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seasonal variation of disinfection by-products formation in during chlorination of treated water from Yangtze River: implication for human exposure

Shao-Gang Liu^{1,2}, Zhi-Liang Zhu^{1*}, Chen-feng Fan¹, Yan-Ling Qiu¹, Jian-Fu 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

2. Key Laboratory of Chemical and Biological Transforming Process of University of Guangxi

Guangxi University for Nationalities
Nanning, 536000, China

Corresponding author: liushaogang2005@163.com (L S-G) and zzl@tongji.edu.cn (Z Z-L)

Abstract— In this study, the effect of seasonal variation and Fe(III) concentrations on the formation and distribution of trihalomethanes (THMs) and haloacetic acids (HAAs) during chlorination of treated water samples from Yangtze River were examined. The corresponding lifetime cancer risk of THMs and HAAs was also estimated using the parameters and procedure issued by US Environmental Protection Agency. The results indicated that the mean concentration of THMs (mean, 108.1 µg/L) are significantly higher than that of other seasons, which is related to high bromide ion in raw water during the salt intrusion, and while five HAA5 concentrations were higher in autumn (mean, 25.0 µg/L) than those of other seasons. At the same time, in presence of Fe(III) increase THMs and HAA5 levels. Total cancer risk in spring (1.16×10^{-4}) increased about 2 times than those of summer (5.36×10^{-5}) in our experimental conditions. In addition, in the presence 0.5 mg/L Fe(III), cancer risk increased 10% in spring than those in the absence of Fe(III) under the same conditions. Results showed that the lifetime cancer risk for THMs and HAAs followed the order, oral, inhalation, and dermal. Thus, the seasonal and Fe(III) effects need to be considered in human health risk assessment studies, especially in the area of coastland and estuary area.

Keywords—trihalomethanes; haloacetic acids; chlorination; disinfection by-products; cancer risk assessment

I. INTRODUCTION

Chlorine (Cl₂) is used as the most common disinfectant because it is extremely efficient to eliminate pathogens and protect humane health against waterborne diseases. However, chlorine reacts with the natural organic matter of humic and fulvic acids contained in water to generate disinfection by-products (DBPs) [1]. Trihalomethanes (THMs) and haloacetic acids (HAAs) are two primary species of DBPs that are found in water disinfected with chlorine. As a result, they have been intensively studied during the chlorination of drinking/natural waters [2, 3]. Nowadays, some of these administrations are Environmental Protection Agency (EPA) had regulated the maximum contaminant level (MCL) of four THM species

(chloroform, bromodichloromethane, dibromochloromethane, and bromoform), and five HAA species (monochloro-, dichloro-, trichloro-, monobromo- and dibromoacetic acid) was set to 80 and 60 µg/L by EPA, respectively.

Several epidemiologic studies have reported that populations exposed to chlorination by-products through three possible routes: oral ingestion, inhalation, and dermal absorption [4, 5]. Recently, many studies partially have been conducted to assess the potential cancer risks from the exposure of the THMs in drinking water [6-8]. In those studies, the greater degrees of risk are found to be associated with chlorination of raw water with higher bromide and organic carbon concentrations. cancer risks and hazard index of THMs was calculated through different exposure routes for tap water, and reported that exposure through oral ingestion had higher risk than through dermal absorption and inhalation. Similar result was also reported by [9], which concluded that the highest risk was from the exposure to chloroform through oral ingestion. As regard as HAAs, exposure to HAAs occurs mainly through oral ingestion, and does not appear to occur readily through inhalation or dermal absorption [10-12].

Varying water quality (e.g. natural organic matter (NOM), seasonal variations, etc), treatment characteristics of the processing of drinking water (e.g., pH, chlorine dose, etc) and different exposure would lead to change of cancer risks. Recent studies showed that presence of trace metal shifts the type of DBPs and contributes the formation of DBPs in chlorinated drinking water, such as Cu(II), Mg(II), Ca(II) [13, 14]. Except for above-mention metal ions, Fe(III) extensively comes from many sources in drinking water, such as corrosion of ferric pipes, geographical variations, and ferric coagulation extensively used. However, very little information was available concerning effect of dissolved Fe(III) on disinfection by-product formation as well as human exposure risk during chlorination of treated water samples. As a result, it is interesting to investigate the differences of THM formation in the presence of Fe(III) or not and examine to controlling factor for the differences of lifetime cancer risk.

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For present study, the main aim of this work were: (1) to investigate the concentration of THMs and HAA5 in season variation in the water sources of Yangtze river; (2) to investigate effect of Fe(III) concentrations on the formation and species of THMs and HAA₅; Furthermore (3) to assess the multipathway exposure lifetime cancer risks, especially compared the presence of Fe(III) or not.

II. MATERIALS AND METHODS

A. Collection of water samples

Water source was from Yangtze River which is located near to the East China Sea (31°324' N, 121°516' E) in different seasons. The same source water is treated in Zhabei Water Plant (ZWP), which supplies for 1,000,000 populations in Shanghai. The typical chlorine dose is reported to be 3.5 mg/L. Treated water samples for this study were collected at sand filtration site and filtered immediately through a pre-rinsed 0.45-μm cellulose filter and stored in the dark at 4°C until further analysis.

B. Materials and Analytical procedure

All chemicals were ACS 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. Fe(III) used in the experiments were added in the form of ferric (III) sulfate (Fe₂(SO₄)₃). A free chlorine (HOCl) stock solution (2000 mg/L) was prepared from 5% sodium hypochlorite (NaOCl) (Sinopharm, Shanghai) and periodically standardized by the N, N-diethyl-p-phenylenediamine (DPD)-ferrous ammonium sulfate (FAS) titrimetric method [15].

C. Analytical procedure

Residual chlorine of THM and HAA samples with were quenched with sodium thiosulfate and ammonium chloride, respectively. THM analysis was performed using US EPA Method 551.1, which includes liquid-liquid extraction (LLE) with pentane. For HAA, The five HAAs were monochloroacetic acid (MCAA), monobromoacetic acid (MBAA), dichloroacetic acid (DCAA), trichloroacetic acid (TCAA), and dibromoacetic acid (DBAA) analyzed by liquid/liquid extraction with methyl-tertiary-butyl-ether (MTBE) followed by derivation with acidic methanol and analyzed by GC/ECD according to USEPA Method 552.2. both THM and HAA analysis was carried out by use of by Gas Chromatograph (Finnigan TRACE GC, Thermo, USA) with an Electron Capture Detector (ECD). 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). Calibration standards were prepared using the standard mixture purchased from J&K Chemical Co., USA (Accustandard, Inc., purity >99%). Non-purgeable dissolved organic carbon (NPOC) measurements were conducted according to Standard Method 3510B using a Shimadzu 500A Model TOC analyzer. Bromide ions were analyzed with an AS11-HC anion separation column using a Dionex 1000 ion chromatography system (Dionex, Sunnyvale, CA).

D. Exposure and risk assessment

Based on the THMs and HAAs data obtained from chlorination of treated water samples in this study, the estimate of the lifetime cancer risk associated to THM and HAA is based on United States Environment Protection Agency (USEPA) guidelines. The detailed description is presented in the literature [16, 17], and it is not reproduced here. In these estimations, THM and HAA exposure to the body was assessed from the equations as shown in Table 1. US EPA (1990) has recommended various values for the standard values for adults were used. The average body weight of adult is 70 kg. The lifetime of residents was assumed to be the standard 70 years for both male and female. The average water ingestion rate considered for oral cancer risk calculations was 2.0 L/day, as assumed for adults by the USEPA. In addition, the primary sources of the slope factor (SF) values for THMs and HAAs were obtained form [18, 19].

TABLE 1 Equations for calculation of body exposure through multi-pathway

Oral exposure	$CDI_{oral} = \frac{C_m \times EF \times ED \times IR_w}{BW \times AT}$
Dermal exposure	$CDI_{dermal} = \frac{C_m \times EF \times ED \times SA \times K_p}{BW \times AT}$
Inhalation exposure	$CDI_{inhalation} = \frac{C_m \times EF \times ED \times K \times IR_a \times K_p}{BW \times AT}$

$$\text{Total lifetime cancer risk} = \sum_{i=1}^n (CDI_i \times SF_i)$$

C_m : The concentration of chemical m in water (mg/L); EF: Exposure frequency (days/year); ED: Exposure duration (year); ET: the exposure time (h/day); IR_a : Daily indoor inhalation rate (m³/day); IR_w : Daily water ingestion rate (L/day); K: Volatilization factor (dimensionless); SA: Skin-surface area available for contact (cm²); K_p : The chemical-specific dermal permeability constant (cm/h); BW: Body weight (kg); AT: The average time (days); CDI: The dose of stressor from the specified exposure route i (mg/kg/day); m: the number of different chemical (dimensionless); SF_i: Slope factor from the specified exposure route i (mg/kg/day)⁻¹; i: oral, dermal and inhalation exposure, expressed as the exposure route is oral, dermal and inhalation exposure, respectively;

III. RESULT AND DISCUSSION

A. Water quality of treated water samples

Figure 1. Seasonal variation in the NPOC concentrations and bromide ions concentrations in treated water samples from Yangtze River (error bars show one standard deviation).

In order to investigate the seasonal variation in DBPs concentration and distribution, water samples were collected from different seasons under same reaction conditions. Seasonal variation in NPOC concentrations and bromide ions in treated water is shown in Figure 1. Average raw water bromide ions concentration was found to be 0.72 mg/L for spring, while it was 0.04 mg/L in summer. The high bromide

concentration in Yangtze River water samples may be related to intrusion of seawater to the surface since this district is located near East China Sea. The phenomenon usually occurs in the drought periods of spring and winter every year.

B. Seasonal variation of DBP formation and distribution

Figure 2. Seasonal variation in (a) THMs (b) HAA₅ concentrations in chlorination of treated water from Yangtze River. ((Reaction conditions: time; 48 h; temperature: $22 \pm 1^\circ\text{C}$; Br⁻: ambient concentration; Cl₂ dose: 3.5 mg/L). (error bars show one standard deviation)).

The seasonal variations in THM and HAA in water samples are illustrated in Fig 2 (a) and (b). It was found that the highest TTHM concentrations were measured in spring (mean, 108.1 µg/L) whereas the lowest were measured in autumn and winter (mean; 65.9 µg/L and 75.5 µg/L, respectively) samples. As regards HAA₅, Fig.2 (b) shows that the highest concentrations in water samples were found that the higher measured value obtained in autumn (mean, 25.0 µg/L), and the lowest value obtained in spring. The findings are in general agreement with the literature information [20], who also found TCAA and DCAA were the major species in published UK and Turkey survey. Moreover, the concentration of total THMs in spring and summer was higher than the standard values of the USEPA, WHO and EU(exclude for total HAA). The results are according with reporter of some countries[21]. In addition, as shown in Fig.2, the brominated THM and HAA species are more dominant in spring and winter than those of by-products in summer. The reason probably is attributable to the presence of high level NPOC and bromide concentrations during spring and winter in water samples.

C. Fe(III) affecting the DBP formation and speciation

Figure 3. Effect of Fe(III) concentrations on the formation of THMs and HAA formation. (Experiment conditions: pH:7.5; time: 48 h, temperature: $22 \pm 1^\circ\text{C}$; Cl₂ dose: 3.5 mg/L; reaction time: 2 d).

Figure 3 presents the effect of Fe(III) concentrations on the formation of total THM and HAA in four seasons of water samples. The results show that THMs concentration increased with increasing Fe(III) concentration from 0 to 1.0 mg/L Fe(III) significantly promoted formation of total THMs, while there was slight net change in total HAA₅ concentration. The similar results were reported by Rossman et al. [22], who found THM formation significantly increased and slight

change in HAAs formation in the presence of ferric pipe deposit. However, the complexity of DBPs formation with multiple consecutive steps makes difficult to propose how the metal ions intervene in the process. One reason can infer that Fe(III) can bind to the carboxylate groups of the substrates and by forming a complex which have a catalytic effect upon phenolic compounds polymerization would increase the reactivity of the substrates towards chlorination. In addition, addition of Fe(III) is also expected to increase the aggregate size of the humic substances as observed in the case of Mg(II) and Ca(II) addition due to intermolecular associations induced by the metal ions present, it will prompt the DBPs formation [23]. According to previous investigations, the total iron in finished water were usually in range of 0.3–0.5 mg/L [24]. Therefore, 0.5 mg/L concentration was selected for a further detailed study to investigate the effect of Fe(III) on cancer risk with seasonal variations.

D. Assessment of cancer risk

The multi-pathway cancer risk from treated water samples for human body was calculated. This research focused on the assessment of the risk of cancer from exposure to THMs and HAAs through three routes: (1) oral ingestion exposure; (2) inhalation exposure; (3) dermal absorption exposure. Risk assessment was calculated for two cases: Case I–non presence of Fe(III) and Case II–in presence of Fe(III), respectively.

1) Effect of seasonal variation on cancer risk in DBPs

Figure 4. Effect seasonal variation via different exposure pathways total cancer risk with and without Fe(III), (Experimental conditions: 0.5 mg/L Fe(III), pH: 7.5; Cl₂ dose: 3.5 mg/L; reaction time: 2 d).

As shown in the Figure 4(a), effect of Fe(III) on the total cancer risk in spring (1.16×10^{-4}) is more significant than those of summer (5.36×10^{-5}). The total cancer risk in spring increased 10% with Fe(III), while cancer risk have no significant change in summer with or without 0.5 mg/L Fe(III). The cancer risk through oral ingestion was also higher than through dermal absorption and inhalation exposure. Except for the cancer risk of THMs, the major cancer risk of HAAs was contributed by DCAA under our experimental conditions. This was also in accordance with the high reference dose of DCAA. Through the oral ingestion and dermal absorption, the cancer risk for each chemical followed the order: TBM > DBCM > BDCM > TCM > DCAA > TCAA. However, the order of the

cancer risk through the inhalation exposure for each chemical was: TCM>DBCM>BDCM>TBM>DCAA>TCAA.

To inhalation exposure, the cancer risk for chloroform was highest among total THMs and HAAs (shown in Figure 4(c)). This could be explained by the cancer slope factor of inhalation being far higher than other chemicals in THMs and HAAs. The mainly reason is which have the high inhalation risk of chloroform comes from its high Henry's constant (H), mass transfer coefficient and high inhalation slope factor, compared with the brominated-THMs [19]. This observation is consistent with the results reported by [25], in which inhalation exposure to THMs is suggested to be an important pathway for THM. In addition, it should be note that CHBr_3 were found to contribute a higher cancer risk in spring than did the other three THMs and HAAs because the measured concentrations were much higher in spring. The order of cancer risk of THMs and HAAs in spring was different from that in summer due to the bromide ion effect in water source. The reason may be presence of Fe(III) contribute bromide ions substitute chlorine atoms in CHCl_3 to brominated-THMs [26], which are likely to cause more carcinogenesis.

IV. CONCLUSIONS

In this study, the effect of seasonal variation and co-presence of Fe(III) on THMs and HAAs formation was investigated during chlorination of treated water samples. The cancer risks of lifetime exposure to THMs and HAAs from different routes were also estimated. The results showed that the highest TTHMs levels were detected in spring while the lower were from fall and winter water samples. As for HAA₅, The highest HAA₅ levels were detected in autumn while the lower were from spring. The lifetime cancer risk for THM and HAA followed the order, oral ingestion and inhalation, dermal. According to USEPA Guidance [27], the cancer risk is in the range of 10^{-4} – 10^{-6} which is an acceptable risk. As a result, this is a case of acceptable risk. The lifetime cancer risk estimation showed that total cancer risk in spring (1.16×10^{-4}) increased about 2 times than those of summer (5.36×10^{-5}) under our experimental conditions, while in presence 0.5 mg/L Fe(III) increased about 10% in spring than that of absence of Fe(III). From the results of cancer risk assessment, it is necessary to pay much attention to effect of Fe(III) and seasonal variation on the DBPs associated with lifetime risk in coastal region where there frequently occurred the salt intrusion to source waters, so as to minimize the cancer risk of DBPs.

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