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Nitrogen Origins and the Role of Ozonation in the Formation of Haloacetonitriles and Halonitromethanes in Chlorine Water Treatment

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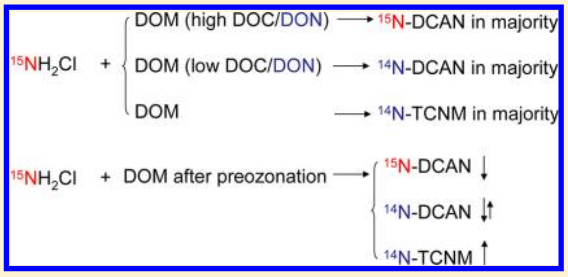
Supporting Information

ABSTRACT: Nitrogenous disinfection byproducts (N-DBPs) such as haloacetonitriles (HANs) and halonitromethanes (HNMs) are formed during water chlorination. Preozonation is sometimes applied to control trihalomethane (THM) formation, but this may risk promoting the formation of HNMs and HANs. The role of ozone in the formation of HANs and HNMs in natural waters remains unclear. The nitrogen sources involved in HAN and HNM formation during the chloramination of dissolved organic matter (DOM) with and without preozonation were evaluated using ^{15}N-labeled monochloramine. The origin of the nitrogen involved in HAN formation was found to depend on the ratio of dissolved organic carbon to nitrogen. In nitrogen-rich solutions HAN nitrogen was mainly from DOM constituents. The formation of ^{15}N-labeled dichloroacetontrile (DCAN) accounted for approximately 30% of the DCAN produced from all hydrophilic acidic and neutral isolates, which have low carbon to nitrogen ratios, while it reached over 50% for the hydrophobic acidic, basic, and neutral isolates with high carbon to nitrogen ratios. Unlabeled trichloronitromethane (TCNM) accounted for over 90% of the total TCNM produced from most of the isolates. The remaining less than 10% of the TCNM was probably generated through an aldehyde pathway. Preozonation reduced DCAN but enhanced the yield of TCNM. The destruction of amino acids and amine structures and subsequent formation of nitro groups by preozonation may help explain the reduced DCAN and increased TCNM formation.



INTRODUCTION

Chlorine is the disinfectant most commonly used in water treatment owing to its ease of use, low cost, and effective germicidal properties. However, chlorine also reacts with dissolved organic matter (DOM) to form disinfection byproducts (DBPs) such as trihalomethanes (THMs) and haloacetic acids (HAAs). Levels of these byproducts are regulated by U.S. EPA and other regulatory agencies worldwide. To reduce the formation of THMs and HAAs, alternatives to chlorine disinfection have been sought. Monochloramine (NH_2Cl) is often used as a secondary disinfectant to maintain chlorine residual and to reduce THM and HAA formation in distribution systems.[1,2] However, other DBPs such as haloacetonitriles (HANs) have been reported in chloramined waters, and sometimes in higher concentrations than in chlorinated water.[3−5] Halonitromethanes (HNMs) have been detected in chloraminated water, particularly after preozonation.[6,7] HANs and HNMs have been reported to be much more geno- and cytotoxic than THMs and HAAs.[8,9]

HANs are known to form from the substitution of hydrogen atoms by chlorine atoms in nitriles.[10] Two pathways have been proposed for nitrile formation involving the chlorination or chloramination of amino acids (Scheme S1 in the Supporting Information).[10] The "aldehyde pathway" involves the formation of an aldehyde first, followed by a reaction between NH_2Cl and aldehyde to form a nitrile, in which reaction NH_2Cl serves as the nitrogen source. The "decarboxylation pathway" involves the N-terminal amino group in amino acids or peptides.[11−14] When an N-terminal amino group is dichlorinated, hydro-

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chloric acid elimination may precede a concerted decarboxylation (i.e., decarboxylation coupled with chloride loss) to form a nitrile. In this pathway, the nitrile's nitrogen originates from dissolved organic compounds. During chloramination both the aldehyde and decarboxylation pathways may be followed simultaneously. Tests with ^{15}N-labeled NH_2Cl and a range of model organic nitrogen compounds have indicated that both NH_2Cl (the aldehyde pathway) and the model organic compounds (the decarboxylation pathway) serve to form dichloroacetonitrile (DCAN).[14,15] Their relative importance in the chloramination of natural waters remains, however, uncertain. It is known only from a case study that 90% of the DCAN nitrogen involved during ^{15}N-labeled monochloramination of Suwannee River natural organic matter (NOM) was derived from $^{15}NH_2Cl$, suggesting the importance of the aldehyde pathway in practice.[5] No other published study has evaluated the nitrogen source involved in HAN and HNM formation during the chloramination of natural water.

Ozonation is capable of reducing THM and HAA precursors;[16−18] it is known to generate aldehydes such as formaldehyde, acetaldehyde, glyoxal, and methylglyoxal.[19,20] Because of this formation of aldehydes, more HAN formation is expected when preozonation is applied prior to chloramination, through the aldehyde pathway. However, reduced HAN formation has been observed during the ozonation−chloramination of authentic waters.[14,16] The reasons behind this need to be explored.

Chlorination and chloramination of organic nitrogen compounds such as amino acids, amines, and nucleic acids form trichloronitromethane (TCNM) at 0.01−0.08% yield.[14,21,22] It has been proposed that chlorine and chloramines may oxidize the amine nitrogen to a nitro group to form TCNM.[21] A recent study has demonstrated, however, that the nitrogen in TCNM originates not only from organic nitrogen compounds, but also from NH_2Cl during chloramination.[15] In addition, the TCNM formation during chloramination does not correlate well with the organic nitrogen content of the dissolved organic matter.[3] The impact of preozonation on TCNM formation in natural waters is unknown.

This study was designed to assess the nitrogen sources in the formation of HANs and HNMs upon chloramination of DOM and the impact of preozonation. ^{15}N-NH_2Cl was reacted with solutions of DOM isolates, with or without preozonation. Gas chromatography−mass spectrometry (GC/MS) coupled with electron ionization (EI) and negative chemical ionization (NCI) were used for HAN and HNM analysis. Besides DOM isolates, several model organic nitrogen compounds and aldehydes were also tested to elucidate the possible pathways.

MATERIALS AND METHODS

Reagents and Solutions. A stock solution of free chlorine (HOCl) was prepared by diluting 5% sodium hypochlorite (NaOCl) (from Sigma) to 1000 mg/L as Cl_2. Monochloramine (NH_2Cl) solutions were prepared daily by reacting equal volumes of ammonium chloride and sodium hypochlorite solutions at a weight ratio of 4 mg/L Cl_2 to 1 mg/L N-NH_4^+. Labeled ^{15}N-NH_2Cl was prepared by mixing ^{15}N-NH_4Cl (98% from Sigma) with chlorine in the same way. The resulting solutions were standardized using DPD titration method.[23] Ozone was generated by a laboratory ozone generator. The ozone concentration of the stock solution was determined using the direct UV absorbance method (measuring UV absorbance at 258 nm with a molar absorptivity of 2950 M^{-1} cm^{-1}).[23] Calibration standards, internal standards, and surrogate standards for the HAN and TCNM analyses were purchased from Supelco. Model compounds, including glycine, L-tryptophan, L-tyrosine, L-asparagine, and β-alanine, were purchased from Sigma. Acetaldehyde, phenylacetaldehyde, and phenylacetonitrile standards were obtained from J&K Chemical.

DOM Fractionation and Characterization. Water from three sources was collected and fractionated. There were two drinking water sources—the Dongjiang and Beijiang rivers in China's Guangdong Province—and a wastewater effluent after secondary treatment. These samples will be referred to as DJ, BJ, and WWTP, respectively. Each sample was fractionated into four isolates—the hydrophobic acidic (HPOA), hydrophobic neutral (HPON), hydrophobic basic (HPOB), and hydrophilic acidic and neutral (HPI-A+N)—using the method developed by Leenheer[24] with slight modification. The fractionation protocol is shown in Figure SI-1. A model solution made by dissolving Suwannee river NOM (Cat. No. 1R101N, from the International Humic Substances Society) was used as a reference, and this will be referred to as SRNOM. The properties of the DOM isolates and SRNOM are listed in Table 1.

Table 1. Properties of DOM Isolates[a]

	isolate description	SUVA (Lmg^{-1} m^{-1})	DOC/DON (mg C/mg N)	bromide (mg/L)
Dongjiang river (DJ)				
1	HPOA	2.6	27	ND
2	HPOB	1.2	NM	ND
3	HPON	1.8	28	ND
4	HPI-A+N	1.4	12	0.21
Beijiang river (BJ)				
5	HPOA	3.9	42	ND
6	HPOB	1.1	NM	ND
7	HPON	1.6	36	ND
8	HPI-A+N	0.8	13	ND
secondary wastewater effluent (WWTP)				
9	HPOA	2.4	20	ND
10	HPOB	1.2	NM	ND
11	HPON	1.5	15	ND
12	HPI-A+N	0.9	10	0.15
Suwannee river NOM (SRNOM)				
13		3.9	48	ND

[a]HPOA−hydrophobic acidic; HPOB−hydrophobic basic; HPON−hydrophobic neutral; HPI-A+N−hydrophilic acidic and neutral. NM: not measured; ND: below detection limit (0.015 mg/L).

Experimental Procedures. The DBP formation experiments were conducted in capped amber glass bottles at room temperature (22 ± 1 °C) in the dark, and the reaction was allowed to proceed for 3 days. The stock solution of the DOM isolates or model organic-N compounds was diluted to 3 mg/L DOC and buffered at pH 7.2 using 10 mM phosphate buffer before use. For the ozone pretreatment tests ozone stock solution was added to achieve an ozone concentration of 3 mg/L. After reaction for 5 min any residual ozone was quenched with sodium thiosulfate. Chloramination, with or without preozonation, was initiated by adding 15 mg/L Cl_2 monochloramine to the test solutions to ensure that monochloramine residuals could be detected after the 3-day incubation period in all samples. After the incubation the samples were quenched

and extracted immediately with methyl tert-butyl ether (MTBE) using the USEPA 551.1 method.[25] The extracts were subjected to DBP analysis to obtain the total HANs and TCNM concentrations.

The nitrogen sources involved in TCNM and DCAN formation were studied by dosing unlabeled and labeled ^{15}N-NH_2Cl to solutions containing DOM or organic-N compounds buffered at pH 7.2 with and without preozonation. The reaction conditions were as described above. After being stored in the dark for 3 days, the mixture was quenched, extracted with MTBE, and concentrated by N_2 blow down. Briefly, a 250-mL sample was extracted in a separatory funnel with 20 mL of MTBE containing 1,2-dibromopropane as the internal standard supplemented with 12 g of anhydrous sodium sulfate. The extracts were collected and purged with N_2 to a final volume of 0.5 mL. The HAN and TCNM contents of the resulting solution were determined using GC/MS.

Acetaldehyde, phenylacetaldehyde, and phenylacetonitrile at 0.16 mM were also dosed with unlabeled 1.6 mM NH_2Cl at pH 7.2. The mixture was subsequently quenched and extracted with MTBE and the resulting solution was analyzed using GC/MS.

Analytical Methods. DOC and total nitrogen concentration were measured using a Shimadzu TOC-V_{CPH} analyzer. UV absorbance at 254 nm was measured with a UV−visible spectrophotometer (Shimadzu, Multispec-1501). Nitrite, nitrate, and bromide ion concentrations were measured using ion chromatography (Metrohm 882 compact IC plus) with an anionic column (metrosepA supp 5). Ammonia was measured using a flow injection analyzer (FIA, QuickChem FIA+, 8000 Series). Dissolved organic nitrogen (DON) concentrations were determined by subtracting the measured nitrite, nitrate, and ammonia concentrations from the total nitrogen after dialysis.[26]

GC-ECD analysis of DBPs was carried out using an Agilent 7890 gas chromatograph with an HP-5 fused silica capillary column (30 m × 0.25 mm I.D. with 0.25-μm film thickness, J&W Scientific). GC/MS coupled with NCI analysis of TCNM was carried out using an Agilent 7890 gas chromatograph coupled with a 5975C mass-selective detector (MSD). The column used was a DB-5MS silica capillary column (30 m × 0.25 mm I.D. with 0.25-μm film thickness, J&W Scientific). Methane was the reagent gas. DCAN was analyzed using a Finnigan Trace GC apparatus coupled with a trace DSQ MS with EI. The column used was a DB-5MS silica capillary column (30 m × 0.25 mm I.D. with 0.25-μm film thickness, J&W Scientific). The analytical methods are described in greater detail in the Supporting Information. Ions with m/z of 74 and 75 were used to quantify the unlabeled and ^{15}N-labeled DCAN concentrations, respectively.[15] TCNM was analyzed by methane chemical ionization using m/z 46 and 47 ions as the quantification ions for unlabeled TCNM and ^{15}N-labeled TCNM, respectively.[15]

Because no standards for ^{15}N-labeled DCAN or TCNM were commercially available, the concentrations of ^{15}N-labeled DBPs were obtained indirectly. The percentages of unlabeled and labeled DCAN and TCNM were calculated based on their spectral abundance obtained from GC-MS. The concentrations were then obtained by multiplying the percentages by the actual concentrations as determined from GC-ECD.

RESULTS

Characteristics of DOM Isolates and Corresponding DBP Formation. Please refer again to Table 1 for the sources and characteristics of the DOM isolates. The HPOA isolates had high SUVA values and DOC/DON ratios. The HPI-A+N isolates had low DOC/DON ratios as a result of their higher organic nitrogen content. The HPI-A+N isolates also had low SUVA values.

Figure 1 displays the formation of TCNM and total HANs (including DCAN, bromochloroacetonitrile (BCAN) and dibromoacetonitrile (DBAN)) from DOM isolates. The HAN yields ranged from 0.002 to 0.014 μmol/mg C with an average value of 0.004 μmol/mg C. The TCNM yields ranged from undetectable to 0.009 μmol/mg C with an average value of 0.003 μmol/mg C. The HPI-A+N isolates generated the most HAN and TCNM upon chloramination, while the HPOB isolates exhibited the lowest yields of TCNM. The formation of HAN and TCNM from each isolates is shown in Figure SI-2.

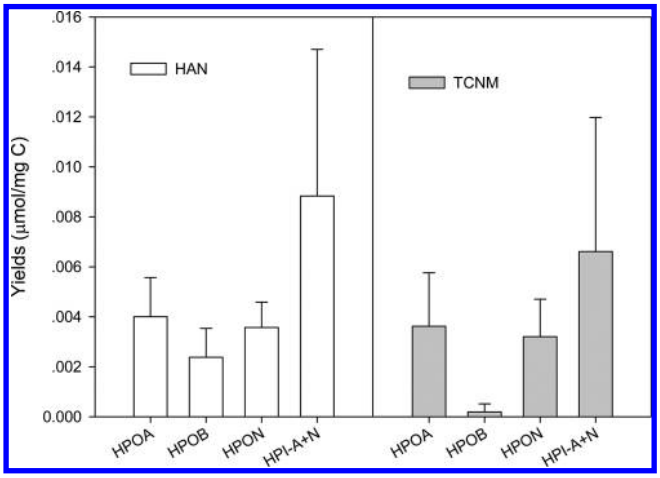

Figure 1. Formation of HANs and TCNM during chloramination of DOM isolates without preozonation (the error bars are the standard deviation from average values). Note: HPOA−hydrophobic acidic; HPOB−hydrophobic basic; HPON−hydrophobic neutral; HPI-A+N−hydrophilic acidic and neutral.

Bromide at 0.21 and 0.15 mg/L was found only in the HPI-A+N isolate from the DJ and WWTP waters, leading to the formation of BCAN and DBAN after chloramination without preozonation. But DCAN was the dominant HAN specie and occupied over 60% of total HANs in HPI-A+N isolates. If only DCAN was considered, the HPI-A+N isolates also generated the highest amount compared to other DOM isolates. The presence of brominated HNMs in these two HPI-A+N isolates was confirmed by the GC/MS spectra, including those typical of dibromonitromethane (DBNM), bromochoronitromethane (BCNM), bromodichloronitromethane (BDCNM), and chlorodibromonitromethane (CDBNM) (shown in Figure SI-3), but they were not quantified due to a lack of standards. The following discussion therefore focuses on the formation of DCAN and TCNM only. It should be noted that ozone oxidizes bromide to hypobromous acid (HOBr), which also reacts with DOM to form brominated DBPs. In HPI-A+N isolates containing bromide, brominated DBPs may have different formation mechanism from chlorinated ones.

^{15}N-Labeled N-DBP Formation from DOM Isolates with or without Preozonation. Figure 2 displays the

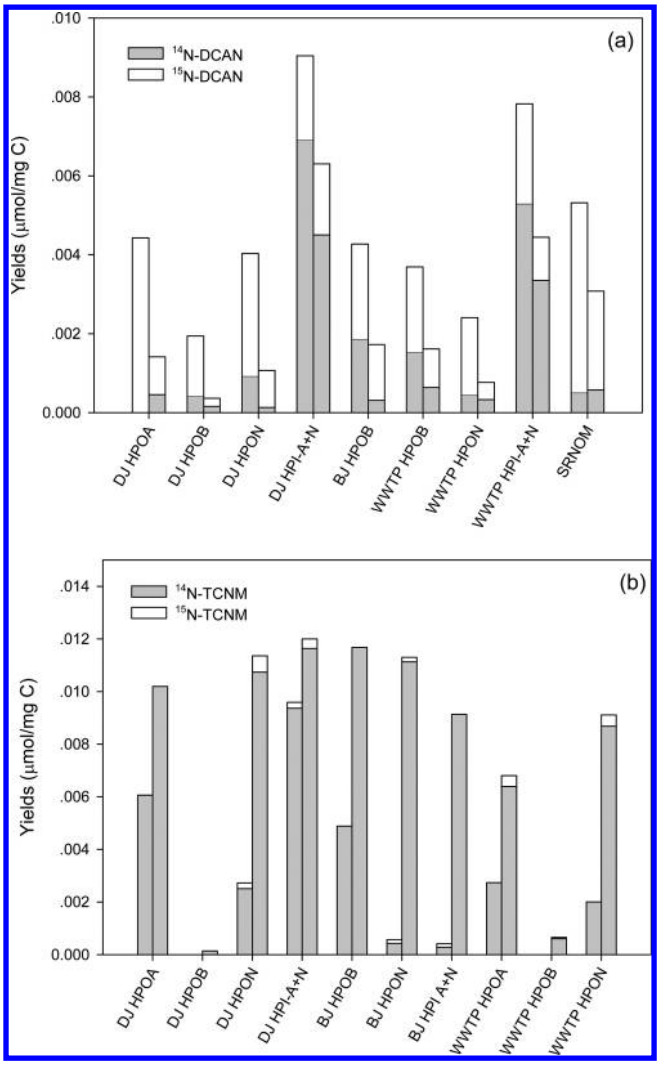

Figure 2. Concentrations of unlabeled and labeled (a) DCAN and (b) TCNM during chloramination of DOM isolates without preozonation (left bar) and with preozonation (right bar).

distribution of ^{15}N-labeled and unlabeled DCAN and TCNM during the chloramination of DOM isolates with and without preozonation. Figure 2a shows that ^{15}N-labeled DCAN was dominant from the hydrophobic isolates and ^{14}N-DCAN was dominant from the hydrophilic isolates. ^{15}N-labeled DCAN accounted for approximately 30% of the total DCAN produced by HPI-A+N isolates, and it was over 50% for the hydrophobic (HPOA, HPOB, and HPON) isolates.

Figure 3 displays the relationships between the DOC/DON ratios of the isolates and the percentages of ^{15}N-labeled DCAN. In general, DOM isolates with low DOC/DON ratios (nitrogen-rich) produced less ^{15}N-labeled HAN. This confirms that the nitrogen in HAN originates from both DOM and monochloramine, and that the nitrogen content of any DOM affects the level of incorporation from each source. On the other hand, Figure 2b shows that unlabeled TCNM was the dominant TCNM in all isolates and accounted for over 90% of the total TCNM in most of them. No relationship was observed between the formation of TCNM and the DOC/DON ratios. This suggests that certain specific organic nitrogen structures in the isolates, rather than DON, are more likely to be TCNM precursors.

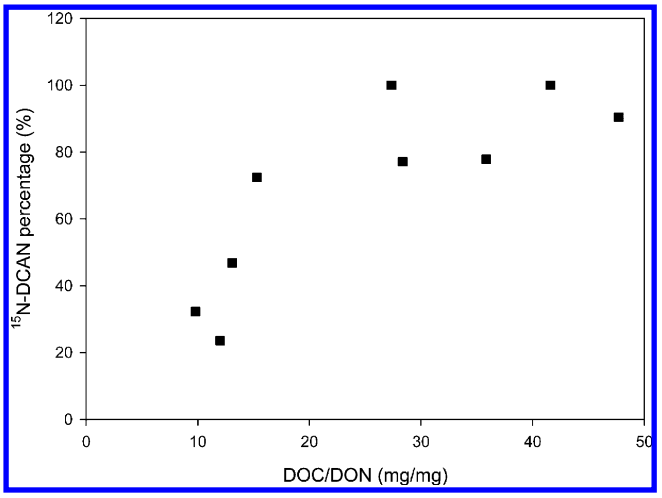

Figure 3. Percentages of ^{15}N-DCAN vs DOC/DON ratios of DOM isolates without preozonation.

Preozonation reduced the formation of ^{15}N-DCAN and total DCAN during subsequent chloramination. Preozonation also resulted in a decrease in ^{14}N-DCAN formation for most of the DOM isolates. Increases in ^{14}N-DCAN formation were observed with the DJ HPOA and SRNOM isolates after preozonation. HPOA isolates generally had higher aromatic content and larger molecular weight.[19,27] Previous studies have reported that ozonation significantly modifies the molecular weight of HPOA isolates but little influences the hydrophilic isolates.[19,28] Ozone selectively reacts with electron rich sites and may even break aromatic rings. The nitrogen in a ring structure may be released after ozonation and attacked by chlorine atoms during the subsequent chloramination, thus enhancing the formation of ^{14}N-DCAN in HPOA isolates. Aldehydes are known to be produced during ozonation, and they could react with chloramines to form nitriles and ^{15}N-DCAN.[10] However, the results observed in this study show the opposite trend. As for TCNM, after preozonation the concentration of unlabeled TCNM was enhanced in all of the DOM isolates. To elucidate the mechanism responsible, organic-N model compounds were selected for further ^{15}N-chloramination studies.

^{15}N-Labeled N-DBP Formation from Model Organic-N Compounds. Tryptophan, tyrosine, alanine, and asparagine were selected as DCAN precursors due to their higher yields of DCAN.[15] They were chloraminated by adding ^{15}N-monochloramine, and the origins of the nitrogen in the resulting DCAN were evaluated. The percentage of ^{15}N-labeled DCAN in the total DCAN ranged from 23% (aniline) to 89% (asparagine). In combination with the other three compounds, including aspartic acid, pyrrole, and methylpyrrole, evaluated in a previous study,[15] the percentage of ^{15}N-labeled DCAN in the total DCAN correlated moderately with the DOC/DON ratios of model compounds—high percentages of ^{15}N-labeled DCAN occurred in compounds with high DOC/DON ratios, as is shown in Figure SI-4. It should be noted that the percentages of ^{15}N-labeled DCAN varied from 33 to 89 for pyrrole, aspartic acid, and asparagine, which had the same DOC/DON ratios of 3.4:1. The percentage of ^{15}N-labeled DCAN was the lowest in alanine with a DOC/DON ratio of 2.8:1. It seems that an electron withdrawing group on one side helps the decarboxylation and release of an imine. It goes to the aldehyde pathway and further chloramination forms ^{15}N-labeled DCAN. The

hydrolysis of imine to form aldehyde is dependent on the R group connected to CH_2 next to it. The stronger the electron withdrawing group R, the lager possibility the formation of aldehyde. The functional groups of R, an indole group in tryptophan, chlorinated intermediates NCl_2-CO- in asparagine, and chlorinated phenol in tyrosine, were electron withdrawing groups. They may attract more electrons than −COOH in aspartic acid and −H in alanine. Therefore, more percentages of ^{15}N-DCAN come from the aldehyde pathway in tryptophan, tyrosine, and asparagine than in aspartic acid and alanine.

As for tyrosine and asparagine with ^{15}N-chloramination, the total DCAN yields were reduced after preozonation. Preozonation reduced ^{15}N-DCAN formation by 12% during subsequent chloramination of asparagine and by 45% with tyrosine. ^{14}N-DCAN formation was reduced or remained similar to that in the preozonated samples (shown in Figure SI-5).

Glycine, tryptophan, and asparagine were selected as TCNM precursors.[14,15,29] Preozonation enhanced the formation of unlabeled and labeled TCNM during subsequent chloramination. Among the organic-N compounds tested, ^{15}N-labeled chloramination of glycine generated mainly unlabeled TCNM. ^{15}N-labeled TCNM was dominant during ^{15}N-labeled chloramination of tryptophan and asparagine (Figure SI-6). The difference could be due to the different structures of these organic-N compounds and they undergo different pathways to form TCNM. Based on the mechanism proposed by Hu et al.[6] and Yang et al.,[15] chlorinated imine may be an intermediate for TCNM formation. A release of −RCHO group is proposed as a step leading to TCNM formation. The electron withdrawn groups such as indole group in tryptophan and chlorinated intermediates NCl_2-CO- in asparagine tend to make the C−C bond break easily, leading to formation of TCNM. Chlorinated imine from chloramination of tryptophan was not observed and $NCl_2-CO-CH_2-CH=^{15}NCl$ was found during chloramination of asparagine. It partially supported the formation of ^{15}N-TCNM from the proposed pathway. TCNM formation from chloramination of glycine may includes the oxidation of $-NCl_2$ to $-NO_2$.[21]

Some intermediates were identified in the chloramination of the model organic-N compounds. The compounds identified during the chloramination of tyrosine included 4-hydroxyphenylacetic acid nitrile ($HO-C_6H_4-CH_2-CN$), its monochlorinated form ($HO-C_6H_3Cl-CH_2-CN$), and (4-hydroxyphenyl) acetaldehyde ($HO-C_6H_4-CH_2-CHO$). The mass spectra interpretation is shown in Figure SI-7. Figure 4 displays the percentage formation of unlabeled and labeled of DCAN and nitrile during ^{15}N-labeled monochloramination of tyrosine with and without preozonation. The signal obtained without preozonation was set as 100%. Interestingly, the percentages of ^{15}N-labeled DCAN and ^{15}N-labeled monochlorinated nitrile were similar, as is shown in Figure 4. This confirmed nitriles as the main DCAN precursors. The nitrile and chlorinated phenol groups in the intermediate render the methylene carbon acidic, promoting its chlorine addition. Hydrolysis releases DCAN (Figure SI-8). The concentrations of (4-hydroxyphenyl) acetaldehyde during the chloramination of tyrosine were further analyzed. Ozonation followed by postchloramination resulted in a 30% decrease in its formation, which corresponds well with the observed 30% decrease in ^{15}N-labeled DCAN formation and is comparable to a 35% decrease in the

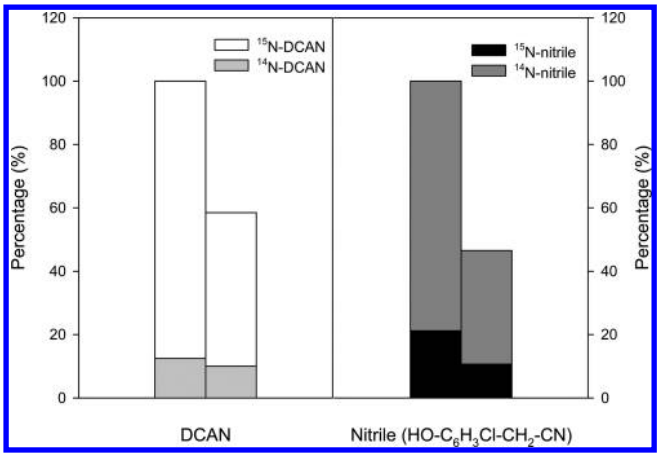

Figure 4. Percentage formation of unlabeled and labeled DCAN and nitrile during ^{15}N-labeled monochloramination of tyrosine with and without preozonation (left bar: without preozonation; right bar: with preozonation).

formation of 4-hydroxyphenylacetic acid nitrile. It also supports that ^{15}N-DCAN is formed from the aldehyde pathway.

During chloramination of asparagine, the GC/MS-NCI spectra suggest that $NCl_2-CO-CH_2-CH=NCl$ is an intermediate and that the nitrogen in the −CH=NCl imine group originates mainly from monochloramine. The mass spectra interpretation is shown in Figure SI-9. Neither nitriles nor aldehydes were found in the chloramination of glycine and alanine using GC/MS-EI or GC/MS-NCI. Chloral hydrate (CCl_3-CHO) was identified in the chloramination of alanine, as shown in Figure SI-10.

Reaction of Aldehydes with Monochloramine. Acetaldehyde and phenylaldehyde react with monochloramine. During the chloramination of acetaldehyde the DCAN yields were 0.02% after 3 days and 0.03% after 7 days. Phenylaldehyde was chosen to represent the (4-hydroxyphenyl)acetaldehyde generated during chloramination of tyrosine because of its similar structure, but neither (4-hydroxyphenyl)acetaldehyde nor the corresponding nitrile was available.

With increasing reaction time, enhanced formation of phenylacetonitrile was observed. No DCAN formation was observed until the fifth day. After reacting for 7 days the yields of phenylacetonitrile and DCAN were 5.4% and 0.04%, respectively (Figure SI-11). Phenylacetonitrile also reacted with monochloramine and 0.04% DCAN after 7 days, which is consistent with the results from the chloramination of phenylaldehyde (Figure SI-12).

DISCUSSION

Two pathways have been delineated for nitrile formation from amino acids (Scheme S1) and amines (Scheme S2). In the "decarboxylation pathway" the nitrile nitrogen originates from organic nitrogen compounds. The aldehyde pathway features inorganic chloramine reactions with aldehydes, where the inorganic chloramines serve as the source of the nitrile nitrogen.

Preozonation reduced DCAN formation through the decarboxylation pathway for most of the DOM isolates tested, indicating the destruction of organic nitrogen compounds by ozone. Ozone reacts with many amino acids and amines, and the rupture of C−N bonds has been detected in some cases.[30] Inorganic nitrogen species such as ammonia, nitrite, and nitrate

are sometimes detected as the end products formed from amine nitrogen.[30−32] Oxidation of amines by ozone may also form nitro groups,[33] which are TCNM precursors but not DCAN precursors. The amino acids and amines available for HAN formation are therefore reduced after ozonation, leading to less HAN formation through the decarboxylation pathway.

Preozonation also reduced DCAN formation through the aldehyde pathway. Aldehydes are byproducts of ozonation. Accordingly, the isolate of ^{15}N-labeled DCAN should increase after ozonation. In fact, however, a reduction in ^{15}N-labeled DCAN was observed after preozonation. The aldehydes formed in significant amount from ozonation were formaldehyde, acetaldehyde, glyoxal, and methyl glyoxal, among which acetaldehyde may form DCAN after reaction with monochloramine.[10] The concentrations of acetaldehyde in various NOM isolates after ozone treatment ranged from 0.4 to 3.9 μg/L.[19] The DCAN concentrations after the reaction of acetaldehyde with NH_2Cl for 3 days ranged from 2×10^{-6} to 2×10^{-5} μmol/L based on the 0.02% DCAN yield from acetaldehyde. So the enhanced formation of acetaldehyde after ozonation contributed little to DCAN formation during subsequent chloramination.

Unlike DCAN, TCNM generation was enhanced by preozonation, which is consistent with previous findings. Interestingly, the nitrogen in the TCNM originated mainly from DOM rather than monochloramine. It exhibited a trend similar to that in the chloramination of glycine, but not of tryptophan or alanine. Chloramines may oxidize the nitrogen in $-NH_2$ precursors from their −3 oxidation state to a +3 nitro group, as shown in Scheme S3.[21] In DOM isolates, less than 10% of the TCNM was probably generated through an aldehyde pathway. Previous studies hypothesized a pathway of TCNM formation from chlorination and chloramination of amino acids and chlorinated imines may be one of the intermediates for TCNM formation.[6,15] However, intermediates other than chlorinated imines were not confirmed from the model compounds in this study. In DOM isolates, oxidation of amine precursors to nitro groups seems to be the predominating pathway for TCNM formation. Compared to chlorine or chloramines, ozone may be more effective in oxidizing $-NH_2$ precursors from their −3 oxidation state to a +3 nitro group,[33] and therefore lead to more HNM formation during subsequent chloramination.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Additional information referred to in the text. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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