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RESEARCH ARTICLE

Characteristics and removal mechanism of the precursors of N-chloro-2,2-dichloroacetamide in a drinking water treatment process at Taihu Lake

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HIGHLIGHTS

- N-Cl-DCAM, an emerging N-DBP in drinking water was investigated.
- A new BAC has a better removal efficiency for N-Cl-DCAM precursors than an old BAC.
- N-Cl-DCAM precursors are more of low molecular weight and non-polar.
- Adsorption of GAC plays a major role in removal of N-Cl-DCAM precursors by an O_3-BAC.

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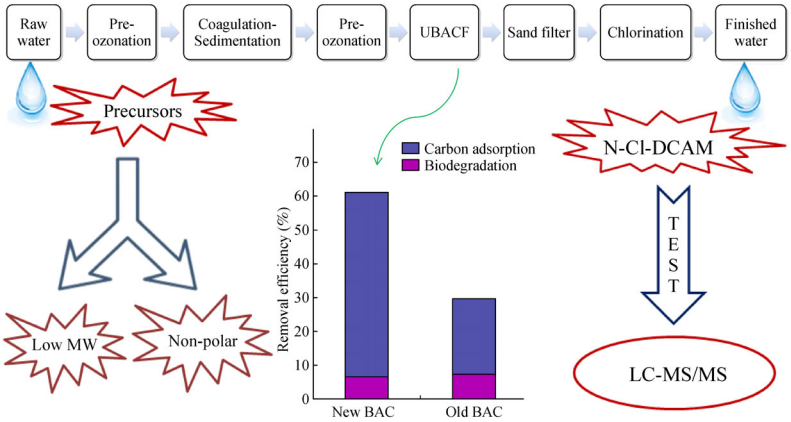
GRAPHIC ABSTRACT



ABSTRACT

N-chloro-2,2-dichloroacetamide (N-Cl-DCAM) is an emerging nitrogenous disinfection by-product (N-DBP) which can occur in drinking water. In this study, an analytical method based on liquid chromatography with tandem mass spectrometry (LC-MS/MS) was developed to validate the concentration of N-Cl-DCAM, which was found to be 1.5 μg/L in the effluent of a waterworks receiving raw water from Taihu Lake, China. The changes of N-Cl-DCAM formation potential (N-Cl-DCAMFP) in the drinking water treatment process and the removal efficiency of its precursors in each unit were evaluated. Non-polar organics accounted for the majority of N-Cl-DCAM precursors, accounting for 70% of the N-Cl-DCAM FP. The effect of conventional water treatment processes on the removal of N-Cl-DCAM precursors was found to be unsatisfactory due to their poor performance in the removal of low molecular weight (MW) or non-polar organics. In the ozonation integrated with biological activated carbon (O_3-BAC) process, the ozonation had little influence on the decrease of N-Cl-DCAM FP. The removal efficiency of precursors by a new BAC filter, in which the granular activated carbon (GAC) had only been used for four months was higher than that achieved by an old BAC filter in which the GAC had been used for two years. The different removal efficiencies of precursors were mainly due to the different adsorption capacities of GAC for individual precursors. Low MW or non-polar organics were predominantly removed by GAC, rather than biodegradation by microorganisms attached to GAC particles.

1 Introduction

Nitrogenous disinfection by-products (N-DBPs) produced

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by the reaction of chlorine and nitrogenous compounds, especially dissolved organic nitrogen (DON) compounds, have caused increasing concern for the drinking water treatment industry in recent years (Chu et al., 2016). Among the detected N-DBPs, haloacetonitriles (HANs), haloacetamides (HAMs), halonitromethanes (HNMs), and nitrosamines (NMs) have attracted much attention (Krasner et al., 2006; Goslan et al., 2009; Bond et al., 2015; Liew et al., 2016). Some studies have indicated that N-DBP levels are lower than those of carbonated DBPs (C-DBPs), although they have a much higher cytotoxicity and genotoxicity than regulated C-DBPs (e.g., haloacetic acids (HAAs) and trihalomethanes (THMs)) in drinking water (Muellner et al., 2007; Plewa et al., 2008; Chu et al., 2009; Wagner et al., 2012).

N-chloro-2,2-dichloroacetamide (N-Cl-DCAM; its structural formula is shown in Fig. 1) is a newly discovered N-DBP, which has been erroneously classified as a dichloroacetamide (DCAM) species in previous reports. This is because its nitrogen-bound chlorine is readily reduced by most commonly used quenching agents used in the measurement of N-DBPs, such as, ascorbic acid, sodium sulfite, and sodium thiosulfate (Kimura et al., 2015). Yu and Reckhow (2017) first reported the presence of N-Cl-DCAM in chlorinated waters in 2016 and showed that ammonium chloride was found to be the only reducing agent that did not cause a reduction in N-chloro-haloacetamides (N-Cl-HAMs) to their corresponding HAMs over a relatively long period of sample storage. Yu and Reckhow (2017) also showed that chlorination is more likely than chloramination to form N-Cl-DCAM in drinking water, and N-Cl-DCAM is considered more toxic than dichloroacetonitrile (DCAN) and DCAM. However, less information is available regarding the occurrence and changes of N-Cl-DCAM in drinking water treatment processes. It is difficult to directly remove the DBPs generated by chlorination in waterworks. The main way to remove DBPs is to remove their precursors, and therefore reduce their formation potential (FP) (Nishijima andSpeitel, 2004; Bond et al., 2012). Therefore, it is necessary to study the characteristics of N-Cl-DCAM precursors and the changes of its FP in waterworks. A time-of-flight mass spectrometry (TOFMS) method has been used to detect N-Cl-DCAM (Yu and Reckhow, 2017), which has limited the investigation of N-Cl-DCAM levels due to the high cost of the instrument. To reduce the time and cost of detection, while achieving a similar detection precision in water samples, it is necessary to establish a new detection method.

In a previous study of other N-DBPs (Lin et al., 2016), the conventional drinking water treatment process, including coagulation, sedimentation, and sand filtration, did not significantly remove the N-DBP precursors. In contrast, ozone integrated with biological activated carbon (O_3-BAC) technology, which is widely used as an advanced treatment process, had a good removal efficiency for some specific natural organic matter (NOM) fractions, such as synthetic organic chemicals and DBP precursors, including those of DCAN and DCAM (Nishijima andSpeitel, 2004; Simpson, 2008; Chu et al., 2012a; Chu et al., 2012b; Wang et al., 2017). Another study showed that BAC filtration was a feasible approach for the direct removal of HAAs from pool water (Tang and Xie, 2016). However, the removal effect of the BAC process on the precursors of different DBPs has been found to vary because of the specific characteristics and removal mechanisms of the precursors by the BAC filter. How to remove N-Cl-DCAM precursors in the drinking water treatment process, including the use of a BAC filter, has not been reported. Currently used BAC processes mainly include the down-flow BAC filter (DBACF)and the up-flow BAC filter (UBACF).The DBACF is located after the sand filtration stage and is widely used in waterworks in China (Schideman et al., 2007). However, from practical operational experience, an uneven distribution of microorganisms and higher water head loss has been reported on the DBACF (Velten et al., 2011).To resolve this, the UBACF has been introduced as a new process between the sedimentation tank and the sand filter. However, there is little literature available regarding the effectiveness of N-DBP removal by UBACF.

In this study, a liquid chromatography with tandem mass spectrometry (LC-MS/MS) system (AB 5500, AB Sciex, Framingham, MA, USA) was used to establish a new detection method for measuring the N-Cl-DCAM concentration. The actual N-Cl-DCAM concentration in drinking water was measured and the N-Cl-DCAM FP in the treatment process of a drinking water treatment plant (DWTP) was investigated to determine the features of precursors and their removal efficiency by different treatment processes. By comparing the difference in the removal efficiency of N-Cl-DCAM precursors between new and old UBACF, we explored the removal mechanism of N-Cl-DCAM precursors by the up-flow BAC filter.

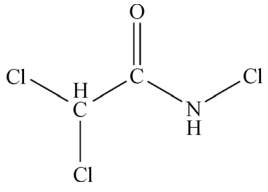

Fig. 1 N-Chloro-2,2-dichloroacetamide (N-Cl-DCAM) (MW = 162.5 g/mol).

2 Materials and methods

2.1 Chemicals and reagents

A DCAM standard was obtained from Alfa Aesar (Karlsruhe, Germany). Pure N-Cl-DCAM is not available on the market. According to the previously reported

method (Yu and Reckhow, 2017), N-Cl-DCAM is obtained from the reaction of DCAM and free chlorine at the same stoichiometric level (i.e., $Cl_2/N = 1:1$) when the pH value of a solution of DCAM and free chlorine is adjusted to 9.0. After the reaction, the residual chlorine in the solution is almost undetectable. Other reagents were purchased from the Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). The ultra-pure water used in the experiment was prepared from a Millipore Milli-Q Gradient water purification system.

2.2 Water samples

All water samples were taken from a drinking water treatment process in a waterworks that received raw water from Taihu Lake, China. The water quality of Taihu Lake during the sampling campaign is presented in Table 1. A process diagram of the waterworks is shown in Fig. 2. The ozone dosages at pre- and post-ozonation, determined according to the removal efficiency of pre-ozone and O_3-BAC processes on ammonia nitrogen and organic matter in water, especially DBP precursors, were 0.5 and 1.2 mg/L, respectively, and the contact time was 6 min. There were two UBACFs with different usage times for the granular activated carbon (GAC); one where GAC had only been used for four months (called New BAC) and another where GAC had been used for over two years (called Old BAC). The characteristics of the two types of GAC are shown in Table 2. The height of the activated carbon filter layer was 2.5 m. The UBACF had a constant up-flow rate of 10 m/h, which maintained a 23% expansion of the carbon bed and a hydraulic retention time of 15 min. The backwashing of the UBACF was achieved using a combination of air and water. Air-washing was initially performed at an intensity of 14 L/m^2/s and a backwash time of 5 min, followed by water-washing that was achieved by increasing the up-flow rate of the influent (12 m/h) and then returning to a normal operating process after a 30 min wash. The backwash cycle was 10 days.

Table 1 The water quality characteristics of Taihu Lake

Parameters	Value
Turbidity (NTU)	18±1.44
UV_{254} (cm^{-1})	0.064±0.007
COD_{Mn} (mg/L)	4.07±0.32
NH_3-N (mg/L)	0.142±0.011
DOC (mg/L)	5.30±0.39
DON (mg/L)	0.278±0.028
Br^- (μg/L)	113±16

Table 2 The characteristics of the new and old GAC used in the BAC filters

Parameters	Value	
	New GAC	Old GAC
Usage time of GAC	4 months	2 years
Particle size (%)		
> 1.70 mm	0.2	0.1
1.70–0.425 mm	99.3	99.5
< 0.425 mm	0.5	0.4
Pore volume (mL/g)	0.65	0.55
Specific surface area (m^2/g)	810	760
Biomass (nmol/g)	92	97
Biological activity (mg·O_2/(L·cm^3))	43.2	47.6
Iodine adsorption (mg/g)	914	856
Methylene blue adsorption (mg/g)	224	183

All water samples were collected in amber glass bottles, and then the water samples were instantaneously filtered through a 0.45 μm microporous filter membrane and stored in the dark at 4°C until experimental detection.

2.3 Chlorination of water samples

The N-Cl-DCAM FP was used to represent the content of DCAM precursors in water. According to previous reports, N-Cl-DCAM is a product of the chlorination of water, rather than chloramination. Therefore, the N-Cl-DCAM FP was investigated through chlorination of water samples. The DBPs FP test has been reported such ways as the UFC method, a shock dose method (Tang et al., 2012) and the methods developed by Krasner et al. (Krasner et al., 2006; Compton et al., 2011). The above shock dose method uses a sufficient Cl_2 dose of 20 mg/L, regardless of the DOC and ammonia concentrations. However, dilution trials are needed in this method. In this study, the FP of DBPs was determined on the basis of the method developed by Krasner et al. (Krasner et al., 2006). The method, which included a sufficient level of chlorination was used to determine the N-Cl-DCAM FP. The water samples were chlorinated in a brown glass bottle. A sodium hypochlorite solution (active chlorine of 6%) was used as the free chlorine stock solution. The chlorine dosages for FP detections were calculated using Eq. (1).The DOC was tested with a total organic carbon (TOC) analyzer (TOC-V CPH; Shimadzu, Tokyo, Japan). Ammonia nitrogen was

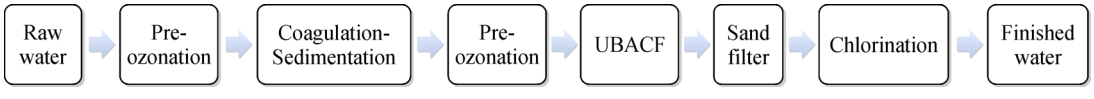

Fig. 2 A process diagram of the waterworks.

determined by the method described in GB/T 5750.7-2006.

$$\mathrm{Cl_2\ dosage(mg/L)} = 3 \times C_{\mathrm{DOC}}(\mathrm{mg/L}) + 7.6 \times C_{\mathrm{NH_3-N}}(\mathrm{mg/L}) + 10(\mathrm{mg/L}). \quad (1)$$

After chlorination, the water samples were immediately shaken to mix them thoroughly, and then stored in the brown glass bottle at 25°C±2°C, and protected from exposure to light for 24 h (Krasner et al., 2006; Dotson et al., 2009; Compton et al., 2011). According to the results of Yu and Reckhow (2017), ammonium chloride was found to be the only reducing agent that did not cause a reduction in N-Cl-HAMs to their corresponding HAMs over a relatively long period of sample storage. In contrast, the other seven analytes instantly disappeared from the selected ion chromatogram after the spiked samples (1 μmol/L for each N-Cl-HAM) were treated with the same concentrations of ascorbic acid, sodium sulfite, and sodium thiosulfate, respectively (Yu and Reckhow, 2017). Therefore, 10% ammonium chloride solution was used to quench the residual chlorine in the water sample to terminate the reaction after 24 h.

2.4 Analytical method

During the experimental work, three samples were tested at each concentration level and the final results were averaged. Statistically significant factors and interactions were defined at the 95% confidence level. A linear regression analysis was conducted using SPSS 18.0 (SPSS Inc. Chicago, IL, USA).

2.4.1 Molecular weight (MW) distribution analysis

The MW fractionation was carried out by using the cutting method, and the ultrafiltration cup system was used for MW separation (Zheng et al., 2018). The effective volume of the ultrafiltration cup was 300 mL. A magnetic stirring device was operated using nitrogen gas to supply a pressure of 0.1 MPa. Prior to fractionation, the membranes were dipped in ultra-pure water for 24 h, and then washed repeatedly until the dissolved organic carbon (DOC) content of the effluent dropped below 0.1 mg/L. In fractionation, water samples were pressurized through 10, 3, and 1 kDa membranes in turn. The water sample was sequentially cut to have an MW of 10, 3, and 1 kDa, and the N-Cl-DCAM FP of the effluent of the three membranes was detected. The mass concentration of organic matter in four MW ranges (<1 kDa, 1 to 3 kDa, 3 to 10 kDa, and >10 kDa) was obtained using a subtractive method (Eqs. (2)–(5)).

$$\mathrm{N-Cl-DCAMFP_{>10\,kDa}} = \mathrm{N-Cl-DCAMFP_{Raw\ water}} - \mathrm{N-Cl-DCAMFP_{10\,kDa\ effluent}}, \quad (2)$$

$$\mathrm{N-Cl-DCAMFP_{3\ to\ 10\,kDa}} = \mathrm{N-Cl-DCAMFP_{10\,kDa\ effluent}} - \mathrm{N-Cl-DCAMFP_{3\,kDa\ effluent}}, \quad (3)$$

$$\mathrm{N-Cl-DCAMFP_{1\ to\ 3\,kDa}} = \mathrm{N-Cl-DCAMFP_{3\,kDa\ effluent}} - \mathrm{N-Cl-DCAMFP_{1\,kDa\ effluent}}, \quad (4)$$

$$\mathrm{N-Cl-DCAMFP_{<1\,kDa}} = \mathrm{N-Cl-DCAMFP_{1\,kDa\ effluent}}. \quad (5)$$

2.4.2 Polarity and non-polarity analysis

The polarity rapid analysis method (PRAM) (Rosario-Ortiz et al., 2007; Chen et al., 2014) was used to classify the polarity of organics. This is a solid phase extraction method that can selectively adsorb organic matter according to its polarity (Liao et al., 2015). A C_{18} column with a non-polar filler was used to adsorb non-polar organics. During the test, the water sample to be tested was filtered through a 0.45 μm glass fiber membrane (GF/F, Whatman, Buckinghamshire, UK) and slowly passed through the C_{18} column at a filtration rate of 1 mL/min. The N-Cl-DCAM FP in the effluent was then determined. The non-polar and weakly polar organics were adsorbed and retained. In the C_{18} column, the filtrate contained only polar organic matter, the raw water and filtrate were collected, the relevant water quality indicators were determined, and the corresponding indicators of non-polar and weakly polar organic substances were obtained by subtraction.

2.4.3 High-throughput sequencing and data analysis

Approximately 10–20 g of BAC was extracted and refrigerated for later testing. All sample sequences are clustered on the basis of the distance between the sequences, and then the sequences were partitioned into diverse operation classification units (OTU) according to the comparability between the sequences. The statistical analysis of bioinformatics data are usually performed on OTUs at a similar level of 97%. On the basis of the OTU clustering results, we obtained representative that were clustered into OTUs. By default, the most abundant sequence was selected as the representative OTU for various OTU analyses. To obtain the species classification information corresponding to each OTU, the Ribosomal Database Project (RDP) classifier method was used to classify the OTU. The Naïve Bayesian assignment algorithm was used to calculate the probability value

assigned to this rank for each sequence at different levels. It is generally considered that when the probability value (i.e., RDP classification threshold) is greater than 0.8, the classification result is credible (when the length of the sequencing fragment is less than 250, this value can be appropriately lowered to 0.5, for example, only the V3, V6, and V4 area is measured). In the study, the reference used was the universal primer in the V3–V4 region, the positive primer 341F: 5-CCTACGGGNGGCWGCAG-3, and the reverse primer 805R: 5-GACTACHVGGGTATC-TAATCC-3. The results of the taxonomic analysis revealed the kind of microorganisms contained in the sample and the sequence number of each microorganism in the sample, i.e., the relative abundance of each microorganism. (Vargas-Albores et al., 2017).

2.4.4 Analysis of GAC characteristics

The biomass on activated carbon was measured based on the adenosine triphosphate (ATP) content in the cell. Approximately 3–5 g of activated carbon were taken from the BAC filters during the operating cycle. Two parts were used for each sample, with one part dried and used to measure the dry weight, while the other part was placed into the brown reagent bottle. Then, 10 mL methanol, 5 mL chloroform, and 4 mL pure water were added to the brown reagent bottle with activated carbon, and the solution was allowed to stand for 12 h after being shaken for 10 min. Then, 5 mL chloroform and 5 mL pure water were added, and the bottle was left to stand for another 12 h. A 5 mL sample of the solution was taken from the intermediate layer, placed in a 50 mL colorimetric tube with a pipette, and evaporated to dryness in the water bath. Then, pure water was added to 25 mL followed by 4 mL of 50 g/L potassium persulfate. The solution was heated for 30 min in a pressure cooker, allowed to cool, and then pure water was added to 50 mL. Then, 1 mL ascorbic acid and 2 mL molybdate were added, and the solution was allowed to stand for 15 min before measurements were conducted.

The biological activity was expressed as biomass respiration potential. The detailed experimental procedures were consistent with (Urfer and Huck, 2001).

2.4.5 New method for the detection of N-Cl-DCAM

Dichloroacetamide and sodium hypochlorite were mixed at the same stoichiometric ratio $Cl_2/N = 1:1$ under the conditions of pH = 9 to prepare a 1 mg/L standard solution of N-Cl-DCAM (MW = 162.5 g/mol), which was placed in a brown injection bottle. Then 1 mg/L N-Cl-DCAM standard solution was diluted with pH = 9 sodium bicarbonate buffer solution, to produce standard solutions with mass concentrations of 1, 2, 5, 10, 20, and 50 μg/L, respectively. Then, LC-MS/MS (AB 5500, AB Sciex, USA) was used to analyze the standard solutions used for calibration. The peak time of N-Cl-DCAM was 0.9–1.0 min, and in some embodiments, the peak time was 0.916 min. The N-Cl-DCAM standard working curve was constructed by taking the N-Cl-DCAM concentration as the x-coordinate and the N-Cl-DCAM peak area as the y-coordinate. The linear correlation coefficient of N-Cl-DCAM was greater than 0.999 within the range of 1–50. The method detection limit (MDL) was less than 0.5 μg/L, the recovery was 87.3%–112.5%, and the relative standard deviation (RSD) was less than 10.0%. The standard working curve used in one experiment is shown in Fig. 3. A total ion flow chromatogram of 5 μg/L N-Cl-DCAM standard solution is shown in Fig. 4.

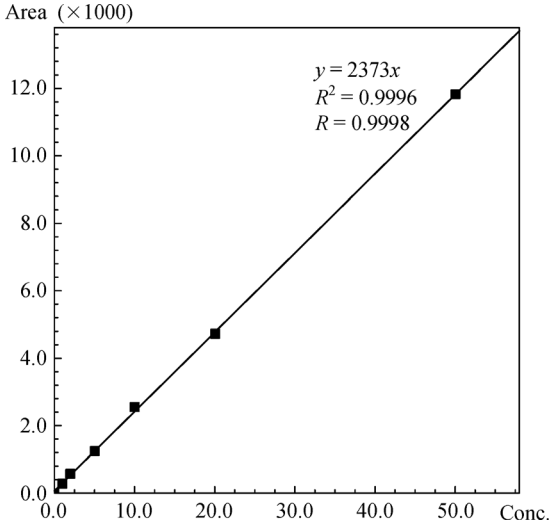

Fig. 3 Standard calibration graph for N-Cl-DCAM.

The standard solution and water samples were detected by LC-MS/MS, with a C_{18} column (100 × 2.1 mm × 1.7 μm; Waters, Milford, MA, USA). The column temperature was maintained isothermally at 40°C and the automatic sampler temperature was kept at 15°C. Milli-Q water (solvent A) and 100% acetonitrile (solvent B) were used as mobile phases, with a constant flow rate of 0.3 mL/min. The preliminary gradient was 0–1 min, 5% B; 2–4 min 5% to 90% B; switched back to 5% B for 0.1 min; and 4–6 min 95% B. The volume of samples used for testing was 5 μL.

The MS conditions were as follows: negative ion mode; precursor ion, 159.9 and 161.9 Da; MS detector temperature, 550°C; curtain gas, 35 psi; collision gas, 9 psi; spray gas, 55 psi; auxiliary heating gas, 55 psi; ionization voltage, −4500 V; scanning mode, multi-response monitoring mode (MRM); MRM conditions, quantitative ion pair, 159.9/70.9, declustering potential, −50 V, collision energy, −11 V, dwell time, 160 msec; qualitative ion pair 1, 161.9/72.9, declustering potential, −50 V, collision energy, −10 V, dwell time, 160 msec; qualitative ion pair

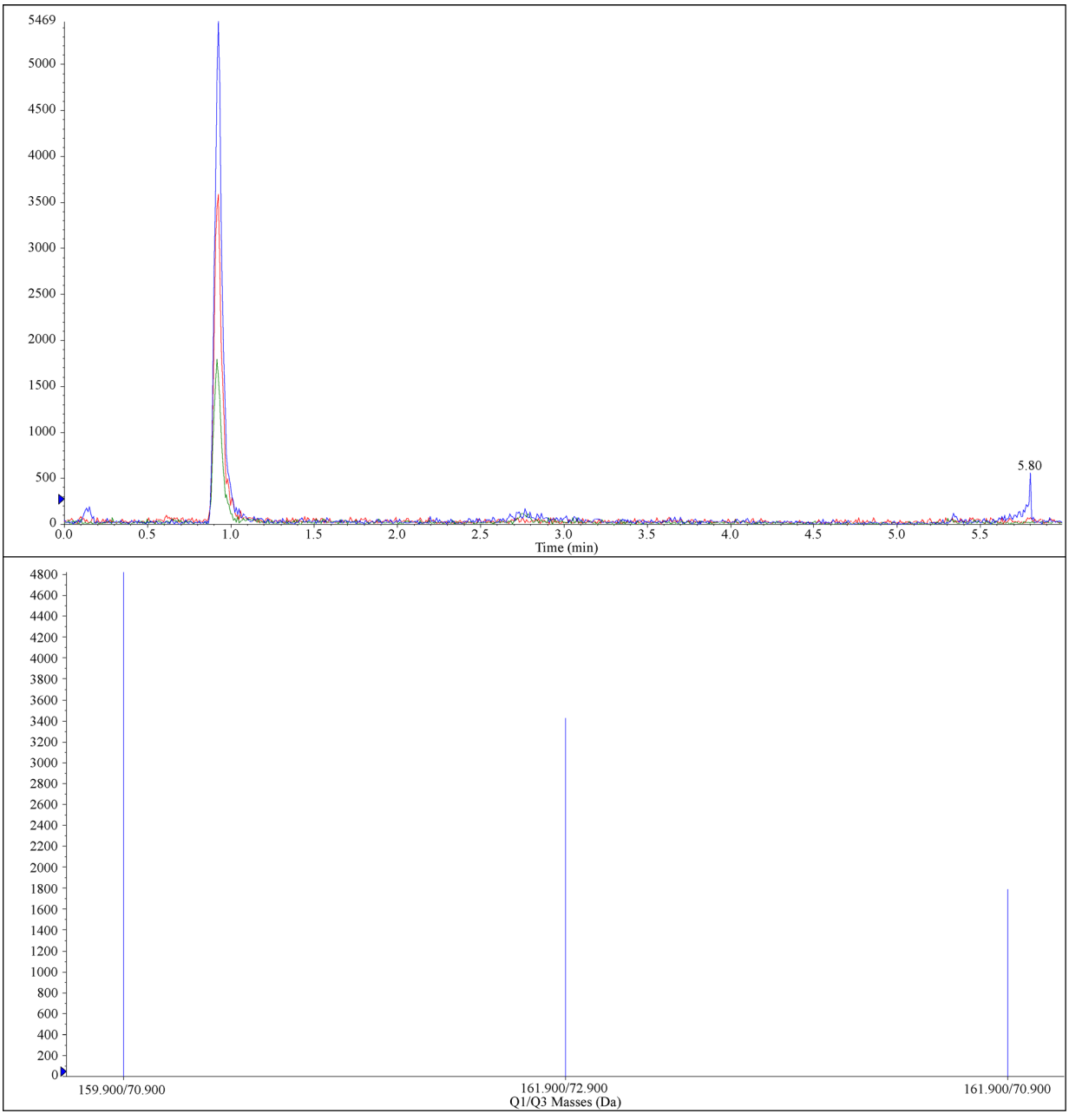

Fig. 4 Total ion flow chromatogram of a 5 μg/L N-Cl-DCAM standard solution.

2, 161.9/70.9, declustering potential, −50 V, collision energy, −10 V, dwell time, 160 msec.

2.5 Method validation

To verify the feasibility of the method, the same batch of water samples was also analyzed for the quantification of N-Cl-DCAM FP using ultra performance liquid chromatography/quadrupole time-of-flight mass spectrometry (UPLC/TOFMS),following a previously reported method (Yu and Reckhow, 2017). All tests were performed simultaneously using three parallel samples, and the test results were averaged. It was found that the results obtained by the new method were similar to those of the confirmed method; thus, further proving that this method was feasible in terms of actual measurements. The test results are shown in Table 3. A total ion flow chromatogram of raw water is shown in Fig. 5.

2.6 Sterilized GAC adsorption experiment

A bench-scale experiment was conducted to simulate the actual operation of GAC without the biodegradation of the attached microorganism. In this experiment, the activated

Table 3 A comparison of the N-Cl-DCAM FP obtained using the LC-MS/MS method and the UPLC/TOFMS method

Samples	AB 5500LC-MS/MS (μg/L)	SPE-UPLC/ESI/qTOF (μg/L)
Raw water	5.55±0.30	5.69±0.29
Pre-ozonation	5.26±0.22	5.12±0.18
Sedimentation	4.57±0.25	4.67±0.27
Post-ozonation	4.29±0.20	4.15±0.16
New BAC	1.67±0.11	1.53±0.13
Old BAC	3.01±0.15	3.14±0.12

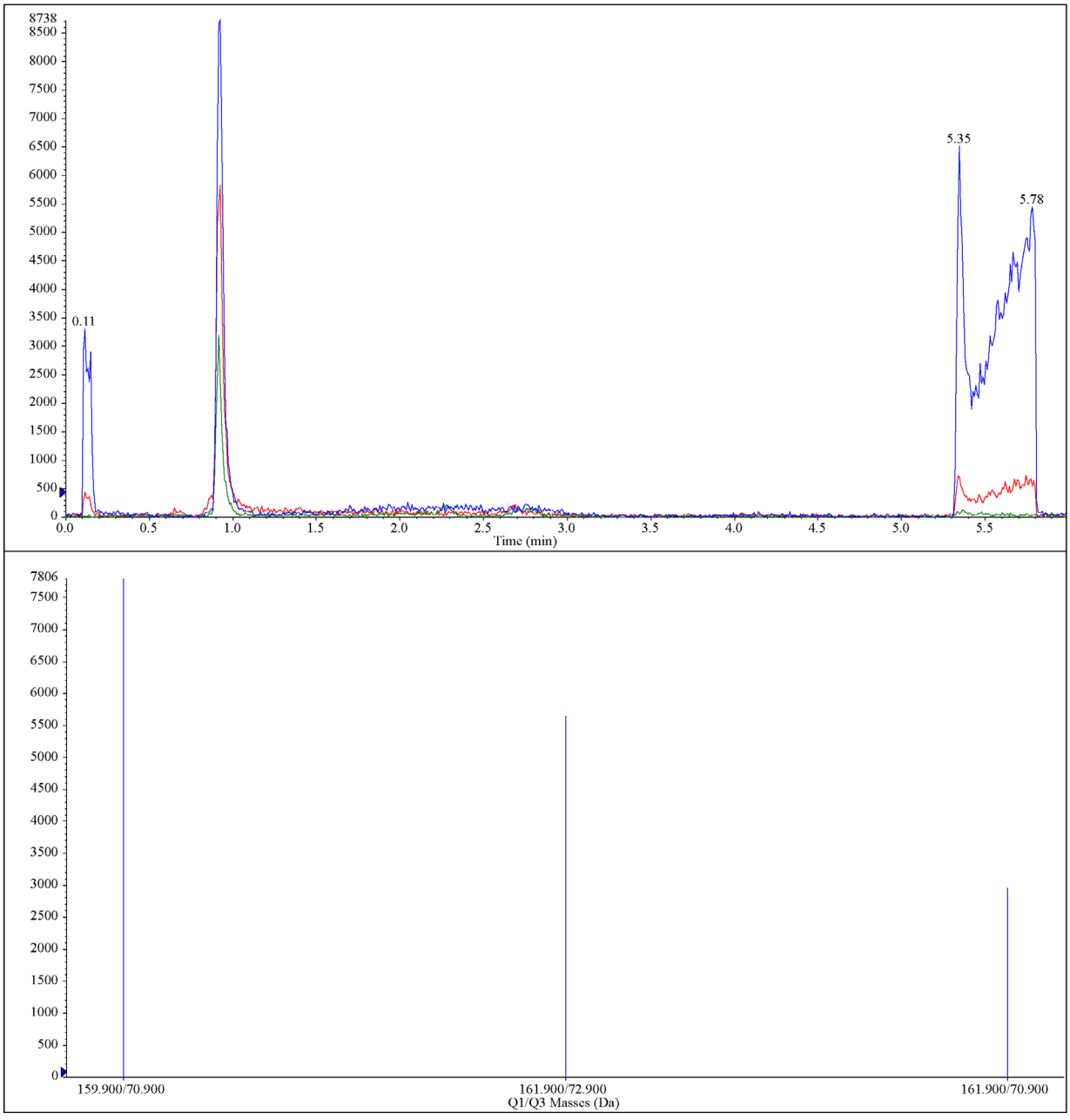

Fig. 5 Total ion flow chromatogram of raw water.

carbon particles were taken from the new and old BAC filters respectively, after inactivating microorganisms with sodium azide and fully backwashing, to treat the effluent from the same ozone contact tank using the filter columns. Unsterilized activated carbon was used as the control. The influent of the columns was the effluent of the same ozone contact tank, lifted by the centrifugal pumps. The filter columns were made of plexi glass material, with a height of 5 m and diameter of 30 cm. The bottom of the filter columns was filled with a 20 cm deep gravel layer and 30 cm deep fine sand layer for support. The tops of the supporting layers were filled with a 2.5 m depth of new inactivated carbon, new biological activated carbon, old inactivated carbon, or old biological activated carbon, respectively. The mass of activated carbon in each filter column was 50 kg. The up-flow rate of the filter columns was 10 m/h and their hydraulic retention time was 15 min. In this experiment, the absolute values of carbon adsorption were calculated using Eq. (6), the carbon adsorption rate was calculated using Eq. (7), and the biodegradation rate was calculated using Eq. (8):

$$X(\mu g/kg) = \frac{A \times v \times T \times (C_0 - C_1)}{M}, \quad (6)$$

$$Y_1(\%) = \frac{C_0 - C_1}{C_0 - C_2} \times 100\%, \quad (7)$$

$$Y_2(\%) = 1 - Y_1, \quad (8)$$

where X is the absolute value of carbon adsorption, Y_1 is the carbon adsorption rate, Y_2 is the biodegradation rate, A is the cross-sectional area of the filter columns, v is the up-flow rate of the filter columns, T is the hydraulic retention time of the filter columns, M is the mass of activated carbon in each filter column, C_0 is the N-Cl-DCAM FP concentration in the effluent from the ozone contact tank, C_1 is the N-Cl-DCAM FP concentration in the effluent from new or old inactivated carbon, and C_2 is the N-Cl-DCAM FP concentration in the effluent from new or old biological activated carbon.

3 Results and discussion

According to the analysis of statistical significance, the p-value in the test was less than 0.05.

3.1 Quantification of N-Cl-DCAM in the finished water

The N-Cl-DCAM concentration in chlorinated water in the waterworks was determined to be 1.5 μg/L. Using the UPLC/TOFMS method, the N-Cl-DCAM concentration in the same batch of water samples was determined to be 1.6 μg/L. In a previous study (Yu and Reckhow, 2017), the N-Cl-DCAM concentrations in 11 tap water samples collected from seven private US residences ranged from 1.40 to 3.48 μg/L. Therefore, the N-Cl-DCAM concentrations in the water samples collected in this study were comparable to those reported in tap water from elsewhere.

3.2 Variations of the N-Cl-DCAM concentration and its removal

N-Cl-DCAM is produced in water subjected to chlorination (Yu and Reckhow, 2017). Due to differences in the components of water and the DON content, which is considered to be the main precursor of N-DBPs in water (Chow et al., 2009), the N-Cl-DCAM concentration generated by chlorinated water samples can differ. The N-Cl-DCAM FP was used to reflect the variations of N-Cl-DCAM precursors during water treatment. The results are shown in Fig. 6.

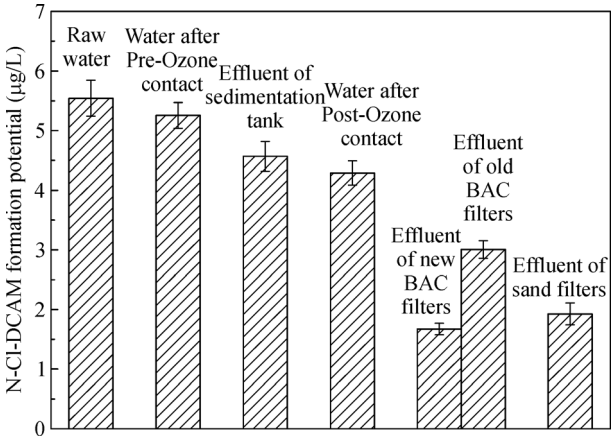

Fig. 6 The N-Cl-DCAN FP in the effluent of different processes.

The N-Cl-DCAM FP of the raw water was 5.6 μg/L, while in the effluent from the pre-ozone, sedimentation, post-ozone, new BAC filter, old BAC filter, and sand filter treatments the values were 5.3, 4.6, 4.3, 1.7, 3.0, and 1.9 μg/L, respectively. According to the N-Cl-DCAM FP results, coagulation combined with the sedimentation process removed 13.12% of the N-Cl-DCAM FP precursors, which indicated that the conventional treatment process had a poor removal efficiency for N-Cl-DCAM precursors. The removal of N-Cl-DCAM FP by ozonation was 5%–6%, which indicated a slight decrease in the N-Cl-DCAM FP after ozonation. Ozonation mineralized part of the low MW organic matter to CO_2 and H_2O (Ratpukdi et al., 2010). This removed small amounts of the N-Cl-DCAM precursors generated by low MW compounds. The purification efficiency of the two BAC filters was obviously different.

Compared with the old BAC filter, the new BAC filter had a significantly better N-Cl-DCAM FP removal

efficiency. The removal of old and new BAC filters were 61.07% and 29.84%, respectively. The influent to both the old and new BAC filters was received from the same ozone contact tank, which indicated that the influent N-Cl-DCAM precursors in the old and new BAC processes were the same. The difference in N-Cl-DCAM FP removal between the old and new BAC processes was likely caused by the different physical and biological properties in the BAC filter treatments.

To determine the cause of these differences, a further investigation was conducted to analyze the effects of the different characteristics of old and new BAC processes on the removal of the precursors of N-Cl-DCAM.

3.3 Analysis of the characteristics of new and old BAC filters

The removal of pollutants by BAC filters occurs due to the combined effects of GAC adsorption and the biodegradation of microorganisms attached to GAC. The biomass of microorganisms attached to the GAC was similar for both BAC filters (Table 1). A high-throughput sequencing analysis was conducted on the microorganisms in the BAC filters to obtain the microbial population distribution on the GAC (Fig. 7). The bacterial communities in the two samples were mainly *Ensifer, Bacillus*, and *Hydrogenophaga,* and their total abundance in the old and new BAC was 37.2% and 42.8%, respectively, which indicated that the population distribution of microorganisms was also similar in the BAC filters. A previous study indicated that *Ensifer* can effectively remove and degrade organic compounds such as metformin, anisole, and amino acids by effectively attacking targets such as esters, ethers, and amide bonds (Ge et al., 2014). *Bacillus* are able to convert humic acids in water into inorganic compounds (Bolotin et al., 2017). *Hydrogenophaga* can use biological hydrogen as an energy source to efficiently decompose dissolved organic matter in water through respiration to remove DON (Du et al., 2015), and reduce the risk of DBPs being generated by subsequent chlorine addition, which is consistent with the results of previous studies. The biomass and biological activity were similar, indicating a similar biodegradability caused by the microorganisms of the two types of BAC processes. In addition to biodegradation, GAC could adsorb the precursors of N-Cl-DCAM which were present in raw water and were produced by the microbial metabolites (Gerrity et al., 2011; Chu et al., 2012a; Tan et al., 2017; Bei et al., 2020). As can be seen from Table 1, the absorbability of GAC in old BAC filters was much worse than that in new BAC filters. The GAC in the new BAC filter displayed strong adsorption, whereas a large amount of organic matter was retained in the pores of the GAC in old BAC filters and backwashing could not completely elute these substances from the pores of the carbon (Simpson, 2008). Because the filter was used for a longer period of time, pollutants gradually accumulated in the pores of the activated carbon, resulting in a decrease in adsorption performance. Therefore, the differences in the removal efficiency of N-Cl-DCAM precursors between the old and new BAC filters was possibly due to the different adsorption levels of activated carbon, rather than biodegradation.

To further clarify the impact of the physical and biological effects of BAC filters on the decrease of the precursors of N-Cl-DCAM, a laboratory-bench-scale system was used to simulate the actual operation of the carbon filter. The results are shown in Table 4. The absolute values of carbon adsorption for the new and old carbon were 8.8 and 3.9 μg/kg, respectively. The removal of N-Cl-DCAM FP by biological activated carbon in new

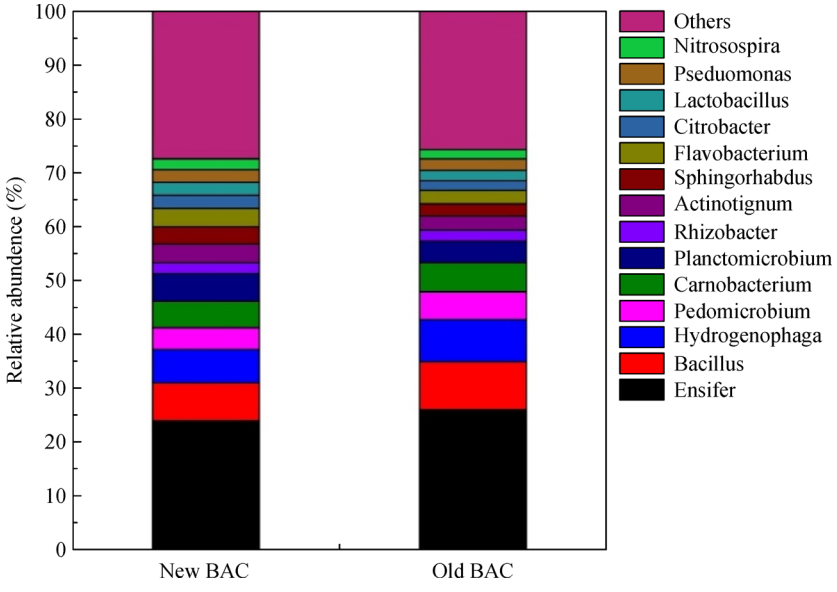

Fig. 7 Relative abundances of bacterial genera on the new and old BAC.

Table 4 Removal of N-Cl-DCAM FP by biological activated carbon and inactivated carbon

Samples	N-Cl-DCAM FP (μg/L)
Effluent of post-ozone contact tank	4.3±0.2
New carbon	
Effluent of biological activated carbon filters	1.7±0.1
Effluent of inactivated carbon filters	1.9±0.1
Old carbon	
Effluent of biological activated carbon filters	3.0±0.2
Effluent of inactivated carbon filters	3.3±0.2

and old carbon filters were 61.07% and 29.84%, respectively, while the removal by inactivated carbon were 54.55% and 22.61%, respectively. Therefore, the reduction of N-Cl-DCAM precursors by the new BAC process was significantly superior to that by the old BAC process. In addition, the carbon adsorption rates of new and old carbon was 89.31% and 75.78%, respectively. The biodegradation rates of new and old carbon were only 10.69% and 24.12%. This indicated that the abatement of the precursors of N-Cl-DCAM through BAC processes was mainly dependent on the adsorptive effect of activated carbon. The different adsorption capacities of GAC were responsible for the different N-Cl-DCAM FPs in the effluent of the old and new BAC filters.

3.4 Analysis of N-Cl-DCAM precursor characteristics

3.4.1 Analysis of MW distribution

To investigate the removal efficiency of different MW organics in the N-Cl-DCAM precursors by the O_3-BAC process, the effluent of each process was screened. The results are shown in Table 5. Low MW organics in N-Cl-DCAM precursors accounted for a large proportion of the total organics, among which organics with MW < 1 kDa accounted for about 40% of the N-Cl-DCAM FP. The conventional water treatment process can remove many of the large MW substances, but it has no obvious effect on the removal of low MW organics, especially those < 1 kDa (Kim and Yu, 2005).There was no obvious removal of low MW organic matter by the ozonation process. This was mainly because the ozone process can change the properties of organic matter in water, with ozone able to oxidize large MW organic matter into low MW organic matter (von Gunten, 2003; Karnik et al., 2005; Chuang and Mitch, 2017). The new and old BAC had different organic matter removal percentage in each MW range. Figure 8 shows the MW distribution of organics in the effluent of the ozone, new BAC, and old BAC treatments. It can be seen that the new BAC process had a significantly better removal efficiency for N-Cl-DCAM precursors than the old BAC process, especially for organic matter with MW < 1 kDa. Because the biomass and microbiological populations of the new BAC and old BAC were similar, the biodegradation effect of the old and new BAC on different MW organics was similar. The differences between the removal efficiencies of different MW organics by the new BAC and old BAC were attributed to the adsorption of activated carbon.

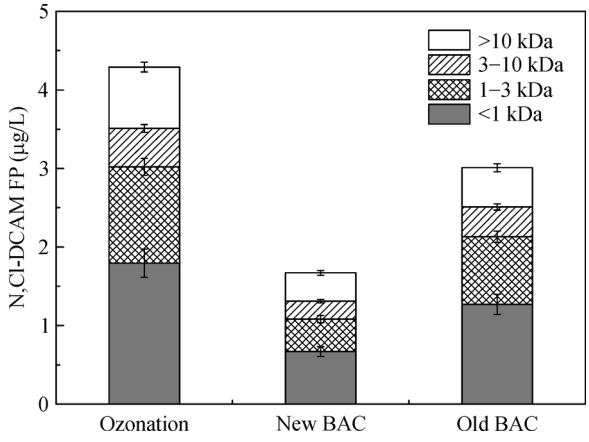

Fig. 8 The MW distribution of organic matter in the effluent of new and old BAC filters.

The inactivated carbon adsorption experiment described in Section 3.3 further confirmed the above conclusion, with different MW organics detected in the N-Cl-DCAM precursors in the influent and effluent of each process. The results are shown in Table 6. The absolute values of carbon adsorption of the new and old carbon for organics with MW < 1 kDa among the N-Cl-DCAM precursors were 3.5 and 1.4 μg/kg, respectively. The adsorption of low MW organic matter by new carbon was clearly better than that for the old carbon. Additionally, the carbon

Table 5 The MW distribution of N-Cl-DCAM precursors in the different processes

Samples	N-Cl-DCAM FP (μg/L)	MW < 1 kDa (μg/L)	MW = 1–3 kDa (μg/L)	MW = 3–10 kDa (μg/L)	MW>10 kDa (μg/L)
Raw water	5.6±0.3	2.2±0.2	1.6±0.2	0.7±0.1	1.1±0.1
Pre-ozone	5.3±0.2	2.2±0.2	1.5±0.1	0.6±0.1	0.9±0.1
Sedimentation	4.6±0.3	1.8±0.1	1.3±0.1	0.6±0.1	0.8±0.1
Post-ozone	4.3±0.2	1.8±0.2	1.2±0.1	0.5±0.1	0.8±0.1
New BAC	1.7±0.1	0.7±0.1	0.4±0.1	0.2±0.1	0.4±0.1
Old BAC	3.0±0.2	1.3±0.1	0.8±0.1	0.4±0.1	0.5±0.1

Table 6 Removal of different MW N-Cl-DCAM precursors by biological activated carbon and inactivated carbon

Samples	MW < 1 kDa (μg/L)	MW = 1–3 kDa (μg/L)	MW = 3–10 kDa (μg/L)	MW>10 kDa (μg/L)
New carbon				
Effluent of biological activated carbon filters	0.7±0.1	0.4±0.1	0.2±0.1	0.4±0.1
Effluent of inactivated carbon filters	0.8±0.1	0.5±0.1	0.3±0.2	0.4±0.1
Old carbon				
Effluent of biological activated carbon filters	1.3±0.1	0.8±0.1	0.4±0.1	0.5±0.2
Effluent of inactivated carbon filters	1.4±0.1	0.9±0.2	0.4±0.1	0.6±0.1

adsorption rates of new and old carbon for low MW organic matter among the N-Cl-DCAM precursors were 92.86% and 77.08%, respectively, which indicates that the carbon adsorption of BAC played a major role in removing small-molecule N-Cl-DCAM precursors.

3.4.2 Analysis of polarity and non-polarity

The polarity characteristics of organic matter were investigated from the reactivity of different molecular structures toward N-Cl-DCAM formation. As shown in Table 7, the non-polar fraction accounted for about 60% of the DOC in the raw water, while the polar components only accounted for about 40%. After chlorination, the non-polar fraction was confirmed to account for most (nearly 70%) of the N-Cl-DCAM FP; thus, indicating that the non-polar fraction tended to form more N-Cl-DCAM than the polar fraction; i.e., the non-polar portion of the N-Cl-DCAM precursors was dominant.

Table 7 Polar and non-polar properties of N-Cl-DCAM precursors

Samples	DOC (mg/L)	N-Cl-DCAM FP (μg/L)
Raw water	4.9±0.3	5.6±0.3
Non-polar	2.9±0.2	3.9±0.3
Polar	1.9±0.2	1.7±0.1

The changes of the polar and non-polar properties of N-Cl-DCAM precursors in the effluent of each treatment process were investigated, and the results are shown in Table 8. The removal of polar organics by the ozonation process was lower than that of non-polar organics. This may be because the ozonation process oxidizes non-polar organics in water and converts them into organics with polar functional groups, such as hydroxyl, carboxyl, and aldehyde groups (Liao et al., 2015). Previous studies have shown that the conventional water treatment process is effective at removing polar organic matter (Liao et al., 2015). The removal of polar and non-polar substances was different for the new and old BAC filters. Figure 9 shows the polar and non-polar properties of N-Cl-DCAM precursors in the effluent treated by new and old BAC filters. It can be seen that the new BAC had a significantly

Table 8 The polar and non-polar properties of N-Cl-DCAM precursors in the different processes

Samples	N-Cl-DCAM FP (μg/L)	Non-polar (μg/L)	Polar (μg/L)
Raw water	5.6±0.3	3.4±0.3	1.7±0.1
Pre-ozone	5.3±0.2	3.7±0.3	1.6±0.1
Sedimentation	4.6±0.3	3.2±0.2	1.4±0.1
Post-ozone	4.3±0.2	2.6±0.2	1.7±0.2
New BAC	1.7±0.1	0.9±0.1	0.8±0.1
Old BAC	3.0±0.2	1.8±0.1	1.2±0.1

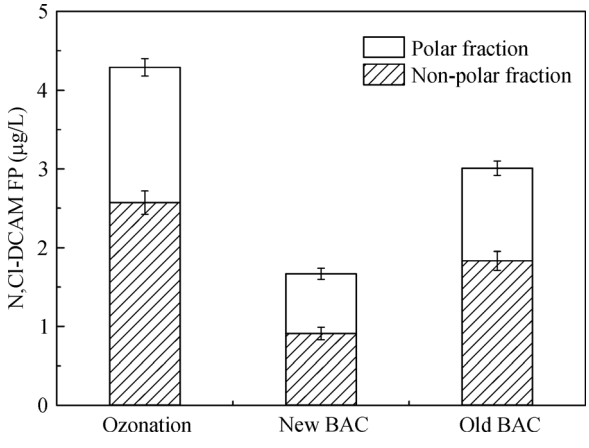

Fig. 9 Polarity and non-polarity of organic matter in the effluent of new and old BAC filters.

better removal efficiency for non-polar organic matter. A previous study found that activated carbon mainly adsorbs non-polar substances in water (Leenheer, 1981). In this study, through the experiment described in Section 3.3, the polarity of organics in the N-Cl-DCAM precursors in the influent and effluent of each process was tested. The results are shown in Table 9. The absolute values of carbon adsorption of the non-polar substances among the N-Cl-DCAM precursors by the new and old carbon were 5.4 and 1.9 μg/kg, respectively, which shows that the adsorption of non-polar substances by the new carbon was clearly better than that by the old carbon. The carbon adsorption rates of the non-polar substances among the N-Cl-DCAM pre-

Table 9 Removal of polar and non-polar organics of N-Cl-DCAM precursors by biological activated carbon and inactivated carbon

Samples	Non-polar (μg/L)	Polar (μg/L)
New BAC		
Effluent of inactivated carbon filters	1.1±0.1	0.89±0.1
Effluent of biological activated carbon filters	0.9±0.1	0.8±0.1
Old BAC		
Effluent of inactivated carbon filters	2.0±0.2	1.3±0.1
Effluent of biological activated carbon filters	1.8±0.1	1.2±0.1

cursors by new and old carbon were 90.96% and 71.62%, respectively, which indicates that the non-polar substances in the N-Cl-DCAM precursors were removed by the BAC process, and were mainly dependent on adsorption by activated carbon.

4 Conclusions

In this study, an LC-MS/MS system was used to establish a new detection method for measuring the N-Cl-DCAM concentration in water samples. N-Cl-DCAM was present in drinking water at a concentration of 1.5 μg/L, and raw water had an N-Cl-DCAM concentration of 5.6 μg/L in samples from a waterworks receiving raw water from Taihu Lake, China. Organics with an MW < 1 and non-polar organic substances accounted for the majority of N-Cl-DCAM precursors. By comparing the changes of N-Cl-DCAM FP in the effluent from different processes, it was found that the effect of a conventional water treatment process on the removal of N-Cl-DCAM precursors was poor, and the removal efficiency of a new BAC filter was better than that of an old filter, which was mainly due to the adsorption of GAC. The removal of N-Cl-DCAM precursors by a BAC filter was mainly dependent on adsorption by GAC, while degradation by microorganisms attached to the GAC was not important. To effectively remove N-Cl-DCAM precursors in existing water treatment processes, it will be necessary to further study removal methods for low MW and non-polar N-Cl-DCAM precursors.

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