

The effect of the molecular mass of the organic matter in raw water on the formation of disinfection by-products

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ABSTRACT

This research used an ultra-membrane filtration system to divide raw water into four different organic groups with different molecular masses. The effects of each organic group on the quantity of disinfection by-products formed after a reaction with chlorine dioxide was investigated. The experimental results show that the four organic groups of different molecular masses were: $10\text{ kD} < \text{average molecular mass (AMM)} < 0.45\ \mu\text{m}$; $5\text{ kD} < \text{AMM} < 10\text{ kD}$, $1\text{ kD} < \text{AMM} < 5\text{ kD}$, and $\text{AMM} < 1\text{ kD}$. Their distribution proportions were 10.8%, 46.8%, 13.3% and 29.1%, respectively. In the reactivity between the organic substances and chlorine dioxide, it was discovered that the reaction breaks down the organic substance large molecules into smaller molecules and cannot directly mineralize the large organic molecules into inorganic carbon. In comparison, the small organic substance molecules (5–1 kD, $\text{AMM} < 1\text{ kD}$) contributed most disinfection by-products per unit organic carbon (THMs/DOC, THAAs/DOC).

Key words | chlorine dioxide, disinfection by-product (DBP), molecular mass, ultra-filtration (UF) system

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INTRODUCTION

Chlorine is used as a disinfectant in most traditional water treatment plants. Because water sources have been over-developed, the pollution caused by organic pollutants is becoming much more serious. Higher dosages of disinfectants are required for water purification processes. This increases the chloro-organic disinfection by-products (DBPs) in the water (Bellar *et al.* 1974; Rook 1974; Oliver 1983; Koch & Krasner 1989; Peters *et al.* 1990). Among these DBPs, organic DBPs are hazardous to human beings and may cause health problems such as cancer, tumours and mutations (National Cancer Institute 1976; Bull & Kopfler 1991; Craun *et al.* 1994). Reducing the formation of organic halogenides has therefore become a very important research topic for scholars, experts and treatment plants (AWWA Research Foundation & KIWA 1985; Krasner *et al.* 1989; Arora *et al.* 1990; Myer 1990; White 1992).

The many formation factors involved in DBPs include organic precursors, disinfectants, pH, temperature, ionic strength, etc. The most important factors are the types of organic precursor and disinfectant and their dosages (Amy *et al.* 1998; Muller 1998). This research used chlorine dioxide as a substitute for chlorine as the disinfectant so as to reduce the formation of organic halogenides (Lykins *et al.* 1986; Narkis 1995). Although ClO_2 is widely used in the drinking water in Europe, the USA and other countries worldwide, it has not yet been used in water treatment facilities in Taiwan. Previous studies on ClO_2 focused on the disinfection efficiency for the removal of harmful microorganisms (see, for example, Narkis 1995; Huang *et al.* 1997), bad odour control (White 1992; Edwards and Amirtharajah 1993) and ferrous or manganese ion removal (Aieta & Berg 1986; White 1992). Few investigations have

Table 1 | The basic quality of the raw water

	Temp. (°C)	pH	TDS (mg/L)	Alkalinity (mg/L)	SS (mg/L)	DOC (mg/L)	Cl ⁻ (mg/L)	Br ⁻ (mg/L)	NH ₃ -N (mg/L)	Cl ₂ (mg/L)
Oct. 1998	20.5	7.4	171	169	7.5	1.97	3.71	0.03	0.08	< 0.1
May 1999	17.8	7.8	189	147	3.9	2.03	2.21	0.01	0.05	< 0.1

looked into DBP formation. Most studies paid more attention to trihalomethanes in DBP formation (Lykins *et al.* 1986; Monscvitz & Rexing 1981) compared with chlorine when ClO₂ was used as an alternative disinfectant.

In this study, raw water was used as the research object to study the individual contributions of various amounts of organic matter of different molecular masses to the DBPs. This would provide a reference basis for water purification plants to control DBPs produced in the filtration technology.

MATERIALS AND METHODS

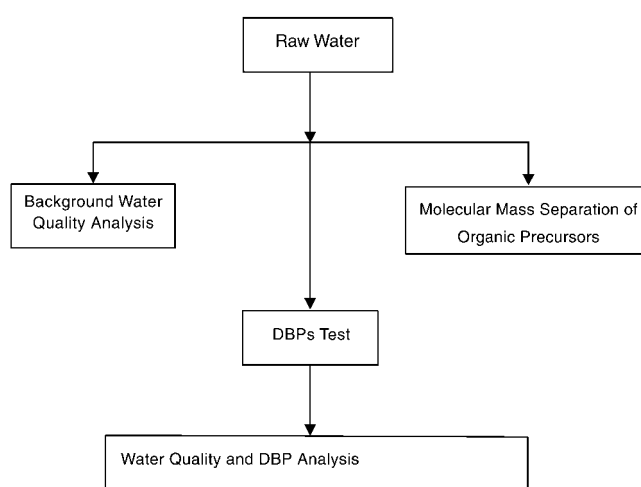
Materials

The preparation of ClO₂

Chlorine dioxide was produced from sodium chlorite activated using a 10% HCl solution (*Standard Methods for the Examination of Water and Wastewater* 1995). The chlorine dioxide gas was driven off using air bubbling and passed through a chlorine-absorption bottle. The chlorine was then absorbed into a distilled water-cooled ice bath. The obtained ClO₂ solution that included no free residual chlorine was placed in brown bottles and kept in a refrigerator in darkness. The concentration was measured using the N,N-diethyl-p-phenylenediamine (DPD) method just before application.

Water sample

The water sample used for this experiment was raw water. (The source of the raw water was the Da Cha Creek, in

**Figure 1** | The experimental procedure of DBPs.

Taichung, Taiwan, before it enters the Fung Yuan water treatment plant. The basic quality of this raw water is shown in Table 1.) Additional experiments involved adding chlorine dioxide to four organic groups at different molecular masses generated by separation using a raw water ultra-filtration system.

Procedure

This research incorporated a batch experiment using the following steps (Figure 1). In this DBP test, the experiment used a BOD bottle as the reaction tank. For the reaction the bottle was filled with 5 mL of phosphate buffer solution and various amounts of ClO₂. After the addition of the appropriate amount of sampled water, the bottle was placed in a container with a constant temperature of 20°C.

Table 2 | The distribution of organic substances with various molecular masses in raw water

Distribution of the molecular masses	0.45 μm –10 kD	10–5 kD	5–1 kD	AMM<1 kD
DOC (mg/L)	0.22 (10.8%)	0.95 (46.8%)	0.27 (13.3%)	0.59 (29.1%)
UV ₂₅₄ /DOC	0.0031	0.0029	0.0035	0.0051

The entire experiment required 7 days. The sampling times were 1, 4, 24, 96 and 168 hours respectively. Three bottles were collected for analysis. The samples were immediately analysed for ClO_2 residual concentration. A 10 ml portion from the 0.2 μm filtrate was collected to analyse the inorganic DBPs (Cl^- , Br^- , ClO_2^- and ClO_3^-) using an ion instrument (DIONEX, series 4500, column AS-12A, 4 mm (10–12), P/N 46034). To the remaining samples, 1 g of $\text{Na}_2\text{S}_2\text{O}_3$ was added to terminate the reaction. One portion of this sample was used for dissolved organic carbon (DOC) analysis. The purpose of measuring this item was that organic matter exists in raw water in dissolved carbon forms. In the experimental step, a water sample was filtered with 0.45 μm Teflon film and the DOC value was determined using organic carbon analysis chromatography (O.I. Corporation Model 700) as an important organic parameter in this study. The trihalomethane (THM), haloacetonitrile (HAN) and haloketone (HK) samples were prepared in a 40 ml brown glass bottle (with Teflon ring and screw-on cap) with 100 mg NH_4Cl as the preservative. Water was added to the above solution to fill the bottle. Samples were capped with Teflon-lined seals, returned to the laboratory in a cooler and stored in a cold room until analysed. The analytical methods followed EPA 501.2 methodology. The pH was adjusted to pH 4.5 in the field and samples were extracted with normal pentane, containing dibromomethane and 1,2-dibromopropane as an internal standard. THMs were analysed using a HP5890II plus gas chromatography, equipped with an electron capture detector (GC-ECD), a one-column injector and a J&W DB-5 capillary column. The HAA water samples were prepared by adding 150 ml NH_4Cl per 100 ml of the sample with the pH adjusted to below 0.5. Samples were extracted with methy-tert-

butylether (MTBE) esterized by diazomethane and analysed using GC-ECD based on EPA standard 502.2.

The analysed items for the water sample analysis included the ClO_2 residual concentration, Cl^- , Br^- , ClO_2^- , ClO_3^- , THMs, HAAs, HANs, HKs, etc.

Quality control

All samples were collected in duplicate with control samples included for all target analytes. All DBP methods incorporated surrogate internal standards; quantification was based on response factors established by multi-level calibration with fortified samples analysed under identical conditions. For the THMs, raw water samples (matrix spikes; $n = 10$) were analysed at a fortification level of 5 $\mu\text{g/L}$ (chloroform = 25 $\mu\text{g/L}$). The overall recovery was $99.1 \pm 3.1\%$. The precision of the HAA method was estimated at $\pm 20\%$. The mean HAA recovery was typically $>93\%$ as estimated from the recovery of the added MBBA internal standard. DBPs identified by GC-ECD were confirmed by gas chromatography–mass spectrometry.

RESULTS AND DISCUSSION

The distribution and effect of organic substances with various molecular masses in raw water

Table 2 shows the molecular mass distribution of the organic matter in Da Cha Creek raw water and the DOC concentration values. The table shows the broad distribution of the organic substances in the raw water. Middle-sized molecules (5–10 kD) occupied 46.8%. Small

Table 3 | The variation of molecular mass through the UF system after the reaction of the raw water with ClO_2

Dosage		1 mg ClO_2/L	10 mg ClO_2/L
DOC (mg/L)	Initial		2.03
	Final	1.65	1.54
	0.45 μm –10 kD*	0.17	0.10
	10–5 kD*	0.64	0.68
	5–1 kD*	0.30	0.26
	AMM < 1 kD*	0.54	0.50
DBPs	THMs ($\mu\text{g}/\text{L}$)	13	11
	THAAs ($\mu\text{g}/\text{L}$)	27.4	31
	ClO_2 (mg/L)	0.4	3.88
	ClO_3^- (mg/L)	N.D.	0.28

*The DOC value of raw water after reaction.

molecules (AMM < 1 kD) occupied 29.1%. In Table 2, the parameter that represents the content of non-saturated bonds in the organic substance is SUVA (Specific Ultra-Violet Absorbance, $\text{UV}_{254}/\text{DOC}$). This value showed that the small molecules (AMM < 1 kD) had a higher absorption value, indicating that this area had the most organic substances with non-saturated bonds. This area also had a higher ability to form DBPs.

Study of organic matter with various molecular masses

The chlorine dioxide dosages used in this research were 1 mg ClO_2/L with an additional high concentration dosage of 10 mg ClO_2/L to simulate post-rainstorm flow. The testing method used a raw water and chlorine dioxide (to simulate a pre-chlorination process) direct reaction, followed by sieving using the ultra-filtration system to observe the molecular mass variations. The results of DBP formation were analysed and are shown in Table 3. Comparing Tables 2 and 3, we can see that after the raw water

reacts with the chlorine dioxide, the water-soluble organic substances have a tendency to move towards the areas with smaller molecules. This indicated that the chlorine dioxide can indeed break down the large organic molecules into smaller molecules, but cannot mineralize the large molecules into inorganic carbon.

In the DBP formation study, although chlorine dioxide usually acts as an oxidant instead of a halogenate agent, it has free radical characteristics just like ozone. Chlorine dioxide can be ionized into hydroxyl free radicals (HO) under higher pH conditions, and further oxidation can be achieved when it reacts with hydrocarbons and produces an intermediate with an odd number of electrons. There are many articles that have indicated that many chloro-compounds are produced by chlorine dioxide with organic matter although the number of chloro-compounds is lower than those formed by chlorine (Lindgren & Nilsson 1974; Kolar & Lindgren 1982; Ozawa & Kwan 1984; Rav-Acha & Choshen 1987). It is believed that ClO_2 intermediate precedes the electron transfer reaction and forms chlorate (ClO_3^-) and hypochlorite (ClO^-). The hypochlorite ion (ClO^-) then reacts with the organic matter and produces chloro-DBPs. This possible mechanism for the formation of HOCl is chlorine dioxide reacting with the unsaturated double bond organic matter and producing ROClO . HOCl is formed by the hydrolysis of ROClO (Lindgren 1971). If the water contains bromide ions, the ClO_2 could oxidize bromide to form hydrobromous acid, which subsequently reacts with organic matter and yields CHBr_3 with an increased bromide concentration and ClO_2 . In our study, the quantity of organic DBPs, TTHMs and THAAs increased as the reaction time increased, but did not drastically increase with an increase in dosage concentration (Li *et al.* 1996). When a normal concentration of 1 mg/L of ClO_2 was added, the quantity of TTHMs and THAAs was about 11 $\mu\text{g}/\text{L}$ and 23 $\mu\text{g}/\text{L}$, respectively. If the ClO_2 dosage was changed to 10 mg/L, the amount of TTHMs and THAAs produced was about 13 $\mu\text{g}/\text{L}$ and 31 $\mu\text{g}/\text{L}$, respectively. Furthermore, halo ketones (HKs), haloacetic nitriles (HANs) were not detected in this study.

The free radicals were the usual type with chlorine dioxide and they occurred in the oxidation–reduction reaction with a single electron. Chlorine dioxide is stable

Table 4 | The formation of DBPs after the reaction of the raw water and the ClO₂

Molecular cut off		0.45 μm-10 KD		10 KD-5 KD		5 KD-1 KD		AMW<1 KD	
Dosage (mg/L)		1	10	1	10	1	10	1	10
DOC	Initial	0.22		0.95		0.27		0.59	
	Final	0.15	0.11	0.75	0.71	0.24	0.23	0.49	0.48
Removal Ratio (%)		31.4	50	20.6	35	12.3	13.2	17.0	19.2
ClO ₂ ⁻		0.3	2.9	0.2	2.2	0.4	3.0	0.1	2.1
ClO ₃ ⁻		N.D.	0.1	N.D.	N.D.	N.D.	0.1	N.D.	N.D.
THMs (μg/L)		9.0	10.5	5.7	6.3	11.6	13.4	25.2	30.1
DBPs	THMs/DOC* (μg/mg)	128.6	95.5	28.5	26.3	386.7	335.0	315.0	273.6
	THAAs (μg/L)	29.1	33.9	6.2	7.9	14.0	14.9	55.4	60.1
	THAAs/DOC** (μg/mg)	415.7	308.2	31.0	32.9	466.7	372.5	692.5	546.4

*Final amount of THMs/DOC removal.

**Final amount of THAAs/DOC removal.

in an acidic environment and it has a tendency to be ionized into ClO₂⁻ and ClO₃⁻ under alkaline conditions: in neutral or alkaline conditions, it is easier to produce acidic radicals:



or



Under high pH conditions, there tends to be an electron exchange reaction:



The pH used in this research was 7.4–7.8. The results show that ClO₂⁻ is the primary by-product and has a clearer dosage relationship. The quantity produced drastically increases as the dosage concentration increases.

For the independent study of various molecular masses, raw water was sieved using the ultra-filtration system into various molecular masses and then reacted with the chlorine dioxide to understand the feasibility of using chlorine dioxide in a micro-filtration system. In the DOC removal comparison, the chlorine dioxide had a low DOC removal rate for small molecules (Table 4). In compliance with the foregoing experimental results, the reaction between the chlorine dioxide and the organic substances in the water decomposed the large organic molecules. In the DBP analysis, the organic substances with small molecular masses (especially the AMM<1 kD) were the primary preliminary materials for forming THMs and HAAs. These results relate to the SUVA of the previous experiment. The DBPs (THMs/DOC and THAAs/DOC) derived from each DOC unit still contributed the most for the organic substances with smaller molecular masses (5–1 kD, AMM<1 kD). This verifies the research by Goel *et al.* (1995): the greater the number of non-saturated bonds in the organic substance, the higher the

UV₂₅₄ absorption and the greater the formation of DBP trihalomethanes related to the non-saturated organic carbon bonds.

In the control by membrane filtration study to reduce the production of DBPs, by adding 1 mg ClO₂/L and 10 mg ClO₂/L, the 10 kD membrane reduced the quantity of THMs and THAAs to (17.5%, 17.4%) and (27.8%, 29%). If a 5 kD membrane is used, the quantity will increase to (28.6%, 27.9%) and (33.7%, 35.8%). The reduced quantity of THMs and THAAs were (51.1%, 50.1%) and (47.1%, 48.6%) for the 1 kD membrane. Therefore, this research discovered that the appropriate membrane filtration technology could control or reduce the quantity of DBPs formed.

CONCLUSION

Ultra-filtration technology can separate raw water into various molecular mass intervals, which is helpful to further analyse and study the water quality and provide a superior treatment technology for DBPs. This experiment demonstrated that organic carbon distribution in raw water is primarily concentrated into two portions (5–10 kD, AMM < 1 kD). Applying the UV₂₅₄ absorption value allows us to see more non-saturated bonds in the organic substances with smaller molecules (AMM < 1 kD) and the experimental results show that this area has the highest production of DBPs. In the DBP study, the inorganic DBPs were mainly chlorine acid radicals. The chlorine acid radical production quantity and chlorine dioxide dosage are directly proportional to one another and irrelevant to the molecular mass of the organic matter. The main organic DBPs formed were THMs and HAAs. The produced quantity of these species increases as the chlorine dioxide dosage increased, but there were no multiple relationships in this increase. There is an obvious difference in species production based on the molecular mass of the organic matter. The main formation interval falls in the range of molecular mass less than 1 kD. This phenomenon will supply some operational options at water treatment facilities.

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