

Formation characteristics of haloacetic acids from phenols in drinking water chlorination

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ABSTRACT

Haloacetic acids (HAAs) are typical chlorination disinfection by-products in drinking water. Apart from natural organic matter, synthetic organic compounds in raw water contribute to HAAs due to their high frequency of detection in raw water and high reactive activities with chlorine. Formation characteristics of HAAs from synthetic organic compounds were investigated using seven phenols as models in the chlorination process. Two HAAs, trihaloacetic acid (TCAA) and dihaloacetic acid (DCAA), were generated and TCAA was the main product. The molar yields of HAAs varied between 0.087 mol/(mol phenol) from resorcinol to 0.251 mol/(mol phenol) from 2,4,6-trichlorophenol at pH 7.0. Phenols having para- or ortho-substituent groups were found to have higher reactive activities than those having meta-substituent groups in forming HAAs. HAA formation potential (HAAFP) of raw water was significantly enhanced with spiked phenols. These results indicate that synthetic organic compounds in raw water have high activities in yielding HAAs, and more research should be focused on their behaviors in drinking water disinfection.

Key words | chlorination, drinking water, HAAs, phenols

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INTRODUCTION

It has been well documented that chlorination disinfection by-products (DBPs) are produced through the reaction of chlorine with natural organic matter (NOM) (Boyce & Hornig 1983; Reckhow *et al.* 1990; Bond *et al.* 2012). Among these DBPs, haloacetic acids (HAAs), which are potentially carcinogenic after trihalomethanes, are typically the second most abundant class on a mass basis in drinking water (Krasner *et al.* 2006; Yan *et al.* 2012). The most common of the nine chlorinated and/or brominated HAAs are dichloroacetic acid (DCAA) and trichloroacetic acid (TCAA) (Qi *et al.* 2004). As HAAs are known or suspected carcinogens, their concentrations in drinking water have been regulated in the water standards of the WHO, EC, and US EPA among others. As an example, the US EPA has limited a total of five HAAs with the maximum contaminant level of 60 µg/L under the Stage 1 Disinfectants/Disinfection By-products Rule (Hozalski *et al.* 2001).

Previous studies have generally regarded NOM as the main precursor of HAAs, for NOM is the predominant

organic compound in clear raw water (Reckhow *et al.* 1990). With serious water pollution in many regions, large quantities of synthetic organic compounds, e.g., phenols, nitrobenzenes, anilines, and chlorobenzenes have been detected in raw water (Chen *et al.* 2005; Li *et al.* 2006). Although their levels are generally in the range of ng/L to µg/L, these organic compounds usually have higher reactive activities with chlorine than NOM does (Hu *et al.* 2002; Dodd & Huang 2004); therefore, the contribution of these organic compounds to HAA formation requires further investigation.

Phenols are widely used in the production of pesticides, dyes, drugs, plastics, antioxidants, and in leather preservation (Vermeulen *et al.* 2005). Due to their high levels and frequencies of detection in raw water, 11 phenols were classified by the US EPA as priority pollutants in the environment, and these include phenol, 3-methylphenol, 4-nitrophenol, 2,4-dichlorophenol, and 2,4,6-trichlorophenol (Mattinez *et al.* 1996). Thus, phenols

could be selected as a model in researching the formation characteristics of HAAs from synthetic organic compounds.

In previous studies, it was found that chlorination of phenols progressed in a number of steps. The first step is the chlorination of the aromatic ring, which leads to the formation of mono-, di-, and trichlorophenols (Patnaik *et al.* 2000; Ge *et al.* 2006, 2008). With the following steps of ring cleavage and hydrolysis, phenols may generate HAAs, THMs, and other DBPs (Boyce & Hornig 1983; Rebenne *et al.* 1996; Blatchley *et al.* 2003). Some dihydroxybenzenes and monohydroxybenzenes are chosen as model compounds in researching the chlorination kinetics of the THM formation mechanism from humic acid. As we know, resorcinol was determined to have a much higher THM formation potential than other phenolic compounds, and hence is regarded as the main component of humic acid in forming THMs (Rebenne *et al.* 1996; Yang & Shang 2004). Rebenne *et al.* (1996) investigated the chlorination of phenols and the formation of chloroform, demonstrating that the yields of chloroform are dependent on the type and position of the substituents of phenols. Further investigations were conducted by Gallard & von Gunten (2002), who found that resorcinol had the highest molar yield while *p*-nitrophenol had the lowest of 13 phenols in chloroform formation at pH 8.0. However, the formation of HAAs may be quite different from that of THMs in the chlorination process. For example, THMs have been enhanced in alkaline media while HAAs are enhanced in acid media in the chlorination of phenol (Guo & Chen 2009). Bond *et al.* (2009a) have studied the disinfection by-products formation and fraction behavior of natural organic matter surrogates and proved that ferulic acid has higher activity than resorcinol in yielding HAA₉. Guo & Chen (2009) investigated the halogenating reaction activity of five aromatic organic compounds (AOCs) and demonstrated that the chlorination or bromination reaction activities for the AOCs with electron donating functional groups were higher than for those with electron withdrawing functional groups. To our knowledge, the formation characteristics of HAAs from phenols have never been investigated in detail and remain uncertain.

Based on the above background, in this investigation we selected seven phenols as model synthetic organic

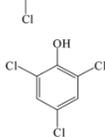
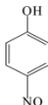
compounds and investigated their behavior in forming HAAs in chlorination. The objectives are: (1) to show the chlorination kinetic process of phenols in forming HAAs; (2) to compare the formation characteristics of HAAs from phenols with different substituent groups; (3) to present the variation of HAA formation potential (HAAFP) from raw water spiked with phenols; and (4) to discuss a possible rate-determining step of phenols in forming HAAs.

MATERIALS AND METHODS

Materials

Trichloroacetic acid (TCAA), dichloroacetic acid (DCAA), and chloroacetic acid (CAA) with purities greater than 99% were obtained from Acros Organics. 1,000 mg/L TCAA, DCAA, and CAA stock solutions were prepared in tert-butyl methyl ether (MtBE). Seven model phenols: phenol, 4-monochlorophenol (4-MCP), 2,4-dichlorophenol (2,4-DCP), 2,4,6-trichlorophenol (TCP), resorcinol, 3-methylphenol (*m*-cresol), and 4-nitrophenol (4-NP) were also purchased from Acros Organics with purities greater than 98%. Their physicochemical properties are listed in Table 1. 1,000 mg/L of phenol and resorcinol stock solutions were prepared which was based on the mass of raw material and diluted to target concentration with Milli-Q pure water (Milli-Q SP VOC, Millipore, Bedford, MA). Meanwhile, 1,000 mg/L of 4-MCP, 2,4-DCP, *m*-cresol and 4-NP, and 250 mg/L 2,4,6-TCP standard solution were also prepared with raw material and then diluted to target concentration with Milli-Q pure water, and 5–10 mL methanol in 100 mL aqueous solution (reagent for high-performance liquid chromatography, HPLC) were added due to their low aqueous solubility, respectively (spiked methanol does not yield HAAs in the chlorination process proved by our experiment). A stock of free chlorine solution was prepared from commercial sodium hypochlorite (NaOCl, 5% active chlorine) and then diluted with Milli-Q pure water. The acute concentration of sodium hypochlorite solution was standardized by sodium thio-sulfate titration.

Table 1 | Selected physicochemical properties of phenols

Compound	Molecular formula	MW (g/mol)	lgK _{ow}	S _w (g/100 mL, H ₂ O, 25 °C)	pK _a
Phenol		94.1	1.51	8.02	9.95
2-Monochlorophenol		128.5	2.15	2.10	8.44
2,4-Dichlorophenol		163.0	3.25	0.50	7.77
2,4,6-Trichlorophenol		197.5	3.75	0.042	6.19
4-Nitrophenol		139.1	1.79	1.63	7.08
m-Cresol		108.1	1.96	0.51	10.0
Resorcinol		110.1	0.88	147.3	9.91

Data from Gnam & Sheldon (1995) and Wagner & Schulz (2001).

Chlorination procedure

Kinetic experiment

Sodium hypochlorite was added with a concentration of 423 µmol/L in 500 mL aqueous solution, and then pH was adjusted to 7.0 by 50 mL phosphoric acid buffer solution and measured with a pH-meter (Mettler-Toledo, Switzerland). Then, 10 µmol/L phenol, 4-MCP, 2,4-DCP, 2,4,6-TCP, resorcinol, m-cresol, and 4-NP were added to the amber glass reactors, respectively, and placed in an air bath with temperature maintained at 25 ± 1 °C and reciprocating rate at 120 rpm. Samples of 25 mL were taken out at 0.08, 0.16, 0.5, 1, 2, 4, 6, 10, 14, 24, 36, and 48 h.

Spiked raw water experiment

Sodium hypochlorite was added with a concentration of 423 µmol/L in 500 mL natural water, which contained

2.29 mg/L humic acid, with pH adjusted to 7.0, then 1 µmol/L phenol and resorcinol were added and the same chlorination procedure as before was followed. Samples of 25 mL were taken out at 0.5, 2, 10, 24, 48, and 72 h.

Impact of pH

Sodium hypochlorite was added with a concentration of 423 µmol/L in 500 mL aqueous solution, pH was adjusted to 6.0, 7.0, 8.0, and 9.0, and 106 µmol/L phenol was spiked in amber glass reactors. Samples of 25 mL were taken out at 5, 10, 20, 30, 60, 120, 180, and 240 min.

The residual sodium hypochlorite in all samples was decomposed by adding excess sodium thiosulfate, and then samples at different reaction times were analyzed by gas chromatography-electron capture detector (GC-ECD) (Shimadzu GC-14C).

Analysis conditions

HAA concentrations for all samples were analyzed using a modified version of US EPA method 552.2. A 25 mL sample was acidified with 1.5 mL concentrated sulfuric acid and extracted with 3 mL of MtBE spiked with 300 $\mu\text{g/L}$ 1,2-dibromopropane as internal standard. Approximately 12 g of sodium sulfate was added to enhance the extraction. Then, 1 mL MtBE extraction was removed and mixed with 2 mL 10% sulfuric acidified ethanol and incubated for 2 h at 50 °C for HAA derivatization. After the derivatization, the solution was back-extracted with 5 mL 10% sodium sulfate solution to remove the excess methane. 1 μL MtBE extraction was injected under splitless injection mode for GC-ECD analysis with a SPB-5 fused silica capillary (25 m length \times 0.32 mm i.d. \times 0.25 μm film thickness). The column temperature was kept at 40 °C for 3 min and increased from 100 °C to 240 °C at a rate of 10 °C/min, held for 2 min. The concentrations of HAAs were determined by comparing the peak height of the samples and the calibration curves of the standards. The correlation coefficient of calibration curves of HAAs was greater than 0.99. The detection limits of DCAA and TCAA were 0.020 and 0.019 $\mu\text{g/L}$, respectively.

RESULTS AND DISCUSSION

Formation of HAAs from phenols in chlorination

Seven phenols: phenol, 4-MCP, 2,4-DCP, 2,4,6-TCP, resorcinol, m-cresol, and 4-NP were selected to investigate the formation characteristics of HAAs from phenols in water chlorination.

TCAA and DCAA were detected in the chlorination process and TCAA was the main product. Figure 1 shows the variation of TCAA and DCAA in reaction time from the seven phenols. TCAA and DCAA quickly yielded a response in 5 min when the phenols were in contact with chlorine, and then increased rapidly with time, especially in the initial 30 min. The plateau of HAA yield was observed to be 14 h from phenol, 4-MCP, 2,4-DCP, 2,4,6-TCP, m-cresol, and resorcinol, whereas it was delayed until 36 h from 4-NP.

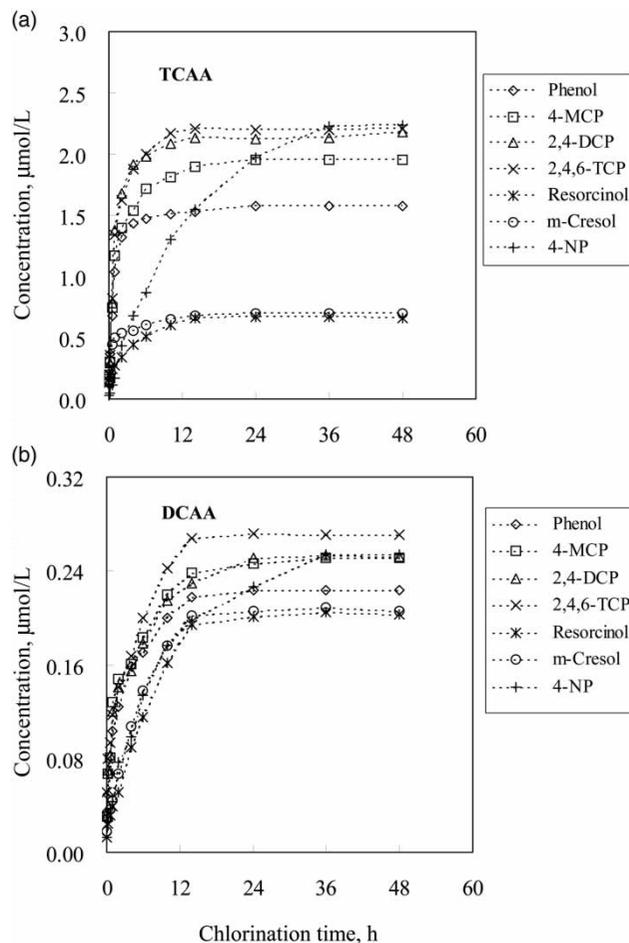


Figure 1 | Comparison of HAA formation in chlorination of different phenols (phenols = 10 $\mu\text{mol/L}$, $[\text{HOCl}] = 423 \mu\text{mol/L}$, pH 7.0).

Moreover, molar yields and formation rates of TCAA and DCAA were compared in the chlorination of the seven phenols. In Figure 1(a) and Table 2, it is noted that the highest molar yield and formation rate of TCAA was obtained from 2,4,6-TCP (0.224 mol/mol phenol). Meanwhile, 2,4-DCP (0.212 mol/mol phenol), 4-MCP (0.195 mol/mol phenol), and phenol (0.157 mol/mol phenol) also had high molar yields and formation rates of TCAA. For 4-NP (0.220 mol/mol phenol), although the formation rate of TCAA was far lower than that of 2,4,6-TCP, the molar yield of TCAA was almost as high as that of 2,4,6-TCP. However, dramatically lower molar yields and formation rates of TCAA were obtained from m-cresol (0.070 mol/mol phenol) and resorcinol (0.067 mol/mol phenol). The comparison of molar yield and formation rate of DCAA from

Table 2 | Molar yields of HAA formation from chlorination of phenols at pH 7.0

Compound	Molar yields of HAAs, mol/mol phenol	
	TCAA	DCAA
Phenol	0.157	0.022
4-Monochlorophenol	0.195	0.025
2,4-Dichlorophenol	0.212	0.025
2,4,6-Trichlorophenol	0.224	0.027
4-Nitrophenol	0.220	0.025
m-Cresol	0.070	0.020
Resorcinol	0.067	0.020

seven phenols is presented in Figure 1(b) and Table 2. Although minor differences occurred under the same chlorination conditions, the highest molar yield of DCAA from the seven phenols was still obtained from 2,4,6-TCP (0.027 mol/mol phenol), while the lowest yield of DCAA was achieved from m-cresol (0.020 mol/mol phenol) and resorcinol (0.020 mol/mol phenol).

These results indicate that phenols have high reaction activities with chlorine and generate HAAs in water disinfection. The formation potential of TCAA and DCAA is strongly related to the type and position of the substituent group of phenols. Summarizing the results, it is noted that phenols having *para*- and *ortho*-substituent groups have higher molar yields of HAAs, e.g., 4-MCP, 2,4-DCP, 2,4,6-TCP, and 4-NP; whereas phenols having a *meta*-substituent group have lower molar yields of HAAs, e.g., resorcinol and m-cresol. These results were similar to the report of Bond *et al.* (2009a, b, 2012), who found in studying the disinfection by-products formation and fraction behaviour of natural organic matter surrogates that ferulic acid has high HAA formation while resorcinol has low HAA formation. However, our data were dramatically different from the investigations of THMs formation in the chlorination of phenols. Gallard & von Gunten (2002) studied the formation of chloroform from 13 phenols at pH 8.0 and reported that the highest molar yield was from resorcinol (0.95 mol/mol phenol) and the molar yields of CHCl₃ from phenol, 4-MCP, 2,4-DCP, and 2,4,6-DCP was between 0.10 and 0.11 mol/mol phenol, while the lowest molar yield of CHCl₃ was from 4-NP (0.05 mol/mol phenol). In

addition, the electron withdrawing substituent group of phenols was found to decrease the formation rate of HAAs, e.g., -NO₂, for the electron withdrawing substituent group would block the electrophilic substitution in the first step of chlorination.

Chlorination of raw water with spiked model phenols

To better understand the formation process of HAAs from phenols in an actual aquatic environment, phenol and resorcinol were selected and then added to raw water in chlorination (the physicochemical properties of the raw water are listed in Table 3).

DCAA and TCAA were detected in the chlorination process and the results are shown in Figure 2. It was observed that concentrations of TCAA were enhanced with spiked phenol or resorcinol in raw water, while DCAA was affected little in this process. TCAA increased by 0.12 µmol/L in the initial 30 min with spiked phenol in raw water, and thereafter, approximately increased by 0.20 µmol/L at 72 h. This indicated that the HAAFP of the raw water was significantly enhanced. However, TCAA only increased by 0.05 µmol/L in the initial 30 min, with a final increase of 0.08 µmol/L at 72 h with spiked 1 µM resorcinol in the raw water. These results were consistent with the above formation potentials of HAAs from seven model phenols in chlorination, which further demonstrated that phenol had higher molar yields of HAAs than resorcinol.

Effect of pH on formation of HAAs from phenol in chlorination

Due to its high frequency of detection and concentration in raw water, phenol was selected from the seven model phenols to further investigate the effect of pH on the

Table 3 | Physicochemical properties of raw water

No.	Item	Value	No.	Item	Value
1	pH	6.61	2	Humic acid, mg/L	2.53
3	Carbonate, mg/L	116.04	4	Sulfate, mg/L	31.03
5	Chloride, mg/L	17.18	6	Phosphate, mg/L	0.01
7	Nitrate, mg/L	9.32	8	Phenol, mg/L	0.016

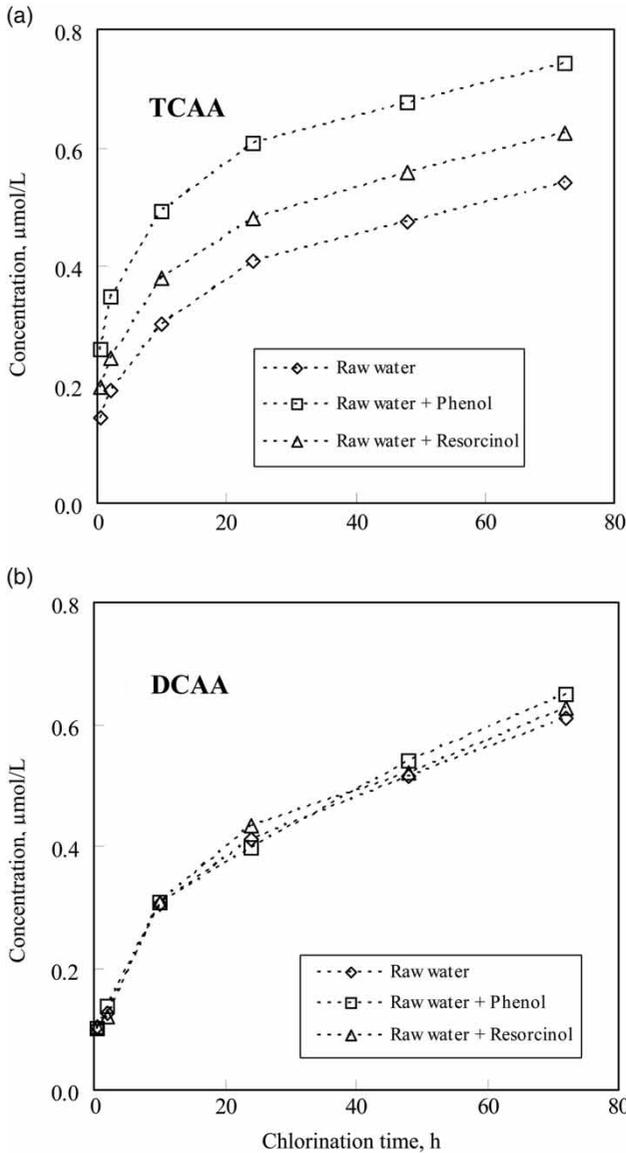


Figure 2 | Chlorination of raw water with addition of phenol and resorcinol (phenols = $1 \mu\text{mol/L}$, $[\text{HOCl}] = 423 \mu\text{mol/L}$, pH 7.0).

formation of HAAs. From Figure 3 it can be seen that the formation of TCAA was observed to be significantly influenced by pH while a minor influence was obtained on the formation of DCAA. With the increase of pH, the yield of TCAA declined gradually. For example, in the initial 5 min, the concentration of TCAA achieved $0.30 \mu\text{mol/L}$ at pH 6.0 while it was only $0.53 \times 10^{-3} \mu\text{mol/L}$ at pH 9.0. At 240 min, TCAA decreased from 1.64 to $0.36 \mu\text{mol/L}$ when pH increased from 6.0 to 9.0. However, the concentration

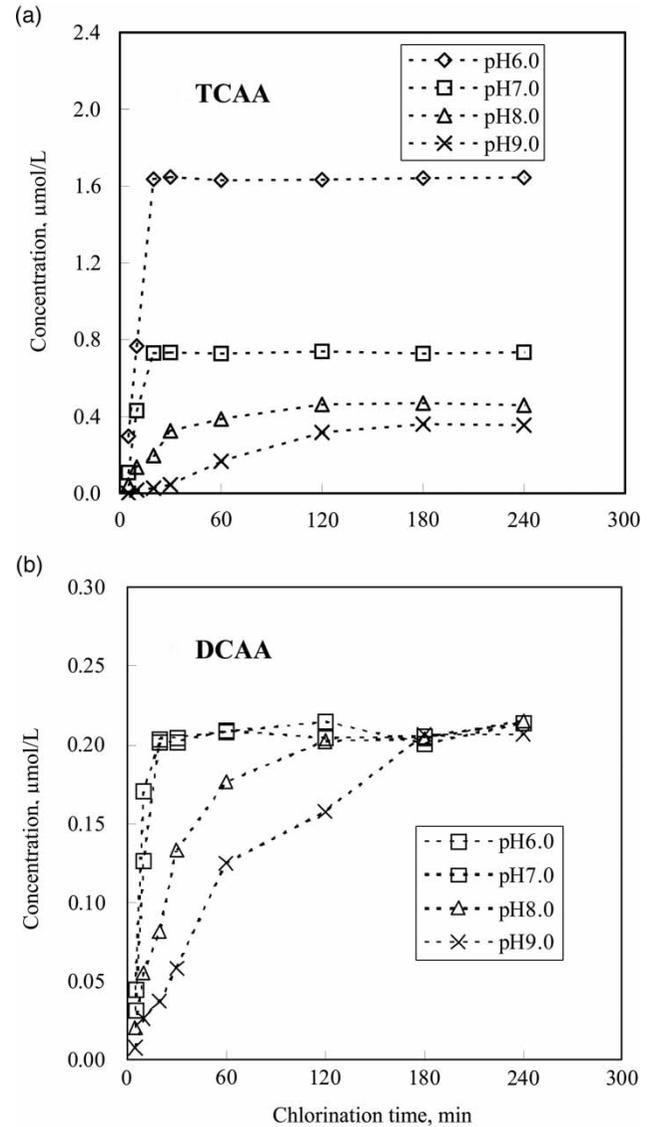


Figure 3 | Effects of pH on formation of HAAs from chlorination of phenol (phenol = $106 \mu\text{mol/L}$, $[\text{HOCl}] = 423 \mu\text{mol/L}$).

of DCAA varied little over the same pH range. The difference in pH effect on yields of DCAA and TCAA may be due to the different hydrolysis intermediates. DCAA precursors have been found to be less hydrophobic than TCAA (Liang & Singer 2003). Similar phenomena were reported by Guo & Chen (2009), who had tested the effect of pH on HAA formation for the reaction of aqueous chlorine with phenol and found that HAA production decreased with increase of the pH.

Rate determining step in the formation of HAAs from phenols

Chlorination of phenols is a successive progress. The first step is the chlorination of the aromatic ring, leading to the formation of mono-, di-, and trichlorophenols (Patnaik *et al.* 2000; Ge *et al.* 2006, 2008). With the next steps of ring cleavage and hydrolysis, phenols gradually produce HAAs (Boyce & Hornig 1983; Rebenne *et al.* 1996; Blatchley *et al.* 2003). Thus, the yield of trichlorophenol was a necessary step in the formation of HAAs. In our previous experiments, five chlorophenols were detected quantitatively by HPLC in the chlorination process, including 2-monochlorophenol (2-MCP), 4-monochlorophenol (4-MCP), 2,6-dichlorophenol (2,6-DCP), 2,4-dichlorophenol (2,4-DCP), and 2,4,6-trichlorophenol (2,4,6-TCP) (Ge *et al.* 2006, 2008).

Figure 4 shows the distribution of chlorophenols including MCP (2-MCP and 4-MCP), DCP (2,4-DCP and 2,6-DCP), TCP (2,4,6-TCP) and HAAs in chlorination of phenol at various pH values at 240 min (the ratio of each component remained steady at 240 min). It was observed that the concentration of TCP was only 3.83 $\mu\text{mol/L}$ at pH 6.0 while at pH 9.0, 74.62 $\mu\text{mol/L}$ was achieved; however, the

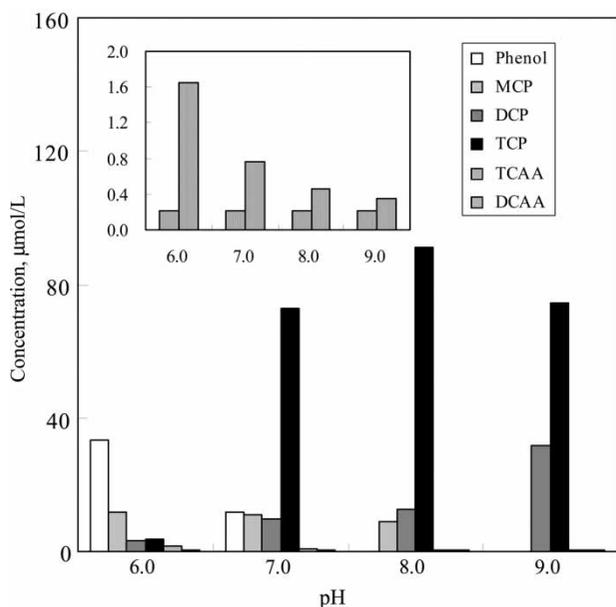


Figure 4 | Chlorination products of phenol at various pH values (phenol = 106 $\mu\text{mol/L}$, [HOCl] = 423 $\mu\text{mol/L}$, $T = 240$ min).

concentration of HAAs was not in proportion to the concentration of TCP in solution. For HAAs it was 1.86 $\mu\text{mol/L}$ at pH 6.0 while it was only 0.57 $\mu\text{mol/L}$ at pH 9.0. This indicates TCP is not a rate-determining intermediate in generating HAAs.

Mechanistic studies by Reckhow & Singer (1986) have linked a rise in levels of DCAA to diketone and then aldehyde formation after oxidation. Conversely, and in agreement with the resorcinol data, TCAA formation has been likened to THM formation and may proceed through common intermediates (Reckhow *et al.* 1990; Bond *et al.* 2009a, b). These results suggest hydrolysis is a key rate-limiting step in yielding HAAs, and further investigation may need to be conducted in determination of the hydrolysis products and the other DBPs being formed in chlorination of phenols.

CONCLUSION

In drinking water treatment, synthetic organic compounds could react with chlorine and contribute to HAAs. Using phenols as models of synthetic organic compounds, it was observed that TCAA and DCAA were generated and TCAA was the main HAA in chlorination. HAA yields from phenols depended on the type and position of the substituents linked to the benzene ring. The sequence of molar yield of HAAs is 2,4,6-TCP > 4-NP > 2,4-DCP > 4-MCP > phenol > *m*-cresol, resorcinol. Phenols that have *para*- and *ortho*-substituent groups have higher activities than those having a *meta*-substituent group in forming HAAs. Moreover, the HAAFP of raw water was significantly enhanced with spiked phenols. These results indicated that some synthetic organic compounds in raw water have high activities in forming HAAs and more research should be conducted on their behaviors in water chlorination.

ACKNOWLEDGEMENTS

We gratefully acknowledge the financial support from the Program for New Century Excellent Talents in University of China (NCET-10-0148), Research Foundation of

National Natural Science Foundation of China (No. 21277114).

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First received 30 January 2013; accepted in revised form 10 April 2013. Available online 12 September 2013