



Effect of ferric and bromide ions on the formation and speciation of disinfection byproducts during chlorination

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Abstract

The effects of ferric ion, pH, and bromide on the formation and distribution of disinfection byproducts (DBPs) during chlorination were studied. Two raw water samples from Huangpu River and Yangtze River, two typical drinking water sources of Shanghai, were used for the investigation. Compared with the samples from Huangpu River, the raw water samples from Yangtze River had lower content of total organic carbon (TOC) and ferric ions, but higher bromide concentrations. Under controlled chlorination conditions, four trihalomethanes (THMs), nine haloacetic acids (HAAs), total organic halogen (TOX) and its halogen species fractions, including total organic chlorine (TOCl) and total organic bromide (TOBr), were determined. The results showed that co-existent ferric and bromide ions significantly promoted the formation of total THMs and HAAs for both raw water samples. Higher concentration of bromide ions significantly changed the speciation of the formed THMs and HAAs. There was an obvious shift to brominated species, which might result in a more adverse influence on the safety of drinking water. The results also indicated that high levels of bromide ions in raw water samples produced higher percentages of unknown TOBr.

Key words: disinfection byproducts; total organic halogen; chlorination; ferric ion; bromide ion

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Introduction

Since the recognition of chloroform as a ubiquitous disinfection byproduct (DBP), numerous chlorine- and bromide-containing DBP species with potentially adverse health effects have been found in drinking water (Rook, 1974; Krasner et al., 1989; Yang, 2007), such as trihalomethanes (THMs), haloacetic acids (HAAs), and halonitriles (HANs). Research on THMs and HAAs, two major classes of DBPs, has been widely conducted. Some of these DBPs have been identified as potentially carcinogenic agents (Btyant et al., 1992). As a result, the United States Environmental Protection Agency (US EPA, 1998) has regulated the maximum contaminant level (MCL) of THMs and HAAs at 80 and 60 $\mu\text{g/L}$, respectively, in stage I of the disinfection/disinfection byproducts rule (D/DBP Rule).

The formation of DBPs and their species distribution is a complex phenomenon and depends on many factors such as characteristics and concentration of natural organic material (NOM) (e.g., dissolved organic carbon, DOC) and water quality parameters (e.g., pH, NH_4^+ and background inorganic matrix, especially bromide concentration). Many

researchers have demonstrated how water quality and treatment factors influence levels of bromide substitution in THMs and HAAs byproduct classes (Pourmoghaddas et al., 1993; Symons et al., 1993; Qi et al., 2004). However, limited studies have attempted to characterize or quantify the trace metal effect of bromide substitution in THMs and HAAs byproduct classes, especially ferric ions. Bower (2002) showed iron oxide-pipe deposits on chlorine DBP formation in the distribution system. Our previous study found ferric ions increased the formation of Br-THMs in alkaline environments (Zhu et al., 2007). Ernset et al. (2003) tested the catalytic effect of copper on THMs formation. However, the relationship between ferric ions and formation of DBPs (e.g., THMs, HAAs) has not been well-established. The formation mechanisms of chlorinated DBPs and their relationship with NOM are also ill-defined.

In recent years, investigations on DBPs have focused on the formation of THMs and HAAs. However, toxicological studies have shown that only about 25% of total mutagenicity of chlorinated drinking water has been identified, suggesting that unidentified DBPs might contain a substantial amount of toxicologically important compounds (Richardson, 1998), especially bromine related DBPs. A

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group parameter, total organic halogen (TOX), has been widely used as an estimate of total amount of halogenated organic materials (Dressman and Stevens, 1983; Hua and Reckhow, 2007). Both THMs and HAAs account for approximately 50% of TOX (Reckhow and Singer, 1984); therefore, the relationship between TOX and NOM should be taken into account in further studies.

Iron exists in ground and surface waters as either ferrous (Fe^{2+}) or ferric (Fe^{3+}) ions. Generally, iron concentrations are less than 0.50 mg/L in aerated water, although concentrations in groundwater can be higher (Vikesland and Valentine, 2002). A maximum contaminant level goal of 2 mg/L has been set for ferric in drinking water supplies in the United State (US EPA, 1996). Although the average concentration of ferric in tap waters is less than 0.1 mg/L, concentrations greater than 0.6 mg/L have been reported due to corrosion of ferric pipes, with deposits consisting of a complex mixture of iron oxides and hydroxides (e.g. goethite and magnetite). On the other hand, in many drinking water treatments, ferric salt has been used as a coagulant (ferric chloride and polyferric sulfate), with a dose range of 5–6 mg/L, which might transport a significant amount of ferric ions into the drinking water system. According to previous investigations, total irons in finished water were usually in the range of 0.3–0.5 mg/L (Henderson, 2001).

Bromide is naturally present in raw water of coastal cities due to saltwater intrusion, and also in the groundwater (Voudrlas and Reinhard, 1988). A nationwide survey of bromide concentrations in the USA showed that the bromide concentration in water resources is usually around 62 $\mu\text{g/L}$, but can exceed 500 $\mu\text{g/L}$ in certain groundwaters near the coast or under special geological circumstance (Amy et al., 1995). In general, bromide contributes to the formation of bromide-DBPs through its reaction with chlorine to form hypobromous acid (HOBr), which subsequently reacts with natural organic materials to form brominated and mixed chlorinated-brominated compounds (Roberts et al., 2002; Cowman and Singer, 1996).

Considering the frequent salt intrusions in drinking water sources of the Yangtze River in recent years, drinking water quality may be adversely affected because of higher halogen content and the coexistent ferric ions. Consequently, we investigated the effects of coexistent ferric and bromide ions on the formation and species distribution of DBPs during the chlorination of different raw water samples, which were collected from two typical drinking water sources of Shanghai. Specific attention was paid to total organic halogen (TOX) and its halogen species fractions.

1 Experimental

1.1 Raw water samples

Raw water samples were collected from intakes of drinking water plants at the Yangtze River ($31^{\circ}32'4''\text{N}$, $121^{\circ}51'6''\text{E}$) and Huangpu River ($31^{\circ}32'1''\text{N}$, $121^{\circ}53'5''\text{E}$) in China, which are the major drinking water sources of

Table 1 Characteristics of raw water samples

Parameter	Yangtze River water	Huangpu River water
Collection date	2/20/2009	2/24/2009
TOC (mg/L)	3.0 ± 0.1	8.5 ± 0.2
DOC (mg/L)	2.8 ± 0.1	7.5 ± 0.1
pH (25°C)	7.9 ± 0.1	7.3 ± 0.1
NH_4^+ (mg/L)	0.15	0.20
Br^- ($\mu\text{g/L}$)	720	100
I^- ($\mu\text{g/L}$)	< 10	< 10
Total Fe^{3+} (mg/L)	0.14	0.20
SUVA ^a (L/(mg·m))	1.80	3.10
UV ₂₅₄ (cm^{-1})	0.053	0.136
Alkalinity (mg/L as CaCO_3)	109.40	103.45
Hardness (mg/L as CaCO_3)	203	180

^aSUVA (specific ultraviolet absorbance) was calculated from ultraviolet absorbance at 254 nm (UV₂₅₄) divided by the dissolved organic carbon (DOC) concentration.

Shanghai. The characteristics of these water samples are summarized in Table 1. The Yangtze River and Huangpu River water samples were collected in February, 2009, filtered with a 0.45- μm filter (cellulose acetate), and stored at 4°C in the dark until the experiments were conducted. The concentration of dissolved organic carbon (DOC) in the Yangtze River and Huangpu River water samples was (2.8 ± 0.1) and (7.5 ± 0.1) mg/L, respectively. The absorbance at 254 nm was 0.053 and 0.136 cm^{-1} , corresponding to SUVA₂₅₄ (specific UV absorbance at 254 nm) of 1.80 and 3.10 L/(mg·m), respectively. As a result, the Yangtze water samples were regarded as low SUVA (1.80 L/(mg·m)) with humic content, while Huangpu water samples were high SUVA (3.10 L/(mg·m)) with humic content. These two kinds of water samples contained different types of NOM precursors, as evidenced by their different SUVA values.

1.2 Chemicals

All chemicals were analytical reagent grade or better, and all solvents used in extractions were high-purity grade. Reagent water was obtained from a Millipore Super-Q plus water system. Ferric ions used in the experiments were added in the form of ferric(III) sulfate ($\text{Fe}_2(\text{SO}_4)_3$). High purity potassium bromide (99.95%) was purchased from Aldrich to prepare the stock solution. A free chlorine (HOCl) stock solution (2000 mg/L) was prepared from 5% sodium hypochlorite (NaOCl) and periodically standardized by N,N-diethyl-*p*-phenylenediamine (DPD)-ferrous ammonium sulfate (FAS) titrimetric method (APHA et al., 1998).

1.3 Experimental procedures

Yangtze River and Huangpu River water samples were treated with chlorine after being spiked with ferric or bromide ions to investigate the impact of coexistent bromide and ferric ions on DBPs formation during chlorination.

Chlorination was conducted in 500 mL chlorine demand-free, glass-stopped bottles. All samples were buffered with 2 mmol/L of phosphate solution to pH 7.5 (except pH experiments). The target free chlorine residual was 0.5 mg Cl_2/L , after 48 hr contact time. Samples were stored headspace-free at (22 ± 1)°C in the dark for 48 hr.

All samples were then quenched and analyzed for DBPs including the THMs, HAAs, dihaloacetonitriles, halo ketones, chloropicrin, and TOX including TOCl and TOBr. The above designed tests were carried out to determine the impact of pH and the presence or absence of ferric ions and bromide ions on DBPs formation for different water samples.

1.4 Analytical methods

Chlorine residuals were analyzed at the time of sampling by DPD ferrous titration (APHA et al., 1998). The DBPs determined for all samples included four chlorine and bromine containing THMs (CHCl_3 , CHBrCl_2 , CHBrCl_2 , and CHBr_3), nine chlorine and bromine containing HAAs (monochloro-, monobromo-, dichloro-, bromochloro-, dibromo-, bromodichloro-, dibromochloro-, trichloro-, and tribromoacetic acid (MCAA, MBAA, DCAA, BCAA, DBAA, BDCAA, DBCAA, TCAA, and TBAA)), three dihaloacetonitriles (dichloro-, bromochloro-, and dibromoacetonitriles, HANs), two halo ketones (dichloro- and trichloropropanone, HKs), chloropicrin (CP), chloral hydrate (CH), and TOX. Unknown TOX was calculated as the difference between the measured TOX and the sum of the chlorine-equivalent concentrations of measured specific DBPs. In addition, total organic chlorine (TOCl) and total organic bromine (TOBr) were analyzed for finished water samples. Both THM and HAA samples were quenched with sodium thiosulfate and ammonium chloride, respectively. The TOX samples were quenched with sodium sulfite and acidified with nitric acid at pH 2. All samples were refrigerated at 4°C and analyzed within two weeks. THMs, HANs, HKs, and CP were quantified by liquid/liquid extraction with pentane and by a Gas Chromatograph (Finnigan TRACE GC, Thermo, USA) with an electron capture detector according to US EPA Method 551.1. The HAAs were analyzed by liquid/liquid extraction with methyl-tertiary-butyl-ether followed by derivatization with acidic methanol and analyzed by GC/ECD according to US EPA Method 552.2. Calibration standards were prepared using the standard mixture purchased from J&K Chemical Co., USA. Calibration curves had at least six points, and calibration standards were also extracted with the same protocol as samples to compensate for extraction efficiency effects. The column used was a DB-5MS fused silica capillary column (30 m × 0.25 mm i.d. with 0.25 μm film thickness; J&W Scientific, USA). At the beginning of each analytical run, solvent blanks and solvent samples containing the internal standard were injected into the GC condition to verify that interferences were absent. Other quality assurance/quality control (QA/QC) procedures, such as QC check standards and matrix spikes were taken through the analysis.

The TOX was determined using a Euroglas ECS 1200 TOX Analyzer (Euroglas, Delft, The Netherlands). The method was based on US EPA Standard Method 5320B with minor modifications. Both TOCl and TOBr were analyzed by high-temperature combustion and offline ion chromatography (Hua and Reckhow, 2006). The DOC con-

centrations were determined with a TOC-VCPN Analyzer (Shimadzu Corp., Japan) according to Standard Method 5310B. Bromide and iodine ions were analyzed with an AS11-HC and AS16-HC anion separation column using a Dionex 1000 ion chromatography system (Dionex, Sunnyvale, USA). Ultraviolet (UV) absorbance at 254 nm was measured using a Shimadzu UV-3000 spectrophotometer based on US EPA Standard Method 5910 B.

2 Results and discussion

2.1 Effect of ferric ions on DBPs

To understand the effect of ferric ions on DBPs formation, ferric ions were spiked into water samples before chlorination. According to previous publications, ferric ions might exist in natural waters in the range of 0.3–0.5 mg/L. Therefore, the concentration of spiked ferric ions was 0.5 mg/L in the experiments. Figure 1 shows the impact of ferric ions on the formation and distribution of THMs and HAAs.

The effect of saltwater intrusion is one of the most important factors considered in our study. Yangtze River water with higher bromide ion levels was collected in the season of saltwater intrusion. In Fig. 1a, CHBr_3 was the most abundant THM species (55.8%), followed by CHClBr_2 (29.7%), CHCl_2Br (10.1%), and CHCl_3 (4.3%) for Yangtze River water without added ferric ions. While in the presence of 0.5 mg/L Fe^{3+} , the formation of these four THMs species increased to 106 μg/L, with an increment of 11% compared to that in the absence of ferric ions.

Figure 1b shows for Huangpu River water samples, CHCl_3 was the most abundant THM species (70.7%), followed by CHCl_2Br (17.3%), CHClBr_2 (10.3%) and CHBr_3 (1.7%) without added ferric ions. This was related to the low bromide concentration and high TOC (or SUVA) value of Huangpu River water. There was no significant difference in total THMs between the two water samples in chlorination. Data showed that total formed THMs was 106.3 and 94.4 μg/L under added or not added ferric ions, respectively in Yangtze River water, while was 98.5 and 94.8 μg/L, respectively, in Huangpu River water. The results also indicated that high concentration bromide ions significantly affect the speciation of the formed THMs, with a shift in THMs to more brominated species at high bromide levels. In the presence of ferric ions during chlorination, a little promotion of THMs production was found for Yangtze River water and Huangpu River water.

As shown in Fig. 1c, after the chlorination of Yangtze River water under no added ferric ions, the most abundant HAAs species was MCAA (44.5%), with other formed HAAs including MBAA (20.7%), DCAA (6.7%), TCAA (2.9%), BCAA (13.4%), DBAA (3.9%), and BDCAA (3.9%). Figure 1d shows the formed HAAs species after chlorination of Huangpu River water, with only MCAA, MBAA, DCAA, and TCAA detected. The formation of DBAA was found only in Yangtze River water with original bromide ions, and the MBAA concentration was obviously higher for Yangtze River water compared to

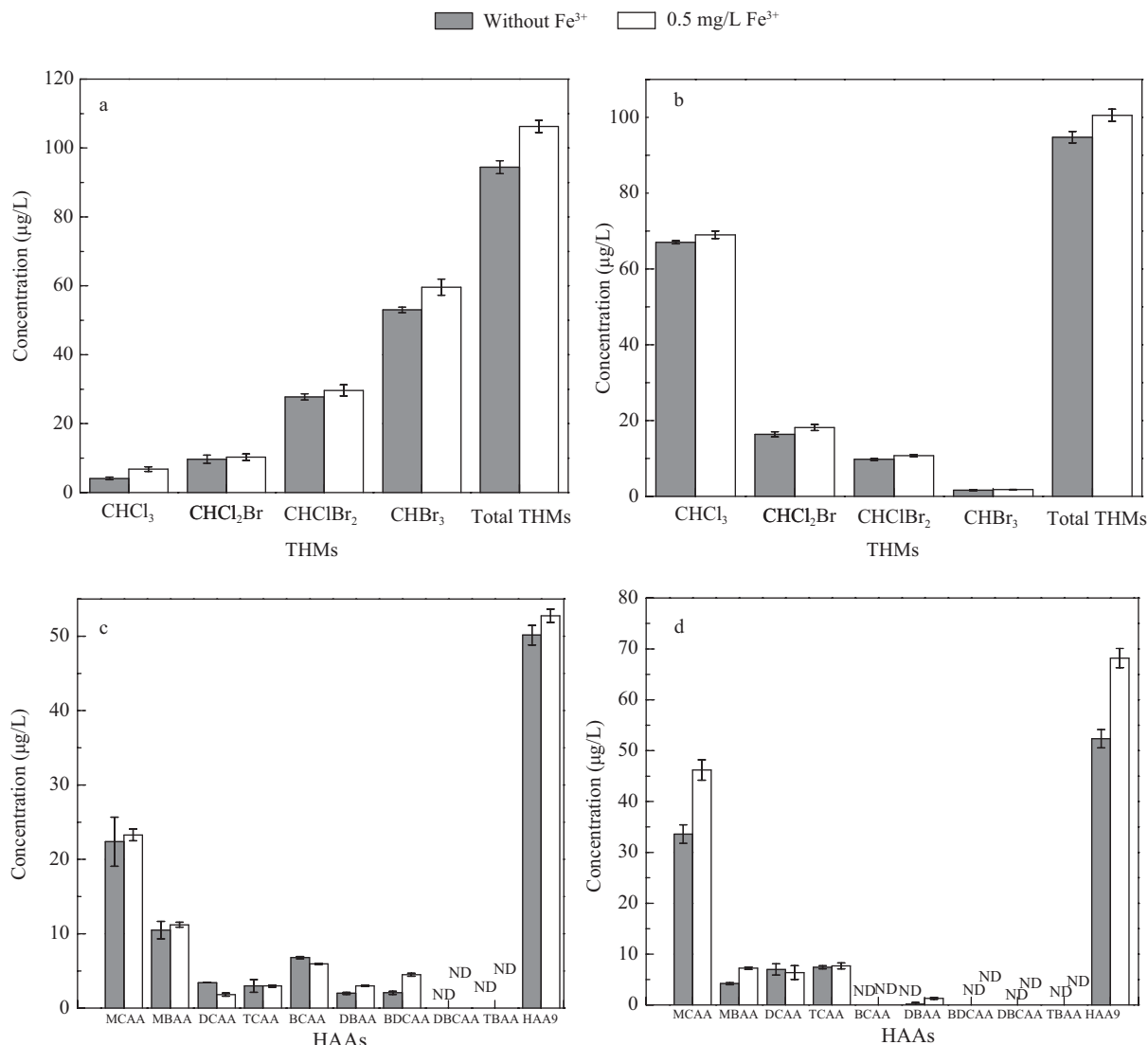


Fig. 1 Effects of ferric ions on the formation and species distribution of THMs and HAAs. Experimental conditions: contact time 48 hr, temperature $(22 \pm 1)^\circ\text{C}$, Br^- ambient concentration, Fe^{3+} 0 or 0.5 mg/L spiked, pH 7.5, Cl_2 dosage 3.5 mg/L for Yangtze River water (a, c) and Cl_2 dosage 6.0 mg/L for Huangpu River water (b, d).

Huangpu River water. This effect is similar with previous research (Chang et al., 2001). Under chlorination of Yangtze River water, ferric ions significantly increased the formation of MCAA, MBAA, DBAA, and BDCAA. For Huangpu River water, the formation of total HAAs and two HAAs species (MCAA and MBAA) increased obviously with the addition of ferric ions.

For the increase in total formed HAAs, the possible reason may be related to the higher SUVA value (Liang and Singer, 2003) in Huangpu River water with more HAAs precursors. It implied that the presence of ferric ions changed the reactivity between chlorine, bromide and NOM, which led to a net increase in these DBPs concentrations. Furthermore, during chlorination of Yangtze River water, DBPs species such as DCAN, DCP, TCP and CH were not detected under the experimental conditions. For Huangpu River water HPW, DBPs species, including DCAN, DCP, TCP and CH, were detected with the concentrations $< 5 \mu\text{g/L}$ after chlorination (data not shown). This may attributed to the higher TOC values and ammonia in Huangpu River water.

2.2 Effect of pH on the formation of THMs and HAAs

In the presence of ferric ions during chlorination, solution pH had an obvious impact on the formation and distribution of THMs and HAAs. The effect of pH on DBPs is shown in Fig. 2. To discuss the relationship between dissolved organic substances and the formation of DBPs, all formed DBPs concentrations were normalized as per unit DOC concentration.

Focusing on the yield of DBPs per unit DOC concentration showed a general trend where higher solution pH promoted the formation of THMs, but was adverse for HAAs under the experimental pH range. As for the effect of added ferric ions, in most of the cases it promoted the formation of total DBPs, and this tendency was more obvious for THMs for Yangtze River water and HAAs for Huangpu River water.

Since the composition of the raw water samples was very complicated, the influence of pH on the formation of different DBPs for both Yangtze and Huangpu water was complicated. The pH change may affect the formation

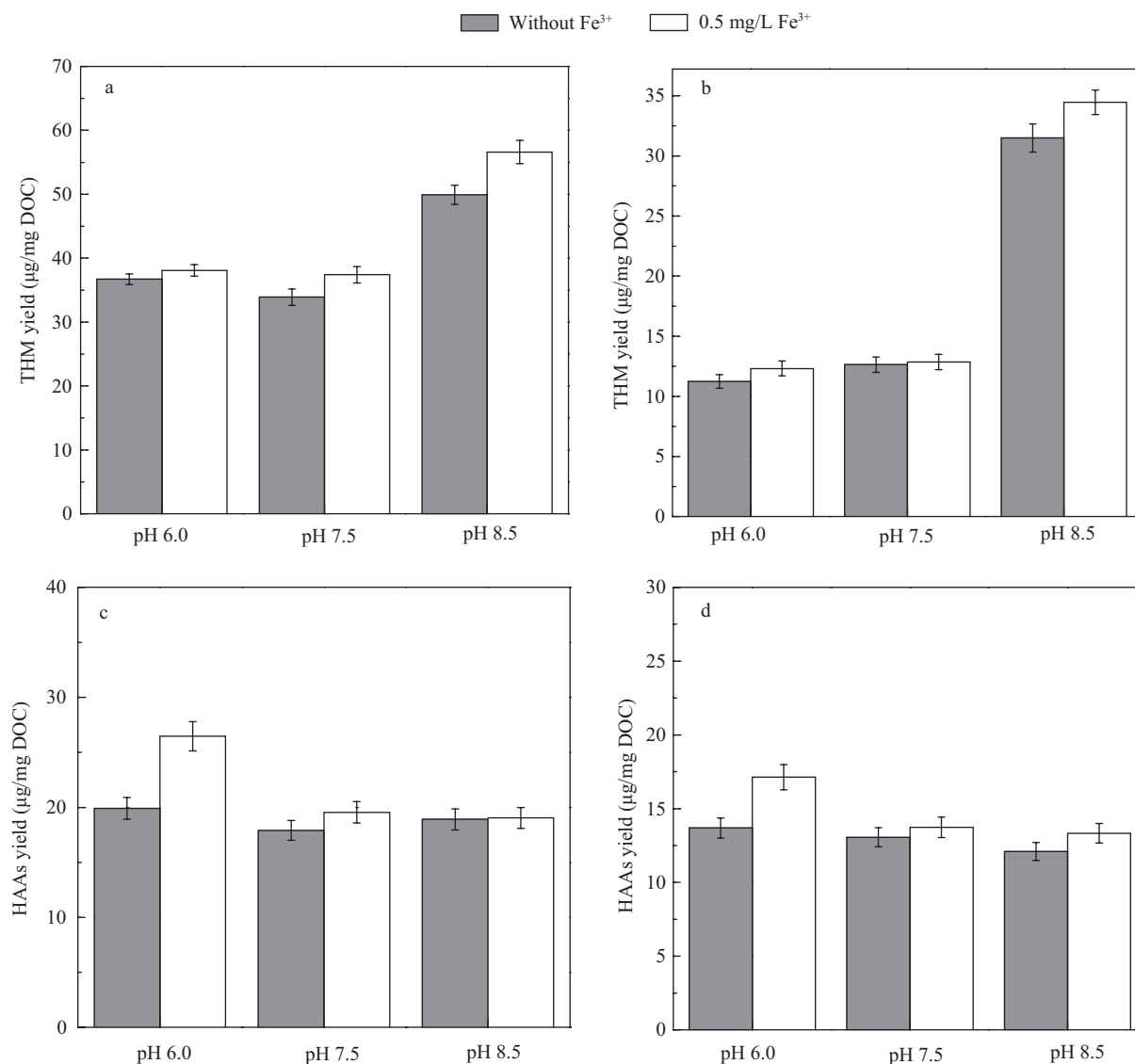


Fig. 2 Effect of pH on the formation and distribution of THMs and HAAs. Reaction conditions: contact time 48 hr, temperature (22 ± 1)°C, Br⁻ ambient concentration, Fe³⁺ 0 or spiked 0.5 mg/L, Cl₂ dosage 3.5 mg/L for Yangtze River water (a, c) and Cl₂ dosage 6.0 mg/L for Huangpu River water (b, d).

of DBPs during chlorination in several major ways. First, the distribution of HOCl/OCl⁻ depends on solution pH. HOCl, a more powerful oxidant than OCl⁻, dominates at low pH values. Second, charge and reactivity of organic precursors are dependent on solution pH. Third, individual DBP formation mechanisms can be affected by pH change. Reckhow and Singer (1985) proposed a conceptual model to describe the formation mechanisms of THMs and HAAs from fulvic acids. Under alkaline conditions, THMs are produced by base-catalyzed hydrolysis reactions. In contrast, trihaloacetic acid is predominately produced under acidic conditions. The pH change in drinking water not only affects Fe³⁺ hydrolysis but also the state of DBPs precursor, so as to affect reactivity between NOM and chlorine. Korshin et al. (1997) reported that the hydrophilic fraction of organic acids was transferred to the hydrophobic fraction of neutral material. With the increase in solution pH during the chlorination of our two water samples, the total concentration of THMs increased gradually; however, the formation of HAAs exhibited a reverse tendency. The

addition of Fe³⁺ enhanced the formation of both THMs and HAAs.

2.3 Effect of bromide ions on the formation of THMs and HAAs

To further understand the effect of coexistent bromide and ferric ions on DBPs, the effect of bromide concentrations on the formation and distribution of THMs and HAAs was investigated for Huangpu River water samples, because it had a lower Br/TOC ratio (Fig. 3). It was found that, with the increase in added bromide concentrations, total formed THMs rose significantly, but total HAAs only increased slightly. When water samples with added bromide ions were spiked with a definite concentration of ferric ions, different effects were observed on the formation of THMs or HAAs. For Huangpu River water samples, the coexistent ferric and bromide ions showed a more significant effect on the formation of HAAs than that of THMs.

As previously discussed, increasing bromide concen-

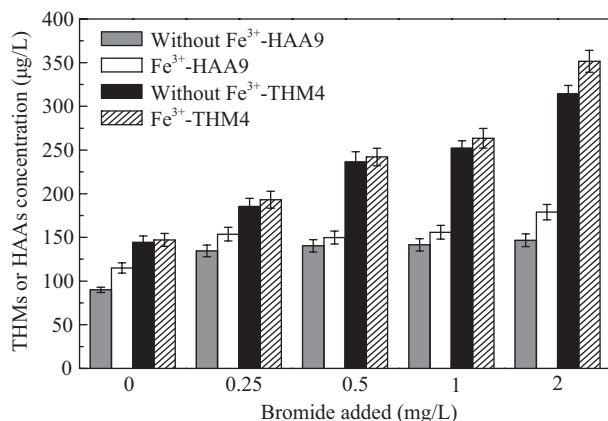


Fig. 3 Effect of bromide ions on the formation of THMs and HAAs. Reaction conditions: contact time 48 hr; temperature (22 ± 1)°C; Br ambient concentration; Cl₂ dosage 6.0 mg/L; Fe³⁺ 0 or 0.5 mg/L; TOC 7.5 mg/L; pH 7.5; Huangpu River water.

tration might markedly shift DBPs toward bromine-containing species, and especially the formation of higher bromine-incorporated species such as CHBr₂Cl, CHBr₃, DBAA, DBCAA, and TBAA. Higher levels of bromide ions have a significant co-effect with ferric ions on the formation of both THMs and HAAs, with a similar result reported previously (Cowman and Singer, 1996). We found co-existent ferric and bromide ions significantly promoted the formation of total THMs and HAAs for raw water samples, which may be attributed to the possible catalysis action of ferric ions for DBPs formation under the experimental conditions.

2.4 Effect of bromide ions on TOX formation

While THMs and HAAs have received attention in recent years for the detection and analysis of DBPs in drinking water chlorination, many other DBPs also exist and their reduction plays an important role on the guarantee of drinking water safety. Both TOX and its halogen fractions can provide more general information beyond the THMs and HAAs.

In this study, TOX and its halogen fractions were all normalized to the unit of µg Cl/L to account for different halogen atomic masses (Hua and Reckhow, 2006). Huangpu River water samples were selected for the TOX experiment. Figure 4 shows the formation of TOX, TOCl and TOBr at varying levels of bromide ions with added or no added ferric ions.

With increasing bromide concentrations in the presence or absence of ferric ions, TOCl concentrations gradually decreased and TOBr gradually increased. The higher bromide ions concentration promoted the formation of more bromine containing DBPs. Additional ferric ions increased the formation of TOX, with the main contribution attributed to the increase in TOBr in most of cases.

At 0.5 mg/L bromide concentration, the molar ratio of TOCl/TOBr was 3.45 and 2.94 for Huangpu River water (HPW) in the absence and presence of ferric ions, which corresponded to an initial Cl₂/Br molar ratio of 13.98. At 2.0 mg/L bromide addition, an initial Cl₂/Br molar ratio of 3.49 produced a TOCl/TOBr ratio of 0.25 and

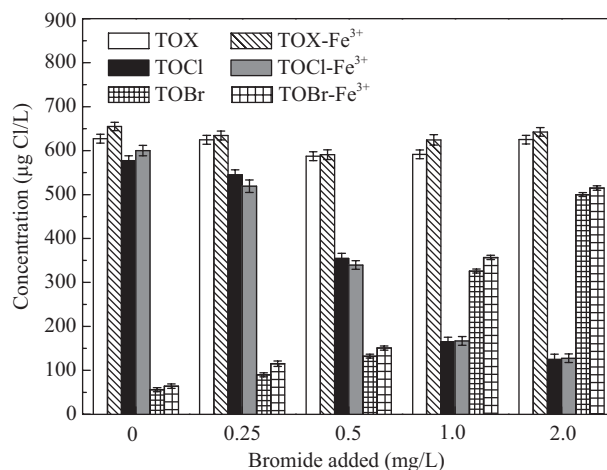


Fig. 4 Effect of bromide on the formation of TOX, TOCl and TOBr. Reaction conditions: contact time 48 hr; temperature (22 ± 1)°C; Cl₂ dosage 6.2 mg/L; Fe³⁺ 0 or 0.5 mg/L; TOC 7.5 mg/L; pH 7.5; Huangpu River water.

0.24 for two cases, respectively. These data indicated that bromide substitution with NOM was approximately one order of magnitude faster than chlorine substitution, which supported previous studies (Acero et al., 2005).

The formation of unknown TOX (UTOX), unknown TOCl (UTOCl), and unknown TOBr (UTOBr) was also determined in the presence or absence of ferric ions. The UTOX was calculated from the difference between TOX and the sum of the chlorine-equivalent concentrations of measured specific DBPs. Both UTOCl and UTOBr were calculated from the difference between TOCl and TOBr and measured chlorine or bromide related specific DBPs, respectively. Under added or no added ferric ions, the ratio for UTOX/TOX, UTOCl/TOCl, and UTOBr/TOBr are presented in Fig. 5. These indicated that higher levels of bromide ions in raw water samples tended to produce higher percentages of unknown TOBr.

Previous studies (Croue et al., 2000; Huang and Yeh, 1997; Dressman and Stevens, 1983; Reckhow and Singer, 1984) have suggested that bromide is more active with the hydrophilic and low MW fractions than the hydrophobic and high MW fractions in the formation of THMs and HAAs. In contrast to bromide, chlorine is more active with

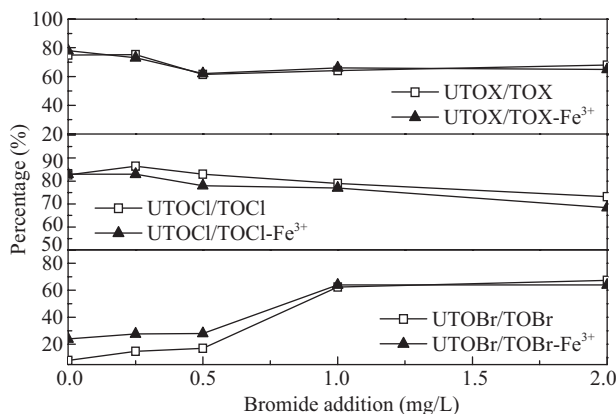


Fig. 5 Effect of bromide ions on the formation of unknown TOX, TOCl and TOBr in the presence or absence of Fe³⁺. Reaction conditions: contact time 48 hr; temperature (22 ± 1)°C; Cl₂ dosage 6.0 mg/L; Fe³⁺ 0 or 0.5 mg/L; TOC 7.5 mg/L; pH 7.5; Huangpu River water.

hydrophobic and high MW compounds in the formation of THMs, HAAs, and TOCl. Additionally, Fe^{3+} may be incorporated with hydrophobic fractions to reduce active precursor sites for chlorine. As a result, the presence of ferric ions produced more TOBr and reduced the formation of TOCl in some extent.

2.5 Implications on drinking water treatment

For water sources containing higher concentrations of ferric and bromide ions, especially in coastal areas, drinking water suppliers should pay more attention in their treatment process to remove ferric and bromide ions, so as to avoid the possible risk of the toxicity of halogenated DBPs, especially for TOBr.

3 Conclusions

The results of this study showed that coexistent ferric and bromide ions significantly increased the formation of THMs in alkaline conditions, but the formation of HAAs appeared in weak acid conditions. The SUVA value of water samples had a close relationship with the formation of DBPs. It was found that, with the increase in bromide ion concentrations, coexistent ferric ions increased TOX and TOBr formation obviously. This suggested that, for coastal areas, more attention should be paid to the drinking water safety as frequent saltwater intrusion increases the risk of bromine contained DBPs for drinking water disinfection by chlorination, especially with the coexistence of ferric ions.

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