



# Effects of metal ions on disinfection byproduct formation during chlorination of natural organic matter and surrogates



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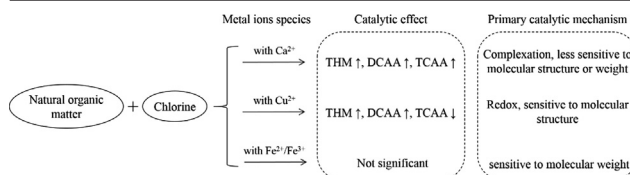
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## HIGHLIGHTS

- Primary catalytic mechanism of calcium and cupric were complexation and redox reaction, respectively.
- Catalytic effect of calcium was less sensitive to molecular structure or weight.
- Catalytic effect of cupric was greatly dependent on molecular structure.
- Catalytic effect of ferric and ferrous iron critically depended on molecular weight.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

### Article history:

Received 12 April 2015

Received in revised form 25 August 2015

Accepted 25 September 2015

Available online 23 October 2015

Handling editor: Jun Huang

### Keywords:

Catalytic effect

Model compounds

Trihalomethanes (THMs)

Haloacetic acids (HAAs)

Complexation

## ABSTRACT

The effects of calcium, cupric, ferrous and ferric ions on the formation of trihalomethanes (THMs) and haloacetic acids (HAAs) were investigated using natural organic matter (NOM), small molecular weight NOM surrogates and natural water samples. The results showed that the effects were greatly dependent on the disinfection byproduct (DBP) precursor structure and molecular weight, and metal ions species. While using NOM as precursors, addition of 4.00 mM calcium ions increased the formation of THMs, dihaloacetic acids (DHAAs) and trihaloacetic acids (THAAs) by 24–47%, 51–61% and 15–25%, respectively. Addition of cupric ions at 0.02 mM increased the formation of THMs and DHAAs by 74–83% and 90–100%, respectively, but decreased the formation of THAAs by 26–27%. Similar effect was not observed when 0.04 mM ferrous or ferric ions were added. The effects of calcium and cupric ions on DBP formation were generally more evident for the NOM surrogates than that for NOM. The primary catalytic effect of calcium ions was due to complexation and less sensitive to molecular structure or weight, while that of cupric ions was attributed to redox reactions and greatly dependent on molecular structure. Both ferric and ferrous iron had substantial effects on the DBP formation of surrogates (citric acid and catechol in particular), which implied that the catalytic effects of ferric and ferrous iron mainly depended on molecular weight. The catalytic effect of cupric ions was also observed on natural water samples, while the effects of calcium, ferrous and ferric ions on natural water samples were not evident.

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## 1. Introduction

Disinfection byproducts (DBPs) in drinking water are unintentionally formed by reactions between chemical disinfectants and the natural organic matter (NOM) that are ubiquitous in water.

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DBPs are a very complex mixture, which include 600 + identified species and much more species that are yet to be identified (Krasner et al., 2006; Bond et al., 2012). Many DBPs (e.g. halobenzoquinones) have been associated with various human cancers and reproductive complications (Hrudey and Charrois, 2012). Trihalomethanes (THMs) and haloacetic acids (HAAs) are among the few DBPs currently regulated around the world (Wang et al., 2015) partly because they are usually the two predominant DBP groups by mass and molarity and can to some extent represent the total DBP content, and partly because both THMs and HAAs are the primary decomposition end-products of many unstable and potentially more toxic intermediate DBPs (Zhai and Zhang, 2011; Bond et al., 2012). The formation and control of THMs and HAAs have been investigated in many studies (Westerhoff et al., 2004; Reckhow et al., 2004; Hua and Reckhow, 2007; Liu et al., 2008). Because of the complex chemical composition and molecular structure of NOM (Kornegay et al., 2000; Sutton and Sposito, 2005), simple organic compounds are usually used as NOM surrogates to determine the mechanisms of DBP formation (Boyce and Hornig, 1983; Chang et al., 2006; Bond et al., 2009; Zeng and Arnold, 2013; Hua et al., 2014). Previous studies have suggested that activated aromatics, amines and  $\beta$ -dicarbonyl species are among the main functionalities of NOM that are more responsible for the formation of THMs and HAAs (Reckhow and Singer, 1985; Zhai and Zhang, 2011; Bond et al., 2012; Pan and Zhang, 2013).

The inorganic components of natural water affect the formation of DBPs during the disinfection process. The most notable inorganic component, which has been extensively studied, is bromide ions (Hua et al., 2006; Hu et al., 2009; Shi et al., 2013). Several other inorganic anions, such as nitrite and chloride, can also alter DBP concentrations and speciation during chlorination (Navalon et al., 2008; Hu et al., 2009). Furthermore, metal ions, which are ubiquitous in natural water and water distribution systems and may be deliberately added for water treatment, react with DBP precursors and disinfectants. NOM can form complexes with hardness ions (e.g. calcium, ferrous and ferric ions) (Stumm and Morgan, 1996; Liu et al., 2007), which may substantially change the reactivity of the NOM to the disinfectants. NOM can also be chemically or physically bound to the surface of ferric or aluminum coagulant flocs. Some transition metal ions (e.g. cupric ions) can catalyze the decomposition of the disinfectants leading to the formation of more powerful oxidants, which react with NOM and change their properties. The concentrations of various metal ions could differ drastically among different water sources (Crittenden et al., 2012). For example, the calcium and ferrous iron concentrations can vary from  $\sim 1$  to  $>50$  mg L<sup>-1</sup> and from  $<0.05$  to  $>0.5$  mg L<sup>-1</sup>, respectively. The dissolved ferric iron concentration is usually very low ( $<1$  mg L<sup>-1</sup>), which greatly depends on the NOM concentration and properties. Primarily due to anthropogenic contamination, the cupric ion concentration in surface water can be up to several mg L<sup>-1</sup> (Liu et al., 2007). The study of the effects of metal ions on DBP formation and speciation is therefore of both theoretical and practical significance.

A few studies have been conducted regarding metal ions effects. Among the metals, copper has drawn particular attention due to its significant catalytic effect. Duggirala (1996) first reported that the presence of a small amount of cupric ions remarkably increased the formation of THMs and proposed that the increase may be attributed to a complexation between the cupric ions and DBP precursors. Fu et al. (2009) further investigated the role of cupric ions in chlorination and found that copper fortifies the formation of hydroxyl free radicals, which in turn break down the large NOM molecules. Calcium, magnesium and ferric ions were also found to be capable of influencing the formation of DBPs by complexation with DBP precursors. Navalon et al. (2009) found that the formation of THMs was enhanced by 32% when 30–100 mg L<sup>-1</sup> magne-

sium or calcium ions were added to natural water or model compound solution before chlorination. They suggested that the complexation between the dissolved metal ions and DBP precursors was the crucial step in the metal catalysis, although they did not study the effect of calcium on HAA formation. Liu et al. (2011) investigated the presence of ferric ions during NOM chlorination and found that 0.5 mg L<sup>-1</sup> ferric ion increased THM levels by 10% in springtime Yangtze River water. Liu et al. (2012) revealed that several metal ions (magnesium, ferrous, manganese, cupric and aluminum) enhanced HAA formation but inhibited THM formation when using tannic acid as the DBP precursor. The authors proposed that two different mechanisms (metal complexation and enhancement of hydroxyl radical generation) were involved in the chlorination process. The effects of metal ions on the chlorination of algae has also been investigated, and iron and manganese were found to reduce HAA yields during the chlorination of *Chlorella vulgaris* due to a metal hydroxide/oxide coating on the algae (Ge et al., 2011).

Previous studies suggested that the calcium, cupric and ferric ions had catalytic effect on DBP formation, the degree of which however differed among the water sources (i.e. contained NOM) and the metal ions. In addition, two general mechanisms, complexation and free radical generation, were proposed for the interpretation of the catalytic effects exerted by all the metal ions. NOM are inherently heterogeneous in terms of the molecular weight and molecular structure. In this study, the catalytic effects of four selected metal ions (calcium, cupric, ferrous and ferric ions) on both macromolecular NOM (i.e. fulvic acid and humic acid) and small molecular weight NOM surrogates that represent different NOM fragments were investigated. The objective of this study was to investigate the role of NOM structure and size in the metal ion-induced catalytic effects on the formation and speciation of THMs and HAAs, and to explore the primary catalytic mechanisms for each selected metal ion.

## 2. Materials and methods

### 2.1. Original water samples

NOM (humic acid and fulvic acid) solutions, NOM surrogate solutions and natural water samples were used in this study. All the NOM and NOM surrogate working solutions were freshly prepared by diluting their respective stock solutions. A humic acid (HA) stock solution of 1.0 g L<sup>-1</sup> was prepared by dissolving commercial HA (Sigma–Aldrich, Switzerland) into an alkaline solution (NaOH, pH = 12), then the pH of the solution was gradually adjusted to neutral using 1.0 M hydrochloric acid (A.R., Beijing Chemical Works, China). The solution was then filtered through a 0.45  $\mu$ m membrane filter (HAWP04700, Millipore, USA) and was stored in a refrigerator (4 °C) until use for a maximum of 30 d. The HA working solution (obtained by diluting the stock solution by 100-fold) had a total organic carbon (TOC) concentration of 1.6 mg L<sup>-1</sup>. A fulvic acid (FA) stock solution was prepared by directly dissolving commercial FA (JONLN, China) into ultrapure water. The FA stock solution was diluted 100-fold to obtain the working solution, which had a TOC concentration of 1.1 mg L<sup>-1</sup>.

The NOM surrogates were selected primarily based on the conceptual molecular structure for FA/HA (Fig. S1 in Supplementary Information). They include two aliphatic carboxylic acids (pyruvic acid and citric acid) and three dihydroxybenzenes (catechol, resorcinol and hydroquinone). The chemical structures for the five selected surrogate compounds are illustrated in Fig. 1. All surrogate compounds were obtained in analytical grade (Sinopharm Chemical Reagent Co. Ltd, China). All stock solutions of surrogate compounds were prepared at concentration of 1.0 g L<sup>-1</sup>. The working solutions were prepared by diluting the respective stock solutions by 1000-fold.

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