



Seasonal variation effects on the formation of trihalomethane during chlorination of water from Yangtze River and associated cancer risk assessment

Shaogang Liu^{1,2}, Zhiliang Zhu^{1,*}, Chenfeng Fan¹, Yanling Qiu¹, Jianfu Zhao¹

1. State Key Laboratory of Pollution Control and Resource Reuse, Key Laboratory of Yangtze Aquatic Environment of Ministry of Education, Tongji University, Shanghai 200092, China. E-mail: liushaogang2005@163.com

2. Department of Chemical and Ecological Engineering, Guangxi University for Nationalities, Nanning 536000, China

Received 10 October 2010; revised 24 December 2010; accepted 29 December 2010

Abstract

For the system of water samples collected from Yangtze River, the effects of seasonal variation and Fe(III) concentrations on the formation and distribution of trihalomethanes (THMs) during chlorination have been investigated. The corresponding lifetime cancer risk of the formed THMs to human beings was estimated using the parameters and procedure issued by the US EPA. The results indicated that the average concentration of THMs (100.81 $\mu\text{g/L}$) in spring was significantly higher than that in other seasons, which was related to the higher bromide ion concentration resulted from the intrusion of tidal saltwater. The total cancer risk in spring reached 8.23×10^{-5} and 8.86×10^{-5} for males and females, respectively, which were about two times of those in summer under the experimental conditions. Furthermore, it was found that the presence of Fe(III) resulted in the increased level of THMs and greater cancer risk from exposure to humans. Under weak basic conditions, about 10% of the increment of THMs from the water samples in spring was found in the presence of 0.5 mg/L Fe(III) compared with the situation without Fe(III). More attention should be given to the effect of the coexistence of Fe(III) and bromide ions on the risk assessment of human intake of THMs from drinking water should be paid more attention, especially in the coastland and estuaries.

Key words: trihalomethanes; Fe(III); chlorination; disinfection byproducts; cancer risk assessment

DOI: 10.1016/S1001-0742(10)60573-6

Citation: Liu S G, Zhu Z L, Fan C F, Qiu Y L, Zhao J F, 2011. Seasonal variation effects on the formation of trihalomethane during chlorination of water from Yangtze River and associated cancer risk assessment. *Journal of Environmental Sciences*, 23(9): 1503–1511.

Introduction

Disinfection of drinking water has been widely practiced in drinking water treatment to protect of public health. Chlorine (Cl_2) is used as the most common disinfectant due to its high efficiency to eliminate pathogens and protect human health against waterborne diseases. However, chlorine reacts with the natural organic matter (NOM), such as humic and fulvic acids, contained in water source can generate undesirable disinfection byproducts (DBPs), which are classified as probable or possible human carcinogens (Bull, 1995; Cantor et al., 1998; Hsu et al., 2001), especially halogenated disinfection byproducts including trihalomethanes (THMs) and haloacetic acids (HAAs) (Bellar et al., 1974; Rook, 1974). Therefore, more and more attention has been paid to the chlorination of drinking/natural waters (Krasner et al., 2006; Ates et al., 2007; Zhao et al., 2009; Chang et al., 2010). The main chlorine byproducts were THMs and HAAs. THMs consist of four compounds: chloroform (CHCl_3), bro-

modichloromethane (CHCl_2Br), dibromochloromethane (CHClBr_2) and bromoform (CHBr_3). The United States Environmental Protection Agency (US EPA, 1999) reported that these four THMs are human carcinogens, of which CHCl_3 , CHCl_2Br and CHBr_3 are carcinogen class B₂ (human carcinogen) and CHClBr_2 is carcinogen class C (probable human carcinogen). As a result, the US EPA (1998) proposed the maximum total contaminant level (MCL) of four THM species to 80 $\mu\text{g/L}$ under Stage I of the Disinfectant/Disinfection Byproducts Rule. These DBPs are regulated because of their potential health risk, as well as their role as surrogates for the control of other halogenated DBPs of health concern.

Main factors impacting DBP formation in chlorination of drinking water include the amount of NOM in particular humic substances, concentration of bromide ion, pH, pipe deposits, seasonal variations, temperature, and contact time of water in distribution system (Liang and Singer, 2003; Toroz and Uyak, 2005; Ates et al., 2007; Li et al., 2009). In addition, recent studies have shown that the presence of dissolved metal ions such as Cu(II), Mg(II), and

*Corresponding author. E-mail: zzl@tongji.edu.cn

jescc.cn

Ca(II) shifts the type of DBPs and enhances the formation of DBPs in chlorinated drinking water (Blatchley et al., 2003; Li et al., 2008; Fu et al., 2009). Compared with above-mentioned metal ions, Fe(III) comes from many sources in aqueous environment, such as oxidation of ferrous ion, corrosion of iron pipes and application of ferric salt often used as coagulants in drinking water treatment. However, limited attention has been paid to the possible change of DBPs during chlorination in the presence of dissolved Fe(III).

Epidemiological studies of THMs have indicated that people are exposed to chlorination byproducts through three possible routes: oral ingestion, inhalation and dermal absorption (King et al., 2000; Villanueva et al., 2004; Karagas et al., 2008). Several studies have been conducted to assess the potential cancer risks from the exposure to THMs in drinking water (Black et al., 1996; Lee et al., 2004; Villanueva et al., 2006). In some studies, the higher cancer risk is found to be associated with the chlorination of raw water with higher bromide and organic carbon concentrations (Black et al., 1996; Derya et al., 2008). Cancer risks and hazard index of THMs are calculated through different exposure routes for tap water. It was reported that the exposure to chloroform through oral ingestion had higher risk than that through dermal absorption and inhalation (Tokmak et al., 2004). In addition, variation in water quality and characteristics of the treatment process could also lead to the change of cancer risk. However, very little information was available concerning the effect of dissolved Fe(III) on disinfection byproducts formation as well as human exposure risk during chlorination of water samples. Accordingly, it is interesting to investigate the effect of Fe(III) on the formation of THMs and the possible controlling factors for cancer risk.

The objective of this study was to investigate the possible synergetic effect of Fe(III) and bromide ions on the formation of THMs, especially in coastal areas with salt-water intrusion. The effects of seasonal variation and pH on the formation and species distribution of THMs were determined. For the water samples from Yangtze River in different seasons, the difference of lifetime cancer risk resulted from the exposure to THMs after the chlorination was also estimated. This work can be helpful for the further understanding and controlling of the potential risk of the DBPs from drinking water, especially in coastal areas or estuaries.

1 Materials and methods

1.1 Water samples

Water source were collected from Yangtze River which is located near the East China Sea (31°324'N, 121°516'E). The source water was treated in Zhabei Water Plant, Shanghai. Zhabei Water Plant has a capacity of 280,000 m³/day, and the treatment process of drinking water consists of coagulation, flocculation-sedimentation, sand filtration and chlorination. The typical chlorine dose is 3.5 mg/L. Water samples for this study were collected at sand

filtration site prior to disinfection, filtered immediately through a pre-rinsed 0.45- μ m cellulose filter and then stored in the dark at 4°C until further analysis.

1.2 Materials

All chemicals were of analytical reagent grade, and all solvents used in extractions were of 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 sulfate. An aqueous chlorine (HOCl) stock solution (2000 mg/L) was prepared from commercial sodium hypochlorite (NaOCl, 5% active chlorine) and periodically standardized by the colorimetric analysis of *N,N*-diethyl-*p*-phenylenediamine (DPD) method (APHA et al., 1998).

1.3 Analytical procedure

The reaction of THMs formation was quenched with sodium thiosulfate. THMs were determined by purge and trap following the US EPA method 524.2. Briefly, 5 mL of the aqueous solution containing THMs was purged with a He flow (40 mL/min) for 11 min and the stream was passed through a Vocab 3000 cartridge. Then, the He purge was stopped and volatile compounds trapped onto the cartridge were desorbed by heating the cartridge at 150°C. The desorbed volatile compounds were introduced into a GC-MS (Thermo ultatrace chromatograph and mass detector, USA) with a DB-5MS fused silica capillary column (30 m \times 0.25 mm \times 0.25 μ m, J&W Scientific, USA) and a quadrupole analyzer. The oven temperature of the GC was programmed from 40°C for 5 min, ramped to 280°C at a rate of 8°C/min. Calibration was made by comparing the THMs with an external standard commercial kit of known THMs concentrations. For all the THMs, the method detection limit (MDL) was below 0.2 μ g/L and the precision (variation of the values for the same sample) was less than 1 μ g/L. Calibration standards were prepared using the standard mixture purchased from J&K Chemical Co. (USA). Total organic halide (TOX) was determined using a Euroglass ECS 1200 TOX analyzer (the Netherlands) based on standard method 5320 B (APHA, 1998) with minor modifications. Total organic chlorine (TOCl) and total organic bromine (TOBr) were analyzed by a high-temperature combustion and offline ion chromatography (Hua and Reckhow, 2006).

The nonpurgeable organic carbon (NPOC) concentrations were measured with a Shimadzu TOC-VCPN analyzer (Japan) according to standard method 5310B. The concentration of bromide ions was analyzed with an AS11-HC anion separation column using a Dionex 1000 ion chromatography system (USA). The ultraviolet (UV) absorbance at 254 nm was measured using a Shimadzu UV-3000 spectrophotometer based on standard method 5910 B.

1.4 Exposure and risk assessment

Based on the THMs data obtained from chlorination water samples in this study, a human health risk assessment developed by the US EPA (2005) and adopted by Lee et al.

(2004) in Hong Kong and Tokmark et al. (2004) in Ankara Turkey was applied. It was often used to estimate both carcinogens and non-carcinogens risks due to exposure to THMs through oral ingestion, dermal adsorption and inhalation exposure.

The body exposure to THMs was assessed from the equations as follows.

$$\text{Oral exposure: } \text{CDI}_{\text{oral}} = \frac{C_m \times F_E \times D_E \times R_{w1}}{W_B \times T_A} \quad (1)$$

$$\text{Dermal exposure: } \text{CDI}_{\text{dermal}} = \frac{C_m \times F_E \times D_E \times A_S \times K_p \times T_E}{W_B \times T_A} \quad (2)$$

$$\text{Inhalation exposure: } \text{CDI}_{\text{inhalation}} = \frac{C_m \times F_E \times D_E \times K \times R_{al} \times T_E}{W_B \times T_A} \quad (3)$$

where, CDI (mg/(kg-day)) is the chronic daily intake; C_m (mg/L) is the concentration of chemical m in water; F_E (days/yr) is exposure frequency; D_E (yr) is exposure duration; T_E (hr/day) is the exposure time; R_{al} (m^3/day) is daily indoor inhalation rate; R_{w1} (L/day) is daily water ingestion rate; K is volatilization factor; A_S (cm^2) is skin-surface area available for contact; K_p (cm/hr) is the chemical-specific dermal permeability constant; W_B (kg) is body weight; and T_A (day) is the average time.

In addition, the standard values for adults recommended by US EPA (1989) were used, except for partial parameters which China population data were adopted. For instance, Chinese (National Bureau of Statistics of China, 2004) have the average body weight of 67.7 kg for males and 59.6 kg for females, and the average life span is 74 years for males and 78 years for females. The average water ingestion rate used in oral cancer risk calculations was 2.0 L/day, as assumed for adults by the US EPA. The primary sources of the slope factor (SF) values for THMs were adopted (US EPA, 1999, 2007).

The total lifetime cancer risk of DBPs through multi-pathway exposure and routes in drinking water is calculated as follows:

$$\text{Total lifetime cancer risk} = \sum_{i=1}^n (\text{CDI}_i \times \text{SF}_i) \quad (4)$$

where CDI_i (mg/kg/day) is the chronic daily intake from the specified exposure route i ; n is the number of different exposure routes; SF_i ($\text{mg}/(\text{kg}\cdot\text{day}))^{-1}$ is slope factor of chemical from the specified exposure route i .

2 Result and discussion

2.1 Water quality of treated water samples

To obtain the seasonal variation in DBPs level and distribution, samples were collected from spring (March–May), summer (June–August), autumn (September–November) and winter (December–February) in 2009, respectively. The characteristics of water quality are shown in Table 1. The water quality parameters in treated water samples represented the average values of three months in the season. It should be noted that using NPOC might overestimate the level of inorganic carbon in some samples. As shown in Fig. 1, the average bromide ions concentration in spring

(0.72 mg/L) was higher than that in summer (0.04 mg/L), which might be related to the intrusion of seawater as this district was located near East China Sea. This phenomenon usually occurs in the drought periods of spring and winter.

2.2 Seasonal variation of DBPs formation and distribution

The seasonal variations in the concentrations of THMs and TOX (Cl, Br) are shown in Fig. 2. The highest concentration of total THMs (TTHMs) was observed in spring (100.81 $\mu\text{g}/\text{L}$), and the low concentrations were observed in autumn and winter (65.95 and 78.20 $\mu\text{g}/\text{L}$, respectively). Moreover, the concentrations of TTHMs in spring and summer were found to be higher than the Stage I limit of 80 $\mu\text{g}/\text{L}$ set by US EPA (1998). The results were consistent with the reported data by Derya et al. (2008).

The levels and species distribution of DBPs varied greatly with the change of seasons, because of the variable NOM characteristics of water sources in different seasons as suggested by previous publications (Toroz and Uyak, 2005; Baytak et al., 2008; Garcia-Villanova et al., 2010). It is clear that the predominant DBPs groups are THMs and HAAs. Bromoform was found as the major composition of formed THMs during chlorination of treated water in spring and winter, the followed species by the concentrations were DBCM, BDCM and chloroform. The high TTHMs concentration in spring was mainly due to relatively high NPOC (3.0 mg/L) in water samples, compared with that from other seasons (< 3.0 mg/L) (Fig. 1). Based

Table 1 Water quality of treated water samples from Yangtze River in 2009

Parameter	Mean	Med	SD	Min	Max
NPOC (mg/L)	2.8	2.45	0.3	2.1	3.2
pH	7.85	7.6	0.2	7.2	7.9
Br^- ($\mu\text{g}/\text{L}$)	300	200	25	40	720
SUVA (L/(mg-cm))	1.80	1.6	0.1	1.3	2.1
UV_{254} (cm^{-1})	0.054	0.052	0.012	0.042	0.069

NPOC: non-purgeable organic carbon.

Sample size is 24.

SUVA (specific ultraviolet absorbance) was calculated from ultraviolet absorbance at 254 nm (UV_{254}) divided by the non-purgeable dissolved organic carbon. All the values in the table are of the seasonal average.

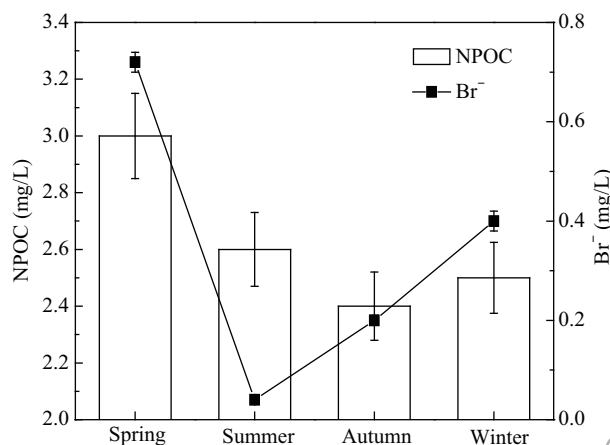


Fig. 1 Seasonal variation in NPOC and bromide ion concentrations in treated water samples collected from Yangtze River. Error bars show one standard deviation.

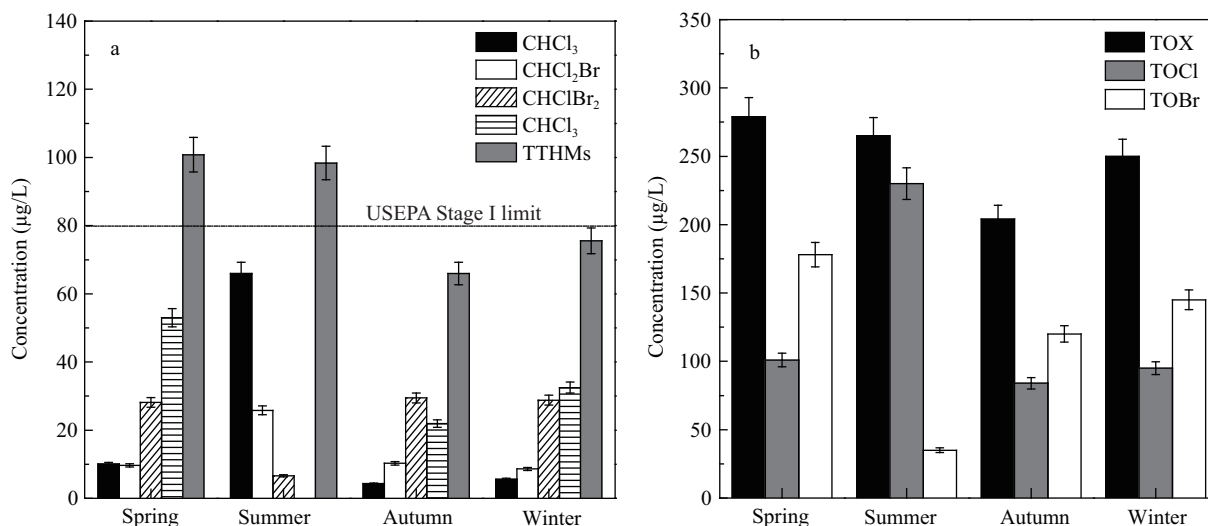


Fig. 2 Seasonal variation in THMs (a) and TOX (Cl, Br) (b) concentrations after chlorination of treated water samples collected from Yangtze River. Experimental conditions: contact time 48 hr; temperature $22 \pm 1^\circ\text{C}$; Cl_2 dosage 3.5 mg/L. Error bars show one standard deviation.

on the results of statistical analysis, the concentration of NOM and THMs formation was fairly correlated (Ates et al., 2007). It is known that THMs formed in the presence of high concentrations of organic matter during chlorination. In addition, the higher concentration of THMs in spring probably is attributable to the presence of high bromide concentration during that season in Yangtze River water.

TOX (Cl, Br) was also determined to assess the occurrence of other halogenated organics. TOX measurements indicated that besides THMs and HAAs some unidentified DBPs or halogenated organics also existed in the water after chlorination, including haloacetonitriles (HANs), halogenated ketones and so on. Kristiana et al. (2009) reported that in source waters, the contribution of halides in THMs and HAAs to TOX on a mass basis ranged between 6%–36% and 4%–20%, respectively. It was found that water samples collected in spring had produced higher amounts of TOBr/TOX than that in summer. The main possible reason was that high bromide levels contained water samples might produce higher TOBr/TOX after chlorination.

2.3 Effect of Fe(III) on THMs formation

The effect of Fe(III) concentrations on THMs formation was studied. Figure 3 shows that THMs concentration increased with increasing Fe(III) concentration from 0 to 1.0 mg/L. The existence of Fe(III) obviously promoted the formation of THMs. The similar results were reported by Rossman et al. (2001), who found that THMs formation in the experimental conditions increased with the presence of pipe deposit. It may be reasonable to suggest that Fe(III) can bind to the carboxylate groups of the substrates and by forming a complex to increase the reactivity of the substrates towards chlorination. Meanwhile, the co-existence of bromide ion and Fe(III) might enhance the formation of Br-contained THMs. Furthermore, addition of Fe(III) is also expected to increase the aggregation size of the humic substances as observed in the case of Mg(II) and Ca(II) addition. It was considered that the presence of metal ions will prompt the DBPs formation due to intermolecular

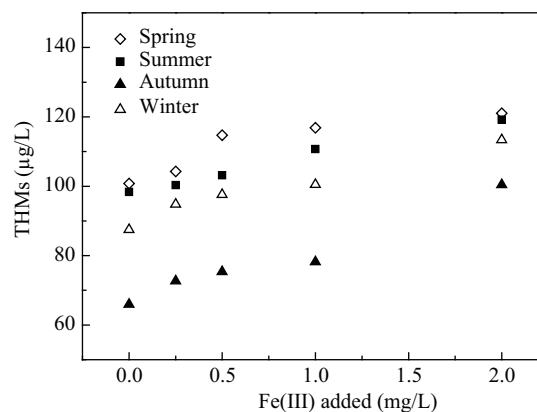


Fig. 3 Effect of Fe(III) concentrations on the formation of THMs. Experimental conditions: pH 7.5; contact time 48 hr; temperature $22 \pm 1^\circ\text{C}$; Cl_2 dosage 3.5 mg/L.

associations (Chassapis et al., 2010).

2.4 Effect of pH on THMs formation

Solution pH affects the speciation and amount of DBPs formed during chlorination. The comparison experiment was conducted to investigate the pH effect on THMs

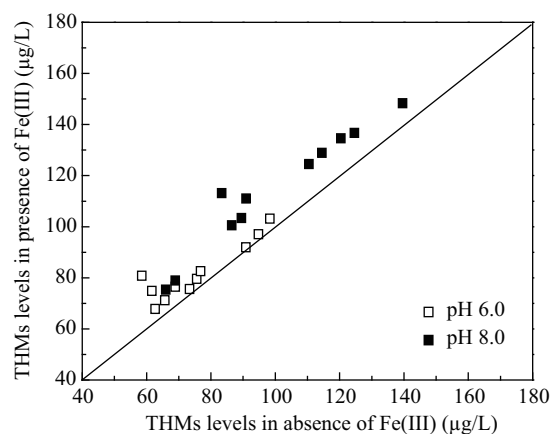


Fig. 4 Effect of pH on the formation of THMs in the absence or presence of Fe(III). Experimental conditions: Fe(III) 0.5 mg/L; contact time 48 hr; temperature $22 \pm 1^\circ\text{C}$; Cl_2 dosage 3.5 mg/L; water samples collected from four seasons.

formation in the presence or absence of Fe(III) (Fig. 4). It was found that the concentration of THMs under weak basic condition (pH 8) was higher than that at pH 6, and the presence of Fe(III) significantly increased the amount of THMs after chlorination. *t*-Test was used to examine whether the effect of pH on THMs concentrations was statistically significant. Comparison was made between the presence and absence of Fe(III), and *p*-values for all THMs (0.004 at pH 6 and < 0.001 at pH 8) were found to be lower than 0.05, suggesting significant variability for different pH values. *t*-Test also indicated that the difference in THMs concentrations under weak basic conditions with Fe(III) was more significant than that under weak acid conditions. The possible reason is that humic substances mainly contain two kinds of groups, carboxylic and phenolic groups. These groups existed in a more ionized state at high pH values and affected the total charge of the humic substances, which enhanced the apparent affinity of this particular binding site for the metal. The complexation mechanisms allowing for better binding with the Fe(III) species (in the pH range of 6–9, Fe(III) species is mainly $\text{Fe}(\text{OH})_2^+$) would result in the increment of the reactivity of substrates towards chlorination (Tiphaine et al., 2006). Another possible explanation might be that high pH values energetically favored a more expanded molecular configuration of the humic polymer, and therefore binding sites were readily accessible to the ferric ions. This might further facilitate metal–ligand coordination so as to increase the NOM reactive sites to chlorine to form additional DBPs (Hassan et al., 2006).

2.5 Assessment of cancer risk from exposure to THMs

The multi-pathway cancer risks from treated water samples of Yangtze River for male and female residents were calculated, respectively. This works are focused on the assessment of the cancer risks from exposure to THMs through three routes, oral ingestion, inhalation, and dermal absorption exposure. Risks assessment was performed in the absence and presence of Fe(III), respectively. In addition, the assessment was conducted at the average concentration of each compound to estimate the average risk.

The results of the average risk assessment calculated from the average concentrations of THMs in four seasons in the absence of Fe(III) are shown in Table 2. It was found that the average cancer risk in spring was the highest among four seasons (8.23×10^{-5} for male and 8.86×10^{-5} for female), while the average cancer risk in summer was the lowest. According to the guidance of US EPA (1989), if cancer risk is in the range of 10^{-4} – 10^{-6} , it is an acceptable risk. Thus, this is a case of acceptable risk. On the whole, the risk level was lower than the reported cancer risks of THMs intake from tap water in Turkey, Taiwan and Hong Kong (1.18×10^{-4} , 1.80×10^{-4} , and 1.99×10^{-5} , respectively) (Uyak et al., 2005; Hsu et al., 2001; Lee et al., 2004).

The results of the average risk assessment calculated from the average concentrations of THMs in spring in the presence of Fe(III) are shown in Fig. 5. It was found that oral ingestion was the principal pathway, followed by dermal absorption and inhalation. The cancer risks of

Table 2 Cancer risk assessment of THMs in different seasons in the absence of Fe(III)

Season	THM* ($\mu\text{g/L}$)	Cancer risk _{oral} ($\times 10^{-5}$)		Cancer risk _{dermal} ($\times 10^{-6}$)		Cancer risk _{inhalation} ($\times 10^{-10}$)		Total cancer risk** ($\times 10^{-5}$)	
		Male	Female	Male	Female	Male	Female	Male	Female
Spring	100.81	7.87	8.48	3.60	3.88	3.47	3.74	8.23	8.86
Summer	98.35	3.45	3.71	1.23	1.33	1.74	1.87	3.57	3.84
Autumn	65.95	5.14	5.54	2.38	2.56	1.99	2.14	5.38	5.79
Winter	78.2	5.42	5.87	2.65	2.84	2.1	2.37	5.69	6.15

* Average concentration of three months in one season; ** calculation by US EPA method.

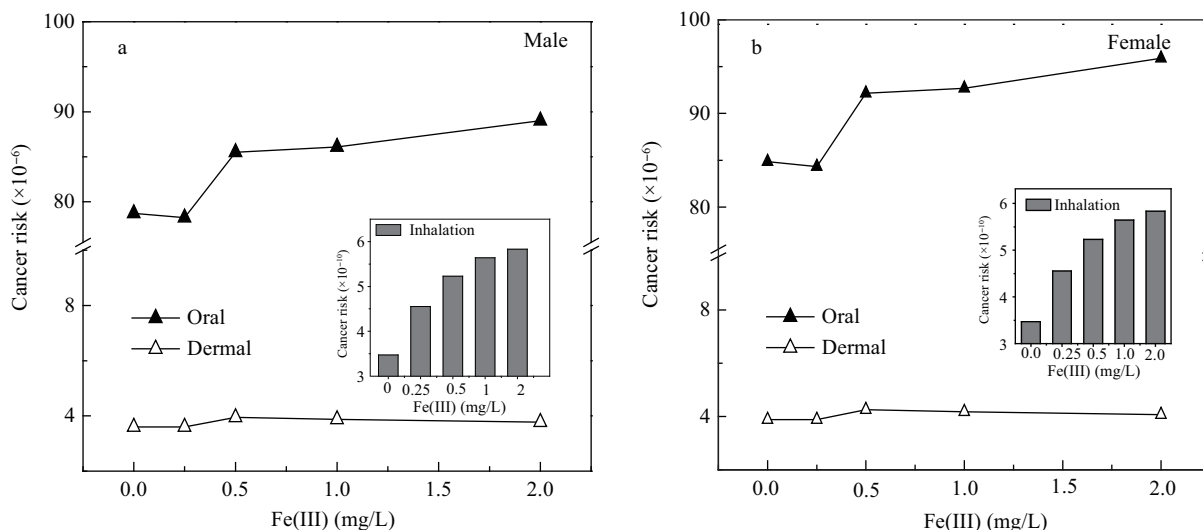


Fig. 5 Total lifetime cancer risk of DBPs via different exposure pathways in drinking water in the presence of different Fe(III) concentrations for male and female. Experimental conditions: contact time 48 hr; pH 7.5; Cl_2 dosage 3.5 mg/L; water samples collected in spring.

THMs through oral ingestion (8.97×10^{-5} – 7.87×10^{-5}) and dermal absorption (3.60×10^{-6} – 3.94×10^{-6}) were lower than 10^{-4} , a negligible risk level defined by the US EPA.

With increasing Fe(III) concentrations, the cancer risks through all the three pathways increased. The possible reason might be that the reaction sites of NOM in the presence of Fe(III) were modified to produce more chloroform which contributed to the cancer risk. It was found that 0.5 mg/L of Fe(III) produced the highest cancer risk under our experimental conditions. According to previous reports, the total irons in finished water were usually in the range of 0.3–0.5 mg/L (Henderson et al., 2001). Therefore, the concentration of 0.5 mg/L was selected for a further detailed study to investigate the effect of pH and seasonal variations on cancer risks in chlorination.

2.6 Effect of seasonal variation on cancer risk from exposure to THMs

In the absence or presence of Fe(III), effect of seasonal variation on cancer risk from exposure to THMs was analyzed. As shown in Fig. 6, effect of Fe(III) on the total cancer risk in spring was more significant than that in summer. The cancer risks from oral ingestion and dermal exposure were higher than that of the inhalation either in the presence or absence of Fe(III) conditions.

To further understand the contribution to cancer risks of different THMs concentrations, percentage contributions to cancer risks of THMs were calculated from the average individual species concentrations. As shown in Fig. 7, without Fe(III) the percentage contributions of CHBr_3 , CHClBr_2 , CHCl_2Br and CHCl_3 to total cancer risk in spring water samples were 61.54%, 25.64%, 11.92%, and 0.90%, respectively. In summer, the percentage contributions to total cancer risk of CHCl_2Br , CHClBr_2 , and CHCl_3 were 70.92%, 14.10%, and 14.98%, respectively. It could be found that more Brominated-THMs were produced in water samples in spring, and Brominated-THMs were the main components resulting in the cancer risk of drinking water. For example, the compound of CHBr_3 was found to contribute a higher cancer risk in spring than other three THMs. In the presence of Fe(III),

the percentage contributions to total cancer risk of the primary THMs increased. According to the previous literature (US EPA, 1991), the compound with the highest cancer risk was CHCl_2Br , followed by CHClBr_2 and CHBr_3 , with slope factors of 0.062, 0.084, and 0.0079 ($\text{mg}/(\text{kg}\cdot\text{day})$)⁻¹, respectively, whereas the slope factor of CHCl_3 was only 0.0061 ($\text{mg}/(\text{kg}\cdot\text{day})$)⁻¹. The slope factors of all brominated-THMs are higher than that of CHCl_3 implying that bromide ion in raw water would generate higher potential of carcinogenic DBPs. In our previous research, it was demonstrated that the presence of Fe(III) promoted the formation of brominated-THMs, which might be more carcinogenic (Zhu et al., 2007). Therefore, drinking water regulations should pay more attention to the species distribution of DBPs individually rather than the total values of THMs and HAAs in coastal areas, where the saltwater intrusion to drinking source waters happened more frequently.

2.7 Effect of pH on cancer risk from exposure to THMs

Cancer risks of THMs through three pathways were calculated under different pH values in water samples collected in spring after the chlorination. The results are presented in Table 3. All cancer risks were higher than 1.0×10^{-6} , except for inhalation (2.44×10^{-10} – 8.46×10^{-10}) of water samples from Yangtze River. In the presence of Fe(III) at pH 8, the effect on the total cancer risk was more significant than that at pH 6. Under weak basic conditions (pH 8), the existence of Fe(III) resulted in an increment of total cancer risk of 6.5% (for male) and 6.8% (for female). This result revealed that oral exposure was the principal pathway for the cancer risk of THMs from drinking water, followed by dermal absorption and inhalation. This finding was consistent with the results by Uyak et al. (2005) who reported that cancer risks of CF, BDCM, and DBCM in tap water through ingestion in Istanbul were higher than the acceptable level, and oral way was found to be the principal pathway. Lee et al. (2004) estimated that for the residents of 19 districts in Hong Kong, oral ingestion is a greater contributor to cancer risk for THMs than inhalation and dermal absorption. However, chloroform is a main contributor to cancer risk of THMs exposure via

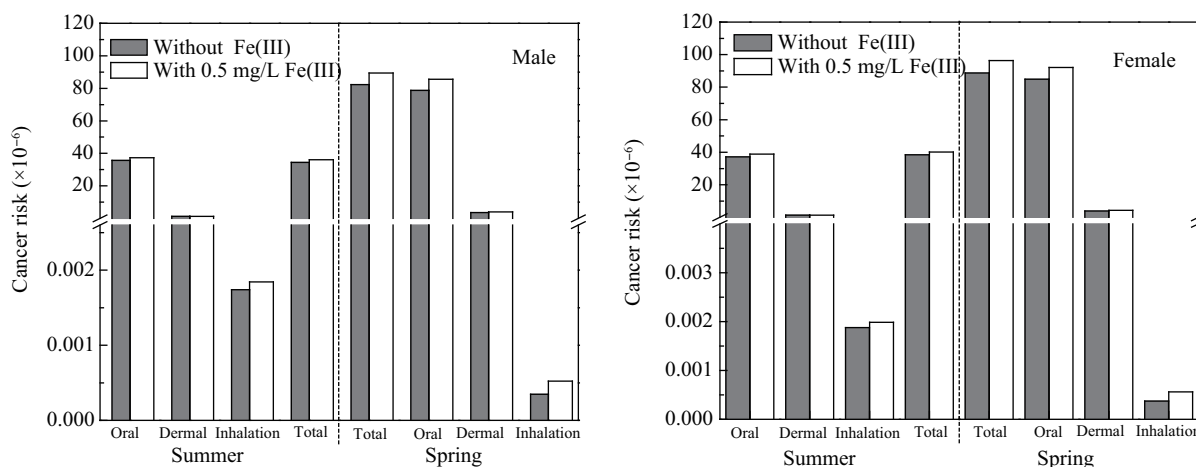


Fig. 6 Effect of seasonal variation on total cancer risk through different exposure pathways. Experimental conditions: pH 7.5; contact time 48 hr; Cl_2 dosage 3.5 mg/L; temperature (22 ± 1)°C.

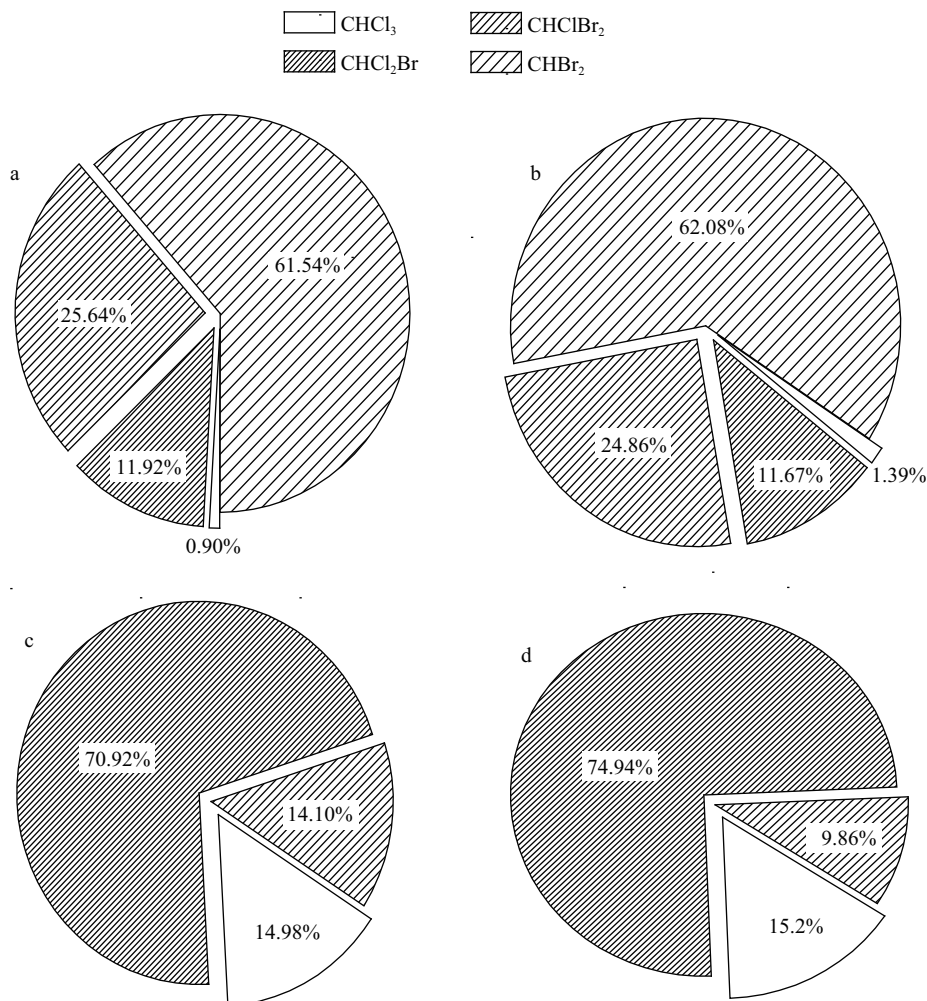


Fig. 7 Percentage contributions of THMs to cancer risks calculated from the average individual species concentration for male in. (a) water spring collected in spring; (b) water samples collected in spring with 0.5 mg/L Fe(III); (c) water samples collected in summer; (d) water samples collected in summer with 0.5 mg/L Fe(III).

inhalation.

2.8 Uncertainty analysis

According to the Guidance of US EPA (1989), the uncertainty of risk assessment of this case study was summarized as follows:

(1) Uncertainties could result from lack of knowledge about the variable parameters of the model. Also, there were uncertainties related to the data that were rarely available. For example, although there were data on the

cancer risks and reproductive toxicology of several of the byproducts, the data were by no means comprehensive. For another, uncertainties could also be found in the lack of long-term and low-dose exposure data.

(2) Cancer risk assessment in this work was only focused on THMs in the presence of Fe(III) during chlorination of treated water samples from Yangtze River. But in the real situation, tap water consists of many carcinogens, especially other carcinogenic chlorination byproducts such as halogenated ketones and chlorophenols. Therefore, the

Table 3 Cancer risks of THMs under different pH in spring water samples

Route	pH 6.0	pH 6.0 with Fe(III)	pH 8.0	pH 8.0 with Fe(III)
Male				
Cancer risk _{oral}	7.51×10^{-5}	7.52×10^{-5}	1.03×10^{-4}	1.11×10^{-4}
Cancer risk _{dermal}	3.41×10^{-6}	3.44×10^{-6}	4.85×10^{-6}	5.28×10^{-6}
Cancer risk _{inhalation}	2.44×10^{-10}	3.14×10^{-10}	6.41×10^{-10}	7.86×10^{-10}
Total cancer risk	7.85×10^{-5}	7.86×10^{-5}	1.09×10^{-4}	1.16×10^{-4}
Female				
Cancer risk _{oral}	8.22×10^{-5}	8.31×10^{-5}	1.11×10^{-4}	1.19×10^{-4}
Cancer risk _{dermal}	3.87×10^{-6}	4.25×10^{-6}	5.23×10^{-6}	5.70×10^{-6}
Cancer risk _{inhalation}	3.74×10^{-10}	5.63×10^{-10}	6.90×10^{-10}	8.46×10^{-10}
Total cancer risk	8.46×10^{-5}	8.47×10^{-5}	1.17×10^{-4}	1.25×10^{-4}

Note: without and with 0.5 mg/L Fe(III); average THMs concentration obtained from two different pH in spring water samples; calculation by US EPA method.

total cancer risk may be higher than the values estimated in this work due to the exposure to other carcinogens.

(3) Uncertainties could be caused by the significant year-to-year variations in hydrology, climate, water quality, seasonal variation in contaminant concentrations DBP precursor levels, treatment practices, distribution system hydraulics, and various exposure routes (e.g., ingestion, inhalation, or dermal absorption) (Arbuckle et al., 2002; Nieuwenhuijsen et al., 2000).

3 Conclusions

Experimental results and investigation showed that the highest total THMs levels were detected in spring while the lower levels in autumn and winter. The lifetime cancer risk of THMs was the highest via oral ingestion, followed by dermal adsorption and inhalation. The effect of Fe(III) on cancer risk was significant at pH 8 than that at pH 6. From the results of cancer risk assessment in this work, it is suggested that more attention should be paid to the effects of Fe(III) and saltwater intrusion on the DBPs associated with the cancer risk resulted from lifetime exposure to THMs from drinking water. In coastal or estuarine areas where the salt intrusion occurs frequently in drought seasons, how to reduce the co-effect of Fe(III) and bromide ions on the amount and species distribution is very important to minimize the cancer risk of DBPs.

Acknowledgments

This work was financially supported by National Mega-Project of Science and Technology of China (No. 2008ZX07421-002) and the National Eleventh Five-Year Pillar Program of Science and Technology of China (No. 2006BAJ04A07).

References

- APHA (American Public Health Association), AWWA (American Water Works Association), WEF (Water Environmental Federation), 1998. Standard Methods for the Examination of Water and Wastewater (20th ed.). American Public Health Association, Washington DC.
- Ates N, Kaplan S S, Sahinkaya E, Kitis M, Dilek F B, Yetis U, 2007. Occurrence of disinfection by-products in low DOC surface waters in Turkey. *Journal of Hazardous Materials*, 142(1-2): 526–534.
- Arbuckle T E, Hrudey S E, Krasner S W, Nuckols J R, 2002. Assessing exposure in epidemiologic studies to disinfection byproducts in drinking water: Report from an International Workshop. *Environmental Health Perspectives*, 110(Suppl. 1): 53–60.
- Baytak D, Sofuoglu A, Inal F, Sofuoglu S C, 2008. Seasonal variation in drinking water concentrations of disinfection by-products in IZMIR and associated human health risks. *Science of the Total Environment*, 407(1): 286–296.
- Bellar T A, Lichtenbert J J, Kroner R C, 1974. The occurrence of organohalides in chlorinated drinking waters. *Journal of the American Water Works Association*, 66(12): 703–706.
- Black B D, Harrington G W, Singer P C, 1996. Reducing cancer risks by improving organic carbon removal. *Journal of the American Water Works Association*, 88(6): 40–52.
- Blatchley E R, Margetas D, Duggirala R, 2003. Copper catalysis in chloroform formation during water chlorination. *Water Research*, 37(18): 4385–4394.
- Bull R J, 1995. Water Chlorination: Essential process or cancer hazard? *Toxicological Sciences*, 28(2): 155–166.
- Cantor K P, Lynch C F, Hildesheim M E, Dosemeci M, Lubin J, Alavanja M et al., 1998. Drinking water source and chlorination byproducts I. Risk of bladder cancer. *Epidemiology*, 9(1): 21–28.
- Chang H H, Tung H H, Chao C C, Wang G S, 2010. Occurrence of haloacetic acids (HAAs) and trihalomethanes (THMs) in drinking water of Taiwan. *Environmental Monitoring and Assessment*, 162(1-4): 237–250.
- Chassapis K, Roulia M, Nika G, 2010. Fe(III)-humate complexes from megalopolis peaty lignite: A novel eco-friendly fertilizer. *Fuel*, 89(7): 1480–1484.
- National Bureau of Statistics of China, 2004. Population Life Expectancy by Region. China Statistical Year Book. China Statistics Press.
- Derya B, Aysun S, Fikret I, Sofuoglu S C, 2008. Seasonal variation in drinking water concentrations of disinfection by-products in IZMIR and associated human health risks. *Science of the Total Environment*, 407(1): 286–296.
- Fu J, Qu J H, Liu R P, Qiang Z M, Liu H J, Zhao X, 2009. Cu(II)-catalyzed THM formation during water chlorination and monochloramination: A comparison study. *Journal of Hazardous Materials*, 170(1): 58–65.
- Garcia-Villanova R J, Mera B B, Paramas A M G, Hierro J M H, Albajar R A, Fonseca I M T, 2010. A multi-year survey of organic disinfection byproducts in drinking waters of Castillay Leon, Spain. The need and difficulty to comply with the legal limit of 2009. *Journal of Environmental Monitoring*, 12(1): 200–207.
- Hassan K Z A, Bower K C, Asce M P E, Miller C M, 2006. Iron oxide enhanced chlorine decay and disinfection by-product formation. *Journal of Environmental Engineering-Asce*, 132(12): 1609–1616.
- Henderson R, Carlson K, Gregory D, 2001. The impact of ferrous ion reduction of chlorite ion on drinking water process performance. *Water Research*, 35(18): 4464–4473.
- Hsu B M, Huang C P, Hsu C L L, 2001. Analysis for Giardia cysts and Cryptosporidium oocysts in water samples from small water systems in Taiwan. *Parasitology Research*, 87(2): 163–168.
- Hua G H, Reckhow D A, 2006. Determination of TOCl, TOBr and TOI in drinking water by pyrolysis and off-line ion chromatography. *Analytical and Bioanalytical Chemistry*, 384(2): 495–504.
- Karagas M R, Villanueva C M, Nieuwenhuijsen M, Weisel C P, Cantor K P, Kogevinas M, 2008. Disinfection byproducts in drinking water and skin cancer? A hypothesis. *Cancer Causes and Control*, 19(5): 547–548.
- King W D, Marrett L D, Woolcott C G, 2000. Case-control study of colon and rectal cancers and chlorination by-products in treated water. *Cancer Epidemiology Biomarkers and Prevention*, 9(8): 813–818.
- Krasner S W, Weinberg H S, Richardson S D, Pastor S J, Chinn R, Scilimenti M J et al., 2006. Occurrence of a new generation of disinfection byproducts. *Environmental Science and Technology*, 40(23): 7175–7185.
- Kristiana I, Gallard H, Joll C, Croue J P, 2009. The formation of halogen-specific TOX from chlorination and chloramination of natural organic matter isolates. *Water Research*, 43(17): 4177–4186.

- Lee S C, Guo H, Lam S M J, Lau S L A, 2004. Multipathway risk assessment on disinfection by-products of drinking water in Hong Kong. *Environmental Research*, 94(1): 47–56.
- Li A, Chen Z L, Shen J M, Zhai X, Yang L, Zhao S Q, 2009. THMs and HAAs Formation by tryptophan during chlorination disinfection. In: Proceedings of 2009 International Conference on Energy and Environment Technology, Vol. 2: 888–891.
- Li B, Liu R P, Liu H J, Gu J N, Qu J H, 2008. The formation and distribution of haloacetic acids 9 in copper pipe during chlorination. *Journal of Hazardous Materials*, 152(1): 250–258.
- Liang L, Singer P C, 2003. Factors influencing the formation and relative distribution of haloacetic acids and trihalomethanes in drinking water. *Environmental Science and Technology*, 37(13): 2920–2928.
- Nieuwenhuijsen M J, Toledano M B, Eaton N E, Fawell J, Elliott P, 2000. Chlorination disinfection byproducts in water and their association with adverse reproductive outcomes: a review. *Occupational and Environmental Medicine*, 57(2): 73–85.
- Rook J J, 1974. Formation of haloforms during chlorination of natural waters. *Water Treatment and Examination*, 23(2): 234–243.
- Rossmann L A, Brown R A, Singer P C, Nuckols J R, 2001. DBP formation kinetics in a simulated distribution system. *Water Research*, 35(14): 3483–3489.
- Tiphaine W, Thierry A, Edward T, Marc F, 2006. Modeling iron binding to organic matter. *Environmental Science and Technology*, 40(23): 7488–7493.
- Tokmak B, Capar G, Dilek F B, Yetis U, 2004. Trihalomethanes and associated potential cancer risks in the water supply in Ankara, Turkey. *Environmental Research*, 96(3): 345–352.
- Toroz I, Uyak V, 2005. Seasonal variations of trihalomethanes (THMs) in water distribution networks of Istanbul City. *Desalination*, 176(1-3): 127–141.
- US EPA, 1989. Risk Assessment Guidance for Superfund. Washington, DC U.S. Environmental Protection Agency. EPA/540/1-89/002. Vol.I.
- US EPA, 1991. Risk Assessment Guidance for Superfund-Vol. I, Part B. Washington, DC: U.S. Environmental Protection Agency. EPA/540/R-92/003.
- US EPA, 1995. Measurement of purgeable organic compounds in water by capillary column gas chromatography/mass spectrometry. Cincinnati, U.S Environmental Protection Agency. Method 524.2.
- US EPA, 1999. Alternative Disinfectants and Oxidant Agency Guidance Manual. April. EPA 815-R-99-014.
- US EPA, 2005. Guidelines for Carcinogen Risk Assessment. Risk assessment forum. Washington, DC. U.S. Environmental Protection Agency. EPA/630/P-03/001F.
- US EPA, 2007. Integrated Risk Information System (IRIS) Database for Risk Assessment. Washington, DC. U.S. Environmental Protection Agency. <http://www.epa.gov/iris>.
- Uyak V, Toroz I, Meric S, 2005. Monitoring and modeling of trihalomethanes (THMs) for a water treatment plant in Istanbul. *Desalination*, 176(1-3): 91–101.
- Villanueva C M, Cantor K P, Grimalt J O, Castano-Vinyals G, Malats N, Silverman D et al., 2006. Assessment of lifetime exposure to trihalomethanes through different routes. *Occupational and Environmental Medicine*, 63(4): 273–277.
- Villanueva C M, Cantor K P, Grimalt J O, Dosemeci M, Malats N, Real F X et al., 2004. Bladder cancer and exposure to disinfection byproducts in water through ingestion, bathing, showering and swimming in pools: Findings from the Spanish bladder cancer. *Epidemiology*, 15(4): S105–S105.
- Zhao S Q, Chen Z L, Yang L, Zhai X, Li A, 2009. THM and HAA formation from sequential use ozone and monochloramine to disinfection in the presence of tannic acid. In: Proceedings of 2009 International Conference on Energy and Environment Technology, Guilin, China October 16–18. Vol. 2: 885–887.
- Zhu Z L, Wang J, Ge Y X, Ma H M, Zhao J F, 2007. Effects of bromide and ferric ions on formation of trihalomethane during disinfection of drinking water by chlorine. *Environmental Science*, 28: 1–4.