher at 3 °C, 10-fold higher at 21 °C and 20-fold higher at 35 °C. 1,1-DCP was the compound showing the greatest increase among the rest volatile CBPs. When chlorine dose increased from 3 mg/L to 30 mg/L, 1,1-DCP concentration became 16-fold higher at 3 °C, 30-fold higher at 21 °C and 120-fold higher at 35 °C. The HAA compound mostly favored from temperature and chlorine dose increase was TCA. When chlorine dose increased from 3 mg/L to 30 mg/L, TCA concentration became 11-fold higher at 3 °C, 22-fold higher at 21 °C and 18-fold higher at 35 °C.

Multifactor analysis of variance was applied regarding three factors: chlorine dose, temperature and reaction time. The results for the CBPs with statistically significant differences are shown in Table III.

Chloroform formation is affected from chlorine dose, temperature, and their interactions. Chloroform concentrations are significantly higher at higher chlorine doses and higher temperatures. Dichlorobromomethane and dibromochloromethane showed the same trends with chloroform. Bromoform formation is affected from the three studied factors chlorine dose, temperature and reaction time (higher concentrations with longer reaction times), and also significant interaction effects were observed between chlorine dose and reaction time.

CH, 1,1-DCP and 1,1,1-TCP formation is significantly affected from chlorine dose. These compounds concentrations increased with increasing chlorine dose. The opposite is true for MBAN, which showed lower concentration at higher chlorine dose, probably because then other species are formed.

Chlorine dose and temperature are the statistically significant factors for MCA formation. MCA concentration increases with increasing chlorine dose and temperature. DCA formation is affected from all three factors, with significant interactions between chlorine dose-temperature. Chlorine dose, temperature and reaction time increase favor DCA formation. Temperature was the only significant factor and had positive effects on both BCA and DBA formation. The same is true for DBA. TCA concentration increases with increasing chlorine dose and temperature. BDCA formation is solely affected from chlorine dose, with higher concentrations resulting from higher chlorine doses.

Finally, chlorine dose and temperature are the significant factors for TBA formation. Higher TBA concentrations are formed at higher chlorine dose, which was also the only compound where higher concentrations were observed at temperatures 4 and 35 °C and significantly lower concentrations at 21 °C. The fact that TBA decomposes to bromoform at 21 °C (Heller-Grossman *et al.*, 1993), is probably the reason for the low TBA concentrations measured at this temperature. Although TBA decomposition rate would be expected to be faster at 35 °C, leading to even lower concentrations in the chlorinated samples, this was not the case according to our study's results. DBPs formation kinetics (including TBA) are also higher at elevated temperature, as suggested by the rapid consumption of residual chlorine. Therefore, the final concentration for this particular compound is probably

TABLE III
 Multifactor analysis of variance results for the CBPs concentrations as a function of temperature, chlorine dose and reaction time

CBPs	Chlorine dose			Temperature			Time			Interactions between factors						Degrees of freedom (total)			
	F-ratio			s. l.			F-ratio			s. l.			F-ratio				s. l.		
	F-ratio	s. l.		F-ratio	s. l.		F-ratio	s. l.		F-ratio	s. l.		F-ratio	s. l.			F-ratio	s. l.	
CHCl ₃	39.316	0.0000 ^a	22.698	0.0000 ^a	1.169	0.3281	6.619	0.0000 ^a	0.286	0.9905	0.378	0.9304	154						
CHCl ₂ Br	22.546	0.0000 ^a	5.375	0.0058 ^a	0.091	0.9851	1.958	0.0771	0.074	1.0000	0.167	0.9947	154						
CHClBr ₂	47.632	0.0000 ^a	6.155	0.0029 ^a	0.429	0.7874	2.566	0.0226 ^a	0.159	0.9994	0.160	0.9955	154						
CHBr ₃	28.570	0.0000 ^a	9.356	0.0002 ^a	2.501	0.0461 ^a	3.801	0.0017 ^a	0.166	0.9993	0.288	0.9687	152						
CH	4.118	0.0081 ^a	0.942	0.3929	0.292	0.8825	0.873	0.5167	0.246	0.9953	0.957	0.4730	155						
1,1-DCP	5.969	0.0008 ^a	1.638	0.1987	0.173	0.9518	0.644	0.6945	0.356	0.9759	0.665	0.7213	153						
1,1,1-TCP	7.562	0.0001 ^a	1.144	0.3220	0.387	0.8179	0.673	0.6716	0.107	0.9999	0.420	0.9070	155						
MBAN	16.235	0.0000 ^a	0.944	0.3921	0.131	0.9706	1.396	0.2216	0.158	0.9995	0.164	0.9950	155						
MCA	6.450	0.0004 ^a	8.516	0.0003 ^a	0.845	0.4992	0.954	0.4594	0.173	0.9992	0.137	0.9974	157						
MBA	1.438	0.2350	6.696	0.0017 ^a	1.096	0.3615	3.842	0.0000 ^a	2.259	0.0421 ^a	6.664	0.0000 ^a	157						
DCA	13.584	0.0000 ^a	29.537	0.0000 ^a	3.525	0.0093 ^a	2.873	0.0118 ^a	1.026	0.4293	0.614	0.7648	157						
BCA	1.999	0.1177	10.320	0.0001 ^a	0.591	0.6701	1.186	0.3184	0.172	0.9992	0.617	0.7622	157						
TCA	10.456	0.0000 ^a	4.756	0.0103 ^a	1.020	0.3997	0.666	0.6774	0.414	0.9557	0.171	0.9944	157						
DBA	1.144	0.3342	5.021	0.0080 ^a	0.413	0.7992	0.157	0.9873	0.074	1.0000	0.078	0.9997	157						
BDCA	8.282	0.0000 ^a	1.263	0.2866	1.864	0.1211	0.322	0.9245	0.338	0.9805	0.973	0.4604	157						
DBCA	2.280	0.0828	3.493	0.0335 ^a	0.254	0.9069	0.532	0.7829	0.192	0.9986	1.427	0.1920	157						
TBA	15.569	0.0000 ^a	4.683	0.0110 ^a	0.642	0.6337	1.321	0.2528	0.562	0.8687	0.186	0.9925	156						

s. l.: significance level.

^aStatistically significant difference (s. l. < 0.05).

the result of the balance between formation and decomposition kinetics. These results also underline the necessity for further investigating DBPs formation and decomposition kinetics under different ranges of conditions.

BCAN, DBAN, MCAN, DCAN, TCAN and CP did not show statistically significant differences (or the number of samples in which they were detected was not sufficient to allow for robust statistical analysis).

4. Conclusions

During bench-scale chlorination of river water from Lesvos Island, Greece, a large number of CBPs were formed, with THMs and HAAs consisting the major species. CH, HANs and HKs occurred at much lower concentrations. CBPs were detected only in chlorinated water samples and not in raw water. This result indicates that their presence in water was exclusively caused from chlorination.

The influence of chlorination conditions on the CBPs formation was in many cases different for different species, a fact that needs to be taken into account during efforts for minimization of their concentrations in drinking water.

Reaction time affects the formation of different categories of CBPs in a different way. THMs and HAAs concentrations increase over time, while the concentrations of volatile CBPs (1,1-DCP, 1,1,1-TCP, CH) decrease after some time interval, due to decomposition.

The pH influence on the CBPs formation is different for individual compounds. In particular, the THMs, MCA, DCA and TCAN concentrations increase with increasing pH, while the CH, 1,1-DCP, 1,1,1-TCP, DCAN, TCA, DBA and BCA concentrations increase at lower pH values. The optimum pH values for the MBA and BDCA formation are between 6 and 8.

Chlorine dose is one of the most important factors affecting CBPs formation and was found to be statistically significant for all the detected compounds. Higher chlorine doses favored higher concentrations, with MBAN being the only exception.

Temperature is another factor that influences the CBPs formation and the highest concentrations were measured at 35 °C. TBA was the only exception, characterized by significantly lower concentrations at 21 °C, probably as a result of a different balance between formation and decomposition kinetics; an observation of interest that requires further investigation.

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