Technical Note

Terminating pre-ozonation prior to biological activated carbon filtration results in increased formation of nitrogenous disinfection by-products upon subsequent chlorination

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HIGHLIGHTS

• DON and SMPs increase in BAC-filtered water after terminating pre-ozonation.
• Terminating pre-ozonation increases N-DBP levels in BAC-filtered water upon chlorination.
• N-DBP precursors were not only derived from the source water but also from the BAC filter.

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ABSTRACT

Previous research demonstrated that ozone dosed before biological activated carbon (BAC) filtration reduces the formation of disinfection by-products (DBPs) upon subsequent chlorination. The current work aimed to evaluate the impact of terminating this pre-ozonation on the ability of the BAC to remove the precursors of N-DBPs. More N-DBP precursors passed into the post-BAC water when the pre-ozonation was terminated, resulting in greater formation of N-DBPs when the water was subsequently chlorinated, compared to a parallel BAC filter when the pre-ozonation was run continuously. Moreover, the N-DBP formation potential was significantly increased in the effluent of the BAC filter after terminating pre-ozonation, compared with the influent of the BAC filter (i.e. the effluent from the sand filter). Therefore, while selectively switching pre-ozonation on/off may have cost and other operational benefits for water suppliers, these should be weighed against the increased formation of N-DBPs and potential associated health risks.

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1. Introduction

In recent years, the presence of halogenated nitrogenous disinfection by-products (N-DBPs), including haloacetonitriles (HANs), haloacetamides (HAcAms) and halonitromethanes (HNMs), in drinking water has gained attention because these compounds are significantly more genotoxic and cytotoxic than the currently regulated carbonaceous DBPs (C-DBPs), such as trihalomethanes (THMs) and haloacetic acids (HAAs) [Plewa et al., 2008; Richardson and Ternes, 2014]. N-DBPs are generally present in drinking water at lower concentrations than THMs [Krasner et al., 2006; Hou et al., 2012]. However, because of population growth and rising water demand, water suppliers are increasingly forced to treat water sources which are polluted with algae and/or municipal wastewater, both of which are known to be key sources of dissolved organic nitrogen (DON) and N-DBP precursors. This
can thus cause a dramatic increase in N-DBP concentrations (Chu et al., 2011; Shah and Mitch, 2012).

Numerous DBPs can be controlled in drinking water systems by more effective removal of dissolved organic matter (DOM)—the main precursors of DBPs—through physical-chemical treatment processes, such as enhanced coagulation and filtration, upstream of the disinfection process. However, N-DBP (e.g., HAN, HNM, HAcAm) precursors exhibit relatively low removal by conventional DWTPs using coagulation-sedimentation-filtration (Bond et al., 2011; Chu et al., 2011; Roccaro et al., 2014). Previous studies have demonstrated that coupling pre-ozonation with biological activated carbon (O$_3$–BAC) can significantly reduce the precursors of regulated C-DBPs and trace organic contaminants (Karnik et al., 2005; Xu et al., 2007; Gerrity et al., 2011). Also, a recent study found that ozonation chemically alters the molecular structures of the precursors, which increases the biodegradability of N-containing organic compounds; the subsequent BAC filtration substantially reduced the formation of the N-DBPs, thus highlighting a synergistic effect of O$_3$ and BAC (Chu et al., 2012). However, it is often the case in water industry practice for pre-ozonation to be intermittently dosed before BAC filtration, for a number of reasons, which may include cost-savings, maintenance of the ozone equipment, or unexpected ozone equipment failure.

Therefore, this study aims to examine the impact of intermittent pre-ozonation on the performance of BAC filtration for controlling N-DBP formation during subsequent chlorination. The formation of chlorinated HAcAms, HANS, HNM$s$, THMs, and HAAs was the focus of the study (rather than brominated and iodinated analogues) because of the low bromide and iodide levels in the studied waters. Changes in DBP precursors in the source water and treated water were the main independent variables of interest in this study.

2. Materials and methods

2.1. Materials

Standards for two HAcAms, dichloroacetamide [DCAcAm] and trichloroacetamide [TCAcAm], were obtained from Alfa Aesar (Karlsruhe, Germany). Standards for two HANS (dichloroacetonic acid [DCAc] and trichloroacetonic acid [TCAc]) were purchased from Sigma–Aldrich (Oakville, ON, Canada). Ultrapure water was produced with a Millipore Milli-Q Gradient water purification system (Billerica, MA, USA). All other materials were at least analytical grade and obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China) unless otherwise noted.

2.2. Pilot-plant process flow

The pilot plant was located in a conventional drinking water treatment plant (DWTP) situated near Lake Taihu, and operated at a flow rate of 1 m$^3$ h$^{-1}$. A chart of the pilot plant process flows is shown in Fig. 1. The raw water used for the pilot-scale treatment processes was obtained from an intake in the Meiliang Bay of Lake Taihu, which is the third largest freshwater lake in China and the potable water source of many cities and towns in Eastern China, including Shanghai, Suzhou, Wuxi and Yixing. In recent years, the accumulation of nutrient-rich sewage and agricultural runoff in this shallow lake has caused severe eutrophication and nuisance algae blooms (Yang et al., 2008). Therefore, the O$_3$–BAC process was added after conventional treatment processes in most of DWTPs in these cities, aimed at improving the final treated drinking water quality.

The conventional treatment sequence in the pilot plant was coagulation-sedimentation (20-mg L$^{-1}$ polymeric aluminum sulfate, 20-min retention time) and sand filtration (7-min retention time), which is common practice among Chinese DWTPs, as shown in Fig. 1. The DWTPs did not use any pre-oxidant before filtration. The quality of the filtered water (i.e. treated by these conventional processes), such as DOC (median = 2.40 mg L$^{-1}$) and DON (median = 0.51 mg L$^{-1}$), is shown in Supplementary Material (SM) Table SM1. O$_3$–BAC was placed after the conventional processes, as shown in Fig. 1. Ozonation was carried out in an ozone contact chamber (4.5-m in height, and 0.4-m in diameter) operated in concurrent flow mode. Ozone was generated from air using an ozonator (HMY-F, Huangming, China) and entered the water in the form of small bubbles through a porous titanium plate. The dissolved ozone dosage was 2.0–2.5 mg L$^{-1}$ (ozone residual was lower than 0.1 mg L$^{-1}$), and the contact time was 30 min. Subsequent to ozonation, the water was fed into the same two granular activated carbon filters (4.0-m in height, and 0.3-m in diameter) where the biological process took place (i.e. BAC). The empty bed contact time, backwashing cycle and filtration rate of the BAC column were maintained at 15 min, 4 d and 7.0 m h$^{-1}$, respectively. The bed depth, effective size, uniformity coefficient, iodine value, methylene blue value, and density of the GAC were 1.6 m, 0.55–0.75 mm, <1.9, 1000 mg g$^{-1}$, 266 mg g$^{-1}$ and 450 g L$^{-1}$, respectively.

2.3. Sampling and chlorination

Both O$_3$–BAC processes were started at the same time and operated in parallel (Fig. 1), and initially achieved the same removal of DOC and DON and the same concentrations of C- and N-DBPs upon subsequent chlorination (Table SM2). Next, ozone dosing was terminated after backwashing in one of the two O$_3$–BAC processes, which is represented as ‘T–O$_3$–BAC’ in the study (ozone was never turned on again after terminating dosing). Another O$_3$–BAC process was operated unchanged, with continuous ozonation applied before BAC filtration, which is represented as ‘C–O$_3$–BAC’. The performance of C–O$_3$–BAC and T–O$_3$–BAC was compared by collecting water samples from the effluent of sand filtration and BAC filtration from the first to fifth backwashing cycles. The removal of each parameter by C–O$_3$–BAC or T–O$_3$–BAC process was calculated by Eq. (1). The removal in each backwashing cycle (four days) was the average removal from sampling on the second, third and fourth day after BAC backwashing.

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\text{Removal (\%)} = \frac{C_A - C_B}{C_A} \times 100\%
\]

\(C_A\)—Concentration detected after sand filtration.

\(C_B\)—Concentration detected after BAC filtration.

None of the collected waters showed any detectable N-DBP background level. The formation yields of DBPs were compared by adding enough chlorine (as Cl$_2$) to the collected water samples (the effluent of the sand filtration, C–O$_3$–BAC, or T–O$_3$–BAC) to provide the desired 24-h chlorine residual of 1 ± 0.5 mg-Cl$_2$ L$^{-1}$. After 24 h storage at room temperature in the dark, the collected water samples were quenched through adding a stoichiometric amount of ascorbic acid and analyzed as quickly as possible (Chu et al., 2013).

2.4. Analysis

CF, DCAN, TCAN, DCNM and TCNM analyses were carried out using a purge & trap sample concentrator (eclipse 4660, OL, USA) and gas chromatograph/mass spectrometry (GC/MS) (Shimadzu-QP2010, Japan), based on USEPA method 524.2 (USEPA, 1992).
DCAcAm and TCACam analyses consisted of liquid-liquid extraction and the above-mentioned GC/MS detection. DCAA and TCAA were determined by gas chromatography with an electron capture detector (Shimadzu-QP2010, Japan). The details of the analyses of these DBPs and other parameters (e.g., turbidity, DOC, DON, NH4+–N, three-dimensional fluorescence excitation-emission matrix [EEM]) are available elsewhere (Chu et al., 2010, 2011).

Apparent molecular weight (MW) of DOM in the BAC-filtered waters was assayed using high-performance liquid chromatography and size exclusion chromatography (e2695, Waters). Separation by size exclusion was performed using a gel column (TSK G3000PWXL, TOSOH) prior to sequential on-line detectors consisting of UV/Visible (Waters 2489) and DOC (Sievers 900 Turbo) detection. The mobile phase solution was made with 0.02 M Na2SO4, 0.05 M KH2PO4, and 0.03 M NaOH. Polyethylene glycols (PEGs) and sodium polystyrene sulfonates (PSSs) (PEGs: 200, 1400 Da; PSS: 3610, 6800, 15450, 31000 Da) were used as standards for calibration (Li et al., 2011).

All comparisons were done by one-way analysis of variance as calculated by SPSS software (Version 17, SPSS Inc., Chicago, IL); p<0.05 was considered statistically significant.

3. Results and discussion

3.1. Removal of C-DBPs

The formation yields of C-DBPs upon chlorination of the effluent water of the sand filter, C–O3–BAC filter and T–O3–BAC filter were measured (Fig. 2). The reduction in C-DBP formation yields by the C–O3–BAC and T–O3–BAC filtration relative to sand filtration was calculated by Eq. (1). C–O3–BAC achieved better reduction of C-DBPs (CF, DCAA and TCAA) than T–O3–BAC (p<0.05). The reduction in C-DBP formation yields closely mirrored the reduction in DOC concentrations, which was expected, since DOC is a known C-DBP precursor indicator measurement (Chellam and Krasner, 2001; Xue et al., 2014). The linear correlation between DOC removal and C-DBP removal held in both the C–O3–BAC and T–O3–BAC waters (Fig. SM1).

3.2. Removal of N-DBPs

The formation yields of N-DBPs upon chlorination of the effluent water of the sand filter, C–O3–BAC filter and T–O3–BAC filter were measured, as shown in Fig. 2. The reduction in N-DBP formation yields by the C–O3–BAC and T–O3–BAC was calculated by Eq. (1). C–O3–BAC filtration achieved stable removal of DCAN (63.4–69.7%), TCAN (88.1–89.2%), DCNM (65.5–69.5%), TCNM (51.7–56.9%), DCAcAm (68.2–71.6%) and TCACam (82.1–88.5%) from the first to fifth backwash cycles (p values of all selected N-DBPs were higher than 0.05).

Some N-DBP concentrations increased in the T–O3–BAC filter after the initial backwash cycle, being 21.3%, 19.6%, 33.5% and 53.7% higher than that in the chlorinated effluent water of the sand filter for DCAN, TCAN, DCAcAm and TCACam (Fig. 2). The increased N-DBP concentrations suggest that new N-DBP precursors were produced into the water in the T–O3–BAC case. Also, the concentrations of DCNM and TCNM were only reduced by 36.3% and 29.5% compared to the chlorinated effluent water of the sand filter.

Fig. 2. The removal of DOC, DON, C-DBPs and N-DBPs. (a and b Show the removal by the C–O3–BAC and T–O3–BAC in first backwash cycle after terminating ozone dosing, respectively; c and d show the removal by the C–O3–BAC and T–O3–BAC in the second backwash cycle after terminating ozone dosing, respectively; e and f show the removal by the C–O3–BAC and T–O3–BAC in the fifth backwash cycle after terminating ozone dosing, respectively. The removal is the average value of the samples collected three times on the second, third and fourth day after BAC backwashing. The error bars represent the standard deviation of three removal values.)
Subsequently, the T–O₃–BAC recovered stable removal ability for N-DBP precursors from the second to fifth backwash cycles ($p > 0.05$), but the removal ability of the T–O₃–BAC filter was still significantly inferior to that of the C–O₃–BAC filter (Fig. 2).

### 3.3. Changes of DBP precursors

As shown in Fig. 2, C–O₃–BAC exhibited a stable removal of DOC (29.7–32.6%) and DON (33.0–36.7%) from the first to fifth backwash cycles ($p$ values of DON and DOC was both higher than 0.05). T–O₃–BAC resulted in a lower DOC and DON removal relative to C–O₃–BAC. Of note, the T–O₃–BAC process significantly increased the DON concentration of the sand-filtered water by 23.9% (from 0.46 to 0.57 mg L⁻¹) in the first backwash cycle. After that, the T–O₃–BAC recovered some ability to remove DON from the second to fifth backwash cycles. The increase in N-DBP formation yields also mirrored the increase in DON concentrations. As in the case of the relationship between DOC and C-DBP concentrations, the linear correlation between DON and N-DBP concentrations held in both the C–O₃–BAC and T–O₃–BAC waters (Fig. SM3). However, the degree of linear correlation between DON and N-DBP concentrations ($R^2 < 0.90$, in Fig. SM3) was lower than that between DOC and C-DBPs ($R^2 > 0.95$, in Fig. SM2), suggesting that it is not only the DON concentration but also the characteristics of the DON in the post-BAC water that influence the N-DBP yield (Chu et al., 2010).

It is known, ozonation transforms higher molecular weight compounds into smaller molecules (Fig. 3) and thereby increases the biodegradable organic matter (Santos et al., 2013), which is then better removed by a subsequent BAC process (Xu et al., 2007; Chu et al., 2012). When ozone dosing was suddenly terminated, a portion of the microorganisms in the BAC may have shifted from exogenous respiration to endogenous respiration due to the reduction in biodegradable organic matter (Yapsakli et al., 2010), which is likely to have resulted in the release of numerous soluble microbial products (SMPs) (Schiener et al., 1998). It is known that a range of SMPs are produced by microorganisms in the BAC process and can be detected in BAC effluent (Barker and Stuckey, 1999; Carlson and Amy, 2000; Kunacheva and Stuckey, 2014). SMPs comprise a wide range of high and low
molecular weight compounds including many DON compounds such as proteins, polysaccharide and amino acids (Rittmann et al., 1987; Chen et al., 2003; Potvin and Zhou, 2011), which can be divided into growth-related utilization associated products (UAPs) and non-growth-related biomass associated products (BAPs). The formation of UAPs and BAPs is directly related to the cell growth rate and the cell endogenous respiration of the microorganisms, respectively (Carlson and Amy, 2000).

As shown in Fig. 3, we investigated the MW distribution of the DOM in effluents of sand filtration, C–O3–BAC filtration and T–O3–BAC filtration, and found C–O3–BAC filtration slightly changed the MW distribution of DOM due to the ozonation oxidation. However, T–O3–BAC filtration substantially increased the percentage of high-MW (>10 kDa) and low-MW (<1 kDa) compared to C–O3–BAC filtration (p < 0.05), which was in accordance with the deduction that SMPs were released in T–O3–BAC filtration, considering that most of the SMPs consisted of the low-MW (<1 kDa, e.g., amino acids) and high-MW (>10 kDa, e.g., proteins, polysaccharide) compounds (Boero et al., 1996; Kunacheva and Stuckey, 2014). However, identification/quantification of specific SMP compounds was not included as part of this study.

EEM spectra were used to characterize the DOM in effluents of sand filtration, ozonation, C–O3–BAC filtration and T–O3–BAC filtration, as shown in Fig. 4. According to the fluorescence regional integration method developed by Chen and colleagues (Chen et al., 2003), the EEM spectra were operationally divided into five regions (Fig. SM2). As shown, DOM in the sand-filtered water (Fig. 4A), ozonated water (Fig. 4B), and BAC-filtered water (Fig. 4C and D) all had two intense peaks in the SMP region (λex > 250 nm, λem < 380 nm) and aromatic protein (AP)-like region (λex < 250 nm, λem > 380 nm), and the fluorescence intensities of the two peaks (SMP and AP) in sand-filtered water was reduced by C–O3–BAC filtration from 553 and 362 a.u. to 246 and 77 a.u. Huminic acid and fulvic acid peaks in the EEM spectra were observed in the untreated source water, but no significant fluorescence peak was found in the humic acid-like and fulvic acid-like region for these treated waters (Fig. 4). This is probably because most of the humic acids and fulvic acids were removed by the conventional treatment processes (Liu et al., 2009; Yan et al., 2006). Previous studies (Chu et al., 2010) reported that SMP-like and AP-like substances, containing elevated organic nitrogen, were the important precursors of N-DBPs (HANs and HACams). The results for the removal of HAN and HACAm formation yields (Fig. 2) and the variation in SMP-like and AP-like peak intensities in EEM spectra (Fig. 4A–C) suggest that the C–O3–BAC process is able to reduce the precursors of these N-DBPs, which supports earlier evidence of this (Chu et al., 2012). However, from Fig. 4D, it was noted that the fluorescence intensities of SMP and AP peaks in the effluent of T–O3–BAC filtration actually increased to 649 and 357 a.u., which mirrored the increase of HAN and HACAm concentrations.

4. Conclusions

In recent years, O3–BAC has become an important process in DWTPs which use polluted water source in China. In some cases, ozone was intermittently dosed (versus continuously) before BAC filtration in DWTPs in order to save costs by the water provider or in emergency situations. This study has showed that the abrupt termination of ozonation results in the presence of some N-DBP (HAN and HACAm) precursors even after only the first backwash cycle, and then substantial formation of HANs and HACams during subsequent chlorination. Moreover, after the first backwash cycle, BAC filtration alone continued to have a lower reduction performance for all measured C-DBPs and N-DBPs compared to C–O3–BAC. The observed recovery in the removal of DON and N-DBPs from the second to fifth backwash cycles was potentially because the microorganisms were gradually able to assimilate the un-ozonated organics, which reduced the release of SMPs and/or other nitrogenous organic matter, however this requires further investigation to confirm.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.chemosphere.2014.10.059.

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