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Effects of ozone pretreatment on the formation of disinfection by-products and its associated bromine substitution factors upon chlorination/chloramination of Tai Lake water

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HIGHLIGHTS

- Preozonation markedly increased some DBPs in chlorination/chloramination.
- Chloramine was a good choice for reducing the bromo- and total DBPs yields.
- The BSFs of DBPs changed with disinfection modes.

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ABSTRACT

This study investigated the effects of preozonation on disinfection by-products (DBPs) formation during chlorination and chloramination of the water collected from Tai Lake. Results showed that the high ozone dose (0.6–1.0 mg O_3/mg DOC) pretreatment reduced the yields of trihaloacetic acids (reduced 62–63% in chlorination), dihaloacetonitriles (reduced 53–55% and 14–26% in chlorination and chloramination, respectively) and trihaomethanes (reduced 19% in chloramination), but markedly increased the formation of halonitromethanes (increased 4.7–5.6 times in chlorination and 2.1–2.7 times in chloramination), haloketones (increased 4.8–7.1 times in chlorination and 2.5–2.9 times in chloramination) and dihaloacetic acids (increased 1.5–2.4 times in chlorination and 0.3–0.6 times in chloramination). Thus the high ozone dose pretreatment should be avoided during chlorination/chloramination of Tai Lake water. Also, chloramination (with and without preozonation) produced much lower DBPs yields as compared with chlorination (with and without preozonation), indicating that chloramine was a better choice to control the DBPs yields. Further analysis also revealed that the bromine substitution factors (BSFs) of DBPs varied with disinfection mode. In chlorinamination, the BSFs generally showed a decrease trend with the ozone dose, yet in chlorination, the BSFs mostly exhibited first an increase and then a decrease trend. Moreover, the BSFs of DBPs in chloramination (with or without preozonation) were dominantly lower than those in chlorination (with or without preozonation).

1. Introduction

As a powerful oxidant, ozone is becoming increasingly popular in water treatment works because it may 1) efficiently kill the bacteria, viruses, and protozoans within a short reaction time; 2) reduce the concentration of heavy metals by oxidizing them into insoluble metal oxides, which are easily removed by post-filtration; 3) reduce or eliminate the color, taste and odor problems in drinking water; and 4) effectively remove a variety of organic micropollutants (Langlais et al., 1991; Lee et al., 2012; Mitrakas et al., 2008; Seo et al., 2010). However, ozone decays rapidly in drinking water and cannot produce a persistent disinfectant residual in distribution system. To provide a long-term guard for microbial safety, chlorine (Cl_2) or monochloramine (NH_2Cl) is often used as a secondary disinfectant in practical application. Therefore, the impacts of ozone on the formation of disinfection by-products (DBPs) during the subsequent chlorination/chloramination should be given attention.

Previous studies showed that the effects of preozonation on the formation of regulated DBPs depended on the water quality parameter, such as SUVA (specific ultraviolet absorbance, obtained by ultraviolet absorbance at 254 nm (UV_{254}) times 100 divided by the dissolved organic carbon (DOC) concentration) (Hu et al., 2010b; Hua and Reckhow, 2007; Yang et al., 2012). For example, during chlorination, preozonation process effectively reduced the formation of trihalomethanes (THMs) and haloacetic acids (HAAs) in waters with high

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SUVA values (>2 L mg^{-1} m^{-1}). Yet for the waters with low SUVA values (<2 L mg^{-1} m^{-1}), the effects of ozonation were less certain, i.e. THMs and HAAs formation reduced, enhanced, or kept stable (Yang et al., 2012). Formation of the emerging unregulated DBPs, such as haloacetonitriles (HANs), haloketones (HKs), and halonitromethanes (HNMs), under sequenced ozonation–chlorination or ozonation–chloramination process had also been studied infrequently. Generally, the preozonation process significantly increased the formation of HNMs whether during chlorination or chloramination (Hu et al., 2010a). However, for the unstable DBPs such as HANs and HKs, mixed effects of preozonation were observed. Several studies reported that preozonation significantly decreased the yields of HANs but increased the formation of HKs during chlorination or chloramination (Hua and Reckhow, 2007; Yang et al., 2012); yet another study showed that the increase or decrease of HANs and HKs upon ozonation–chlorination seemly depended on the ozone dosage (Chiang et al., 2010). Thus, for a specific drinking water, especially for those with SUVA < 2, it is necessary to investigate the effects of ozone, including the ozone dosage, on the formation of all kinds of DBPs in detail, which may provide the basic and useful information for the better control of DBPs in the subsequent water treatment.

Tai Lake, one of the most important drinking water sources in Yangtze River delta in China, is located on the border of Jiangsu and Zhejiang provinces with an area coverage of 2340 km^2 and supplies potable water for the cities around it. However, the deterioration of water quality in Tai Lake had been a public concern. Serious cynobacteria bloom had been observed in Tai Lake for more than a decade. Since the ozonation is powerful in eliminating the bloom related algal toxins, odor and color problems (Langlais et al., 1991), and moreover, a large amount of DOC with low SUVA could be released after the peak of algal bloom (Nguyen et al., 2005; Ye et al., 2011), it is extremely necessary to investigate the effects of preozonation on DBPs formation during chlorination/chloramination of Tai Lake water, and therefore provide the basic information to the upgrade of water treatment technique in related water works.

On the other hand, to alleviate the low water level in winter and the algal bloom occurring in summer, the Tai Lake drew water from Yangtze River every year, which contained high bromide level due to the inburst of salt tide from estuaries (You et al., 2012). Thus, a relatively high level of bromide ion (248 μg/L) was detected in Tai Lake water (Hong et al., submitted for publication). It is known that the presence of bromide ion during chlorination/chloramination would result in the increase of DBPs yields and the formation of DBPs shifting to more brominated species (Chang et al., 2001; Hong et al., 2013; Hu et al., 2010b). As the brominated DBPs have much higher health risks than their chlorinated analogs, some efforts have been made to investigate the bromine substitution degree (BSD) of DBPs formation as a function of disinfection conditions, such as the factors of Br^-/DOC, chlorine/chloramine dose, reaction time, pH and temperature in order to control the brominated DBPs better (Chang et al., 2001; Hong et al., 2013; Richardson et al., 2007). Yet very few studies were carried out to investigate the impacts of preozonation on the BSD of DBPs during chlorination/chloramination, and the investigated DBPs only included THMs and HAAs (Zhang et al., 2008). Preozonation can affect the formation of DBPs, and they would also exert influence on the competition between chlorine (included the chlorine release from the chloramine) and bromine during the reactions with organic matter. So it is necessary to systematically study the effects of preozonation on BSD of DBPs formation, which include the regulated and the emerging DBPs classes.

Regarding the information above, this study aimed to investigate the effects of ozone pretreatment on the formation of a series of DBPs during chlorination and chloramination of the water collected from Tai Lake. Five classes of DBPs were selected that represent both regulated (THMs and HAAs) and emerging DBPs (HANs, HKs and HNMs). As the high level of bromide ion presented in Tai Lake water, bromine substitution factors (BSFs) of DBPs, which was an unbiased index of BSD, among disinfection modes (Cl_2, NH_2Cl, $O_3 + Cl_2$ and $O_3 + NH_2Cl$) were also evaluated.

2. Material and methods

2.1. Water samples

The water sample in Tai Lake was collected from the water intake of Gongohu water works in Nov. 2011 and filtered with GF/F filter (0.45 μm) before used in chlorination/chloramination or ozone-chlorination/chloramination. The detailed water quality parameters were described in our previous study (Hong et al., submitted for publication): DOC = 10.34 mg/L, $UV_{254} = 0.054$, SUVA = 0.52, total dissolved nitrogen = 0.95 mg/L, $NO_3^- - N-$ = 0.2 mg/L, $NO_2^- - N$ = 4 μg/L, organic nitrogen = 0.61 mg/L, and bromide = 248 μg/L.

2.2. Chlorination/chloramination experiments

NaClO was purchased from Sigma (reagent grade, 5%). Monochloramine was prepared by mixing an equal volume of NaClO and NH_4Cl (weight ratio: 4 mg/L Cl_2 to 1 mg/L N) before used (Yang et al., 2007). Both the chlorination and chloramination were conducted in a series of glass tubes with glass septa (the full volume ≈ 135 mL), and Cl_2/NH_2Cl doses were chosen to ensure that a substantial Cl_2/NH_2Cl residual (>2 mg/L) was present after incubation for 1 day so that formation reactions would not be chlorine/monochloramine limited. Whether for chlorination or for chloramination, each condition ran in two replicates. All samples were incubated headspace free in the dark at 20 ± 1° C. After disinfection, the water sample was divided into several parts for DBPs analysis: ammonium chloride (final concentration: 100 mg L^{-1}) was used to quench the chlorine and monochloramine in the water sample for THMs, HANs, HKs and HAAs analysis (refereed to EPA551.1 and EPA552.3), while for HNMs, ammonium sulfate (0.58 g per 45 mL water) was used (Huang et al., 2013).

2.3. Ozone-chlorination and ozone-chloramination experiments

Ozone was produced using an ozone generator (Jiahuan YT-50G, Guangzhou, China) fed with ultra-high purity oxygen, and introduced immediately into the ultrapure water using a diffuser placed at the bottom of the reactor until the ozone reached the equilibrium concentration (about 25 mg/L). Ozonation was conducted in a series of conical flasks with glass septa, and each was completely filled with water samples (≈280 mL, ensuring that the water volume is enough for two replicates in chlorination). Then a pre-calculated volume (82 mL) of water was removed from each flask, and series of ozone stock solution and ultrapure water (82 mL + 0 mL; 49.2 mL + 32.8 mL; 16.4 mL + 65.6 mL) were added in the flasks. In this way, the same DOC concentrations during ozonation were obtained, and ensure the ozone doses were 1.0, 0.6, and 0.2 mg O_3/mg DOC, which were commonly used during drinking water pretreatment (Chiang et al., 2009). After that, the conical flasks were shaken up for 20 min, and the excess ozone was removed by nitrogen flow. Then the ozonated water samples were used for subsequent chlorination/chloramination (same as Section 2.2) as well as the UV_{254} determination. Yet the final UV_{254} values in ozonated water and DBPs yields in ozone-chlorinated and ozone-chloraminated water were recalculated as the total DOC is equal to 10.34 mg/L.

2.4. DBPs analysis

THMs (chloroform (TCM), bromodichloro- (BDCM), chlorodibromo- (CDBM) and tribromomethane (TBM)), HANs (trichloro-(TCAN), dichloro-(DCAN), bromochloro (BCAN) and dibromoacetonitrile (DBAN)) and HKs (1,1-dichloro-(DCP) and 1,1,1,-trichloroproprone (TCP)) were extracted using methyl tert-butyl ether (MTBE), and analyzed by GC/ECD system, which referred to EPA551.1.