Bench scale evaluation of Fe(II) ions on haloacetic acids (HAAs) formation in synthetic water

M. Safiur Rahman and Graham A. Gagnon

ABSTRACT

Cast iron pipes were installed broadly in North American water utilities, particularly in older cities such as Halifax, NS, and other cities in the northeastern portions of Canada and the USA. Many of these cast iron pipes are corroded and are continuous sources of Fe(II) ions in drinking water distribution systems. In this paper, the results of an experimental investigation into the factors influencing haloacetic acids (HAAs) formation in the presence of Fe(II) ions are presented. The experiments were conducted using $NaHCO_3$ buffered synthetic water samples with different characteristics (i.e. pH, phosphate, stagnation time) simulating with water distribution systems. The results showed that Fe(II) ions significantly reduced HAAs formation in different reaction systems at a 95% confidence level. In control water systems, pH had no significant impact, however, in the presence of Fe(II) ions in water, pH had an obvious impact to increase HAAs formation ($\alpha = 0.05$). In contrast, phosphate-based corrosion inhibitor significantly ($\alpha = 0.05$) reduced HAAs formation in the presence of different dosages of Fe(II) ions in water samples for the reaction period of 24, 48, 84 and 130 h, respectively. Significant factors and their rank influencing HAAs formation and distribution were identified using a 2^4 full factorial design approach.
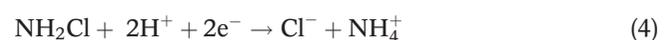
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INTRODUCTION

Approximately 30% of the 600,000 km of water mains in the USA are comprised of unlined cast iron or ductile iron (AWWA 1998). The interior surface of an unlined cast iron water distribution pipe is typically exposed to an oxidizing environment that causes corrosion. Hozalski *et al.* (2008) reported the reduction of pipe wall as a zero-valent iron (Fe(O)); correspondingly when Fe(O) ions come in contact with water, Fe(II) ions are formed in water through iron corrosion (Equation (1)). Oxidants such as oxygen and free chlorine (HOCl and OCl$^-$) or monochloramine are available in drinking water to accept the released electrons (Equations (2)–(4)) (Sarin *et al.* 2004a). Consequently, concentration of ferrous ions Fe^{2+} in iron pipe water systems increases under these corrosion conditions (Kirmeyer *et al.* 2000). Kuch (1984) and Kirmeyer *et al.* (2000) have hypothesized that ferric (Fe^{3+}) oxides present in the iron scale act as an alternative oxidant for allowing the iron corrosion

(and Fe^{2+} release) to occur during water stagnation/ oxygen depletion conditions. However, ferric oxides in iron corrosion are reduced and ferrous ions are formed according to Equation (5) following the 'Kuch Mechanism' (Kuch 1984):

$$Fe(0) \rightarrow Fe^{2+} + 2e^- \qquad (1)$$

$$O_2 + 4H^+ + 2e^- \rightarrow 2H_2O \qquad (2)$$

$$HOCl + H^+ + 2e^- \rightarrow Cl^- + H_2O \qquad (3)$$

$$NH_2Cl + 2H^+ + 2e^- \rightarrow Cl^- + NH_4^+ \qquad (4)$$

$$Fe_{(s)} + 2FeOOH_{(s)} + 6H^+ \rightarrow 3Fe^{2+} + 4H_2O \qquad (5)$$

Therefore, it has been given that Fe(II) ions are being added continuously in drinking water distribution systems from the iron corrosion products (Sarin et al. 2004a). A laboratory study revealed that the release rate of Fe(II) ions ranges from 0.003 mg m^{-1} h^{-1} in iron pipe loops with flowing oxygenated water to 0.01 mg m^{-1} h^{-1} under stagnant anoxic conditions (Sarin et al. 2004b). However, in corroded iron pipe, the corrosion products are the main source of aqueous Fe(II) ions in distribution systems. The concentration of Fe(II) ions was found to be 7.2 mg/L, dry weight basis in a center sample and 17.1 mg/L, dry weight basis in a side sample of 40–50 year-old iron pipe collected from the distribution system in Melbourne, Australia (Lin et al. 2001). Reduction of pipe walls could be mentioned by zero-valent iron or by the ferrous ions contained in or sorbed to iron oxide corrosion products (Hozalski et al. 2008). Several laboratory studies have reported that Fe(O) is a robust reductant that reduces different types of halogenated solvents including chlorinated byproducts: haloacetic acids (HAAs) (Zhang et al. 2004; Hozalski et al. 2008), carbon tetrachloride (Matheson & Tratnyek 1994), trichloro(nitro)methane (chloropicrin) (Pearson et al. 2005), 1,1,1-trichloroethane (Fennelly & Roberts 1998), and pentachlorophenol (Kim & Carraway 2000). It has also been reported that Fe(O) reduces several brominated compounds, for instance, 1,2-dibromoethane (Rajagopal & Burris 1999), 1,2 dibromo-3-chloropropane (Siantar et al. 1996). In addition to the study on impact of zero valent iron (Fe(O)) on reduction of halogenated compounds, Chun et al. (2005) investigated a study using synthetic iron pipe corrosion scales, i.e. magnetite and goethite which contain both Fe(II) and Fe(III) ions; and found that selected disinfection byproducts (i.e. trichlonitromethane, trichloacetonitrile, 1,1,1-trichloropropanone and trichloroacetaldehyde hydrate) were significantly reduced in the presence of magnetite and goethite in solution.

On the other hand, free chlorine is the most widely and effectively used secondary disinfectant for drinking water distribution systems since 1913 in North America to deactivate pathogens and/or to residual concentrations in the distribution system in order to minimize the risk (Madigan et al. 2000). Generally, increased concentration of disinfectant (oxidants) would be expected to increase corrosion (Eisnor & Gagnon 2004). Therefore, it has been hypothesized that the corrosion products and Fe(II) ions react with free chlorine and disinfectant byproducts present in iron pipe water distribution systems.

In recent years, different types of effort have been executed to understand the corrosion mechanisms and to control metal release from corroded pipe. Increasing pH and/or alkalinity are two cost effective and useful methods to reduce the metal corrosion. Phosphate-based corrosion inhibitors are an alternative additive for drinking water for mitigating metal corrosion protection, red water control, and turbidity reduction (Maddison et al. 2001). The possible mechanism of phosphate corrosion inhibitor is that phosphate usually adsorbs to the surface of iron particles and probably involves the interaction of PO_4^{3-} with two Fe^{3+} ions to relatively stable Fe-PO$_4$-Fe linkage or binuclear inner-sphere complexes (Stumm & Sulzberger 1992; Lytle & Snoeyink 2002). Other studies have suggested that phosphate adsorbs onto the iron surface to form a protective film (McNeill & Edwards 2001) that might reduce corrosion. However, in the USA, around 67% of water utilities use polyphosphate or a blend of polyphosphate and orthophosphate and the rest of the utilities (33%) add orthophosphate as a corrosion inhibitor to the finished water (Edwards & McNeill 2002). Unfortunately, published research concerning the reactivity of phosphate-based corrosion inhibitors on the formation of HAAs in the presence and absence of Fe(II) ions in solution iron is not yet well established.

The formation of HAAs and their species distribution is a complex phenomenon and depends on several factors including characteristics of water, treatments procedures, and water distribution pipe materials. Previous studies have mostly reported both the formation of HAAs and their reduction in full scale distribution systems (Singer et al. 1995; Arora et al. 1997; Williams et al. 1997; Pecher et al. 2002; Hozalski et al. 2008; Amold et al. 2010). However, investigations into the effect of Fe(II) ions alone, and along with phosphate-based corrosion inhibitor on HAAs formation for different pH values, are limited in the existing literature. In the present study, the effect of Fe(II) ions and other factors (pH, phosphate dosage and reaction time) on HAAs formation and distribution were investigated using NaHCO$_3$ buffered synthetic water under controlled laboratory conditions. A 2^4 full factorial design with center point approach was followed to prepare the synthetic water samples with the different characteristics. The goal of this

study was to investigate and rank the most significant factors and their interaction influencing HAAs formation in drinking water treatment and distribution systems.

MATERIALS AND METHODS

Reagents, solutions and glassware

$FeSO_4.7H_2O$ (assay: 100%, Fisher Scientific, USA) was used as a source of initial Fe(II) ions in solution. Ammonium chloride (assay: 99.6%), sodium sulfite (assay: 100%) and sodium bi-carbonate (assay: 100%), sodium sulfate (assay: 99.4%), sodium hydroxide (assay: 100%), sulfuric acid (assay: 98%), hydrochloric acid (assay: 36.5–38%) were obtained from Fisher Scientific, USA. Blended phosphate (Virchem 937, Carus Chemical Corporation, USA) composed of 25% zinc phosphate and 75% polyphosphate was used as a source of phosphate.

Humic acid (HA) (technical grade, Sigma Aldrich, USA) was used as a source of natural organic matter (NOM). A stock solution for the HA was prepared by dissolving an aliquot of HA in 1 L Milli-Q water at pH >10. The solution was stirred for 24 h at room temperature (21 ± 1 °C). The solution was then filtered through 0.45 µm filter paper (Micron-PSE, Polysulfone), which produced a HA solution of 280–300 mg/L dissolved organic carbon (DOC). The stock solution was stored at 4 °C for subsequent uses (Vikesland *et al.* 1998; Chang *et al.* 2001; Yang & Shang 2004; Li & Zhao 2006). A chlorine stock solution of 5 mg-Cl_2/L was prepared using a 5% aqueous sodium hypochlorite (NaCl) solution (Fisher Scientific, USA) following Standard Method 5710B (APHA 1998). All solutions were prepared in ultrapure water from a Milli-Q water purified system (Millipore: Milli-Ro 5 plus and Milli Q plus 185). HAA_9 standard stock solution was prepared in a 5 mL volumetric flask containing MtBE (assay 99.8%, Sigma-Aldrich, Germany) by addition of 50 µL HAA_9 mix solution (EPA 552.2 Acids Calibration Mix, Supelco, PA, USA). The stock solution was used to prepare different concentrations (10–100 µg/L) of HAAs standard solutions to calibrate GC. The diluted stock solution will be good up to 24 h. Diazomethane solution was prepared freshly in the Water Chemistry Laboratory, Dalhousie University each day for HAAs extraction. 1–2 di-bromopropane (Assay 99%, Acros Organics, NJ,

USA) was used as internal standard solution in each extracted HAAs solution.

All dish-washed glassware, especially amber color bottles (reactor), used for this study were soaked using a concentrated sodium hypochlorite solution ($\sim$300 mg/L as Cl_2) for at least 24 h. Thereafter, the bottles were rinsed thoroughly three times with deionized water and finally with Milli-Q water, and were heated at 110 °C overnight (APHA 1998).

Batch experiments

Bench scale experiments were conducted for HAAs formation analysis using synthetic water samples consisting of differing characteristics. HA was used as a source of natural organic matter (Vikesland *et al.* 1998; Chang *et al.* 2001; Yang & Shang 2004; Li & Zhao 2006). A required amount of purified HA stock solution was employed as the surrogate for NOM (2.85 mg/L as DOC) in $NaHCO_3$ buffered water systems (5 mg-C/L as dissolved inorganic carbon). HA was chosen because it contains 48.95% carbon (by weight), while natural freshwater contains 48–54% carbon. Prior to the HAAs formation study, NOM in water (2.85 mg/L as DOC) was characterized on the basis of molecular weight (MW) distribution using high performance size exclusion chromatography (HPSEC) (Perklin Elmer, Series 200) with a UV/VIS detector. This study revealed that the MW fraction of 1,500–2,500 Da was predominant in the studied NOM in water (Table 1). The required pH values of the buffered water samples were adjusted using 0.5N HCl and 0.5N NaOH solution. A required amount of a phosphate-based corrosion inhibitor, zinc ortho-polyphosphate was added to obtain 1.5 mg-PO_4/L in solution. After that, all samples were chlorinated and $FeSO_4$ was added to obtain the required amount of Fe(II) ions in the solutions. The solutions were mixed properly and transferred immediately into 250 mL chlorine demand free serum bottles (reactor) with PTFE (polytetrafluoroethylene) faced. The serum bottles were filled with the samples headspace-free. Finally the serum bottles (reactors) were wrapped with aluminum foil to prevent photochemical reaction and kept in the dark for the designated reaction times.

After each designated reaction period (i.e. 3.5, 24, 48, 84 and 130 h) at different water characteristics, the water samples were collected into headspace-free 25 mL glass

Table 1 | Fraction features of NOM molecular weight (MW) before HAAs formation study

Fraction	Range of MW (Da)	M_W	M_N	P	% of the total
1	50–200	174.2 ± 0.1	347.3 ± 0.6	0.50	2.1 ± 0.01
2	> 200–500	274.5 ± 5.6	273.2 ± 4.9	1.00	2.5 ± 0.7
3	> 500–1,000	553.9 ± 9.9	5,19.1 ± 12.7	1.07	14.1 ± 0.2
4	> 1,000–1,500	1,101.9 ± 1.6	2,186.9 ± 4.3	0.50	27.8 ± 0.9
5	> 1,500–2,500	2,604.9 ± 8.8	2,264 ± 6.4	1.15	50.6 ± 0.2
6	> 2,500	58,328.5 ± 1,127.6	56,854.9 ± 547.3	1.03	2.9 ± 0.2

vials with polypropylene screw caps and teflon-lined septa. Chlorinated samples for HAAs analysis were quenched by ammonium chloride to prevent further formation of HAAs after the designated reaction time. All samples were refrigerated at 4 °C not more than 2 weeks prior to extraction. Total experiments were conducted at room temperature (21 ± 1 °C). All of the tests were conducted in duplicate to test the reproducibility of the results. For each batch test, control samples were used following the procedure as in the test sample but without the designed variables (i.e. ferrous ions, phosphate).

Analytical procedure

DOC measurements were performed with a total organic carbon analyzer (TOC-V$_{CPH}$) equipped with an auto-sampler ASI-V (Shimadzu Corp., Kyoto, Japan) according to Standard Method 5310B (APHA 1998). Free chlorine concentration was determined using the colorimetric version of the *N,N*-diethyl-*p*-phenylenediamine (DPD) HACH method 8021 (HACH 2005) at a wavelength of 530 nm using a DR/5000 UV Visible Spectrophotometer (HACH Co., Loveland, Colorado). Concentration of Fe(II) ions was measured colorimetrically with the 1,10-phenanthroline HACH method 8146 (HACH 2005) at a wavelength of 510 nm using a DR/5000 UV Visible Spectrophotometer. Phosphate concentration was measured by an ion chromatograph (761 Compact IC, Metrohm). All pH measurements were made using an Accumet electrode and Accumet Excel, XL50 (Dual channel pH/ion/conductivity) meter (Fisher Scientific, Singapore) calibrated with National Bureau of Standards (NBS) buffers. The pH meter was standardized daily using a three-point calibration with pH 4, 7, and 10 standard solutions (Thermo Fisher Scientific, USA).

Nine HAAs, i.e. monochloroacetic acid (MCAA), mono-bromoacetic acid (MBAA), dichloroacetic acid (DCAA), bromochloroacetic acid (BCAA), dibromoacetic acid (DBAA), bromodichloroacetic acid (DCAA), dibromochloroacetic acid (DBCAA), trichloroacetic acid (TCAA) and tribromoacetic acid (TBAA), were extracted by liquid–liquid extraction with MtBE, methalization with diazomethane following Standard Method 6251B (APHA 1998). HAAs analyses were quantified by gas chromatography (Varian, CP 3800 Gas Chromatography) with electron capture detection (GC–ECD) according to USEPA Method 552.2 (USEPA 1995). Further details on the operating conditions of GC–ECD for HAAs analysis is provided in the supplementary material (SM-I).

Experimental design and data analysis

A 2^4 full factorial design was studied to evaluate the importance and interaction of the ferrous, Fe(II) ions concentrations, pH, phosphate-based corrosion inhibitor dosages and different reaction times on HAAs formation. The range and levels of the studied variables for this study is presented in Table 2. These values were chosen because they are typical values for many water distribution systems. Data that were obtained from each HAAs formation experiment were entered into a computer system and the statistical analysis of the factorial design was performed by using Windows version programs (1) Minitab® 16 (MINITAB Inc., State College, Pennsylvania, USA) and (2) Microsoft Excel® 2010 (Redmond, WA, USA). The analysis provided relevant statistical parameters including the *F*-test associated with probability $p(F)$. The statistical significance of the regression coefficient was determined by the student's *t*-test associated with probability $p(t)$. Unless otherwise

Table 2 | Experimental range and level of different variables on HAAs formation study

Code	Variable	Unit	Low (–)	Center (+)	High (+)
			Level		
A	Fe(II) ions	mg-Fe(II)/L	0	1.5	3
B	pH	Unit	6.5	7.5	8.5
C	Corrosion inhibitor	mg-PO$_4$/L	0	0.75	1.5
D	Reaction time	Hour (h)	3.5	13.5	24

mentioned, all statistical analysis was conducted at a 95% confidence level.

RESULTS AND DISCUSSION

To determine the effects of Fe(II) ions and other factors on HAAs formation and speciation in iron water systems, a methodical investigation was conducted. Bromine was not present in the studied water samples (method detection limit (MDL) for Br was 0.105 mg/L); and, as a consequence, the formation of major brominated species was found to be below the detection limit in most cases throughout the study (MDL for each HAA species is provided in supplementary material, SM-II). Therefore, major brominated species were not included in the results and discussion part. However, the effects of different factors on HAAs formation study are presented below.

Effect of Fe(II) ions and reaction time

To understand the effect of Fe(II) ions on HAAs formation, ferrous iron was added into the buffered synthetic water samples having pH 6.5, DOC 2.85 mg/L. This study was conducted at room temperature ($21 \pm 1\,°C$) for a chlorine to carbon mole ratio of 0.79 and for the different reaction times ranging from 3.5 to 130 h, respectively. As mentioned previously, cast iron pipes are a constant source of Fe(II) ions in drinking water distribution systems (Sarin *et al.* 2004a), while the levels of Fe(II) ions are site specific to the water quality. Fe(II) ions concentration in distribution systems were reported up to 3 mg/L (Kirmeyer *et al.* 2000) and under anoxic condition, aqueous Fe(II) ions concentrations up to 1.11 mg-Fe(II)/L (0.02 mM) were observed

in a pipe loop reactor constructed using a 70 year old galvanized iron pipe (Sarin *et al.* 2004a). Therefore, different dosages of Fe(II) ions concentration ranging from 0.35 to 3 mg/L were chosen for this study.

This study revealed that in the presence of 0.35 mg/L Fe(II) ions, HAAs formation was significantly reduced (41.5–51.9%) compared with the control water system (in the absence of Fe(II) ions and a phosphate-based corrosion inhibitor) in the studied reaction periods ranging from 3.5 to 130 h (Figure 1). This study also revealed that HAAs formation reduced gradually from 41.5 to 71.02% with an increase of total Fe(II) ions concentration from 0.35 to 3 mg/L for the reaction period of 3.5 h. This finding is in agreement with the previous observations which have reported that iron oxides surface (i.e. magnetite, goethite) accelerated the reduction rates of various organic compounds and halogenated byproducts (Amonette *et al.* 2000; Pecher *et al.* 2002; Elsner *et al.* 2004; Chun *et al.* 2005; Lee *et al.* 2008). Lee *et al.* (2008) reported that the degradation rate for TCNM (trichloronitromethane), a non-regulated DBP (disinfection by-product), depends on water-soluble iron in water systems. Fe(II) is a strong reductant (Amold *et al.* 2010) and when the concentration of Fe(II) ions increase, it increases the reactive surface area, via oxidation of Fe(II) to Fe(III) by residual disinfectants along with other oxidants, and consequent precipitation. As numerous studies have reported that free chlorine is used up preliminarily by
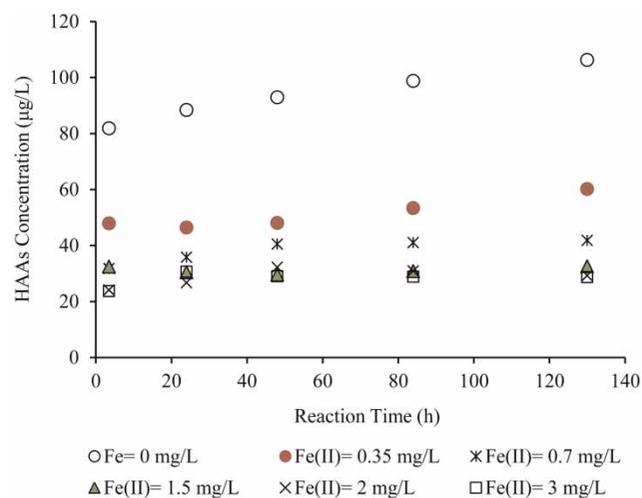
Figure 1 | Effect of Fe(II) ions concentration and reaction time on HAAs formation in synthetic water at pH 6.5, chlorine to carbon mole ratio of 0.79 and $21 \pm 1\,°C$.

iron oxides (Rossman *et al*. 2001), it was therefore hypothesized that less free chlorine might be available to react with precursor material to form DBPs. However, the current bench scale experiments showed that the formation of HAAs was lower in the presence of Fe(II) ions compared with the control water systems, and consequently HAAs formation decreased gradually with the increase of Fe(II) ions concentration in the reaction systems (Figure 1). A possible explanation for this result is that adsorption of higher NOM MW fractions onto iron oxide surface reduces HAAs formation, also higher NOM MW fractions were reported to be the most reactive NOM components in DBP formation study (Marhaba & Van 2000; Chang *et al*. 2001; Lamsal *et al*. 2012). This hypothesis was supported by Zhou *et al*. (2001), who reported that NOM MW fraction for 1,250–3,750 Da predominantly adsorbed onto iron oxide surface following the best fit to the Langmuir adsorption isotherm. The results for MW distribution of NOM for this study revealed that more than 50% MW fraction lay between 1,500 and 2,500 Da (Table 1), which might be adsorbed onto iron oxide surface resulting in the reduction of HAAs formation. The change of NOM MW distribution in different reaction medias was conducted as a part of a separate study to be published later. However, in addition to chlorine and NOM reactivity with Fe(II) ions, it is also believed that the HAAs formed at the initial stage in contact of chlorine with NO, are adsorbed on the iron oxides surfaces.

For all samples, the major portion of HAAs formation was observed at the initial 3.5 h of the reaction period (Figure 1). However, the HAAs formation was monitored up to 130 h (5.5 days) of the reaction periods. It was found that the HAAs concentrations in control water systems were gradually and slightly increased with the increase in reaction times. However, HAAs formation was maintained relatively constant after 48 h of the reaction period in the presence of different dosages of total Fe(II) ions in solutions. Statistical analysis (two-way analysis of variance (ANOVA)) for the HAAs formation data revealed that Fe(II) ions significantly ($p < 0.001$) reduced the formation of HAAs at a 95% confidence level. It implied that the presence of total ferrous ions in solutions changed the reactivity between chlorine and NOM, which led to a net decrease in these HAAs concentrations. However, ANOVA revealed that the reaction time was not statistically significant ($\alpha = 0.05$, $p > 0.05$) in changing HAAs formation at different dosages of Fe(II) ions in the studied iron water systems (Table 3).
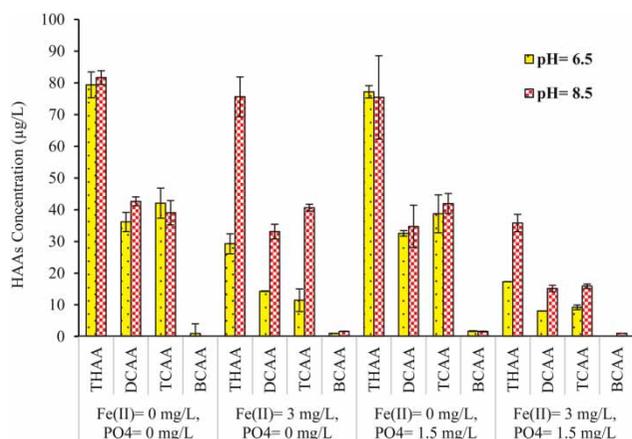
Effect of pH

Typical pH value in drinking water treatment and distribution systems has been reported to be 6.5–9 (Chun *et al*. 2005). Therefore, this study was conducted at pH 6.5 and 8.5 for a reaction period of 24 h, and for a chlorine to carbon mole ratio of 0.79 in four different reaction systems at $21 \pm 1\,^{\circ}C$ temp. This study revealed that in the control water systems, changing the pH values from 6.5 to 8.5 did not significantly affect in changing HAAs formation (Figure 2). This finding was consistent with the reported results by Ye *et al*. (2009), which acknowledged that increasing the pH value from 6.0 to 8.5 did not significantly change the concentration of HAAs. However, in the presence of 3 mg/L Fe(II) ions in solution, changing the pH values from 6.5 to 8.5 led to a 2.5 fold increment of HAAs formation and was observed here following the same reaction conditions. The influence of pH on the formation and distribution of HAAs in iron water systems could be affected due to the following reasons: (1) at a higher pH level, the dissolved metal ions could either directly enhance chloride ions by degrading free chlorine ($OCl^- \rightarrow O_2 + Cl^-$; Gray *et al*. (1977)), (2) dissolved metal ions increase the reactivity

Table 3 | Two-way ANOVA on effect for different concentrations of Fe(II) ions and different reaction times on HAAs formation

Source of variation	SS	df	MS	F	P-value	F crit
Fe(II) conc. (mg/L)	2,022.164	4	505.5411	36.01	< 0.001	3.007
Reaction time (h)	164.3499	4	41.08746	2.92	> 0.05	3.007
Error	224.6792	16	14.04245			
Total	2,411.193	24				

SS: sum of squares; df: degrees of freedom; MS: mean square.

Figure 2 | Effect of pH on HAAs formation and speciation in different reaction systems for a chlorine to carbon mole ratio of 0.79, reaction period of 24 h at $21 \pm 1\,^{\circ}C$ (error bars represent standard deviation at 2σ levels).

of DBP precursors (Blatchley III et al. 2003), and (3) individual HAAs formation mechanisms could be affected by pH change in solution. Free chlorine represents the combination of HOCl and OCl^{-} (pK_a of 7.6), thus hypochlorite ion (OCl^{-}) is in greater proportion at pH 8.5 (i.e. greater than 95%). However, these results demonstrated that a lower pH value of 6.5 might contribute lower concentration of HAAs in the presence of Fe(II) ions. Therefore, the results of this study might have implications for understanding the fact that pH change in drinking water not only affects the Fe(II) ions oxidation but has also an impact on HAAs precursors as well as affecting the reactivity between NOM and chlorine.

This study revealed (Figure 2) that DCAA formation was favored for a high pH value of 8.5 but the adverse trend was observed for the formation of TCAA in the control water systems. Figure 2 demonstrates that TCAA formation exceeds DCAA formation at pH 6.5 in control water. These findings were in agreement with the reported results in the literature (Liang & Singer 2003; Uyak et al. 2007). Conversely, in the presence of Fe(II) ions alone and along with a phosphate-based corrosion inhibitor, an increment for DCAA, TCAA and BCAA formation was observed for changing pH value from 6.5 to 8.5 (Figure 2). This can be attributed due to the fact that changes in pH value can change the iron oxidation rates even though in the presence of phosphate and can alter both the extent of Fe(II) adsorption onto iron oxide surfaces and dissociation of chlorine. However, it is noted that the

impact of pH on HAAs formation is complicated, because the rate of HAA formation and hydrolysis varies for each individual species in different reaction systems.

Effect of PO_4 dosage and reaction time

Phosphate-based corrosion inhibitors are typically dosed into their treated water at a dosage of 0.5–3 mg-PO_4/L (Kirmeyer et al. 2000; Maddison et al. 2001). Therefore, a 1.5 mg/L phosphate dosage was selected for this bench scale study in synthetic buffered water systems. This study revealed the interactions effect of a phosphate-based corrosion inhibitor with the different dosages of Fe(II) ions on HAAs formation at pH value of 6.5. In the presence of a phosphate-based corrosion inhibitor (1.5 mg-PO_4/L) along with the different dosages of Fe(II) ions, HAAs formation significantly (at confidence level of 95%) reduced compared with the presence of Fe(II) ions only for the reaction periods of 24 h ($p = 0.008$), 48 h ($p = 0.042$), 84 h ($p = 0.036$) and 130 h ($p = 0.005$) respectively (Figures 3(b)–(e)). However, for the reaction period of 3.5 h, the phosphate-based corrosion inhibitor (1.5 mg-PO_4/L) did not show a statistically significant ($p = 0.878$) effect on the reduction of HAAs formation (Figure 3(a)). The finding of this study was in agreement with the research by Zhang & Andrews (2012), who conducted batch tests using different metals (Fe, Cu and Pb) coupons along with 1 mg/L phosphate-based corrosion inhibitor and reported that during a short reaction periods (<12 h), the phosphate did not considerably affect HAAs formation. However, the results of this study illustrated that in the presence of a phosphate-based corrosion inhibitor (1.5 mg-PO_4/L) along with Fe(II) ions in water samples, the statistical variation ($\alpha = 0.05$, $p \leq 0.005$) of HAAs formation was higher for the reaction period of 130 h (Figure 3(e)) compared to the reaction periods of 84, 48, 24 and 3.5 h, respectively (Table 4). A possible explanation for this fact is that at the initial stage when Fe(II) ions come in contact with oxidants (i.e. oxygen, chlorine), Fe(II) ions are oxidized to Fe(III) ions and the Fe(III) ions react with phosphate to form ferric phosphate. Einsele (1938) reported that during the stagnation time, especially when increasing the reaction time, Fe(III) species in ferric phosphate were reduced to Fe(II). As a consequence, it could be assumed that more chlorine might be occupied by
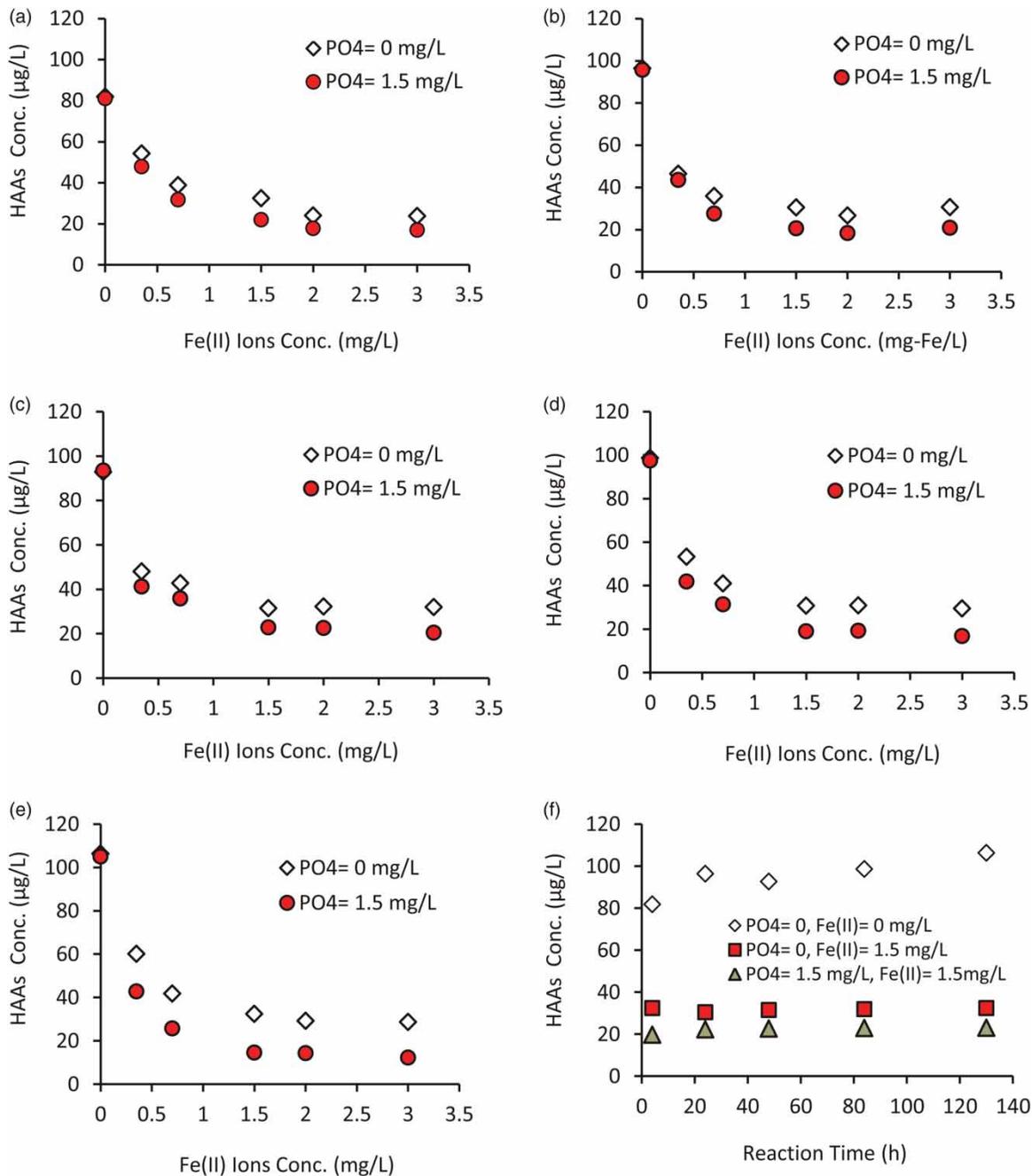
Figure 3 │ Effect of phosphate (1.5 mg-PO₄/L) on HAAs formation in synthetic water at pH 6.5, for chlorine to carbon mole ratio of 0.789, for the reaction periods of (a) 4 h, (b) 24 h, (c) 48 h, (d) 84 h, (e) 130 h, and (f) all reaction periods together.

the regenerated Fe(II) ions, and therefore, less chlorine might be available to react with NOM to form HAAs. In contrast, in the absence of phosphate, Fe(II) ions were converted to Fe(III) ions and these Fe(III) ions were not regenerated to Fe(II) ions which could be reacted with residual chlorine in the iron water systems. Consequently, in the absence of phosphate more chlorine might be available to react with NOM to form more HAAs which agreed reasonably with the reported data that increasing chloride ions increasing DBP formation (Singer *et al.* 1995).

Table 4 │ Student paired *t*-test on effect of phosphate dosage on HAAs formation for different reaction time (h) for a chlorine to carbon mole ratio of 0.789 in synthetic water, pH 6.5, temp 21 ± 1 °C

	Reaction time				
Statistical factors	4 h	24 h	48 h	84 h	130 h
Pooled variance	48.973	14.92	39.51	36.038	36.92
t Stat	1.538	3.324	2.066	2.689	3.79
t Critical	1.943	1.943	1.943	1.943	1.943
$P(T < =t)$	0.874	0.008	0.042	0.036	0.005
Remark	*Insignificant*	*Significant*	*Significant*	*Significant*	*Significant*

HAA speciation and correlation

Several previous studies have provided results that DCAA, TCAA and MCAA are the main HAA species in the chlorinated drinking water supplies (Rodriguez *et al.* 2004; Zhang & Andrews 2012). In the current study, MCAA was not found. However, the results of our study revealed that DCAA and TCAA were found to be the most common HAA species with a content of over 90% of total HAAs. TCAA was the most abundant HAA species (51.9 ± 11.4%), followed by DCAA (45.3 ± 7.5%), and BCAA (1.14 ± 1.6%) respectively in the water systems. This study also illustrated that less formation of DCAA, TCAA and BCAA occurs when 1.5 mg/L phosphate is added in the Fe(II) ions water systems compared with the Fe(II) ions water systems only (Figure 2). Bromine was not present in the synthetic water systems, therefore, no significant major brominated HAA species were observed in this study. However, a small amount of BCAA was found due to the presence of trace amount of bromide in NaOCl solution. Figure 4 shows that in the presence of different dosages of Fe(II) ions, the formation of HAA species are proportionally decreased compared with the control water systems.

The Pearson correlation matrix between all the variables (i.e. Fe(II) ions, pH, phosphate dosage, reaction time, HAAs and HAA species) in synthetic water samples (number of observations 79) was performed using the software, 'IBM SPSS Statistics 20' for Windows (IBM, USA) and the results are presented in Table 5. This study revealed a significant positive correlation between the pH values and the formation of both total HAAs ($r = 0.45$, $p < 0.0001$) and individual HAA species, i.e. DCAA ($r = 0.42$, $p < 0.0001$), TCAA ($r = 0.49$, $p < 0.0001$) and BCAA ($r = 0.74$,
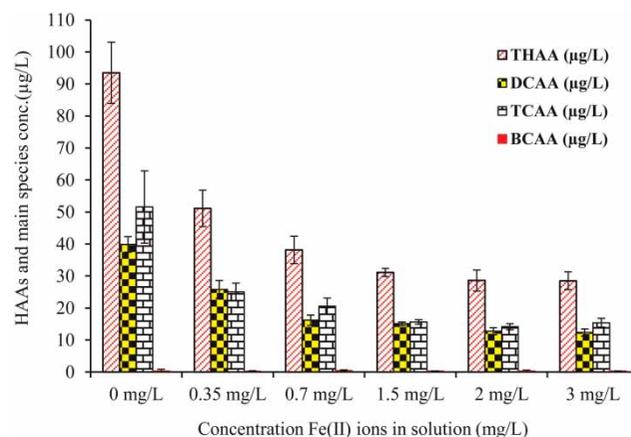
Figure 4 │ Relationship between HAAs formation and speciation with different dosages of Fe(II) ions at room temperature (21 ± 1 °C), for a pH value of 6.5 and a chlorine to carbon mole ratio of 0.79 (error bars represent standard deviation at 2σ levels).

$p < 0.0001$). However, a negative and moderate correlation was observed between the phosphate-based corrosion inhibitor and the formation of THAA ($r = 0.48$, $p < 0.0001$), DCAA ($r = 0.51$, $p < 0.0001$), and TCAA TCAA ($r = 0.46$, $p < 0.0001$) concentration in the same reaction systems. The Pearson correlation showed a moderate and negative relationship between Fe(II) ions and the formation of THAA ($r = 0.47$, $p < 0.0001$), DCAA ($r = 0.43$, $p < 0.0001$), and TCAA ($r = 0.48$, $p < 0.0001$). The correlation coefficients between total HAA and individual species were higher ranging from 0.62 to 0.98 ($p < 0.0001$), showing that each HAA species was strongly related to the other HAA. A moderate correlation between Fe(II) ions and pH ($p = 0.023$) was observed, indicating that an interaction may exist between the two independent variables. Therefore, the affiliation between one of the independent variables (pH or Fe(II) ions) and the dependent

Table 5 │ Pearson correlation coefficients between HAAs, DCAA, TCAA, BCAA, pH, PO_4 dosages, concentration of Fe(II) ions and reaction times

	HAA_9	DCAA	TCAA	BCAA	pH	PO_4	Fe(II)	Time
HAAs	1							
DCAA	0.96[b]	1						
TCAA	0.98[b]	0.88[b]	1					
BCAA	0.69[b]	0.62[b]	0.68[b]	1				
pH values	0.45[b]	0.42[b]	0.40[b]	0.74[b]	1			
PO_4 conc. (mg/L)	− 0.48[b]	− 0.51[b]	− 0.45[b]	− 0.12	−0.04	1		
Fe(II) ions (mg/L)	− 0.47[b]	− 0.43[b]	− 0.48[b]	− 0.07	0.26[a]	0.17	1	
Reaction time (h)	− 0.09	− 0.22	0.01	− 0.19	− 0.36[b]	− 0.04	− 0.16	1

[a]Correlation is significant at the 0.05 level (2-tailed).
[b]Correlation is significant at the 0.01 level (2-tailed).

variable (HAAs) was dependent upon the value of the other independent variables. The Pearson correlation matrix did not show any correlation between reaction time and other variables ($p > 0.05$) with an exception of pH value ($p = 0.001$). This finding from the statistical analysis is similar to the pH monitoring data (not presented here) that acknowledge that an increase of reaction time decreases the pH values in different reaction systems.

Significant factor/s on HAA formation

To investigate the significant factor/s on HAA formation, a full factorial (2^4) design approach with center point was followed to conduct the experiments. All the experiments were conducted in replicate and the repeatability was evaluated by paired t-tests at the 95% confidence level. The experimental data (number of observations 40) were analyzed with a Windows version program Minitab® 16 (MINITAB Inc., State College, Pennsylvania, USA) and the results are summarized in Table 6, which presents the estimated parameter values, their standard errors (SE), and summarizes the hypothesis results for the significance of each parameter. The statistical significance was determined based on student's t-test and the value of probability p. The statistical significance is represented in terms of Prob > t in Table 6. In this study, the negative value of the coefficient indicated that a high level setting of the factor provided lower content of HAAs formation than the low level setting and vice versa for the positive value of the coefficient. The analysis for the HAAs formation results in

Table 6 │ Estimated parameters and their significance in HAAs formation study

Term	Effect	SE Coef.	t-value	p-value	Contribution (%)	Comments
Constant		1.725	32.82	0.000		
Fe(II) ions (mg/L)	− 35.4	1.725	− 10.26	0.000	50.85	*Significant*
pH unit	13.97	1.725	4.05	0.010	7.92	*Significant*
Phosphate (mg-PO_4/L)	− 19.2	1.725	− 5.56	0.003	14.96	*Significant*
Reaction time (h)	4.44	1.725	1.29	0.254	0.80	
Fe(II)*pH	18.53	1.725	5.37	0.003	13.94	*Significant*
Fe(II)*Phosphate	− 9.48	1.725	− 2.75	0.040	3.65	*Significant*
Fe(II)*Time	− 3.31	1.725	− 0.96	0.382	0.44	
pH*Phosphate	− 9.9	1.725	− 2.87	0.035	3.97	*Significant*
pH*Time	2.6	1.725	0.75	0.486	0.27	
Phosphate*Time	4.37	1.725	1.27	0.261	0.77	

Table 6 reveal that the Fe(II) ions concentration (factor A) was the most significant factor ($p < 0.0001$, contribution 50.85%) on HAAs formation followed by the phosphate-based corrosion inhibitor ($p = 0.003$, contribution 14.96%) and pH ($p = 0.01$, contribution 7.92%) respectively at a 95% confidence level. Several interaction factors including AB (Fe(II) ions and pH, $p = 0.003$), AC (Fe(II) ions and phosphate dosage, $p = 0.04$) and BC (pH and phosphate dosage, $p = 0.035$) were also shown to be statistically significant at a 95% confidence level for HAAs formation study. The percentage of contribution for main and interaction factors on HAAs formation is presented in Table 6.

The main effects of the significant variables in this study are plotted in Figure 5(a) to visually assess their impact on HAAs formation. The signs of the effect indicate the direction of the effect. It was observed in Figure 5(a) that the main effects A and C were negative, having slopes of -35.4 and -19.2, respectively, indicating that when Fe(II) ions concentration and phosphate dose changed from a lower to a higher level, it reduced HAAs formation. However, the reverse trend was observed for the main factor of B (pH value) (Figure 5(a)). One of the major benefits of

factorial design approach is that it gives more insight into the interaction between the input parameters (Montgomery 2009). The interactions of AB, AC and BC are plotted in Figure 5(b). The non-parallel lines in these figures are indications of interaction between the two factors. The interaction plots AB (Fe(II) ions and pH) demonstrated that the Fe(II) ions concentration effect was very large when the pH value was at a low level (pH 6.5) and small when the pH value was at a high level (pH 8.5). However, AC (Fe(II) ions and PO$_4$) interaction plots showed the opposite trend, indicating that Fe(II) ions had more impact on the reduction of HAAs formation at a high level of phosphate (1.5 mg/L) compared to a low level of phosphate dosage (0 mg/L) (Figure 5(b)). On the other hand, the interaction plot BC (pH and phosphate dosage) indicated that pH had a little effect (slope = 4.07) at a high level of phosphate dosage, but a large effect for a low level of phosphate dosage. Therefore, this study illustrated that the lowest content of HAAs formation would appear to be obtained when the pH value was at a low level (6.5) and the phosphate dosage was at a high level (1.65 mg/L) in iron water systems.
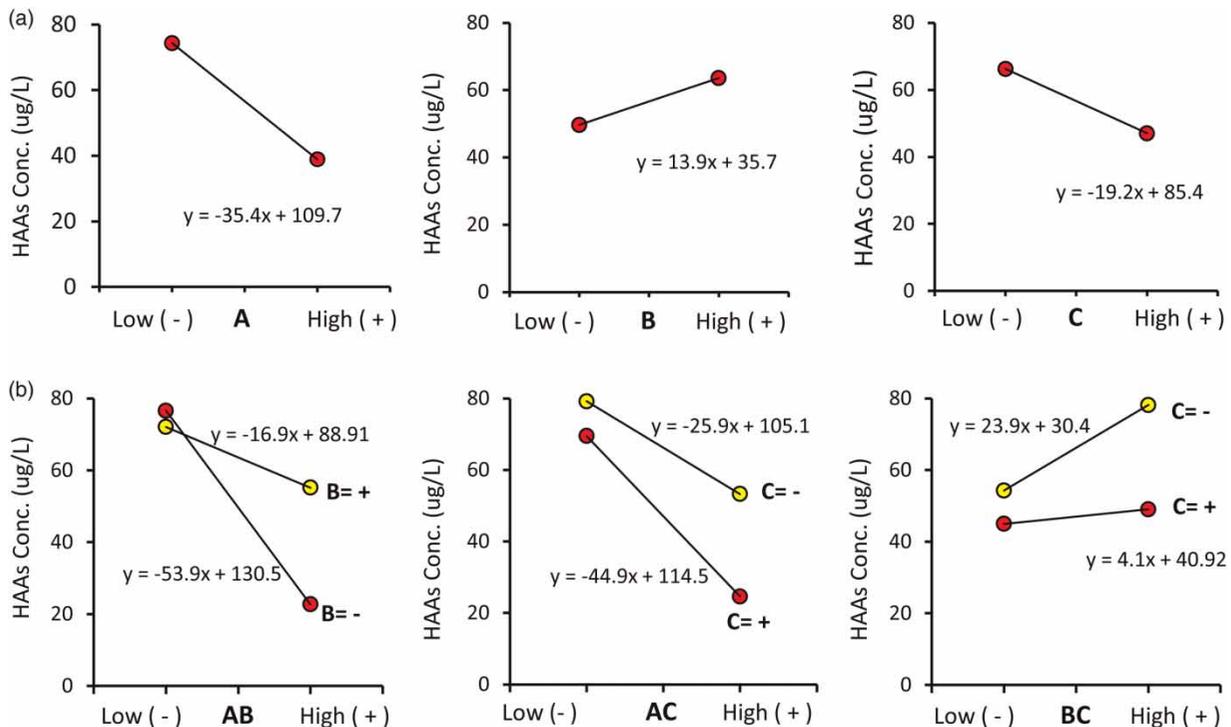

Figure 5 │ Significant (a) main effects and (b) interaction effects on HAAs formation.

SUMMARY AND CONCLUSIONS

The goal of this study was to evaluate the effect of Fe(II) ions concentration, along with a phosphate-based corrosion inhibitor for the different pH values and reaction times on HAAs formation. This study revealed that the formation of HAAs in the presence of Fe(II) ions was lower compared with the control water systems for the different reaction periods. However, in the iron water systems, phosphate significantly (at 95% confidence level) reduced HAAs formation for the different reaction periods studied here. The effect of pH on HAAs formation in the iron water systems was complicated compared to the control water systems, because the rate of HAAs formation and hydrolysis varies for each individual species in the presence of dissolved metal ions. This study revealed that DCAA was favored at a pH value of 8.5 compared to a pH value of 6.5 in the control water systems (in the absence of Fe(II) ions and a phosphate-based corrosion inhibitor), but the adverse trend was observed for TCAA formation in the same reaction systems. However, this study showed that TCAA formation exceeded DCAA formation at a pH value of 6.5 in the same reaction systems. Conversely, in the presence of Fe(II) ions alone, and along with a phosphate-based corrosion inhibitor, an increment for DCAA, TCAA and BCAA was observed for changing the pH value from 6.5 to 8.5. Therefore, the results of this study might have implications for understanding the fact that a pH change in drinking water not only affects the Fe(II) ions oxidation, but also has an impact on HAA formation and speciation as well as to affect reactivity between NOM and chlorine.

The factorial design approach revealed that Fe(II) ions, pH and phosphate-based corrosion inhibitor were the main significant factors for HAAs formation study. However, this study revealed that the main effect of Fe(II) ions concentration (factor *A*) really dominates this process, accounting for over 50.85% of total variability, whereas the main effect pH (factor *B*) and phosphate dosage (factor *C*), account for about 7.92 and 14.96%, respectively. Several interaction factors also showed significant effects at a 95% confidence level on HAAs formation. However, this study conclusively demonstrated that the lowest content of HAAs formation would appear to be obtained in the presence of a phosphate-based corrosion inhibitor (1.65 mg-PO_4/L) at a pH value of 6.5 compared to a pH value of 8.5 in the iron water systems. The results of this study will be an important element for utilities to understand the effects of Fe(II) ions and its interaction with phosphate-based corrosion inhibitor on HAAs formation in water treatment and distribution systems.

REFERENCES

Amold, W. A., Hozalski, R. M., Pearson, C. R. & Moore, K. 2010 TBAA reduction in reactors in simulated distribution systems pipes. *J. Am. Water Works Assoc.* **102** (3), 99–106.

APHA 1998 *Standard Methods for the Examination of Water and Wastewater*, 20th edn. APHA, Washington DC, USA.

Amonette, J. E., Workman, D. J., Kennedy, D. W., Fruchter, J. S. & Gorby, Y. A. 2000 Dechlorination of carbon tetrachloride by Fe(II) associated with goethite. *Environ. Sci. Technol.* **34** (21), 4606–4613.

Arora, H., LeChevallier, M. W. & Dixon, K. L. 1997 DBP occurrence survey. *J. Am. Water Works Assoc.* **89** (6), 60–68.

AWWA 1998 *Water:/Stats, the Water Utility Database: 1996 Survey (CD)*. American Water Works Association, Denver, CO.

Blatchley III, E. R., Margetas, D. & Duggirala, R. 2003 Copper catalysis in chloroform formation during water chlorination. *Water Res.* **37** (18), 4385–4394.

Chang, E. E., Chiang, P. C., Ko, Y. W. & Lan, W. H. 2001 Characteristics of organic precursors and their relationship with disinfection by-products. *Chemosphere* **44** (5), 1231–1236.

Chun, C. L., Hozalski, R. M. & Arnold, W. A. 2005 Degradation of drinking water disinfection byproducts by synthetic goethite and magnetite. *Environ. Sci. Technol.* **39** (21), 8525–8532.

Edwards, M. & McNeill, L. S. 2002 Effect of phosphate inhibitors on lead release from pipes. *J. Am. Water Works Assoc.* **94** (1), 79–90.

Einsele, W. 1938 On the chemical and colloidal chemical reactions in iron phosphate systems from limnochemical and limnogeological points of view. *Archiv. Hydrobiol.* **33**, 361.

Eisnor, J. D. & Gagnon, G. A. 2004 Impact of secondary disinfection on corrosion in a model distribution system. *J. Water Supply Res. Tech. AQUA* **53** (7), 441–452.

Elsner, M., Schwarzenbach, R. P. & Haderlein, S. B. 2004 Reactivity of Fe(II)-bearing minerals toward reductive transformation of organic contaminants. *Environ. Sci. Technol.* **38** (3), 799–807.

Fennelly, J. P. & Roberts, A. L. 1998 Reaction of 1,1,1-trichloroethane with zero-valent metals and bimetallic reductants. *Environ. Sci. Technol.* **32** (13), 1980–1988.

Gray, E. T., Taylor, R. W. & Margerum, D. W. 1977 Kinetics and mechanisms of copper-catalyzed decomposition of hypochlorite and hypobromite – properties of a dimeric copper(III) hydroxide intermediate. *Inorg. Chem.* **16** (12), 3047–3055.

Hach 2005 *DR 5000 Spectrophotometer Procedures Manual*, 2nd edn. Hach Company, Loveland, Colorado.

Hozalski, R. M., Arnold, W. A., Chun, C., LaPara, T. M., Lee, J. Y., Pearson, C. R. & Zhang, P. 2008 Degradation of halogenated disinfection byproducts in water distribution systems. *ACS Symp. Ser.* **995**, 334–348.

Kim, Y. H. & Carraway, E. R. 2000 Dechlorination of pentachlorophenol by zero valent iron and modified zero valent irons. *Environ. Sci. Technol.* **34** (10), 2014–2017.

Kirmeyer, G. J., Pierson, G., Clement, J., Sandvig, A., Snoeyink, V., Kriven, W. & Camper, A. 2000 *Distribution System Water Quality Changes Following Implementation of Corrosion Control Strategies*. AWWA Research Foundation, Denver, USA, 333.

Kuch, A. 1984 Korrosion und Schutzchichtbildung durch Leitungswasser. *Gwf. Gas Wasserfach* **81**, 611–615, 628–633.

Lamsal, R., Montreuil, K. R., Kent, F. C., Walsh, M. E. & Gagnon, G. A. 2012 Characterization and removal of natural organic matter by an integrated membrane system. *Desalination* **303**, 12–16.

Lee, J. Y., Pearson, C. R., Hozalski, R. M. & Arnold, W. A. 2008 Degradation of trichloronitromethane by iron water main corrosion products. *Water Res.* **42** (8–9), 2043–2050.

Li, X. & Zhao, H. 2006 Development of a model for predicting trihalomethanes propagation in water distribution systems. *Chemosphere* **62** (6), 1028–1032.

Liang, L. & Singer, P. C. 2003 Factors influencing the formation and relative distribution of haloacetic acids and trihalomethanes in drinking water. *Environ. Sci. Technol.* **37** (13), 2920–2928.

Lin, J., Ellaway, M. & Adrien, R. 2001 Study of corrosion material accumulated on the inner wall of steel water pipe. *Corros. Sci.* **43** (11), 2065–2081.

Lytle, D. A. & Snoeyink, V. L. 2002 Effect of ortho- and polyphosphates on the properties of iron particles and suspensions. *J. Am. Water Works Assoc.* **94** (10), 87–99.

Maddison, L. A., Gagnon, G. A. & Eisnor, J. D. 2001 Corrosion control strategies for the Halifax regional distribution system. *Can. J. Civ. Eng.* **28** (2), 305–313.

Madigan, M. T., Martinko, J. & Parker, J. 2000 *Brock Biology of Microorganisms*, 9th edn. Prentice-Hall, Englewood Cliffs, NJ, USA.

Marhaba, T. F. & Van, D. 2000 The variation of mass and disinfection by-product formation potential of dissolved organic matter fractions along a conventional surface water treatment plant. *J. Hazard. Mater.* **74** (3), 133–147.

Matheson, L. J. & Tratnyek, P. G. 1994 Reductive dehalogenation of chlorinated methanes by iron metal. *Environ. Sci. Technol.* **28** (12), 2045–2053.

McNeill, L. S. & Edwards, M. 2001 Iron pipe corrosion in distribution systems. *J. Am. Water Works Assoc. A* **93** (7), 88–100.

Montgomery, D. C. 2009 *Design and Analysis of Experiments*, 7th edn. John Wiley & Sons, USA.

Pearson, C. R., Hozalski, R. M. & Arnold, W. A. 2005 Degradation of chloropicrin in the presence of Fe(0). *Environ. Toxicol. Chem.* **24** (12), 48–53.

Pecher, K., Haderlein, S. B. & Schwarzenbach, R. P. 2002 Reduction of polyhalogenated methanes by surface-bound Fe (II) in aqueous suspensions of iron oxides. *Environ. Sci. Technol.* **36** (8), 1734–1741.

Rajagopal, V. K. & Burris, D. R. 1999 Reduction of 1,2-dibromoethane in the presence of zero-valent iron. *Environ. Toxicol. Chem.* **18** (8), 1779–1782.

Rodriguez, M. J., Sérodes, J. B. & Levallois, P. 2004 Behavior of trihalomethanes and haloacetic acids in a drinking water distribution system. *Water Res.* **38** (20), 4367–4382.

Rossman, L. A., Brown, R. A., Singer, P. C. & Nuckols, J. R. 2001 DBP formation kinetics in a simulated distribution system. *Water Res.* **35** (14), 3483–2389.

Sarin, P., Snoeyink, V. L., Bebee, J., Jim, K. K., Beckett, M. A., Kriven, W. M. & Clement, J. A. 2004a Iron release from corroded iron pipes in drinking water distribution systems: effect of dissolved oxygen. *Water Res.* **38** (5), 1259–1269.

Sarin, P., Snoeyink, V. L., Lytle, D. A. & Kriven, W. M. 2004b Iron corrosion scales: model for scale growth, iron release, and colored water formation. *J. Environ. Eng.* **130** (4), 364–373.

Siantar, D. P., Schreier, C. G., Chou, C. S. & Reinhard, M. 1996 Treatment of 1,2 dibromo-3-chloropropane and nitrate contaminated water with zero-valent iron or hydrogen/palladium catalysts. *Water Res.* **30** (10), 2315–2322.

Singer, P. C., Obolensky, A. & Greiner, A. 1995 DBPs in chlorinated North Carolina drinking waters. *J. Am. Water Works Assoc.* **87** (10), 83–92.

Stumm, W. & Sulzberger, B. 1992 The cycling of iron in natural environments – considerations based on laboratory studies of

heterogeneous redox processes. *Geochim. Cosmochim. Acta* **56** (8), 3233–3257.

USEPA 1995 *Determination of Haloacetic Acids and Dalapon in Drinking Water by Liquid–Liquid Extraction, Derivatization and Gas Chromatography with Electron-Capture Detection.* National Exposure Research Laboratory, Office of Research and Development, Cincinnati, OH, USA, Method 552.2.

Uyak, V., Ozdemir, K. & Toroz, I. 2007 Multiple linear regression modeling of disinfection by-products formation in Istanbul drinking water reservoirs. *Sci. Total Environ.* **378** (3), 269–280.

Vikesland, P. J., Ozekin, K. & Valentine, R. L. 1998 Effect of natural organic matter on monochloramine decomposition: pathway elucidation through the use of mass and redox balances. *Environ. Sci. Technol.* **32** (10), 1409–1416.

Williams, D. T., LeBel, G. L. & Benoit, F. M. 1997 Disinfection byproducts in Canadian drinking water. *Chemosphere* **34** (2), 299–316.

Yang, X. & Shang, C. 2004 Chlorination byproduct formation in the presence of humic acid, model nitrogenous organic compounds, ammonia, and bromide. *Environ. Sci. Technol.* **38** (19), 4995–5001.

Ye, B., Wang, W., Yang, L. & Wei, J. E. X. 2009 Factors influencing disinfection by-products formation in drinking water of six cities in China. *J. Hazard. Mater.* **171** (1–3), 147–152.

Zhang, H. & Andrews, S. A. 2012 Effects of phosphate-based corrosion inhibitors on the kinetics of chlorine degradation and haloacetic acid formation in contact with three metal materials. *Can. J. Civ. Eng.* **39** (1), 44–54.

Zhang, L., Arnold, W. A. & Hozalski, R. M. 2004 Kinetics of haloacetic acid reactions with Fe(0). *Environ. Sci. Technol.* **38** (24), 6881–6889.

Zhou, Q., Maurice, P. A. & Cabaniss, S. E. 2001 Size fractionation upon adsorption of fulvic acid on goethite: equilibrium and kinetic studies. *Geochim. Cosmochim. Acta* **65** (5), 803–812.