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Yuru Wang, Julien Le Roux, Tao Zhang, Jean-Philippe Croué

Institutions: Shaanxi Normal University, King Abdullah University of Science and Technology

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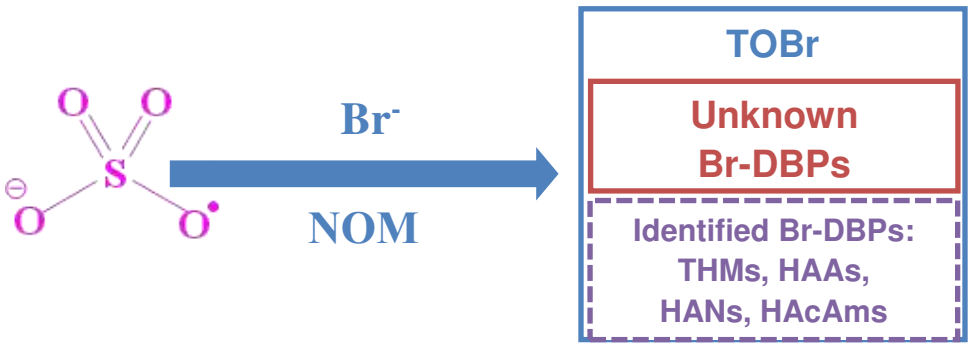
Yuru Wang, Julien Le Roux, Tao Zhang, and Jean-Philippe Croué*

Water Desalination and Reuse Center, King Abdullah University of Science and Technology, Thuwal 4700, Kingdom of Saudi Arabia

* Corresponding author: Tel.: + 966 (0) 2 808 2984.

E-mail address: jp.croue@kaust.edu.sa

TOC Art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THMs, HAAs,
HANs, HAcAms

ABSTRACT

Sulfate radical-based advanced oxidation process (SR-AOP) has received increasing application interests for the removal of water/wastewater contaminants. However, limited knowledge is available on its side effects. This study investigated the side effects in terms of the production of total organic bromine (TOBr) and brominated disinfection byproducts (Br-DBPs) in the presence of bromide ion and organic matter in water. Sulfate radical was generated by heterogeneous catalytic activation of peroxymonosulfate. Isolated natural organic matter (NOM) fractions as well as low molecular weight compounds were used as model organic matter. Considerable amounts of TOBr were produced by SR-AOP, where bromoform (TBM) and dibromoacetic acid (DBAA) were identified as dominant Br-DBPs. In general, SR-AOP favored the formation of DBAA, which is quite distinct from bromination with HOBr/OBr^- (more TBM production). SR-AOP experimental results indicate that bromine incorporation is distributed among both hydrophobic and hydrophilic NOM fractions. Studies on model precursors reveal that low molecular weight acids are reactive TBM precursors (citric acid > succinic acid > pyruvic acid > maleic acid). High DBAA formation from citric acid, aspartic acid, and asparagine was observed; meanwhile aspartic acid and asparagine were the major precursors of dibromoacetonitrile and dibromoacetamide, respectively.

INTRODUCTION

Bromide ion is a ubiquitous component of natural waters and its concentration significantly varies depending on the water source.[1-3] When water is disinfected with chlorine, ozone or chlorine dioxide, bromide ion can be quickly oxidized to hypobromous acid (HOBr), which subsequently reacts with natural organic matter (NOM) to yield brominated disinfection byproducts (Br-DBPs) in an analogous way to hypochlorous acid (HOCl). Elevated bromide levels in source waters have been reported to induce a significant shift in speciation to Br-DBPs, attributed to HOBr being a more efficient substitution agent in comparison with HOCl.[4] It has been shown that Br-DBPs are generally more cyto- and genotoxic than their chlorinated analogues.[5]

In recent years, sulfate radical ($SO_4^{\bullet-}$)-based advanced oxidation processes (SR-AOPs) have gained great scientific and technological interests for the decontamination of groundwater, surface water and industrial wastewaters. Sulfate radical with a high standard reduction potential (2.5 – 3.1 V) can react with a broad spectrum of organic contaminants at near diffusion-controlled limits.[6] $SO_4^{\bullet-}$ can be generated through the activation of persulfates (i.e., peroxymonosulfate (PMS) and peroxydisulfate (PDS)) by alkaline, UV, heat, or transition metals.[7-10] Compared to hydrogen peroxide, persulfates in solid state are relatively stable, therefore favoring storage and transportation. The strong oxidative capacity, relative stable nature, and high aqueous solubility of its precursor compounds (i.e., PMS and PDS), in combination with a variety of $SO_4^{\bullet-}$-generating techniques, make sulfate radical an excellent alternative for eliminating recalcitrant organic pollutants. Recently, promising treatment efficiency of SR-AOPs for waters with various challenging matrices (e.g., landfill leachate) has

been reported.[11-13] Moreover, there has been interest in the application of SR-AOPs as alternative disinfectants.[14]

Similarly to hydroxyl radical, the inorganic constituents of waters are usually competing scavengers of $SO_4^{\bullet-}$. Halide ions are known as important sink of $SO_4^{\bullet-}$. Particularly, bromide ion is of special concern because its reactivity with $SO_4^{\bullet-}$ is approximately 13-fold higher than that of chloride ion.[15, 16] In the presence of bromide ions, bromine atom ($Br^{\bullet}$) formation by $SO_4^{\bullet-}$ oxidation is quite fast. Once $Br^{\bullet}$ is formed, it quickly reacts with bromide ion to produce dibromine anion radical ($Br_2^{\bullet-}$).[17] Besides, $Br^{\bullet}$ and $Br_2^{\bullet-}$ can also undergo a series of reactions with Br^- and H_2O, leading to the generation of $BrOH^{\bullet-}$ and $HOBr/OBr^-$ (see Table S1 of the Supporting Information (SI)).[17-21] Direct reaction of bromide ion with the monosubstituted peroxide precursor of $SO_4^{\bullet-}$ (i.e., PMS) also occurs, however, the rate of active bromine formation is extremely low when PMS is used alone without activation (Figure S1).[22] In water, these chain reactions involving reactive bromine species (i.e., $Br^{\bullet}$, $Br_2^{\bullet-}$, $BrOH^{\bullet-}$, and $HOBr/OBr^-$) can be terminated by reacting with NOM to form brominated byproducts, which poses one of the primary issues of concern for the real water/wastewater application of SR-AOPs.

To date, no information is available about bromine-incorporation into organic matter from bromide-containing water during SR-AOPs. Therefore, the objectives of this research were to investigate the formation and speciation of regulated and emerging DBPs with respect to NOM properties, and to study and compare bromine-incorporation by SR-AOPs with bromination by $HOBr/OBr^-$. Brominated trihalomethanes (THMs), haloacetic acids (HAAs), and haloacetonitriles (HANs) are the major Br-DBPs of concern in this study. Total organic bromine (TOBr) was used to evaluate the total incorporation of bromine into organic molecules.

Moreover, a range of structurally diverse model compounds including six amino acids (Group I), three phenolic compounds (Group II), and six carboxylic acids (Group III) which represent important moieties of NOM were tested to identify significant precursors of Br-DBPs and TOBr.[23] Amino acids featuring high levels of organic nitrogen may promote nitrogenous disinfection byproducts (N-DBPs) formation. Haloacetamides (HAcAms), an emerging class of N-DBPs, were therefore monitored for experiments involving amino acids. The $CuFe_2O_4$ activated PMS process was employed to generate $SO_4^{\bullet-}$, rather than UV/PMS or UV/PDS, to avoid any interference from UV irradiation.[24]

MATERIALS AND METHODS

Materials. A detailed description of reagents and preparation procedures of $CuFe_2O_4$ spinel catalyst and bromine stock solution is provided in Text S1 (SI).

NOM Samples and Selection of Model Compounds. Four previously isolated NOM fractions were employed in this study (Table S2, SI). Three hydrophobic NOM fractions (i.e., hydrophobic acids or HPOA obtained from base desorption, hydrophobic or HPO isolated with acetonitrile/water desorption) showing very different chemical composition were selected: SR HPOA isolated from the Suwannee River (Georgia, USA); SPR HPOA isolated from the South Platte River (Colorado, USA) and CR HPO obtained from Colorado River (California/LA Verne, USA). The hydrophilic acid and neutral fraction (BR HPIA+N) isolated from Blavet River (Côte D'Armor, France) was also used in this work. NOM fractions were isolated using two slightly different comprehensive isolation protocols described elsewhere.[25] Three groups of model compounds representing functional moieties of NOM were selected as NOM surrogates. Group I consisted of six amino acids (i.e., asparagine, glutamic acid, phenylalanine, tryptophan, tyrosine, and aspartic acid). Group II included three phenolic compounds (i.e., phenol,

hydroquinone, and salicylic acid). Six carboxylic acids (i.e., citric acid, oxalic acid, malonic acid, succinic acid, maleic acid, and pyruvic acid) were selected as group III to represent low molecular weight acids. Structures and physicochemical properties of the model compounds are presented in Table S3 (SI).

Experimental Procedure. Experiments were conducted in duplicate or triplicate at room temperature (20 ± 2 ºC) in 250 mL capped amber bottles (individual bottle per contact time) under headspace-free conditions. NOM isolate experiments were performed at a concentration of 5-7 mg L^{-1} (final DOC content of 2.2 to 2.7 mg L^{-1} was verified by TOC analyzer) in the presence of 2 mg L^{-1} bromide (25 µM Br^-) buffered with 10 mM tetraborate, unless otherwise indicated. Reactions with model compounds were conducted with 50 µM individual molecule solutions in the presence of 4 mg L^{-1} bromide (50 µM Br^-) buffered with 10 mM tetraborate. Nitric acid and/or sodium hydroxide were used to adjust the initial pH of the solutions. For $SO_4^{\bullet-}$-based tests, the reaction was initiated by adding an appropriate amount of $CuFe_2O_4$ spinel catalyst and PMS (Sigma Aldrich, $KHSO_5 \cdot 0.5KHSO_4 \cdot 0.5K_2SO_4$) stock solution. The $CuFe_2O_4$/PMS system generates $SO_4^{\bullet-}$ as the major radical species and the sulfate radical yield ratio from PMS was approximately 1 mol per mol.[24] The bottles were immediately capped and placed in a shaker (IKA® KS 260) at a speed of 500 rpm to maintain complete homogeneity throughout the reaction. Samples were withdrawn at specific time intervals, immediately quenched with excess sodium nitrite, and then filtered through 0.45 µm glass fiber syringe filters before analysis. Bromination was conducted as a comparison by dosing a predetermined amount of HOBr/OBr^- into the same amount of NOM isolates and model compound solutions buffered with 10 mM tetraborate in 250 mL amber bottles without headspace.

Analytical Methods. *NOM solution analyses.* Dissolved organic carbon (DOC) content was measured by a Shimadzu TOC-Vcsh Analyzer. UV absorbance at 254 nm was recorded using a Shimadzu UV-2550 UV-VIS spectrophotometer. A liquid chromatography-organic carbon detector (LC-OCD Model 8, DOC-LABOR, Germany) with a size exclusion chromatography column was employed to compare NOM compositions. Three-dimensional fluorescence excitation - emission matrices (FEEM) were obtained using an Aqualog® CDOM Fluorometer (Horiba Scientific, Japan). Further details with respect to LC-OCD and FEEM measurements are presented in Text S2 (SI).

Brominated organic compounds and residual oxidant. Samples for TOBr analysis were enriched through adsorption on activated carbon column using a TOX sample preparatory unit (TXA-03, Mitsubishi Chemical Analytech Co., Ltd, Japan). TOBr was then transformed into hydrogen halide under high-temperature (950 ºC) combustion of the activated carbon for at least 30 min via an AOX-200 adsorbable halogen analyzer, and then collected in Milli-Q water as bromide ion. Off-line quantification of bromide ion was performed by ion chromatography (Dionex ICS-1600) equipped with a conductivity detector and a Dionex IonPac® AS-15 column (2 × 250 mm), using a 30 mM KOH solution at a flow rate of 0.4 mL min^{-1} as mobile phase. The obtained Br^- concentration was used to calculate the concentration of TOBr (as μg L^{-1} Br^-). During bromination experiments, residual bromine was monitored at the time of sampling by DPD colorimetric method. Residual PMS was determined using colorimetric method after reacting with Co^{2+} and ABTS to form a colored ABTS radical cation (further details in Text S3, SI).

Br-DBPs analysis. Samples for the analysis of THMs/HAAs were extracted with methyl tert-butyl ether (MTBE) within 1 h after quenching based on the EPA Method 551 and 552,

respectively. HAcAms were extracted with ethyl acetate following a similar method to EPA Method 551. THMs, HANs, and HAcAms were quantified on a gas chromatography (Agilent 7890A) equipped with an electron capture detector (GC-ECD), while MTBE extracts for HAAs were analyzed on an Agilent 7890A GC equipped with Agilent 5975C inert XL MSD with Triple Axis Detector (GC-MSD). DBPs were separated on a DB-1701 (30 m × 250 μm × 0.25 μm) capillary column. Analytical details are provided in the SI (Text S3).

RESULTS AND DISCUSSION

Characteristics of NOM Isolates. The NOM isolates exhibited a wide range of $SUVA_{254}$ values (Table S2). SR HPOA showed the highest $SUVA_{254}$ (4.97 L mg^{-1} m^{-1}), indicating a high degree of aromaticity, followed by SPR HPOA (3.11 L mg^{-1} m^{-1}) and CR HPO (2.08 L mg^{-1} m^{-1}). BR HPIA+N showed the lowest $SUVA_{254}$ (1.27 L mg^{-1} m^{-1}), which is characteristic of low content of aromatic moieties. Our previous works[25] indicated that SR HPOA is characterized by the predominance of fulvic acid structures derived from lignins and tannins (high aromatic/phenolic carbon and carboxyl group contents) and CR HPO mainly incorporates fulvic acid structures derived from terpenoids (lower aromatic carbon and phenolic content, higher methyl group content) incorporating abundant polysaccharides moieties. SPR HPOA showed an intermediate composition with both types of aromatic structures well represented.[25] In general, hydrophilic acids plus neutral NOM such as BR HPIA+N can be described as a mixture of aliphatic hydroxy acids (e.g., low molecular weight acids), N-acetylaminosugars, neutral carbohydrates, and neutral peptides.[25] These differences in composition between the four NOM fractions are in good agreement with the additional structural information obtained by LC-OCD and FEEM analyses (Text S3 and Figures S2 to S4, SI).

Bromine-incorporation into NOM Isolates. Preliminary experiments with SR HPOA were conducted to investigate the formation kinetics of TOBr and Br-DBPs from bromide-containing water by SR-AOP. Recent studies have shown that $SO_4^{\bullet-}$ can lead to complete conversion of Br^- to BrO_3^- in ultrapure water via $HOBr/OBr^-$ as an intermediate path.[2, 26] However, no bromate formation was observed in this study in the presence of NOM. Moreover, the $CuFe_2O_4$ catalyst had negligible impacts on the UV absorbance at 254 nm and TOC of NOM isolates, suggesting insignificant adsorption of NOM on the catalyst (data not shown). Figure 1 illustrates TOBr and Br-DBPs evolution profiles by SR-AOP in the presence of 25 μM Br^- at pH 7.5. TOBr was rapidly formed within the first 4 h, where fast decomposition of PMS (> 70%) was observed. After 4 hours, TOBr concentration slowly decreased throughout the duration of the experiment (24 h), which is probably due to reactions of sulfate radical with TOBr components. Bromoform (TBM) formation showed a similar trend as TOBr, suggesting that TBM can be oxidized by the sulfate radicals remaining in the system, which was confirmed by additional experiments (Figure S5). Yields of both dibromoacetic acid (DBAA) and monobromoacetic acid (MBAA) gradually increased with reaction time. As opposed to TBM, HAAs were not decomposed at longer reaction times. Low levels (< 4 μg L^{-1}) of bromochloroacetonitrile (BCAN) and dibromochloromethane (DBCM) were produced due to the presence of trace chloride in the potassium bromide salt used to prepare the solutions.

Figures 2-4 present the influence of PMS concentration, bromide ion concentration, and solution pH on the formation and speciation of TOBr and Br-DBPs by SR-AOP. In all cases TBM and DBAA were the dominant identified Br-DBPs. TOBr and HAAs increased with increasing PMS dosage, while the formation of TBM exhibited an increasing and then a decreasing pattern because of its destruction with excess sulfate radicals. Increasing bromide

concentration enhanced the formation of TOBr, TBM, and DBAA (Figure 3), which was expected, as an increase in [Br^-] led to a greater concentration of reactive bromine radical species in the system. As shown in Figure 4, the formation of both TOBr and identified Br-DBPs was highly pH-dependent. TOBr and DBAA gradually increased with increasing pH until reaching a maximum at pH 7.5 and then rapidly decreased as pH was further increased to 9.5, which is possibly related to the transformation of $SO_4^{\bullet-}$ to hydroxyl radical through the reaction with OH^-. The high efficiency of $CuFe_2O_4$/PMS system at neutral pH was discussed in detail in a previous study.[24] The significant reduction of TOBr and DBAA at higher pH is also likely related to the non-radical self-dissociation pathway of PMS in alkaline conditions.[27] Besides, hydrolysis of DBAA at pH > 8.0 is believed to be another reason responsible for its reduced concentration at basic pH.[28] TBM formation increased with increasing pH, which is consistent with the commonly accepted explanation that base-catalyzed hydrolysis mechanisms play a significant role in THM formation.[29] This pH dependence of DBAA and TBM formation from NOM by SR-AOP follows the behavior expected for chlorination/bromination of NOM, suggesting that sulfate radical-induced formation of Br-DBPs showed some similarities compared to that of chlorination/bromination. As a result, further studies were conducted to fully address the differences and similarities between the two processes.

Figure 5 illustrates the formation and speciation of TOBr and Br-DBPs from various NOM isolates by SR-AOP in the presence of 25 μM Br^- at pH 7.5 and for a contact time of 2 h in comparison with bromination (a HOBr/OBr^- concentration of 25 μM). The comparison was conducted to test if the bromination trend of these reactive bromine species generated in SR-AOP is different from that of HOBr/OBr^-. Considerable formation of TOBr from NOM isolates by sulfate radical oxidation of bromide-containing water was observed, ranging from 56 - 107 μg

245 mg^{-1} C (Figure S6). On a molar basis, about 6.5 - 12.2% (Figure 5a) of the initial bromide was
246 transformed to TOBr. Nevertheless, SR-AOP produced much less TOBr than the bromination
247 process. Approximately 8.5 - 25% of initial bromine was incorporated into TOBr, likely due to
248 (1) bromine being a preferable substituting agent[4] and (2) possible subsequent decay of
249 brominated compounds by sulfate radical in SR-AOP system.[2] It is known that identified DBPs
250 only account for a fraction of the total organic halogen (TOX). In fact, approximately 50% of the
251 TOX from chlorination of natural waters remains unknown,[5, 30-32] while over 70% formed by
252 chloramines has not been identified.[32, 33] In the present study, quantified Br-DBPs only
253 constituted 22 - 33% of TOBr during SR-AOP, compared to 28 – 48% in bromination (Figure
254 5a). Speciation analysis revealed that DBAA was the predominant Br-DBPs during SR oxidation,
255 accounting for 90 ± 6% of HAAs and 54 ± 6% of total identified Br-DBPs by weight, followed
256 by TBM which contributed to 75 ± 3% of the THMs and 31 ± 3% of total identified Br-DBPs. In
257 contrast, NOM isolates were more susceptible to the formation of Br-THMs upon bromination.
258 TBM was by far the major contributor of total identified Br-DBPs (63 - 86% on a weight basis)
259 upon bromination, while DBAA and TBAA contributed to 5.2 - 10.4% and 3.2 - 5.3%,
260 respectively (Figure 5b and 5c). Besides, bromination tended to incorporate more bromine into
261 HAAs to form mainly DBAA and TBAA, while SR-AOP yielded mainly DBAA and MBAA (to
262 a lesser extent) with negligible TBAA formation, indicating again a different trend in Br-DBPs
263 formation from active bromine species formed in SR-AOP as compared with bromination.
264 For both SR-AOP and bromination, the formation of TOBr and Br-DBPs among different
265 types of NOM isolates exhibited distinct variation, which could be related to the different NOM
266 properties and their reactivities towards the oxidants. TOBr and Br-DBPs formation correlated
267 well to the $SUVA_{254}$ values of the three hydrophobic NOM isolates during SR-AOP.

Interestingly the hydrophilic NOM isolate (i.e., BR HPIA+N) with the lowest $SUVA_{254}$ formed high amounts of both TOBr and Br-DBPs similar to those formed from SR HPOA (Figure 5a).

These results demonstrate that SR-AOP favors the formation of DBAA in comparison to bromination which tends to produce more TBM. The DBAA yields from various NOM isolates during SR-AOP were 2.4 - 5.84 times higher than those from bromination. The hydrophilic fraction as well as hydrophobic acid with the highest $SUVA_{254}$ value were the dominant sources of TOBr and Br-DBPs during SR-AOP, while good correlations ($R^2 > 0.81$) were observed between aromaticity of NOM and Br-DBP formation during bromination. The significant differences in distribution and speciation pattern of Br-DBPs upon SR-AOP and bromination suggest that sulfate radical-induced DBPs formation involves different reaction mechanisms as compared to bromination. In the SR-AOP system, both $SO_4^{\bullet-}$ and bromine radicals (e.g., $Br^{\bullet}$ and $Br_2^{\bullet-}$) can react with organic compounds via abstraction of hydrogen, addition to unsaturated compounds or one-electron oxidation.[15] As such, multiple pathways could be involved in the formation of TOBr and Br-DBPs by SR-AOP. To further understand the importance of precursor characteristics and the DBPs formation mechanisms in SR-AOP system, a broad spectrum of model compounds were tested as precursors.

Formation of TOBr and Br-DBPs from Model Compounds. Table 1 summarizes the incorporation of 50 μM bromide ion (i.e., 4 mg L^{-1}) into 50 μM model compounds by SR-AOP (100 μM PMS and 50 mg L^{-1} $CuFe_2O_4$) at pH 8 and 24 h of contact time. Bromination of 50 μM model compounds by 50 μM HOBr at pH 8 was tested for comparison. Results for 2 h of reaction were also provided in Table S4 (SI). Consistent with the observation of bromine incorporation into NOM isolates, SR-AOP induced higher yields of DBAA and MBAA for nearly all the model precursors in comparison to bromination.

Particularly, LMW acids (Group III) were certainly the most important precursors of TBM during SR-AOP, while TBM yields from amino acids (Group I) and phenolic compounds (Group II) were minimal. Upon SR-AOP and bromination, TBAA mainly originated from LWM acids and phenolic compounds, respectively. For the SR-AOP system, TBM formation from each aliphatic carboxylic acid predominated over the other identified Br-DBPs, whereas DBAA was the major species from amino acids and phenolic compounds. Formation of N-DBPs was observed by both SR-AOP and bromination of amino acids, although generally to a small extent except for asparagine.

Among the studied model compounds, citric acid (a very HPI acid), was the most reactive Br-DBPs precursor upon SR-AOP, yielding the highest amounts of TBM (1144.3 μg L^{-1}), DBAA (434.6 μg L^{-1}), and MBAA (85.3 μg L^{-1}). More than 35.8% of initial bromide ion was incorporated into TOBr, where the identified Br-DBPs accounted for nearly 100% of TOBr. Bromination of citric acid also yielded comparable TBM and to a lesser degree DBAA after 24 h. However, TBM formation from bromination was much slower as only 14.0% was produced within 2 h, whereas more than 68.8% of the 24 h TBM yield was formed in 2 h by SR-AOP. Sulfate radicals are known to efficiently react with most aliphatic carboxylic acids, leading to oxidative decarboxylation of these compounds.[34] Besides, reaction rate constants of $SO_4^{\bullet-}$ scavenging by carboxylate ions are siginificantly higher than their corresponding carboxylic acids due to the fact that the former proceeds by one electron transfer from the carboxylate group to $SO_4^{\bullet-}$ and the latter via hydrogen abstraction from C-H bond.[35] Consequently, decarboxylation of aliphatic carboxylic acids by $SO_4^{\bullet-}$ through one electron transfer is favored in this study as most LMW acids were deprotonated into carboxylate anion at pH 8 (see Table S3 for the pK_a values). For citric acid, $SO_4^{\bullet-}$ first abstracts one electron from the carboxylate group of β-carbon

followed by the loss of CO_2 and the formation of a corresponding C-centered radical ($HOC^{\bullet}(CH_2COO^-)_2$) which then converts the hydroxyl group of the β-carbon to a more stable form of keto group. The resulting 3-oxopentanedioic acid ($HOOC\text{-}CH_2\text{-}C(O)\text{-}CH_2\text{-}COOH$), an aliphatic β-keto acid, favors rapid halogenation at the two enolizable methylene groups doubly activated by adjacent carbonyl groups.[36] Subsequent decarboxylation/hydrolysis or oxidation of the ketone gives rise to substantial TBM, DBAA, and MBAA formation. Bromination of 3-oxopentanedioic acid at pH 8 was reported to be relatively fast.[37] As such, oxidative decarboxylation of citric acid and subsequent transformation into 3-oxopentanedioic acid are believed to be the rate-limiting step responsible for the slower TBM formation kinetics of citric acid by bromination as compared to SR-AOP.

Pyruvic acid, an α-keto acid, was another important TBM precursor by SR-AOP. TBM accounted for 95% of the TOBr formed followed by a small amount of DBAA. Although to a lesser extent, bromination of pyruvic acid also yielded considerable amount of TBM. Chlorination of pyruvic acid was reported to proceed via dominated oxidation pathway (> 98.5%), yielding TCAA as major byproduct.[38] In this study, the electrophilic substitution pathway dominates given the prevailing TBM yields. The reaction pathway discrepancy between SR-AOP/bromination and chlorination is likely due to a higher reactivity of bromine species than chlorine in halogenating reactions. It is reasonable that α-hydrogens in methyl group of pyruvic acid undergo three successive halogenations upon the attack by bromine radicals or bromine to give a tribromopyruvic acid ($CBr_3\text{-}C(O)\text{-}COOH$). Subsequent hydrolysis of this intermediate releases TBM and oxalic acid. Based on the formation of DBAA by SR-AOP, decarboxylation pathway that converts pyruvic acid to acetaldehyde (CH_3CHO) should also occur. The resulting acetaldehyde favors halogenation at α-hydrogens, further oxidation leading to DBAA.

8.1% of initial bromide was incorporated into TOBr formed from maleic acid by SR-AOP, and TBM contributed to 43.6% of TOBr. In contrast, bromination showed different patterns of speciation with 19.1% bromine being converted into TOBr, while TBM accounted for only 3.76% of TOBr. The significantly higher TBM formation by SR-AOP is believed to result from the preference of sulfate radical on oxidizing unsaturated carbon bonds.[39] Initially, the attack of $SO_4^{\bullet-}$ on the carbon-carbon double bond of maleic acid leads to the formation of oxobutanedioic acid (HOOC-C(O)-CH_2-COOH) through hydroxylation along with isomerization. Decarboxylation of oxobutanedioic acid occurs yielding pyruvic acid, which eventually leads to the formation of TBM upon further reactions. It is also probable that oxobutanedioic acid, which is also an aliphatic β-keto acid, contains an activated methylene group especially susceptible to halogenation. After halogenation, decarboxylation likely occurs yielding a dibromopyruvic acid, which can undergo halogenation followed by hydrolysis to yield TBM. Bromination of maleic acid is known to proceed via anti-addition reaction on alkene group to form a stable mixture of dibromomaleic acid enantiomers,[40] which would explain the relatively higher TOBr and considerably lower TBM formation observed.

For the three saturated dicarboxylic acids (i.e., oxalic acid, malonic acid, and succinic acid) subjected to SR-AOP, both TBM and DBAA yields increased with increasing carbon chain length. Insignificant substitution occurred on oxalic acid upon SR-AOP with less than 3.7% of bromine incorporated into TOBr. Oxalic acid being the simplest dicarboxylic acid with its two carbon atoms in the maximum oxidation state, decarboxylation proceeding twice to yield two carbon dioxides should be the dominating reaction pathway, supported by the conclusion of Zhang et al.[24] Upon attack by sulfate radical, malonic acid also undergoes decarboxylation to form acetic acid which can be hardly halogenated due to the inductive effect of carbonyl group

and the absence of an electron donating alkyl group. In this study, succinic acid was the second most significant TBM precursor upon SR-AOP (see Table 1) with more than 14.4% of initial bromine being converted into TBM. It is likely that decarboxylation of succinate occurs twice followed by complete halogenation to yield two TBM. For bromination, both oxalic acid and succinic acid were characterized by a low bromine demand (see Table S5), and low TOBr and TBM formation, where only 2.3% and 1.5% of bromine was incorporated into TOBr, respectively. Similar findings were also observed when oxalic acid was subjected to chlorination.[41] Bromination of malonic acid led to nearly no TBM formation, but yielded significant amount of DBAA with 9% of bromine being incorporated into DBAA after 24 h and more than 71% being formed within the first 2 h. This high DBAA formation can be explained by the presence of an α-carbon flanked by two adjacent carbonyl functional groups enhancing electrophilic substitution. Accordingly, malonic acid undergoes α-bromination twice to give a dibromomalonic acid which subsequently decarboxylates to DBAA.

Upon SR-AOP, asparagine was a predominant precursor of dibromoacetamide (DBAcAm) (117.4 μg L^{-1} at 24 h) which along with DBAA (74 μg L^{-1} at 24 h) were the major Br-DBPs generated. DBAcAm yield (1068.6 μg L^{-1}) from bromination of asparagine was substantial with over 19% of initial bromine being incorporated into DBAcAm, which was more than 8 times of that from SR-AOP. DBAA and DBAN were also produced from bromination of asparagine (233.3 μg L^{-1} and 112.9 μg L^{-1}, respectively). DBAcAm was formed to a considerably higher extent by bromination. Besides, asparagine exhibited a very fast DBAcAm formation rate upon bromination with nearly 100% being formed within 2 h, while DBAN slowly increased from 14.9 μg L^{-1} at 2 h to 112.9 μg L^{-1} at 24 h. This result suggests that the majority of DBAcAm is not likely a result of the dihaloacetonitrile (i.e., DBAN in this study) hydrolysis pathway.[42] In

383 contrast, the side-chain amide group of asparagine plays a key role in DBAcAm formation,
384 similarly to the mechanism of asparagine chloramination proposed by Huang et al.[43] Compared
385 to bromination, the lower DBAcAm formation from asparagine by SR-AOP may result from the
386 oxidation of the side-chain amide nitrogen group by sulfate radical and bromine radicals ($Br^{\bullet}/Br^{-}$
387 (2.00 V)) due to their high redox potential. Small amounts of bromoacetamide (BAcAm) were
388 generally detected from amino acids subjected to SR-AOP with asparagine as the major
389 precursor. However, this was not observed during bromination. Aspartic acid, selected as a
390 hydrophilic surrogate, was the second most reactive precursor of DBAA (198.3 μg L^{-1}) and
391 MBAA (18.3 μg L^{-1}) and the principal contributor of DBAN (29.2 μg L^{-1}) as a result of SR-AOP.
392 Similar formation patterns were also observed from chlorination of aspartic acid.[41] The relatively
393 high formation of DBAA can be explained by the preferential formation of 3-oxopropanoic acid
394 at pH 8 which is an aliphatic β-keto acid compound and a moiety known to have high
395 dihaloacetic acid formation potential.[37, 44] Bromination of amino acids exerted a significant
396 bromine demand, where nearly 100% bromine was consumed within 2 h (Table S5). Asparagine
397 and tyrosine exhibited a high halogenation efficiency with 39.4% and 32.6% of initial bromine
398 being converted into TOBr in 24 h, respectively, while the other amino acids were characterized
399 by lower TOBr formation (< 6%).
400 Model compounds with phenolic groups including tyrosine, phenol, and salicylic acid were
401 major precursors of TOBr upon both SR-AOP and bromination. This would be attributed to the
402 electron-donating effect of hydroxyl group attached to the aromatic ring, therefore facilitating the
403 electrophilic aromatic substitution by both reactive bromine radicals and bromine. For Group II
404 in the SR-AOP system, DBAA was the major identified Br-DBPs followed by TBM and MBAA,
405 while no formation of TBAA was observed (Table 1). On the other hand, bromination of model

406 compounds with phenolic groups produced considerable amounts of TBM followed by small
407 amounts of TBAA and DBAA.

408 **Environmental Significance.** It is proved in our previous study[24] that PMS forms inner-
409 sphere coordination (i.e., specific adsorption, a strong surface interaction which is not influenced
410 by ionic strength) with the surface metal sites of $CuFe_2O_4$. In excess of PMS, one can expect that
411 the bromine species generated in the solution would have limited access to the metal sites of the
412 catalyst because these sites are already occupied by PMS. Figure 1a shows that bromine
413 incorporation into the organic structure (i.e., bromination) finished within 4 hours, while the
414 remaining PMS concentration in the solution was still above 10 μM. Therefore, PMS was in
415 excess during the major bromination reaction. Although this study is based on the specific
416 $CuFe_2O_4$-induced sulfate radical generation process, the result can still largely represent the
417 bromination trend of organic matter in SR-AOPs. Our study reveals that $SO_4^{\bullet-}$ based-AOPs
418 produces brominated byproducts including regulated and emerging Br-DBPs when applied to
419 waters containing bromide ions. At bromide concentrations relevant to natural environment (i.e.,
420 2.5 - 6.5 μM) our results showed that significant amount of TOBr (i.e., 25 - 50 μg mg^{-1} C) with
421 bromoform and dibromoacetic acid as the major identified Br-DBP species (i.e., 3.5 - 6 and 2 - 7
422 μg mg^{-1} C) can be produced from sulfate radical within 2 hours at pH 7.5. When applied as a
423 decontamination strategy for natural waters (i.e., bromide containing ground or surface waters
424 with DOC content ranging from 2 to 10 mg L^{-1}), the potential risk of producing substantial
425 amount of regulated and non-regulated Br-DPBs from sulfate radical oxidation should be
426 considered. In the case of potable water production, the formed Br-DPBs from sulfate radical
427 reaction (i.e., can be viewed as a polishing treatment step) may contribute for a significant part
428 to the DBP content obtained after final disinfection. Moreover, special attention should be given

to those containing a substantial fraction of hydrophilic NOM species not easily removed by conventional water treatment process (e.g., coagulation). Groundwater is also usually characterized by a considerable content of hydrophilic organic matter.[45] Particularly, SR-AOPs have already been applied in ground water remediation.[46] Further investigation is required to elucidate the importance of other halide ions on the formation of halogenated byproducts by SR-AOPs and to monitor the evolution of active halide species as well.

ASSOCIATED CONTENT

Supporting Information. Detailed descriptions of materials and methods as well as supporting tables and figures are included in the SI. This information is available free of charge via the Internet at http://pubs.acs.org.

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Table 1. Formation of TOBr and Br-DBPs from Model Compounds

Compound	TOBr (μg L^{-1})		DBAA (μg L^{-1})		MBAA (μg L^{-1})		TBAA (μg L^{-1})		TBM (μg L^{-1})		DBAN (μg L^{-1})		DBAcAm (μg L^{-1})		BAcAm (μg L^{-1})	
	$SO_4^{\bullet-}/Br^-$	HOBr	$SO_4^{\bullet-}/Br^-$	HOBr	$SO_4^{\bullet-}/Br^-$	HOBr	$SO_4^{\bullet-}/Br^-$	HOBr	$SO_4^{\bullet-}/Br^-$	HOBr	$SO_4^{\bullet-}/Br^-$	HOBr	$SO_4^{\bullet-}/Br^-$	HOBr	$SO_4^{\bullet-}/Br^-$	HOBr
Group I																
L-Asparagine	294.0	1574.2	126.3	233.3	1.1	1.0	ND	ND	ND	ND	2.4	112.9	117.4	1068.6	14.0	ND
L-Glutamic acid	93.0	77.3	17.0	0.16	1.8	ND	ND	ND	0.8	0.090	2.9	1.83	6.1	5.0	4.1	ND
L-Phenylalanine	48.9	61.5	4.1	0.16	1.9	ND	ND	ND	1.0	ND	2.7	2.19	4.5	5.0	3.8	ND
L-Tryptophan	165.8	153.0	2.0	0.65	1.4	ND	ND	ND	ND	4.39	2.3	1.92	4.5	11.3	3.9	ND
L-Tyrosine	1406.2	1302.6	5.9	1.6	1.5	ND	ND	6.1	0.2	85.6	2.4	2.5	4.8	6.9	3.4	ND
L-aspartic acid	609.5	393.9	198.3	0.71	18.3	ND	ND	ND	15.2	36.30	29.2	5.8	6.5	6.3	ND	ND
Group II																
Phenol	1069.0	1988.5	2.8	0.25	0.2	ND	ND	4.0	ND	141.2	NA	NA	NA	NA	NA	NA
Hydroquinone	163.2	314.6	19.1	1.85	1.9	ND	ND	5.5	9.3	32.5	NA	NA	NA	NA	NA	NA
Salicylic acid	1694.2	2054.2	28.9	0.70	1.4	ND	ND	3.4	17.2	51.0	NA	NA	NA	NA	NA	NA
Group III																
Citric acid	1435.0	1185.8	434.6	198.5	85.3	9.9	1.9	4.0	1144.3	966.3	NA	NA	NA	NA	NA	NA
Oxalic acid	147.0	91.5	0.5	0.090	ND	ND	ND	ND	4.6	23.8	NA	NA	NA	NA	NA	NA
Malonic acid	59.4	652.6	8.7	488.1	3.2	20.5	ND	ND	15.9	0.59	NA	NA	NA	NA	NA	NA
Succinic acid	601.1	60.3	14.0	0.12	1.7	ND	4.3	ND	606.9	52.8	NA	NA	NA	NA	NA	NA
Maleic acid	324.9	762.7	3.6	0.15	0.1	ND	2.6	4.6	149.2	30.2	NA	NA	NA	NA	NA	NA
Pyruvic acid	395.0	261.4	29.7	0.69	2.5	2.9	ND	ND	396.4	278.9	NA	NA	NA	NA	NA	NA

Note: Incorporation of bromine into model compounds by SR-AOP: PMS = 100 μM; $CuFe_2O_4$ dose = 50 mg L^{-1}; bromide = 50 μM; model compound = 50 μM; pH=8.0 in 10 mM tetraborate buffer; contact time 24 h. Bromination of model compounds: $HOBr/OBr^-$ = 50 μM; model compound = 50 μM; pH=8.0 in 10 mM tetraborate buffer; contact time 24 h. The results are the average values of duplicate tests. ND: not detected; NA: not applicable.

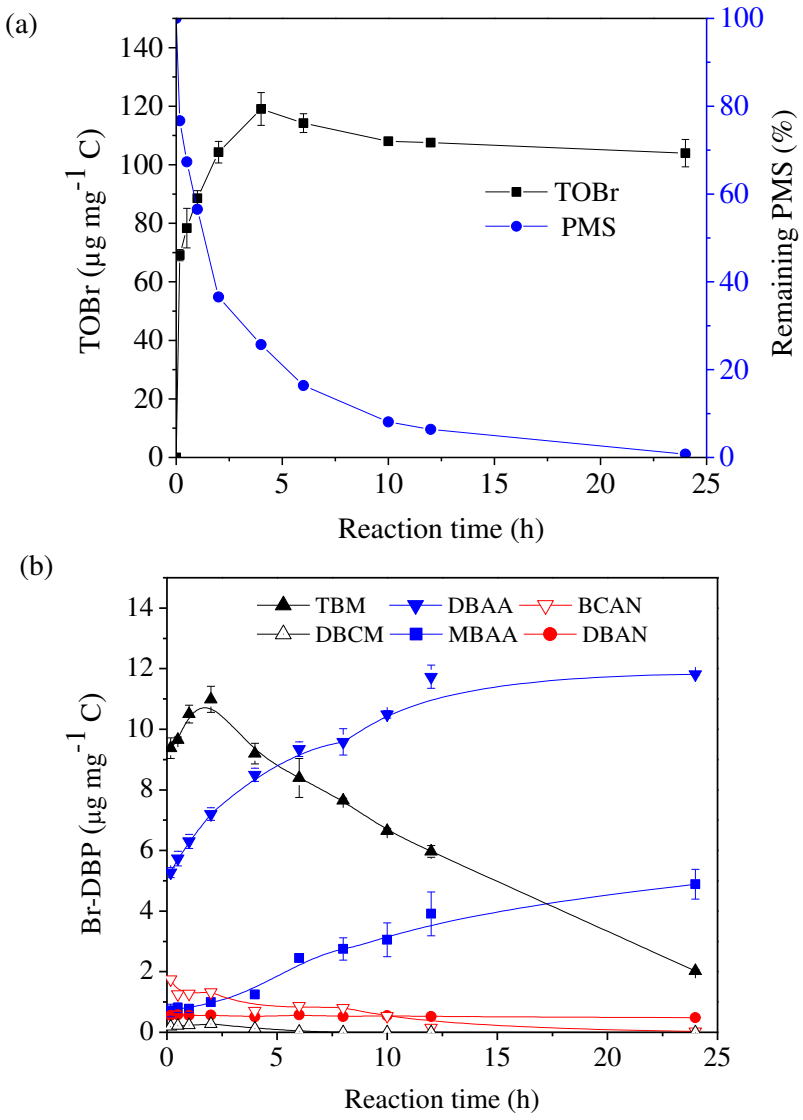

Figure 1. Kinetics of TOBr and Br-DBPs formation from bromide-containing water by SR-AOP: (a) decomposition of PMS and evolution profile of TOBr; (b) evolution profiles of Br-DBP. Experimental conditions: 5 mg solid SR HPOA per liter MQ (2.25 mg L^{-1} DOC); PMS = 50 μM; $CuFe_2O_4$ = 50 mg L^{-1}; Br^- = 25 μM; T = 20 °C; pH = 7.5.

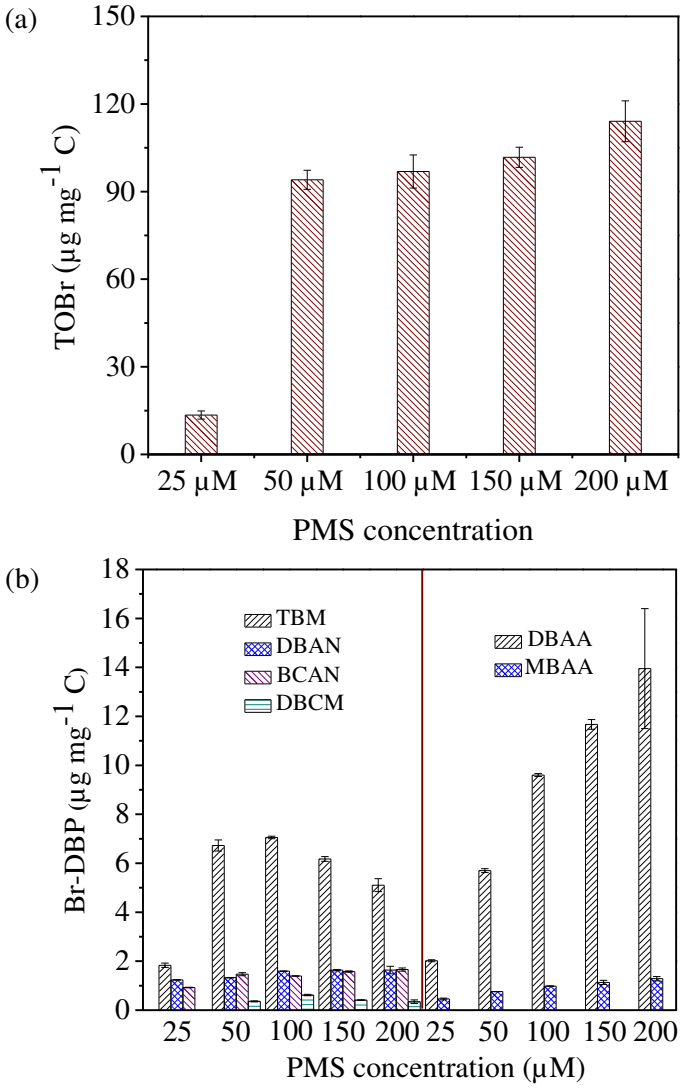

Figure 2. Effect of PMS concentration on the formation and speciation of TOBr and Br-DBPs by SR-AOP: (a) Bromine incorporation into TOBr; (b) THMs, HANs, and HAAs speciation. Experimental conditions: 5 mg solid SR HPOA per liter MQ (2.25 mg L^{-1} DOC); $CuFe_2O_4$ = 50 mg L^{-1}; Br^- = 25 µM; contact time = 2 h; T = 20 °C; pH = 5.5.

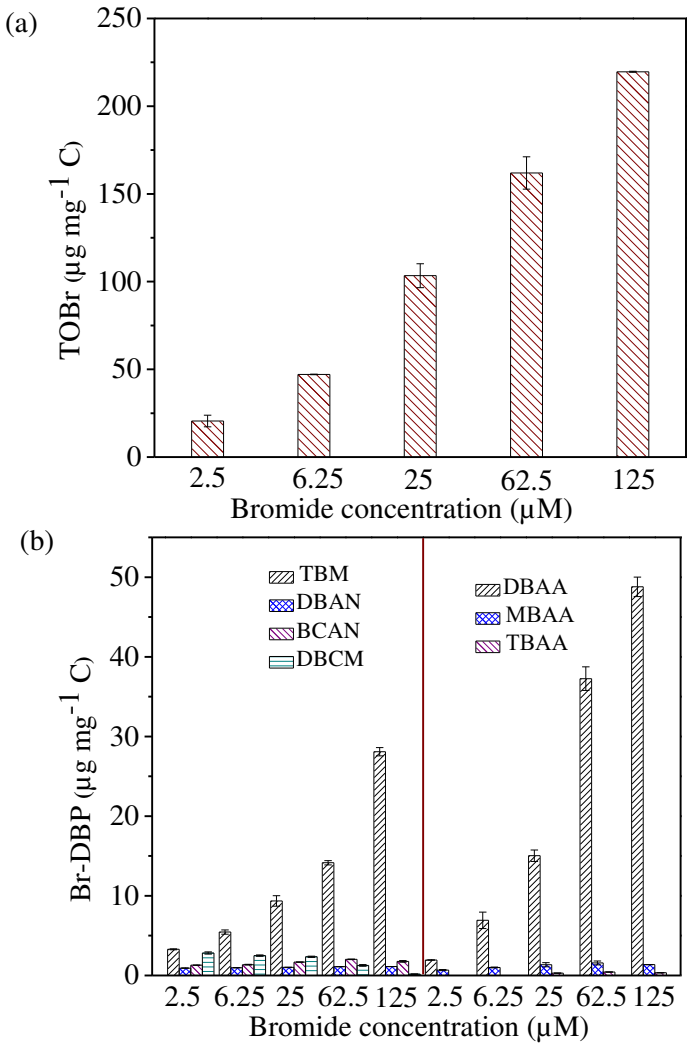

Figure 3. Bromine incorporation into TOBr and Br-DBPs under various bromide concentrations: (a) Bromine incorporation into TOBr; (b) THMs, HANs, and HAAs speciation. Experimental conditions: 5 mg solid SR HPOA per liter MQ (2.25 mg L^{-1} DOC); PMS = 100 µM; $CuFe_2O_4$ = 50 mg L^{-1}; contact time = 2 h; T = 20 ºC; pH = 7.5

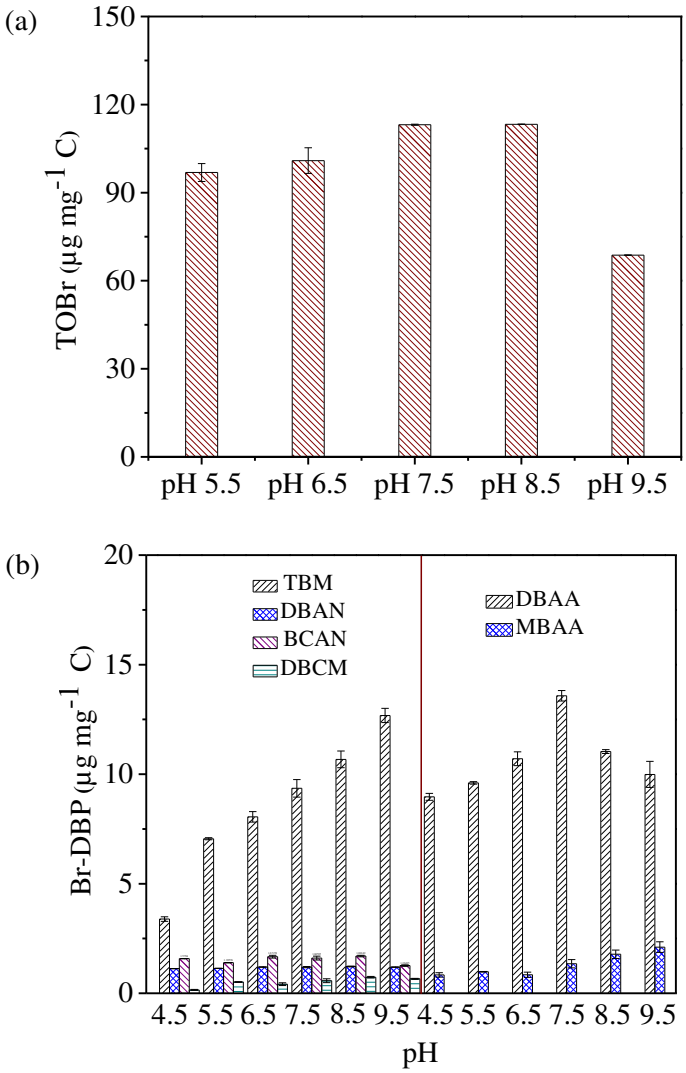

Figure 4. Effect of solution pH on the formation and speciation of TOBr and Br-DBPs by SR-AOP: (a) Bromine incorporation into TOBr; (b) THMs, HANs, and HAAs speciation. Experimental conditions: 5 mg solid SR HPOA per liter MQ (2.25 mg L^{-1} DOC); PMS = 100 µM; $CuFe_2O_4$ = 50 mg L^{-1}; bromide = 25 µM; contact time = 2 h; T = 20 ^oC.

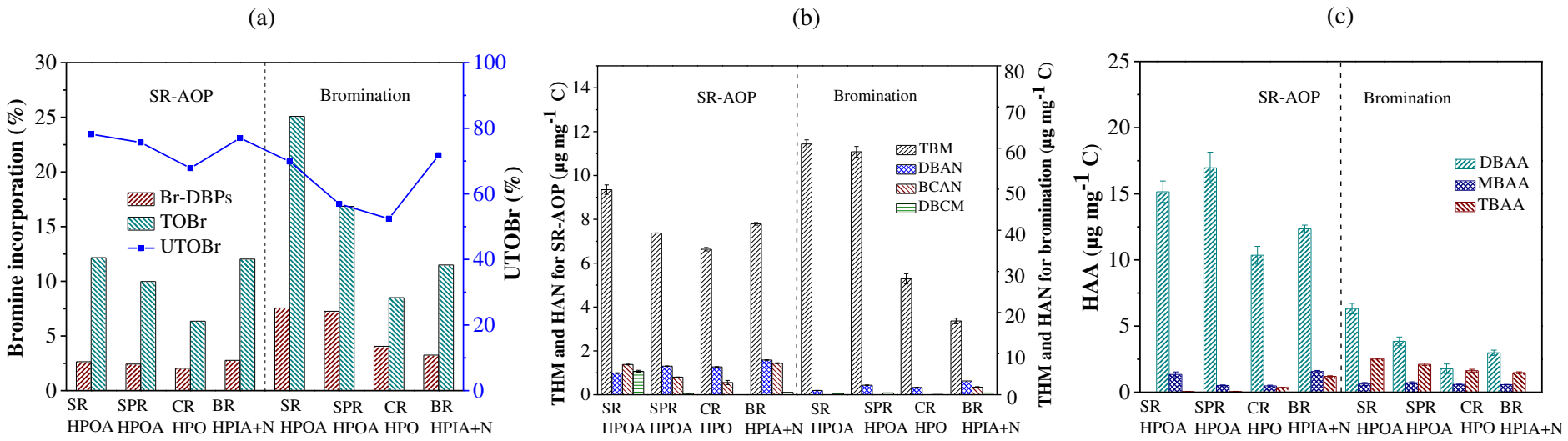

Figure 5. Formation and speciation of TOBr and Br-DBPs from NOM isolates by SR-AOP and bromination: (a) Proportion of unknown compounds in TOBr (UTOBr) and bromine incorporation into TOBr and Br-DBPs; (b) THMs and HANs speciation; (c) HAAs speciation. Experimental conditions: 5 - 7 mg solid NOM isolate per liter MQ; pH = 7.5; contact time = 2 h; T = 20 ºC; for SR-AOP, PMS = 100 μM, $CuFe_2O_4$ = 50 mg L^{-1}, Br^- = 25 μM; for bromination, $HOBr/OBr^-$ = 25 μM.