

## Raw water treatment with Cl<sub>2</sub> and ClO<sub>2</sub>: comparison of two major class of disinfection by-products formation

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**Epidemiological studies have demonstrated the cellular toxicity of trihalomethanes (THMs) and haloacetic acids (HAAs) that usually form during water treatment with chemical chlorine disinfectants such as chlorine and chlorine dioxide. THMs and HAAs formation potential of organic precursor in a surface water source for water treatment with Cl<sub>2</sub> and ClO<sub>2</sub> was studied with reference to key determinants. It was observed that the concentration of THMs and HAAs formed during ClO<sub>2</sub> treatment was significantly lower than that formed during Cl<sub>2</sub> treatment concentration that formed during chlorination. HAAs, dominated with bromo-HAAs were predominantly formed with a negligible amount of THMs during ClO<sub>2</sub> treatment. The combined total of HAAs and THMs formed during chlorine dioxide treatment was only 10–21% of that formed for chlorination. Among the HAAs species, dibromoacetic acid accounted for 86% of total HAAs during chlorine dioxide treatment whereas dichloroacetic acid (36.7%) followed by dibromoacetic acid (20.4%) and bromochloroacetic acid (16.9%) were major constituent formed during chlorination. Species shift towards more toxic bromo-HAAs may pose a concern on shifting water treatment from chlorine to chlorine dioxide, particularly for bromide-containing water.**

**Keywords:** Chlorination byproducts, chlorine dioxide, disinfection byproducts, haloacetic acids, trihalomethanes.

HALOACETIC acids and trihalomethanes are two major-class of regulated disinfection by-products (DBPs)<sup>1</sup> formed when natural water is treated with chlorine or chlorine dioxide. Chlorination is a widely employed method for drinking water disinfection and biofouling control in industrial water utilities such as refineries, steel mills, petrochemical plants, chemical processing plants and electric utilities<sup>2</sup>. However, chlorine reacts with the natural organic matters (NOMs) present in the water to generate chlorination by-products (CBPs) in more or less substantial amounts depending on the quality of raw water<sup>3</sup>. CBPs are the undesirable by-products, epidemiological studies have demonstrated the occurrence of cancer in human due to the exposure to these CBPs<sup>4,5</sup>. Due to their proven toxicological concern, the US Environmental

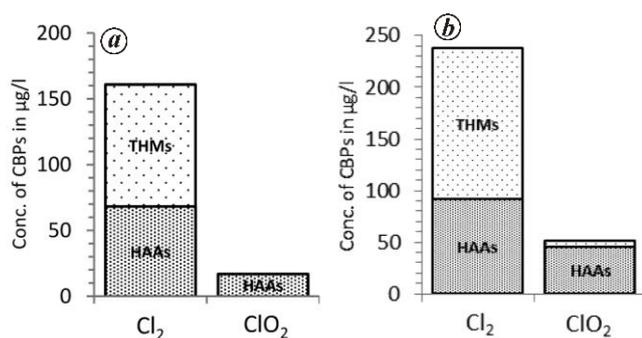
Protection Agency (USEPA) has set a maximum contaminant level goal (MCLG) of 60 µg/l for HAAs and 80 µg/l for THMs<sup>6</sup>. Among the disinfectants other than chlorine, such as chlorine dioxide, chloramine, ozone, chlorine dioxide (ClO<sub>2</sub>) has recently been used as an alternative to chlorine and demonstrated promising behaviour in full-scale distribution system<sup>7</sup>. Though numerous inorganic and biological material present in natural water reacts with ClO<sub>2</sub>, many studies have shown that it forms a lesser amount of HAAs and THMs. The dominant mechanism of the reaction of Cl<sub>2</sub> and ClO<sub>2</sub> with natural organic matters (NOMs) and other constituents of natural water are different; type and level of the resultant organic by-products are thus expected to be different<sup>8</sup>. Though the CBPs form on ClO<sub>2</sub> treatment of natural water is low compared to chlorine<sup>9</sup> various factors like pH, temperature, oxidant concentration, NOMs concentration, precursor reactivity, bromide concentration may affect the formation and distribution of THMs and HAAs<sup>10–12</sup> greatly. Recognizing the importance, extensive studies has been conducted around the world on the various aspects of different classes of CBPs formation. However, a few preliminary studies are available from India and limited to an assessment of the level of THMs present in the treated water<sup>13,14</sup>. Furthermore, such studies on the formation of CBPs during the treatment of real water have been limited to very few water sources worldwide<sup>15</sup>. To comprehend the potential impact of transferring water treatment option from Cl<sub>2</sub> to ClO<sub>2</sub>, it is essential to concurrently quantify the formation of different CBPs class at the same time. Such information is practically lacking. Comprehensive information on the comparative behaviour of CBPs formed during treatment with Cl<sub>2</sub> and ClO<sub>2</sub> is a prerequisite for the water utility managers to evaluate the potential impact of switching to ClO<sub>2</sub> from Cl<sub>2</sub>. The main objective of this study was to investigate the potential NOM precursor of a freshwater source derived from a river for the occurrence of THMs and HAAs as a result of both Cl<sub>2</sub> and ClO<sub>2</sub> treatment. Effect of key determinants such as contact time, oxidant dose and temperature on the CBPs formation potential was evaluated and compared for both the oxidants. Species distribution of THMs and HAAs for both the treatment was studied.

Raw water samples from Palar River, Tamil Nadu, were collected in a pre-cleaned 1 litre amber colour glass jar, brought to the laboratory, filtered immediately by Millipore membrane filter (0.45 µm) and stored at 4°C to minimize the deterioration of NOM precursor. Water samples were treated with a calculated amount of working standard to get a final concentration of 5 and 25 mg/l of Cl<sub>2</sub> or ClO<sub>2</sub> and withdrawn at 30 min and 24 h for extraction and analysis of THMs and HAAs. Details of sample treatment, instrument conditions and statistical summary of analytical parameters is provided as [Supplementary Material](#).

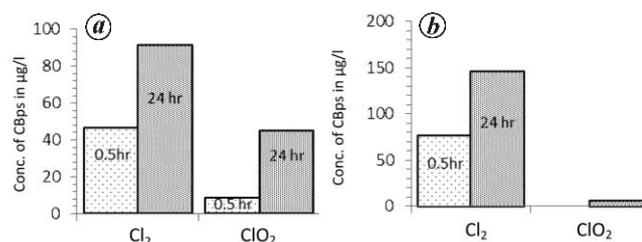
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Effect of three important treatment parameters, i.e. contact time, oxidant dose and temperature on the formation of four THMs and nine HAAs was studied for the same water sample treated with  $\text{Cl}_2$  and  $\text{ClO}_2$ . For both chlorine and chlorine dioxide treatment, CBPs formation showed a general upward trend with an increase in the oxidant dose. Figure 1 illustrates the formation of THMs and HAAs on treatment with both the oxidants. It can be seen that the combined concentration of HAAs and THMs formed during chlorine dioxide treatment was only 10–21% of that formed during chlorination. Formation of THMs was unfavourable compared to HAAs for water treatment with  $\text{ClO}_2$ . Only a small amount of THMs was observed even after 24 h of contact with 25 mg/l of  $\text{ClO}_2$ , and not even detected for 5 mg/l  $\text{ClO}_2$  treatment. However, a significant amount of HAAs was formed, which increased three-fold on increasing the  $\text{ClO}_2$  dose from 5 to 25 mg/l. HAAs was the major CBPs among THMs and HAAs formed during chlorine dioxide treatment, which account for 90–99% of the combined load. On the other hand, THMs are the major fraction for chlorination, which contributed 57% of the combined THMs and HAAs formed. Treatment with chlorine generated a considerably higher amount of CBPs that is 92.68  $\mu\text{g/l}$  of THMs and 68.32  $\mu\text{g/l}$  of HAAs for 5 mg/l  $\text{Cl}_2$  after 24 h contact time. The effect of applied oxidant dose concentration on CBPs formation was more profound in case of chlorine dioxide and 164% increase of combined HAAs and THMs was noticed for an increase of dose from 5 to

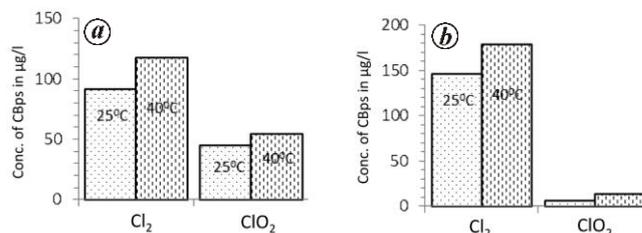
25 mg/l. In comparison, treatment with chlorine demonstrated only a 58% increase of THMs and 34% of HAAs on five-fold increase of dose from 5 to 25 mg/l. Similarly, the effect of contact time on the percentage increase of HAAs and THMs during  $\text{ClO}_2$  treatment was greater than that for chlorination (Figure 2). THMs and HAAs concentration was approximately doubled when contact time increased from ½ h to 24 h for chlorination, whereas five-fold increase in HAAs was observed for the same during  $\text{ClO}_2$  treatment and THMs which was not detected at ½ h was 5.9  $\mu\text{g/l}$  at 24 h. This indicates that the formation of THMs and HAAs is relatively slower for chlorine dioxide, and it follows a rapid initial formation followed by the slower steady formation in case of chlorination. The trend was similar to previous report<sup>16</sup> indicating that the chlorine reacted with the active group more quickly initially and as both free chlorine and precursor concentration diminished over time, the formation of CBPs became slower. CBPs formation potential as a function of temperature is depicted in Figure 3. In general, an increase in temperature accelerates the rate of reaction. However, it may also reduce the semi-volatile and/or unstable CBPs by various decomposition mechanisms<sup>17,18</sup>. The resultant effect of formation and decomposition on the total yield was always observed to be positive during our study. Approximately, 20% enhancement of CBPs was observed on the 15°C increase in reaction temperature from 25°C to 40°C for both the oxidant treatment except for THMs formation during  $\text{ClO}_2$  treatment which increased from 5.92  $\mu\text{g/l}$  to 13.25  $\mu\text{g/l}$ . Thus, temperature does not appear to have a great influence on the overall yield of CBPs. This was due to the formation and simultaneous decomposition of at least some of the CBPs, resulting in a lower net effect. In addition to the total load of CBPs, species distribution among chloro-, bromo- or bromochloro- is also a crucial factor on its toxicological profile. Brominated CBPs are generally more cytotoxic and genotoxic and associated with higher carcinogenicity than their chloro-analogue<sup>5,19</sup>. Thus, it is important to compare and quantify the distribution of species during both the oxidant treatment options. Figure 4 shows the distribution of nine HAAs species and Figure 5 describes the variation in the distribution of four THMs species for  $\text{Cl}_2$  and  $\text{ClO}_2$  treatment. The results showed that out of



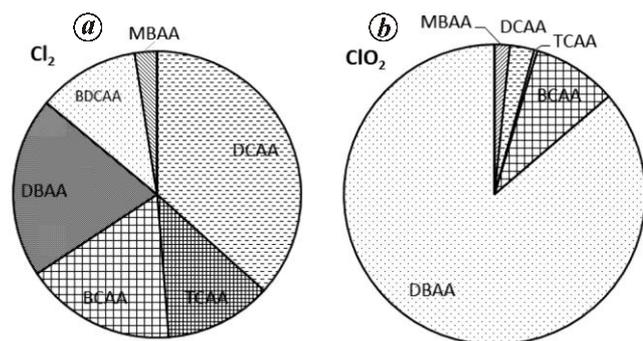
**Figure 1 a, b.** Comparison of the effect of dose on the formation and relative contribution of total HAAs and total THMs during treatment of water with  $\text{Cl}_2$  and  $\text{ClO}_2$ . [ $\text{Cl}_2/\text{ClO}_2$ ]: *a*, 5 mg/l, *b*, 25 mg/l; temp. 25°C, contact time: 24 h.



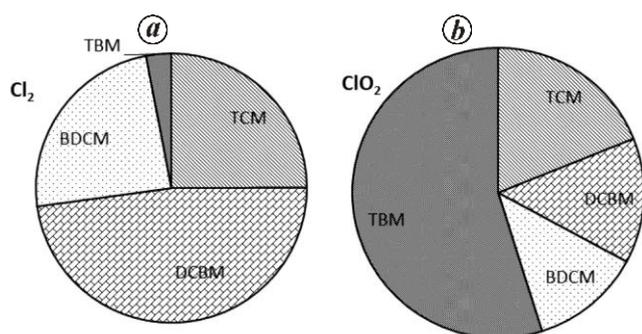
**Figure 2 a, b.** Effect of reaction time on the enhancement of (a) total THMs and (b) total HAAs in the treated water. [ $\text{Cl}_2/\text{ClO}_2$ ]: 25 mg/l.



**Figure 3 a, b.** Effect of temperature on the net yield of (a) total HAAs and (b) total THMs during  $\text{Cl}_2$  and  $\text{ClO}_2$  treatment. [ $\text{Cl}_2/\text{ClO}_2$ ]: 25 mg/l, contact time: 24 h.



**Figure 4.** Distribution of nine HAAs species during chlorine and chlorine dioxide treatment of natural water. MCAA, BDCAA, DBCAA and TBAA were not detected during  $\text{ClO}_2$  treatment; MCAA, MBAA and TBAA were not detected for  $\text{Cl}_2$  treatment. [ $\text{Cl}_2/\text{ClO}_2$ ]: 25 mg/l, contact time: 24 h.



**Figure 5.** Variation in the distribution of four THMs species during chlorine and chlorine dioxide treatment of natural water. [ $\text{Cl}_2/\text{ClO}_2$ ]: 25 mg/l, contact time: 24 h.

nine HAAs species, only five were formed (condition: oxidant dose 25 mg/l, reaction time 24 h) during chlorine dioxide treatment and among those, DBAA accounted for 86% of total HAAs. MBAA (2%), DCAA (2.5%), BCAA (9%) and TCAA (0.3%) were the other HAA species that formed during chlorine dioxide treatment (Figure 4 b). The above observation indicated the presence of diverse precursor type and varying degree of reactivity, which underwent different reaction pathways to form mono-, di-, tri-HAAs. It has been demonstrated that mono-, di- and tri-HAAs were generated from different organic precursors and the extent of formation depends on the availability of respective precursor. The HAAs species distribution pattern for chlorination, however, differs greatly and relatively more distributed among different species. This indicated that the oxidant type plays a significant role in the speciation distribution of HAAs. MCAA, MBAA and TBAA were not observed for chlorination also and probably be the most unstable or thermodynamically unfavourable species. The major species formed during chlorination were DCAA (36.7%) followed by DBAA (20.4%), BCAA (16.9%), TCAA (12%), BDCAA (11%) and DBCAA (2.5%) (Figure 4). HAAs speciation distribution may be dissimilar for different water type and water source from the different place due

to change in the precursor nature. Order of HAAs speciation observed in a recent study<sup>20</sup> was MCAA > DCAA > TCAA, which is different from our observation. In the case of THMs, all the four species were formed for both chlorine and chlorine dioxide treatment, though the total THMs concentration was only 5% for  $\text{ClO}_2$  compared to  $\text{Cl}_2$  (Figure 5 a, b). The average THMs value reported during  $\text{ClO}_2$  treatment of drinking water in a previous study<sup>21</sup> was similar to our observation. TBM was the major THMs species for chlorine dioxide whereas it was the lowest fraction for chlorination. Since the level of THM is very less for  $\text{ClO}_2$ , the significance of species distribution during both the treatment option may not be a crucial factor with respect to comparative health issues. It is clear that the magnitude of reactivity of NOMs precursor towards THMs formation is many folds more for chlorine than chlorine dioxide resulting in high THMs formation during chlorination. This observation is similar to many previous studies<sup>9,22</sup>.

In summary, the study highlighted the important aspect of DBPs formation, which is crucial to take into account while deciding on the shift of disinfection practice from  $\text{ClO}_2$  to  $\text{Cl}_2$ . Treatment of raw water with  $\text{ClO}_2$  generated an extremely low concentration of THMs and replacement of chlorine with  $\text{ClO}_2$  in the water utilities will surely reduce the THMs concentration in treated water significantly. Though HAAs formed during  $\text{ClO}_2$  treatment was always less than that formed during chlorination, it generated a higher proportion of more toxic brominated HAAs when water contains bromide and worsen the toxicological profile of treated water.  $\text{ClO}_2$  reacts more readily with HAAs forming precursor whereas reactivity of chlorine towards THMs forming precursor was greater.

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## Quantitative assessment of crop species diversity in shifting cultivation system of Eastern Himalaya

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**The narrowing of diversity in crop species contributing to the world's food supplies has been considered a potential threat to food security. The present study quantifies crop species diversity in controversial shifting cultivation system (SCS) using primary data from 52 villages spread across six North-Eastern (NE) hill states of India. The findings reveal that SCS is much diversified compared to settled cultivation system. Along with cereals, millets and pulses, the upland tribes grow a variety of horticultural crops on SC land. At the aggregate level, horticultural crops in the sampled states were observed to be much diversified and the mean diversification index value was found to be 0.79 (Simpson's Diversity Index) for the six NE hill states on SC land. The present study documented 25 cultivars of vegetables, 22 cultivars of fruits, spices and plantation crops, and 12 field crops in SCS, besides many minor fruits and underutilized vegetables. However, the most densely populated crop species were rice, maize and finger millet in the case field crops. Vegetable crops included pumpkin, potato and ash gourd, and fruit crops included banana, pineapple and citrus, while spices like ginger, chilli and turmeric were densely cultivated on SC land. Thus, the prevailing crop species in SCS had their own attributes, performances and challenges. Experiences of the present study shall be the guiding benchmark for those who negate the possibilities of agrobiodiversity in SCS.**

**Keywords:** Agrobiodiversity, crop diversity, upland tribes, shifting cultivation.

FOOD security of any country is primarily dependent upon the extent to which different food groups are produced and consumed, which underlines the importance of crop diversity. Crop diversity can be described as plant genetic resources for food and agriculture (PGRFA), and implies the nature of diversity within and among crops, their wild relatives and wild edible plant species. Crop diversity has evolved over thousands of years of interaction

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