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CHLORINE AND CHLORINE DIOXIDE OXIDATION OF NATURAL ORGANIC MATTER IN WATER TREATMENT PLANTS

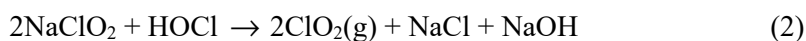
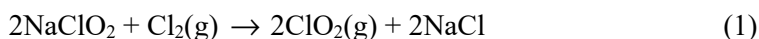
The formation of trihalomethanes (THMs) during chlorine (Cl_2) and chlorine dioxide (ClO_2) treatment was investigated. Water samples were collected from three drinking water sources, namely, Büyükçekmece Lake water (BLW) in Istanbul City, Kızılcapınar Lake water (KLW), and Ulutan Lake water (ULW) in Zonguldak City, Turkey. The results of the study show that Cl_2 treatment forms more THMs in all three water sources compared to ClO_2 treatment. Further, due to the Cl_2 treatment, the maximum THMs concentrations were observed in BLW ($121.15 \mu\text{g}/\text{dm}^3$) samples, followed by KLW ($97.26 \mu\text{g}/\text{dm}^3$) and ULW ($88.52 \mu\text{g}/\text{dm}^3$) samples within the reaction time of 24 h for $5 \text{ mg}/\text{dm}^3$ of Cl_2 dose. However, it was found that the concentrations of THMs formed at three water sources with applied ClO_2 treatment under the same conditions were significantly reduced. As a result of the ClO_2 treatment at the end of the reaction time of 24h, THMs concentrations formed in BLW, KLW, and ULW were recorded as 30.26, 16.53, and $17.71 \mu\text{g}/\text{dm}^3$, respectively. On chlorination, chloroform (CFM) was found the dominant THM species in all water sources. All THM species contents ranged from $1.98 \mu\text{g}/\text{dm}^3$ to $11.23 \mu\text{g}/\text{dm}^3$ and the highest level of dibromochloromethane (BDCFM) was observed as the major THM species among all species in BLW due to the ClO_2 treatment. Also, the formation of inorganic DBPs such as chlorate (ClO_3^-) and chlorite (ClO_2^-) was evaluated during ClO_2 oxidation. The levels of ClO_2^- formed due to the ClO_2 oxidation were higher than those of ClO_3^- levels for BLW, KLW, and ULW samples and varied from 19 to 55%, and from 37 to 60% of the applied ClO_2 doses ($2\text{--}10 \text{ mg}/\text{dm}^3$), respectively. On the other hand, ClO_3^- levels varied between 5 and 9% and 2 and 6% of the applied ClO_2 concentration for the KLW and ULW samples, respectively.

1. INTRODUCTION

The impact of water quality and safety on human life is one of the most significant public health issues [1, 2]. Therefore, most of the drinking water resources require disinfection to eradicate pathogenic organisms and control their growth due to the presence

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of trace organics [3]. Chlorination is widely used all over the world not only for the disinfection of drinking water but also for protecting against microbial contamination with oxidizing potential power [4]. However, as chlorine reacts with natural organic matter (NOM), disinfection byproducts (DBPs) are formed [5, 6]. Of the DBPs formed in chlorinated water, trihalomethanes (THMs) and haloacetic acids (HAAs) represent a significantly high fraction of these chlorination by-products. Also, these products have adverse health effects on human beings and are considered potentially carcinogenic [7]. Many countries have established strict regulations to control disinfection byproducts due to their potential carcinogenic effects. THMs and HAAs have been regulated by the US Environmental Protection Agency (USEPA) with maximum contaminant levels of 80 mg/dm³ for THMs and 60 mg/dm³ for HAAs [8]. The European Community (EC) regulation limits for total THM concentration in drinking water are 100 µg/dm³. In Turkey, the current THMs limit is 100 µg/dm³ [9]. To comply and to reduce the formation of DBPs, some water utilities are looking for alternative disinfectants [10] such as ozone, chloramines, and chlorine dioxide. Among these disinfectants, chlorine dioxide (ClO₂) has mostly been used as an alternative to chlorine, as it produces significantly less THMs and HAAs [11] as compared to other oxidants. Many researchers have also demonstrated that as it does not undergo substitution reactions with natural organic matter (NOM) present in water and thus, disinfection with ClO₂ has reduced THMs and other chlorination by-products [12]. Furthermore, ClO₂ is a more powerful disinfectant than chlorine (Cl₂) for water treatment because of its higher oxidation capacity. For potable water application, ClO₂ is generated from sodium chlorite (NaOCl₂) solutions. ClO₂ can be formed from NaOCl₂ reacting with gaseous chlorine (Cl₂(g)), hypochlorous acid (HOCl), or hydrochloric acid (HCl) [13]:



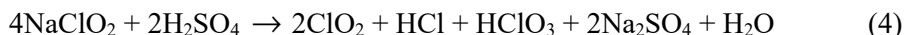
ClO₂ produces low levels of organic by-products compared to chlorine. Chlorite (ClO₂⁻) and chlorate (ClO₃⁻) are the inorganic by-products that result from the use of ClO₂ as a disinfectant. Generally, ClO₂⁻ is the predominant reaction endproduct, with approximately 70% of the ClO₂ converted to ClO₂⁻ and 8–10% is converted to ClO₃⁻ [14]. ClO₂ can signify a potential risk to human health because of these inorganic by-products. The USEPA established a federal drinking water threshold level of 0.8 mg/dm³ for ClO₂ and 1.0 mg/dm³ for ClO₂⁻ [8]. The chief DBPs of ClO₂ are ClO₂⁻ and ClO₃⁻ ions [15]. The main features affecting the formation of chlorite and chlorate ions in drinking water include the applied dose, water temperature, pH, and exposure to sunlight. Further, the mechanism of the reaction of Cl₂ and ClO₂ with NOMs and other constituents of natural water is different. In other words, ClO₂ produces a lower level of organic byproducts than

chlorine. Thus, the objective of this study was to investigate the occurrence of DBPs (chlorite, chlorate, and trihalomethanes) in three drinking water sources as a result of using ClO₂ as compared to Cl₂. Each of these raw water types consists of varying water quality characteristics, including conductivity, pH, ultraviolet absorbance at 254 nm (UV₂₅₄), total organic carbon (TOC) and THMs.

2. EXPERIMENTAL

Source water and sampling. During this study, water samples were taken from Buyukçekmece Lake water (BLW) in Istanbul city and also Ulutan Lake water (ULW) and Kızılcapınar Lake water (KLW) in Zonguldak city, Turkey. The sampling was done from 2016 to 2017 (in September 2016 and August 2017). Approximately 700 000 m³ of drinking water per day is provided by the BLW reservoir in Istanbul. ULW and KLW are reservoirs that provide nearly 38 000 m³ of raw water per day to the drinking-water treatment plant of Zonguldak. Raw water samples were collected as a grab sample, shipped to the laboratory on the same day, and kept in the dark in a refrigerator at 4 °C to retard biological activity before use.

Cl₂ and ClO₂ oxidation. Chlorine and chlorine dioxide treatments of water were carried out in a 500 cm³ amber-color glass bottles. BLW, KLW, and ULW samples were buffered to pH 7.5 with 5 mM phosphate buffer. Chlorine stock (1000 mg/dm³) and working standard (50–200 mg/dm³) solutions were prepared using commercial 4% NaOCl and standardized by iodometric titration (accuracy ±0.18 mg/dm³). It is essential that ClO₂ solutions used for the study to be devoid of chlorine for accurate comparison of THM formation during both the biocide treatment conditions. The chlorine-free ClO₂ solution was generated by acidifying sodium chlorite with 1 M H₂SO₄, followed by stripping the ClO₂ by nitrogen over sodium chlorite solution and dissolving the ClO₂ gas in chilled Millipore Type-I water (18 MΩ·cm). ClO₂ was generated according to the equation



The concentration of ClO₂ was determined by Na₂S₂O₃ titration similar to chlorine analysis. Water samples were treated with the Cl₂ or ClO₂ working standard solutions to get initial oxidant doses of 2, 5, 8, and 10 mg/dm³ to investigate the dose effect on DBP formation within 24 h. Residual oxidant concentrations at various intervals were measured by the DPD-colorimetric method [15].

Analytical procedure. All water samples were analyzed based on procedures described in the Standard Methods (SM) [16]. All standard solutions were prepared in

ultrapure water (Sartorius Co., Germany). Further, raw water samples were filtered using 0.45 μm cellulose acetate filters before chlorination and chlorine dioxide oxidations. TOC analyses were conducted by the high-temperature combustion method according to SM-3510B using a Shimadzu 5000A TOC analyzer equipped with an auto-sampler [16]. The minimum quantification limit of the analyzer was 0.1 mg/dm^3 . UV_{254} absorbance was recorded using a Shimadzu 1601 UV-visible spectrophotometer at a wavelength of 254 nm [16]. THM measurement was conducted by the EPA method 551 of liquid-liquid extraction (LLE) with pentane [17]. THM calibration standards were prepared using certified commercial mix solutions (AccuStandard, Inc., purity N99%). THMs analyses were performed with the HP 7890 Series II gas chromatograph equipped with a microelectronic capture detector (GC- μECD) and its analytical detection limit is $0.1 \pm 0.0001 \mu\text{g}/\text{dm}^3$. A capillary column of DB-1 (30 $\text{m} \times 0.32$ mm I.D. $\times 1.0$ μm , J&W Science) was used. Injections of samples were made in split/splitless mode, with helium as carrier gas and nitrogen as makeup gas. The four THM species were: chloroform (CFM), dichlorobromomethane (DBCFM) dibromochloromethane (BDCFM), and bromoform (BFM).

Analyses of ClO_2^- and ClO_3^- in the water samples were carried out using the Dionex IC 3000 system (USA) equipped with an AS-19 analytical column and an AG-19 guard column as per USEPA method 300.1 [18] and also its analytical detection limit is $0.001 \pm 0.0001 \text{ mg}/\text{dm}^3$.

3. RESULTS AND DISCUSSION

A summary of water quality parameters is presented in Table 1. The ranges throughout the year were as follows: pH 7.43–8.43, turbidity 1.6–13.5 NTU, conductivity: 250–685 $\mu\text{S}/\text{cm}$, total hardness: 61–168 $\text{mg CaCO}_3/\text{dm}^3$, bromide: 75–310 $\mu\text{g}/\text{dm}^3$, and temperature: 6.5–22.8 $^\circ\text{C}$. The NOM surrogate parameters TOC, UV_{254} and SUVA had ranges of 3.79–8.85 mg/dm^3 , 0.05–0.155 cm^{-1} and 1.7–4.09 $\text{dm}^3/(\text{mg} \cdot \text{m})$, respectively. As can be seen from Table 1, pH, temperature, and dissolved oxygen (DO) levels of the three water sources were in the similar range, with Büyükçekmece Lake water (BLW) having the highest pH (8.33) and Kızılcapınar Lake water (KLW) having the lowest (7.35). DO of the Ulutan Lake water (ULW) was marginally higher than those of BLW and KLW. UV_{254} values were not in the same trend, and the highest value was observed for BLW (0.155 cm^{-1}) followed by KLW (0.14 cm^{-1}) and the lowest for ULW (0.05 cm^{-1}). Although the TOC value was the lowest for BLW, it had the highest SUVA value (the ratio $\text{UV}_{254}/\text{TOC}$ of water) (3.45 $\text{dm}^3/(\text{mg} \cdot \text{m})$) as compared to KLW and ULW, respectively. SUVA was a good predictor of the carbon aromaticity content of the NOM and DBP formation in water. SUVA values of about 4–5 $\text{dm}^3/(\text{mg} \cdot \text{m})$ represent highly aromatic NOM [19]. The nutrient content of the water source was reflected by the presence of nitrate (NO_3^-) and total nitrogen amount. The NO_3^- value for ULW was 1.88 mg/dm^3 and

was the lowest among the three water sources. Bromide content in the water was also related to the distribution of DBPs as a result of the water disinfection. As shown in Table 1, the highest bromide concentration was detected in BLW. Previous studies in this region indicated that the BLW source is located near the Marmara Sea coastlines, and therefore, usually, there is some seawater intrusion to this water source [19]. Bromide concentrations in KLW and ULW were found as 0.13 and 0.07 mg/dm³, respectively.

Table 1

Physicochemical characteristics of raw water samples

	BLW		KLW		ULW	
	Range	Average	Range	Average	Range	Average
pH	7.50–8.33	8.07	7.35–8.03	7.68	7.48–7.57	7.35
Turbidity, NTU	2.1–6.8	3.4	1.8–3.8	2.9	1.7–3.1	2.6
Conductivity, $\mu\text{S}/\text{cm}$	385–654	539	175–365	310	220–385	270
Alkalinity, mg CaCO ₃ /dm ³	115–162	142	82–125	121	65–80	75
Hardness, mg CaCO ₃ /dm ³	109–168	148	87–134	125	61–74	69
Temperature, °C	7.3–22.8	15.5	8.4–22.35	14.8	6.5–19.5	14.7
Chloride, mg/dm ³	38–63	52	24–38	29	21–28	25
Oxygen, mg/dm ³	6.98–8.12	7.59	7.21–8.45	8.11	7.45–8.56	8.23
Br ⁻ , mg/dm ³	83–310	240	75–180	120	60–130	80
TOC mg/dm ³	3.79–7.69	4.83	3.85–8.85	5.21	4.01–5.68	4.78
UV ₂₅₄	0.07–0.155	0.12	0.06–0.14	0.11	0.05–0.1	0.08
SUVA	2.03–4.09	2.85	1.85–2.45	2.35	1.7–2.22	2.09

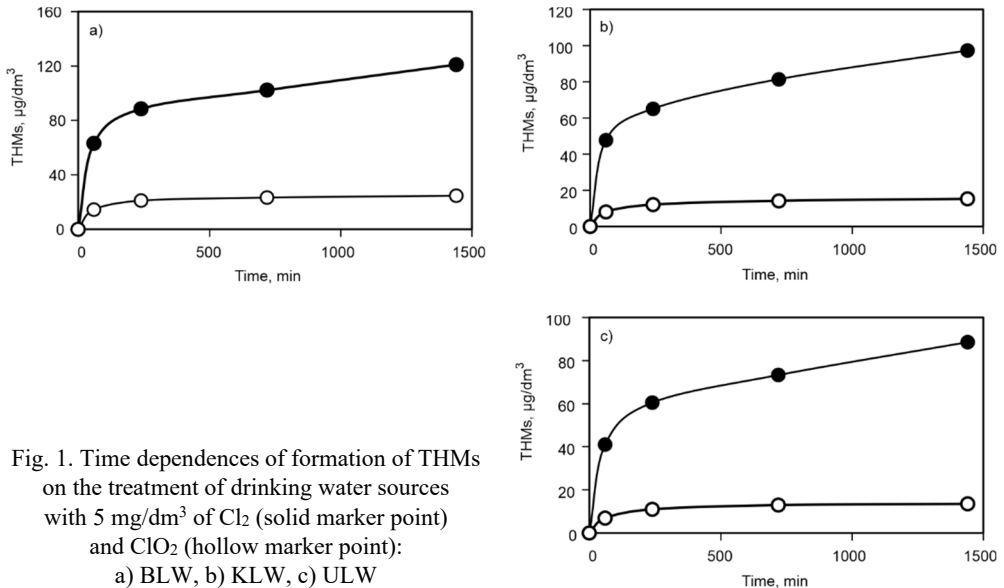


Fig. 1. Time dependences of formation of THMs on the treatment of drinking water sources with 5 mg/dm³ of Cl₂ (solid marker point) and ClO₂ (hollow marker point):
a) BLW, b) KLW, c) ULW

Figure 1 demonstrates the concentration of total THMs (TTHMs) formed, due to Cl_2 and ClO_2 disinfection of BLW, KLW, and ULW samples, dosed with 5 mg/dm^3 , pH 7, reaction times 1–24 h. The formation of trihalomethanes commonly proceeded in two stages. An initial stage was completed rapidly within the first few hours and then, the stage was marked by a steady rate of increase. Approximately 50% of trihalomethanes were produced within the contact time of 1 h. The results up to 24 h reaction time showed that the highest THMs concentrations were recorded as $121.15 \text{ } \mu\text{g/dm}^3$ in chlorinated BLW samples due to the high organic matter and UV_{254} value, followed by KLW ($97.26 \text{ } \mu\text{g/dm}^3$) and the lowest for ULW samples ($88.52 \text{ } \mu\text{g/dm}^3$). The THMs level varied from 63.22 (BLW), 47.65 (KLW), and $41.06 \text{ } \mu\text{g/dm}^3$ (ULW) to 121.15 (BLW), 97.26 (KLW), and $88.52 \text{ } \mu\text{g/dm}^3$ (ULW) for the same conditions.

This observation is similar to those given in the previous report [20], which supports the fact that chlorine first reacts with the active group quickly, thus leading to the rapid initial formation of DBPs like THMs. On the other hand, it was observed that the concentrations of THMs were significantly reduced with applied 5 mg/dm^3 of ClO_2 after the 24 h contact time at all of the water resources (Fig. 1). In other words, by ClO_2 oxidation, the concentrations of THMs decreased from 121.15 to 30.6, from 97.26 to 16.53, and from 88.52 to $17.71 \text{ } \mu\text{g/dm}^3$ for BLW, KLW, and ULW, respectively, for 5 mg/dm^3 of ClO_2 at the end of the reaction time of 24 h. ClO_2 oxidation reduced the formation of THMs and the other halogenated by-products and ClO_2 does not generally take part in the direct substitution reaction with NOM present in the water and thus, it does not produce significant amounts of halogenated organic DBPs. In other words, the mechanism of the reaction of Cl_2 and ClO_2 with NOMs is different. This finding is consistent with the results obtained by Korn et al. [21].

Figure 2 shows the formation and distribution of THMs species from three water resources due to Cl_2 and ClO_2 doses of 2–10 mg/dm^3 after the reaction time of 24 h at room temperature ($25 \text{ }^\circ\text{C}$). The major species of THM formed during chlorination of water from BLW was CFM followed by DBCFM, while for KLW and ULW the predominant THM species were CFM, DCBFM, and DBCFM, respectively. As regards THM, the maximum concentrations were determined in BLW at the Cl_2 dose of 10 mg/dm^3 as 222.95 for CFM, 156.27 for DBCFM, 125.06 for DCBFM, and $67.82 \text{ } \mu\text{g/dm}^3$ for BFM. Further, the CFM concentration varied from 61.33 (BLW), 31.23 (KLW), and $29.75 \text{ } \mu\text{g/dm}^3$ (ULW) for a chlorine dose of 2 mg/dm^3 to 222.95 (BLW), 135.65 (KLW), and $128.85 \text{ } \mu\text{g/dm}^3$ (ULW) for a chlorine dose of 10 mg/dm^3 , whereas the DBCFM concentration varied from 31.08 (BLW), 10.07 (KLW), and $8.24 \text{ } \mu\text{g/dm}^3$ (ULW) to 125.04 (BLW), 57.03 (KLW), and $50.11 \text{ } \mu\text{g/dm}^3$ (ULW) for the same conditions. This observation also indicated that the concentration of THMs species gradually increased on increasing the chlorine concentration. In chlorinated BLW samples, the speciation of THM is a little different from KLW and ULW. The concentrations of CHClBr_2 and CHCl_2Br observed in BLW were higher than those of KLW and ULW under the same chlorination conditions. These results have also shown that the chlorination of high levels of bromide-containing water modifies

the chlorination process, i.e., bromide is rapidly oxidized to bromine and directly affects the formation and distribution of THM species. Besides, the BLW source is located near the Marmara Sea coastlines, and therefore, usually, there is a seawater intrusion to this water source [19, 22, 23]. The amounts of all THM species for three water sources were decreased with ClO₂ oxidation at the same experimental conditions in the present study as shown in Fig. 2.

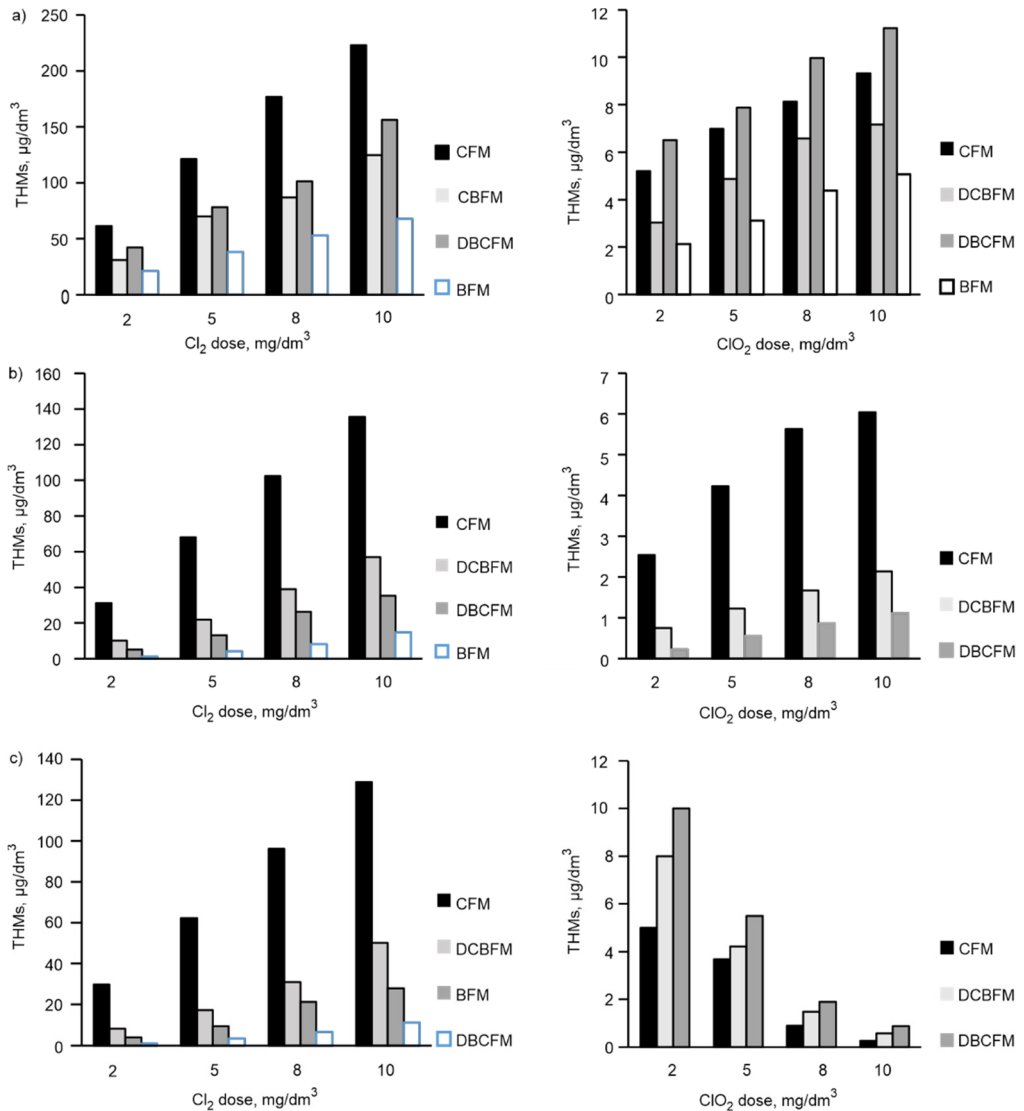
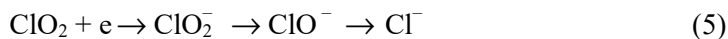


Fig. 2. Distribution of THM species during the treatment of drinking water sources with Cl₂ and ClO₂ (doses of 2–10 mg/dm³) at the reaction time of 24 h: a) BLW, b) KLW and c) ULW

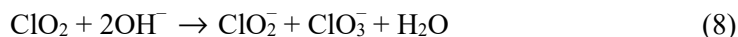
Before chlorination, as the ClO_2 doses of 2–10 mg/dm^3 were added to the samples, the concentrations of THM species ranged from 1.98 to 11.23 $\mu\text{g}/\text{dm}^3$ within the reaction time of 24 h and 25 °C. While the concentrations of DBCFM and BDCFM were detected below 3 $\mu\text{g}/\text{dm}^3$ for KLW and ULW samples, BFM was not found for all ClO_2 doses (Fig. 2). BDCFM was observed to be the single dominant species in the BLW source with ClO_2 oxidation. Its concentration ranged from 6.5 to 11.23 $\mu\text{g}/\text{dm}^3$ at the ClO_2 doses of 2–10 mg/dm^3 . Further, the amount of brominated THM species was higher in BLW as a result of the ClO_2 oxidation. Although chlorine dioxide does not generally take part in the direct substitution reaction with NOM present in water, it reacts with bromides in water following the schemes:



This outcome demonstrated that bromine was more reactive with hydrophilic and low molecular weight precursors as measured by THM formation than their corresponding hydrophobic and high molecular weight precursors and also ClO_2 tended to form more hydrophilic and low molecular weight NOM fractions. However, it should be noted that the application of ClO_2 oxidation reduced the levels of brominated THMs. In other words, the reduction percentages tended to be higher as compared to chlorination oxidation in all water sources.

3.4. FORMATION AND DISTRIBUTION OF ClO_2^- AND ClO_3^-

ClO_2^- and ClO_3^- are the significant inorganic DBPs that result from the use of ClO_2 as a disinfectant. Typically, up to 70% of the applied ClO_2 dose is reduced into chlorite ions and up to 10% is converted into chlorate ions. In an aqueous solution, neutral and alkaline conditions favor the formation of acidic radicals (eq. (8)), and under high pH conditions, ClO_2 tends to react by exchanging electrons to produce chlorite ions (eq. (9))



On the other hand, the ClO_2^- levels varied from 19% to 36%, from 35% to 55%, and from 37% to 60% of the applied ClO_2 dose for BLW, KLW, and ULW water samples, respectively, for 2–10 mg/dm^3 of ClO_2 (Table 2).

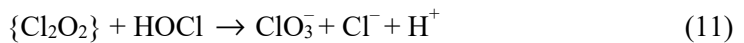
Table 2

Summary of ClO₂⁻ and ClO₃⁻ in the water samples formed during Cl₂ and ClO₂ disinfection

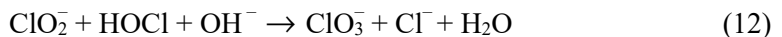
Source	ClO ₂ treatment (2–10 mg/dm ³)		Cl ₂ treatment (2–10 mg/dm ³)	
	ClO ₂ ⁻ /ClO ₂	ClO ₃ ⁻ /ClO ₂	ClO ₂ ⁻ /Cl ₂	ClO ₃ ⁻ /Cl ₂
BLW	0.19–0.36	0.00	nd	0.18–0.23
KLW	0.35–0.55	0.05–0.09	nd	0.14–0.20
ULW	0.37–0.60	0.02–0.06	nd	0.16–0.21

ClO₂⁻/ClO₂, ClO₃⁻/ClO₂, ClO₂⁻/Cl₂ and ClO₃⁻/Cl₂ represent the concentrations of chlorite and chlorate formed per 1 mg/dm³ of ClO₂ and Cl₂ doses, respectively. nd – not detected, treatment conditions: Cl₂ and ClO₂ doses 2, 5, 8 and 10 mg/dm³, contact time from 30 min to 24 h, temperature: 25 °C.

The level of chlorite ion formed in the BLW was slightly lower than that in KLW and ULW samples, which may be due to the presence of higher chloride content (58 mg/dm³) in the BLW compared to that of KLW and ULW. Chlorate levels were lower than that of chlorite for 2–10 mg/dm³ of ClO₂ at three water sources. Further, chlorate was not detected in the BLW sample, and it varied between 5 and 9% and between 2 and 6% of the applied chlorine dioxide concentration for the KLW and ULW samples, respectively. These findings indicated that up to 60% reduction in the conversion of ClO₂ to ClO₂⁻ was observed on increasing the dose from 2 to 10 mg/dm³. As can be seen from Table 2, a substantial amount of chlorate was detected ranging from 14 to 23% in all the chlorinated natural water samples. Chlorate is not directly formed from the reaction between chlorine dioxide and dissolved matter in the water. Chlorate is formed in the chlorine dioxide generation process from feedstock contamination as well as be produced from a generation reaction byproduct. Further, the addition of chlorine to a chlorine dioxide-treated water sample contributes to the formation of chlorate in water. Large excess amounts of Cl₂ results in the over-oxidization of chlorite and directly form chlorate in an aqueous solution [25]



Also, in basic solutions when the hypochlorite ion (OCl⁻) is present, greater amounts of ClO₃⁻ are formed by the following reaction [25]



On the other hand, ClO₂⁻ was not detected in chlorinated samples in this study.

4. CONCLUSION

In the present study, the formation and yield of THMs during Cl_2 and ClO_2 treatments of water samples from Büyükçekmece Lake (BLW), Kızılcapınar Lake (KLW) and Ulutan Lake (ULW) were studied. This study showed the significant influence of various NOM on THM formation. The order of the THM level of three water sources was $\text{BLW} > \text{KLW} > \text{ULW}$ for chlorination. A lower level of THMs was observed with ClO_2 oxidation as compared to chlorine treatment for three water sources. This result also demonstrated that the dominant mechanism of the reaction of Cl_2 and ClO_2 with NOMs and other constituents of natural water is different and thus ClO_2 alone cannot produce a significant amount of halogenated organic byproducts. The major THM species formed during chlorination of water samples from KLW and ULW was chloroform (CFM) followed by brominated THM species while, for BLW, the predominance THM species was dibromochloromethane (BDCFM) and dichlorobromomethane (DBCM). The replacement of chlorine with ClO_2 oxidation in all water sources corresponded to an 80% reduction in the THM concentrations. Additionally, among THM species, BDCFM was observed to be the single dominant compound as $11.23 \mu\text{g}/\text{dm}^3$ during the ClO_2 treatment of BLW at the maximum ClO_2 dose. This result demonstrated that the bromide level of water source plays an important role in the formation and distribution of THMs due to ClO_2 treatment. For three water sources, the distribution order of THM species was $\text{CFM} > \text{DBCFM} > \text{BDCFM} > (\text{bromoform}) \text{BFM}$ for chlorination, whereas it was $\text{BDCFM} > \text{CFM} > \text{DBCFM} > \text{BFM}$ for ClO_2 oxidation. On the other hand, the results of the present study show that ClO_2 is suggested to be a good oxidation reagent for controlling Br-DBP reduction. Therefore, it is of great recommendation for water sources. Also, the results of the present study have shown that ClO_2^- and ClO_3^- levels in the chlorine dioxide-oxidated water varied between 19–31 and 0.0% for BLW, 35–55 and 5–9% for KLW, and 37–60 and 2–6 in ULW, respectively, for 2–10 mg/dm^3 of ClO_2 .

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