



Review

Disinfection byproducts formation from emerging organic micropollutants during chlorine-based disinfection processes

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ABSTRACT

The formation of disinfection byproducts (DBPs) during the water disinfection process has attracted extensive attention due to their potential toxicity. Emerging organic micropollutants (EOMPs) are now ubiquitous in the water environments, and they have been confirmed that could be the precursors for many DBPs during chlorine-based disinfection processes (Cl-DPs). Although there are increasing studies on the formation of DBPs from EOMPs during Cl-DPs, there is still a lack of review paper on this hotspot. In this review, the typical Cl-DPs and their corresponding mechanisms were introduced first. Then, the DBPs formation in the presence of different EOMPs (e.g., pharmaceuticals and personal care products, endocrine disrupting chemicals, and brominated flame retardants) during Cl-DPs were discussed and highlighted, including the pathways, mechanisms, and influencing factors. Moreover, the DBPs detection and control methods have also been summarized and discussed. Finally, future studies and challenges of controlling DBPs formation were proposed. This review gave a comprehensive understanding of DBPs formation from EOMPs during Cl-DPs, and more studies are needed in the future to balance the EOMPs removal against corresponding DBPs formation during disinfection processes.

1. Introduction

Disinfection processes are an important means to ensure water quality safety, which can eliminate pathogenic microorganisms during the drinking water treatment and ensure the quality parameters for safe drinking water consumption in the distribution network [1]. However, disinfection byproducts (DBPs) are formed when disinfectants react with

many precursors in water, such as natural organic matter (NOM), anthropogenic contaminants, brominated and iodinated compounds. Since Rook first reported trihalomethanes (THMs) in 1974s, more than 700 DBPs have been identified in water to date [2,3]. These identified DBPs mainly include carbonaceous DBPs (C-DBPs, such as THMs, haloaceticacids (HAAs), haloketones (HKs), haloacetaldehydes (HALs) etc.), and nitrogenous DBPs (N-DBPs, such as halonitromethanes

Abbreviations: EOMPs, Emerging organic micropollutants; DBPs, Disinfection byproducts; Cl-DPs, Chlorine-based disinfection processes; PPCPs, Pharmaceuticals and personal care products; EDCs, Endocrine disrupting chemicals; BFRs, Brominated flame retardants; C-DBPs, Carbonaceous DBPs; N-DBPs, Nitrogenous DBPs; RCS, Reactive chlorine species; RNS, Reactive nitrogen species; THMs, Trihalomethanes; HAAs, Haloaceticacids; HKs, Haloketones; HALs, Haloacetaldehydes; HNMs, Halonitromethanes; HANs, Haloacetonitriles; HAcAms, Haloacetamides; CF/TCM, Chloroform/Trichloromethane; BDCM, Bromodichloromethane; DBCM, Dibromochloromethane; TBM, Tribromomethane; MCAA, Monochloroacetic acid; DCAA, Dichloroacetic acid; TCAA, Trichloroacetic acid; 1,1-DCP, 1,1-dichloro-2-propanone; 1,1,1-TCP, 1,1,1-trichloropropanone; CH, Chloral hydrate; DCA, Dichloroacetaldehyde; MCAN, Monochloroacetonitrile; DCAN, Dichloroacetonitrile; TCAN, Trichloroacetonitrile; MCNM, Monochloronitromethane; DCNM, Dichloronitromethane; TCNM, Trichloronitromethane; TCACAm, Trichloroacetamide; DCACAm, Dichloroacetamide; TCAM, Trichloroacetamide; HBQs, Halobenzoquinones; HFNs, Halogenated furanones; NAs, Nitrosoamines; HPRs, Halogenated pyrroles; HPs, Halogenated phenols; HSAs, Halogenated salicylic acids; HHBAs, Halogenated hydroxybenzoic acids; CBCs, Chlorobenzyl cyanides; NOM, Natural organic matter; TC, Tetracycline; CTC, Chlortetracycline; OTC, Oxytetracycline; DC, Doxycycline; ENO, Enoxacin; NDMA, N-nitrosodimethylamine; FLE, Fleroxacin; SMT, Sulfamethazine; TMP, Trimethoprim; MNZ, Metronidazole; CAP, Chloramphenicol; NSAIDs, Non-steroidal anti-inflammatory drugs; IBP, Ibuprofen; CBZ, Carbamazepine; BPA, Bisphenol A; TBBPA, Tetrabromobisphenol A.

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(HNMs), haloacetonitriles (HANs), haloacetamides (HAcAms), etc.), and some inorganic DBPs (such as chlorite (ClO_2^-), chlorate (ClO_3^-), bromate (BrO_3^-), etc.) [4–6] (Table 1), and the discovery process of different DBPs is shown in Fig. 1 [7]. Many toxicological studies have shown that most of these identified DBPs have cytotoxicity, neurotoxicity, genotoxicity, carcinogenicity, mutagenicity, and teratogenicity, and the toxicity of DBPs can be roughly ranked as follows: iodinated DBPs > brominated DBPs > chlorinated DBPs. Although the concentration of DBPs in drinking water is generally in the level of ng/L to $\mu\text{g/L}$, many countries have regulated dozens of DBPs (mainly THMs and HAAs) in water quality management due to their frequent discovery and harmful effects [1,4–6,8].

Among various disinfection processes (mainly including chlor(am)ination, ozonation, and UV disinfection), the chlorine-based

disinfection processes (Cl-DPs, using chlorine, hypochlorite salts, chloramine, and chlorine dioxide (ClO_2) as disinfectants) are still the conventional and highly preferred technologies due to their low cost, simple operation, high efficiencies, and persistence in the distribution network [1,8]. Chlorine and hypochlorite salts (such as NaClO) are most used in the chlorination disinfection process, and hydrolysis of these disinfectants to produce HOCl and OCl^- for the disinfection of water. When combining chlorine with ammonia, chloramine (including monochloramine (NH_2Cl), dichloramine (NHCl_2), and trichloramine (NCl_3)) will be generated, and the NH_2Cl is often used as an alternative disinfectant for disinfection. Compared with HOCl and OCl^- , the NH_2Cl exhibits a lower disinfection performance, but it can decrease the formation of regulated DBPs (such as THMs and HAAs) to some extent. ClO_2 is recognized as a safe and effective disinfectant, which possesses excellent disinfection

Table 1

Characteristics of some typical DBPs discussed in this paper.

Category	DBPs	Abbreviation	Chemical formula	Chemical structure
THMs	Chloroform/trichloromethane	CF/TCM	CHCl_3	
	Bromodichloromethane	BDCM	CHCl_2Br	
	Dibromochloromethane	DBCM	CHClBr_2	
	Tribromomethane	TBM	CHBr_3	
HAAs	Monochloroacetic acid	MCAA	CClCOOH	
	Dichloroacetic acid	DCAA	CCl_2COOH	
	Trichloroacetic acid	TCAA	CCl_3COOH	
HKs	1,1-dichloro-2-propanone	1,1-DCP	$\text{C}_3\text{H}_4\text{Cl}_2\text{O}$	
	1,1,1-trichloropropanone	1,1,1-TCP	$\text{C}_3\text{H}_3\text{Cl}_3\text{O}$	
HALs	Chloral hydrate	CH	$\text{CCl}_3\text{CH}(\text{OH})_2$	
	Dichloroacetaldehyde	DCA	$\text{CCl}_2\text{CH}_2(\text{OH})_2$	
HANs	Dichloroacetonitrile	DCAN	$\text{C}_2\text{HCl}_2\text{N}$	
	Trichloroacetonitrile	TCAN	$\text{C}_2\text{Cl}_3\text{N}$	
HNMs	Monochloronitromethane	MCNM	CH_2ClNO_2	
	Dichloronitromethane	DCNM	CHCl_2NO_2	
	Trichloronitromethane	TCNM	CCl_3NO_2	
HAcAms	Trichloroacetamide	TCAcAm	$\text{C}_2\text{H}_2\text{Cl}_3\text{NO}$	
	Dichloroacetamide	DCAcAm	$\text{C}_2\text{H}_3\text{Cl}_2\text{NO}$	

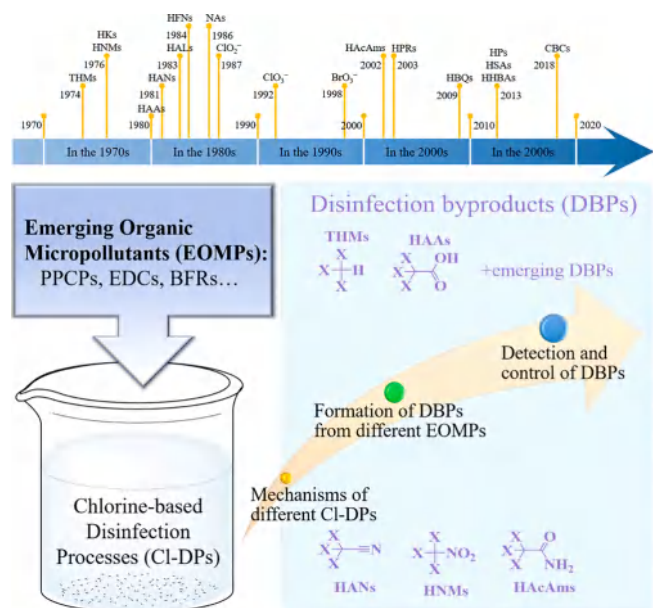


Fig. 1. The discovery process of different DBPs [7], Copyright 2021 Environmental Science; An overview of DBPs formation from EOMPs during Cl-DPs.

performance due to its high oxidation ability. Meanwhile, ClO_2 does not react with NOM (e.g., humic acid), which greatly reduces the formation of DBPs. However, some features, such as high cost, easy to decompose and explode, etc., thus greatly limiting the application of ClO_2 [1,8–10]. Additionally, according to the World Health Organization, the residual chlorine levels should ≥ 0.5 mg/L after contact of 30 min. Meanwhile, it is essential to retain a suitable chlorine dose for providing adequate residual chlorine during storage and utilization, suggesting the dosage of free chlorine for clear water is about 2 mg/L and twice (4 mg/L) for turbid water [11]. Although the Cl-DPs are very effective for water purification, the various DBPs formed by the reaction of disinfectants and precursors should not be ignored. Especially for the emerging organic micropollutants (EOMPs), which are frequently detected in various environments due to overuse and anthropogenic discharge, and have been confirmed that can be as the precursors react with disinfectants to produce many regulated and emerging DBPs during Cl-DPs.

The EOMPs are those organic pollutants that are not included in existing water-quality regulations, but have complex chemical structures and rich polar groups and commonly exist in water environments at low concentrations (ng/L to $\mu\text{g/L}$) [12]. EOMPs in water environment mainly come from industrial wastewater discharge, municipal sewage discharge, and agricultural runoff, including but not limited to pharmaceuticals and personal care products (PPCPs), endocrine disrupting chemicals (EDCs), and brominated flame retardants (BFRs) [13–15]. Different from traditional contaminants, which always exert acute toxicity, EOMPs exert their effects in more subtle ways, like disrupting endocrine, increasing antibiotic resistance and ecotoxicity [16,17]. In general, the conventional drinking water or wastewater treatment processes (e.g., coagulation, sedimentation, filtration, and biological treatment) are not ideal for EOMPs removal [18,19]. However, recent studies have shown that they are likely to react with disinfectants during Cl-DPs. The reactions of EOMPs and disinfectants would cause the benzene ring or piperazinyl ring cleavage, intermolecular rearrangement, hydroxylation, and chlorine substitution of EOMPs, leading to the degradation and removal of EOMPs [20,21]. What's even more concerning, the disinfectants also are likely to react with EOMPs and their intermediates to form various DBPs due to the insufficient degradation performance of disinfectants, in this case, the EOMPs become the potential precursors of DBPs. For example, Ye et al. [9] investigated the formation of DBPs during chlor(am)ination when using four tetracycline

antibiotics (tetracycline (TC), chlortetracycline (CTC), oxytetracycline (OTC), and doxycycline (DC)) as the precursors. The results showed that the DCACAm and TCM were major DBPs produced from tetracycline antibiotics during chlorination, while only DCACAm was the predominant DBPs during chloramination. Furthermore, the DCACAm yields from these tetracyclines were 0.43 %–54.26 % during chlorination and 0.65 %–44.57 % during chloramination, indicating that tetracyclines were the precursors of DCACAm. He et al. [10] reported that five types of halogenated DBPs (i.e., HAAs, HANs, THMs, HKs, and HALs) and ClO_2^- formed during enoxacin (ENO) destruction when using ClO_2 as the disinfectant in the water distribution system. Furthermore, during chlor(am)ination, EOMPs with higher aromaticity and more phenyl or heterocyclic (e.g., some PPCPs and EDCs) may easily convert to aromatic DBPs, then they go through side chain cleavage and ring opening reactions to form aliphatic DBPs, like THMs and HAAs [22]. Studies have also shown that EOMPs containing amine groups, such as ranitidine, chlorpheniramine, and CTC, could act as the precursors of *N*-nitrosodimethylamine (NDMA) DBPs during the Cl-DPs, which is considered to be a powerful carcinogen with high water solubility [23]. These studies have proved that the EOMPs can be the precursors of various DBPs during Cl-DPs, but the current results are not enough to establish the relationship between EOMPs and DBPs formation during Cl-DPs, which should arouse more attention and require more detailed study in the future.

Up to now, many review papers have summarized and discussed the formation of DBPs. For instance, Gilca et al. [1] presented a comprehensive review of the emerging DBPs in drinking water treatment processes, mainly including the classification, occurrence, methods of analysis, environmental and health impacts, prevention and control of these DBPs. Chaukura et al. [24] mainly reviewed the influence factors for DBPs formation and the technologies for DBPs abatement in drinking water. Ding et al. [25] reviewed the unintended effects of engineering agents and materials on the formation of undesirable DBPs during drinking water treatment and distribution. These reviews have made great progress in summarizing the related knowledge of DBPs and grasping the development direction of drinking water disinfection, thus observably accelerating the related research. Although many reviews on DBPs have been published, none of a comprehensive review has been paid to the formation of DBPs from EOMPs during Cl-DPs, which is urgently needed. In this review, the basic disinfection mechanisms of different Cl-DPs have been summarized first. Then, the DBPs formation from different EOMPs during Cl-DPs has been discussed and highlighted, including the pathways, mechanisms, and influencing factors. Moreover, the detection and control of DBPs have also been summarized and interpreted. Finally, the prospects and challenges have been proposed (Fig. 1). All in all, in order to control the formation of various emerging DBPs during disinfection, it is of great importance to understand the interaction between EOMPs and DBPs. This review would inspire some new ideas for efficiently controlling of DBPs formation during Cl-DPs.

2. Mechanisms of different Cl-DPs

Chlorine, hypochlorite salts, chloramine, and ClO_2 are the most used disinfectants in the Cl-DPs. Furthermore, UV radiation are often combined with Cl-DPs to improve the disinfection effect and reduce DBPs formation. To obtain a comprehensive understanding of the Cl-DPs, the fundamental mechanisms of these disinfection processes were summarized as follows.

2.1. Chlorine disinfection process

During chlorination, chlorine usually comes from chlorine gas or NaClO . When chlorine is released in aqueous systems, it forms HOCl and OCl^- , which act as the primary oxidants for EOMPs degradation during chlorination. The redox potential of HOCl is 1.48 V, while that of OCl^- is 0.84 V, making HOCl a more potent oxidant [26]. HOCl is a two-electron

electrophilic reagent and prone to attack electron-rich sites (e.g., primary amine, secondary amines, unsaturated aromatic rings, and phenolic hydroxyl) of organic molecules with its Cl atom, while OCl^- is a stronger chlorinating agent for derivative amino-compounds like ametryn and chlorotoluron [27–29]. The pK_a of HOCl is 7.5 at 25 °C (Eq. (1)), namely, when pH is in the range of 3–7.5, HOCl is the main substance during chlorination [30]. As pH increases from 7.5 to 8, HOCl is converted into OCl^- , so the concentration of OCl^- increase, leading to the decrease of degradation efficiency for most EOMPs (e.g., acebutolol, acesulfame, iodophenols) due to the relatively low reactivity and oxidizing strength compared to HOCl [8,30,31]. Moreover, electrophilic substitution reaction and single-electron transfer reaction are considered to be the main reactions during chlorination, which greatly contribute to the formation of chlorine-substituted products [26].



2.2. Chloramine disinfection process

Among the chloramines, NH_2Cl is the most widely used alternative disinfectant for chlorine due to its stabilization during the continuous disinfection process and less DBPs formation afterward [32]. The mechanism of chloramination is similar to that of chlorination but the disinfectants in chloramination show a lower oxidant capacity than those in chlorination. However, it is noteworthy that the combination between ammonia and chlorine had an impressive synergistic influence on the removal of chlorine-resistant EOMPs like atrazine and *N,N*-diethyl-3-toluamide [33,34]. By decomposing chloramines, reactive species are generated, which would account for the elimination of contaminants [33]. Specifically, $\bullet\text{OH}$, reactive chlorine species (RCS), and reactive nitrogen species (RNS) are generated via Eqs. (2)–(9) [33,34]. Although chloramines have a lower oxidant capacity than that chlorine, chloramines can be considered as a source of nitrogen, leading to the generation of *N*-DBPs, which are more toxic than typical *C*-DBPs [35,36]. For example, chloramine was found to be responsible for the formation of DCAN and DCaAm [37,38]. Nonetheless, a decrease of overall DBPs generation from EOMPs can be seen during chloramination compared with chlorination, which is because chloramination can inhibit the formation of most regulated DBPs, thus could be as a safer disinfection method to be applied [34,39].



2.3. Chlorine dioxide disinfection process

Another alternative disinfectant for chlorine is ClO_2 , which is a broad-spectrum, safe, and effective disinfectant because of its high oxidation performance and decreased formation of DBPs. As a powerful one-electron oxidant, ClO_2 could attack the electron-rich and electron-donating moieties (such as enzymes, anilines, phenols, olefins, amines, sulfide, and nitrides) to plunder electrons, thus causing the inactivation or denaturation of the pathogen [40–42]. Meanwhile, it exhibits a strong adsorption and penetration ability to the cell wall, and has a destructive

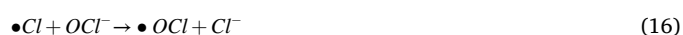
effect on microbial cells, so as to achieve the purpose of disinfection. In comparison to chlorine disinfection, ClO_2 disinfection could decrease the formation of halogenated DBPs and is less affected by pH [40–42]. However, during the disinfection process, ClO_2 would form the ClO_2^- and ClO_3^- (Eq. (10)), which are the widely regulated DBPs. Besides, ClO_2 gas is difficult to store and transport because of its explosive and unstable properties, so it usually needs to be produced on-site [40–42]. Furthermore, the reaction between ClO_2 and EOMPs has also been extensively studied, including antipyrine, diclofenac, etc., oxidation is the primary step to replace the chlorine substitution for EOMPs degradation, so there are no chlorinated DBPs.



2.4. UV/(chlorine, chloramine, ClO_2) combined disinfection processes

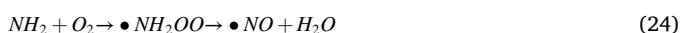
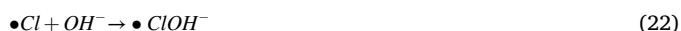
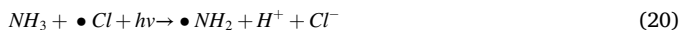
UV irradiation is also a typical disinfection process and does not cause the formation of DBPs. However, UV disinfection is limited due to the occurrence of photoreactivation and dark repair of bacteria. Therefore, in order to improve the disinfection effect and reduce the formation of DBPs, UV irradiation is often combined with these Cl-DBPs. Furthermore, various reactive species could be generated under UV irradiation during the UV/chlorine, UV/chloramine, and UV/ ClO_2 processes, which would significantly affect the processes of EOMPs degradation and DBPs formation.

In the UV/chlorine process, HOCl and OCl^- are photolyzed to yield $\bullet\text{OH}$ and RCS via Eqs. (11)–(18) [43–45]. And HOCl is more capable of generating $\bullet\text{OH}$ than ClO_2^- , which is more likely to scavenge $\bullet\text{OH}$. The oxidation potentials of $\bullet\text{OH}$, $\bullet\text{Cl}$, and $\bullet\text{Cl}_2$ are 2.8, 2.4, and 2.0 V, respectively [45,46], indicating their strong oxidizing ability to degrade EOMPs. Moreover, $\bullet\text{OH}$ is a nonselective oxidant that can decompose a wide range of EOMPs, while $\bullet\text{Cl}$ and $\bullet\text{Cl}_2$ are selective oxidants that prefer electron-rich moieties more (e.g., phenolic and amine groups) [47]. Thus, during UV/chlorine treatment, there are three types of reactions, including chlorine-modulated reactions, UV-induced reactions, and free radicals-driven reactions would exist [48]. The degradation of various EOMPs depends on different types of radicals and reactions. For example, direct photolysis and RCS were responsible for diazotriazole, 5,5-diphenylhydantoin, β -cyclocitral and phenacetin degradation, and $\bullet\text{OCl}$ accounted for iopamidol oxidation, while $\bullet\text{OH}$ was the major radical in clmbazole degradation [45,49–52]. However, during the degradation of EOMPs, various DBPs could also be formed depending on the EOMPs types and experiment conditions. For example, the higher radical exposure in this process might alter the dissolved organic matter properties, enhancing DBPs formation potential [53]. The attack of highly oxidizing RCS favored the opening of heterocyclic, aromatic, and phenolic rings, which could account for the increasing generation of precursors of some DBPs such as TCAA, DCAN, and TCNM, causing the formation of more chlorinated-DBPs [53–55].

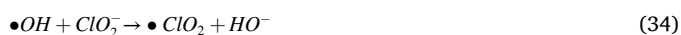


One of the major differences between UV/chlorine and UV/chloramine is the existence of RNS (e.g., $\bullet\text{NO}$ and $\bullet\text{NO}_2$), which are particular

species, preferring to attack organic molecules with electron-rich groups like anilines, phenothiazines, thiols, and phenolic groups [56–58]. Chloramine molecules have N—Cl bonds that can be fractured under UV exposure, forming nitrogenous radicals and $\bullet\text{Cl}$ (Eq. (19)) [59]. Once these radicals form, subsequent reactions are initiated, including the chloramine convert into $\bullet\text{ClOH}^-$, $\bullet\text{OH}$, and RNS, etc. (Eqs. (20)–(25)) [58,60]. In recent, attention has been turned to removing EOMPs by the UV/chloramine process, the related mechanisms involved in chloramine photolysis, the EOMPs degradation, the generation of DBPs, and so on were intensively investigated.



ClO_2 has been reported to undergo photodecomposition by UV irradiation, during the process, ClO_2 was photolyzed to generate $\bullet\text{OCl}$, $\text{O}(^3\text{P})$, and $\bullet\text{Cl}$ at the first stage via Eqs. (26)–(27) [61]. Subsequently, some secondary reactive species were generated via chain reactions [62]. To be specific, $\bullet\text{OCl}$ could react with $\text{H}_2\text{O}/\text{HO}^-$ to generate HOCl , while $\text{O}(^3\text{P})$ would react with dissolved oxygen to yield ozone (Eqs. (28)–(29)) [61,63]. Furthermore, the $\bullet\text{Cl}$ would react with $\text{H}_2\text{O}/\text{HO}^-$ to form $\bullet\text{ClOH}^-$ and $\bullet\text{OH}$ (Eqs. (30)–(31)). However, although the yield of halogenated DBPs could be inhibited in the UV/ ClO_2 process, the significant yield of ClO_2^- and ClO_3^- is a potential concern [61]. Specifically, the ClO_2^- and ClO_3^- could be formed through the chain reactions between these generated reactive species (Eqs. (32)–(36)) [61]. Generally, EOMPs containing electron-donating moieties were more likely to be degraded by UV/ ClO_2 process, but this process might not be able to outcompete the UV/chlorine because of the relatively low formation of radicals [61].



3. DBPs formation from different EOMPs

In recent years, the EOMPs have attracted worldwide attention due to their high detection frequency, high health risks, and challenging to

be removed by traditional water treatment technologies. They are widely used in daily life, industrial and agricultural production, thus the EOMPs can enter the source water through industrial wastewater discharge, municipal sewage discharge and agricultural runoff [13–15]. Although the concentration of these EOMPs is low, their removal efficiency is limited by existing water treatment technologies. Therefore, the reaction of these EOMPs with disinfectants and the formed DBPs during the Cl-DPs should not be ignored. Various EOMPs, including the PPCPs, EDCs, and BFRs all have been proven to be the precursors of DBPs. To better understand the connection between EOMPs and DBPs, the structures of some typical EOMPs, their vulnerable functional groups, and/or main reactions with different disinfectants, as well as corresponding DBPs formation were listed in Table 2. The specific transformation mechanisms, pathways, and more detailed information on the transformation from EOMPs to DBPs were further discussed.

3.1. Pharmaceuticals and personal care products (PPCPs)

PPCPs are widely used in daily life, containing antibiotics, non-steroidal anti-inflammatory drugs (NSAIDs), antiepileptic drugs, β -blockers, blood lipid regulators, and so on [79]. The Cl-DPs may attack and degrade the PPCPs to some extent due to their oxidation property. However, the formation of DBPs during the reaction between disinfectants and PPCPs/intermediates should not be ignored.

3.1.1. Antibiotics

As a common class of pharmaceuticals, antibiotics are widely used in medicine, livestock, and aquaculture industries to treat and prevent infections [9,21,80]. However, the extensive use and incomplete metabolism of antibiotics result in a large number of antibiotics entering the water environment through domestic sewage, medical wastewater, animal feed, and aquaculture wastewater discharge, which could pose a potential threat to human health considering the increased antibiotic resistance as well as ecotoxicity effects [9,21]. The major classes of antibiotics include but are not limited to fluoroquinolones, tetracyclines, sulfonamides, and β -lactams. Concurrently, the Cl-DPs during drinking water or wastewater treatment may convert antibiotics to various intermediates and DBPs, which may be far more toxic than the original compounds. Therefore, it is of great significance to investigate the occurrence, mechanism, and concentration of the formed DBPs during antibiotic degradation in the Cl-DPs.

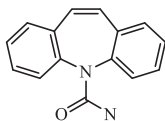
3.1.1.1. Fluoroquinolones. Fluoroquinolones are broad-spectrum antibiotics, commonly applied to treat respiratory diseases and promote the growth of some animals for their low cost and high efficiency [81]. Previous studies reported that the structure of fluoroquinolones plays an important role in its destruction and DBPs formation pathways. For example, the formation of TCM and HANs would be facilitated during chlorination because of the cation and zwitterion of enrofloxacin [82]. Also, fluoroquinolones contain a piperazine ring, which has been proven easily opened or cleared. Subsequently, fragments can be transformed into more stable substances by disinfectants, still with antibacterial properties. For example, fleroxacin (FLE), is often applied to treat urinary tract infections and respiratory disease, and is frequently detected in the aquatic environment. He et al. [64] studied the reactivity and transformation process of FLE by chlorine and ClO_2 treatment. The results displayed that chlorine and ClO_2 can effectively degrade FLE. The piperazine ring cleavage was the principal and initial reaction in both above reactions. Then, the removal of the piperazine group mainly occurred in the chlorine process, while the decarboxylation predominantly happened in the ClO_2 process. The intermediates enhanced first and then declined with time, while three halogenated DBPs (THMs, HAAs, and HANs) risen with time, manifesting that the generated intermediates were further converted into the halogenated DBPs. In addition, although the halogenated DBPs were less during the ClO_2

Table 2
Some studies of the DBPs formation from EOMPs during the Cl-DPs.

EOMPs	Structure	Disinfectant	Main reactions/ vulnerable groups	Potential DBPs formation	Ref.
PPCPs					
Enoxacin		ClO ₂	Piperazine ring fragmentation, hydroxyls addition at C3 and C10	HAAs, HANs, THMs, HKs, HALs	[10]
Fleroxacin		Chlorine or ClO ₂	Piperazine ring cleavage, piperazine group removal (chlorine), decarboxylation (ClO ₂)	THMs, HAAs, HANs	[64,65]
Ciprofloxacin		Chlorine	piperazinyl ring loses two carbons and two hydrogens, piperazinyl ring is opened and a double-bonded oxygen adds to it	Transformation products with antibacterial properties	[66]
Levofloxacin and ofloxacin		Chlorine	Partial loss of piperazine ring, substitution of the carboxyl group with chlorine	Transformation products with antibacterial properties	[66]
Tetracyclines		Chlorine or chloramine	Connected ring systems with electron-rich moieties are likely to be attacked by oxidants	TCM, DCaAm, DCAN, TCM, tetrachloromethane	[9,67]
Sulfamethazine		Chlorine	Desulfonation, S—N cleavage, hydroxylation, chlorine substitution	Transformation products	[21]
Trimethoprim		UV/chlorine	Chlorine substitution, hydroxylation, trimethoxybenzyl moiety is likely to be attacked by •OCl	TCM, CH, DCAN, TCNM	[43]
Metronidazole		Chlor(am)ine	N-denitration, hydroxyethyl group removal	TCM, DCaAm, TCaAm, DCAN	[37]
		UV/chlorine	Hydroxylation, carbonylation, hydroxylation cleavage, demethylation and denitration	1,1,1-TCP, TCAN, DCAN	[68]
Chloramphenicol		UV/chlorine	—C—N— bonds cleavage, nitrite liberation, ring opening	MCNM, DCNM, TCNM	[54]
Ibuprofen		UV/chlorine	hydroxylation and chlorine substitution, decarboxylation, demethylation, chlorination and ring cleavage	TCM, CH, 1,1,1-TCP, 1,1-DCP, DCAA and TCAA	[55,69]
N, N-diethyl-3-toluamide		UV/chlorine	Oxidation and electrophilic halogenation (the tertiary amine and aromatic groups), hydroxylation	TCM, CH, 1,1-DCP, 1,1,1-TCP, DCAA and TCAA	[55]
Acetaminophen/Paracetamol		Chlor(am)ine	Electrophilic substitution, C4—N3 bond cleavage	TCM, DCAN, DCaAm, TCaAm	[36]
Diclofenac		ClO ₂	Decarboxylation, hydroxylation, C—N bond cleavage	Transformation products with enhanced toxicity	[70]

(continued on next page)

Table 2 (continued)

EOMPs	Structure	Disinfectant	Main reactions/ vulnerable groups	Potential DBPs formation	Ref.
Carbamazepine		UV/chlorine	Hydroxylation substitution, ring contraction, chlorine substitution, intramolecular rearrangement, oxidative ring opening	TCM, DCAA, TCAA, DCAN, TCNM	[71]
EDCs	Bisphenol A	Chlor(am)ine	Rearrangement, amine cleavage, decarbonylation	Acridine, 9(10)H-Acridone and other Transformation products	[72,73]
		Chlor(am)ine	Electrophilic substitution, α -C bond and β -C bond cleavage, benzene ring opening	Halogenated bisphenol A, THMs, HAAs, HANs	[74,75]
	Bisphenol S	Chlorine	Chlorine substitution on the benzene ring, oxidative coupling	Monochloro-, dichloro-, trichloro-, tetrachloro-BPS and the biphenyl ether dimer and trimer DBPs	[76]
BFRs	Tetrabromo-bisphenol A	Chlorine	Oxidation, beta-scission, substitution, dimerization	Transformation products	[77]
	2-bromodiphenyl ether	UV/chlorine	C-Br bond homolysis, C-C binding, <i>ortho</i> -position substitution, intramolecular elimination	Toxic dibenzofuran, 2-hydroxydibenzofuran	[78]

process, the formation of ClO_2^- was induced (Fig. 2). Similar to FLE, ENO is also a third-generation fluoroquinolone with a naphthyridine ring. While treating ENO with ClO_2 , it was found that the cleavage of the piperazine group was a crucial step in forming transformation products, just like the FLE [10]. Subsequently, five kinds of halogenated DBPs, including HAAs, HANs, THMs, HKs, and HALs, were formed. However, it was neither ENO nor its intermediates but the ClO_2 -mediated NOM that might facilitate the formation of halogenated DBPs during the oxidation process. Kong et al. [61] reported that the ciprofloxacin was mainly degraded by the radicals ($\bullet\text{HO}$ and $\bullet\text{Cl}$). Although the generation of halogenated DBPs and ClO_3^- is minimal during the co-exposure of ClO_2 and UV radiation, the significant generation of ClO_2^- (0.76 mg/L from 1.35 mg/L of ClO_2) was a potential problem, as its concentration may exceed the drinking water standards in some regions (e.g., Europe and China).

3.1.1.2. Tetracyclines. Tetracycline antibiotics (mainly TC, CTC, OTC, and DC) are widely applied in human and veterinary medicine, curing bacterial infections and promoting animal growth, thus inevitably leading to drug resistance in most bacteria genera. The tetracyclines contain activated benzene rings with electron-rich moieties like an amide group and several hydroxyl groups, enabling them to react with disinfectants and become potential DBPs precursors [83]. Several studies have demonstrated that the presence of tetracyclines during Cl-DPs would lead to emerging DBPs formation. As reported by Zhou et al. [67], the chlorination and chloramination of four tetracyclines (TC, OTC, CTC, and DC) were investigated. The results showed that different tetracyclines yielded different DBPs (including TCM, DCAN, tetrachloromethane, and dichloroacetone) concentrations due to the molecular structures and functional groups. Meanwhile, the fewer DBPs formed in chloramination than in chlorination, except DCAN, which is probably because NH_2Cl could offer the nitrogen source for the nitrile group in DCAN. Ye et al. [9] also reported that the tetracyclines (TC, OTC, CTC, and DC) can form TCM, CH, DCAcAm, TCAcAm, and DCAN DBPs during chlorination and chloramination processes. For chlorination, the DCAcAm and TCM had the highest yield among all detected DBPs, while DCAcAm was the predominant contributor for chloramination (Fig. 3a). Liu et al. [84] also studied the formation of DBPs from tetracyclines (TC and OTC) during chlorine disinfection of ammonium-containing water. The results showed that both NH_2Cl and NHCl_2 played a crucial part in NDMA formation. The mechanism analysis

demonstrated that the dissociation of $-\text{OH}$ on the *meta*-position of the dimethylamine group promoted the generation of NDMA, and the unsymmetrical dimethylhydrazine pathway was the main mechanism of NDMA generation (Fig. 3b). Although it has been proven that tetracyclines can be converted into many emerging DBPs during Cl-DPs, the mechanism and formation pathways of DBPs were complex and still need further investigation.

3.1.1.3. Sulfonamides. Sulfonamides are also the most commonly used and frequently detected veterinary antibiotic in the water environment. Sulfamethazine (SMT), taken for example, has a primary amine functional group to increase the electron density of the benzene ring, making it possible for the benzene ring to be attacked by chlorine via electrophilic substitution. Meanwhile, its secondary and tertiary amine functional groups are also susceptible to chlorine. Moreover, the molecular weight of SMT is relatively low, which enables it to go through ring opening and hydrolysis and form DBPs easily [85,86]. Yang et al. [21] studied the transformation and DBPs formation of SMT during the chlorination process. The results indicated that several DBPs were identified based on different confidence levels. Mechanism analysis demonstrated that the DBPs were generated via desulfonation, S-N cleavage, hydroxylation, and chlorine substitution after chlorination. Xiang et al. [86] also studied the degradation of SMT in UV/ NH_2Cl process. The results indicated that the hydroxylation, nitrosation, and ring-opening reactions were the principal pathway for SMT degradation in UV/ NH_2Cl system. TCM and 1,1-DCP were predominantly formed in dark chlorination, TCM was the main DBPs in UV/ NH_2Cl process, while UV/chlorine process mainly generated TCM, DCAN, and 1,1,1-TCP. Compared with the UV/ Cl_2 treatment, less DBPs formed in the UV/ NH_2Cl process (Fig. 4). Wang et al. [87] also reported that there were 11, 12, and 15 DBPs were proposed for sulfamethoxazole, sulfathiazole, and sulfadimethoxine during chlorination process, respectively. The structures of these DBPs suggested a variety of reaction types, including chlorine substitution, S-C cleavage, S-N hydrolysis, desulfonation, oxidation/hydroxylation, and conjugation reactions. However, the particular mechanism for different kinds of DBPs formed during chlorination of SMT remains unclear and needs to be studied further.

Meanwhile, the existence of trimethoprim (TMP) should not be neglected, and it is often prescribed as a broad-spectrum antibiotic combined with sulfonamides. The DBPs formation and the related mechanism of TMP degradation by the UV/chlorine process were

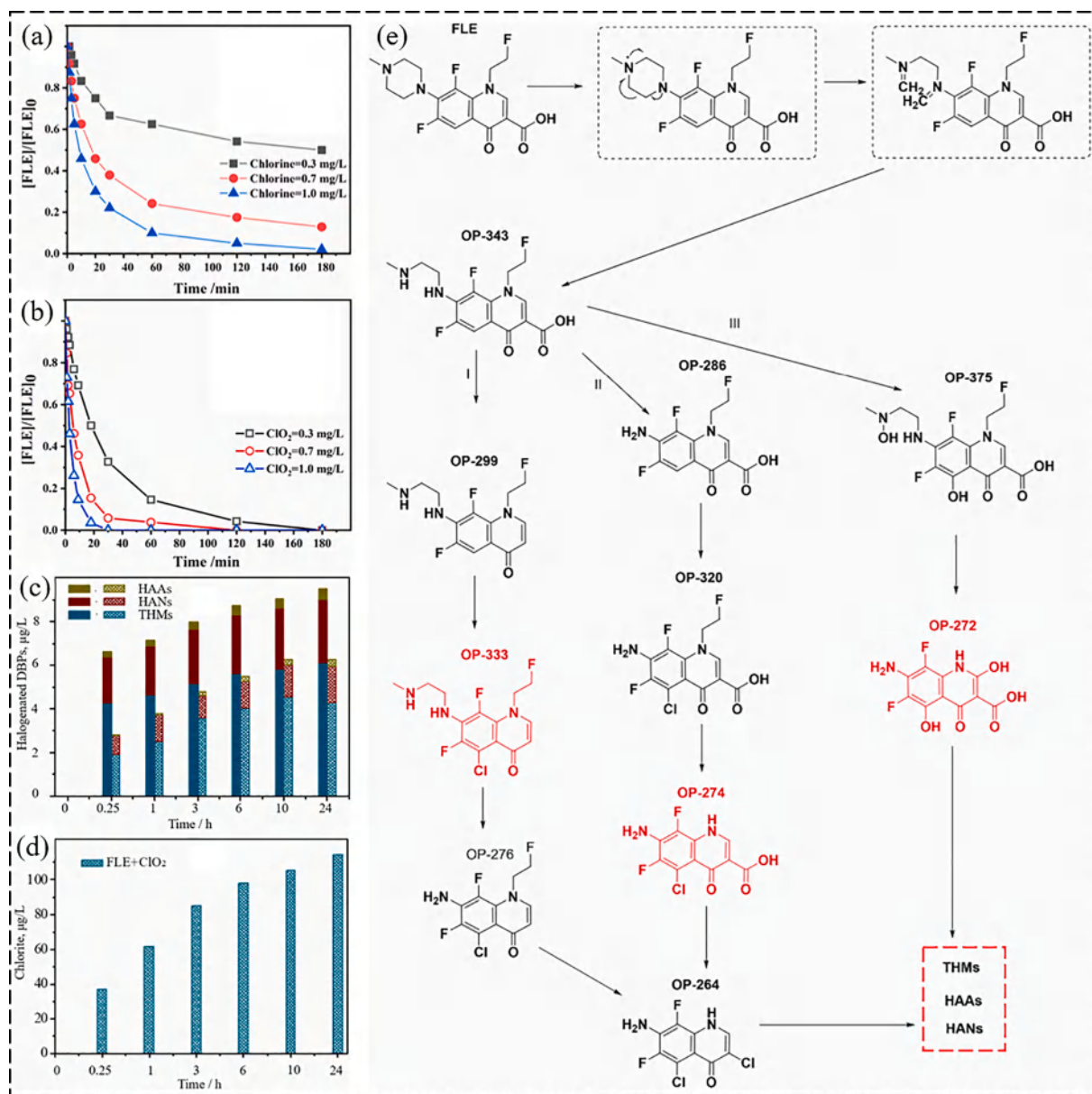


Fig. 2. FLE degradation by chlorine (a) and ClO₂ (b) [64]; Formation of halogenated DBPs (c) and ClO₂ (d) during FLE degradation by chlorine and ClO₂ [64]; The proposed pathways of DBPs formation from FLE during chlorine and ClO₂ process, the red intermediate was only identified in ClO₂ process [64]. Copyright 2022 Chemosphere.

investigated by Wu et al. [43]. As shown in the transformation pathways of TMP, the first step was chlorine substitution induced by RCS alone or in company with HOCl/OCl⁻, then the generated intermediates went through hydroxylation, demethylation, and further oxidation by •OH, HOCl/OCl⁻ or RCS, respectively. Finally, chlorinated DBPs, including CF, CH, DCAN, and TCNM, were generated through ring opening owing to RCS and HOCl/OCl⁻. Since TMP has functional groups like amine, methoxyl, and alkyl in the aromatic moiety as many other PPCPs do, the mechanisms of TMP transformation during the UV/chlorine treatment, especially the involvement of RCS, may be extrapolated to other EOMPs.

3.1.1.4. Nitroimidazoles. Nitroimidazoles (including metronidazole (MNZ), dimetridazole, ronidazole, etc.) are widely applied to prevent and treat infections caused by anaerobic bacteria and protozoan bacteria, and their structure contains an imidazole heterocycle and a nitrogen group [5]. When treated with chlorine, the carbon atom connected with these groups is more likely to be attacked and form DBPs [37,88]. Zhang

et al. [37] studied the DBPs formation of MNZ during chlorination and chloramination processes. It was found that the CF, DCACAm, TCACAm, and DCAN were formed during chlor(am)ination of MNZ, and their yields were overall lower under chloramination than chlorination. The mechanism analysis indicated that the nitroso group in MNZ has the best frontier electron densities (FED²) of 32.89 %, signifying the C9 was more easily substituted by electrophiles (chlor(am)ine). After hydroxyethyl cleavage, the opened ring was more liable to form HACAm under the action of OH⁻. Meanwhile, The FED² of C8 and C11 were 23.07 %, 19.56 % below C9. Thus, the bonds of C8—N4, C9—N4, and C11—N5 might also be broken to form new intermediates with double bonds. These unsaturated double bonds in alkenyl halide could be removed by chlorination, thus forming THMs, especially for TCM. Subsequently, the intermediates could further be transformed into HANs, mainly DCAN (Fig. 5). As for the chloramination of MNZ, although the DBPs formation was overall lower than chlorination, the mechanism was much more complex because both MNZ and chloramine would generate nitrogen to

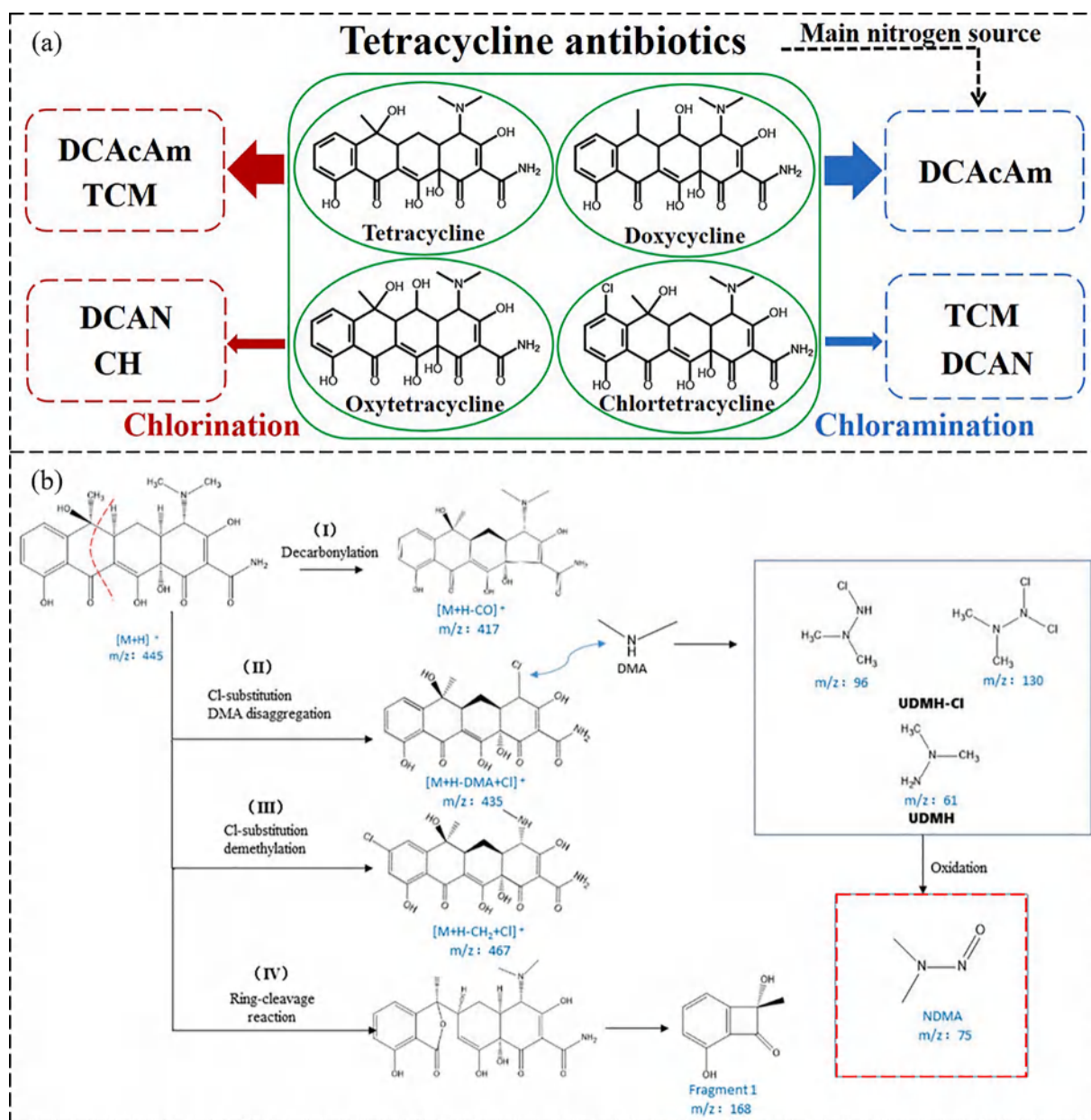


Fig. 3. The generated DBPs from tetracyclines during chlorination and chloramination processes [9] (a). Copyright 2021 Chemosphere; NDMA formation pathway from TC during chlorination [84] (b). Copyright 2021 Science of The Total Environment.

form the *N*-DBPs. Luo et al. [88] also studied the degradation of dimetridazole in the UV/chlorine process. The results indicated that the main degradation processes of dimetridazole included dimerization, demethylation, $\bullet OH$ substitution, chlorination, and ring-opening. And the oxidation of imidazole rings of intermediates via the chlorination and radicals can cause HNMs DBPs formation (e.g., DCNM and TCNM).

3.1.1.5. Chloramphenicol. Chloramphenicol (CAP) is another common antibiotic with aromatic structure, amine, and nitro groups, and it has been widely used in clinical prescriptions, animal husbandry, and aquaculture. The chlorine might be substituted on the benzene ring, leading to the formation of chlorinated and some others DBPs [54]. For example, Dong et al. [54] studied the degradation of CAP and the formation of DBPs during the UV/chlorine treatment. The results showed that three HNMs, including MCNM, DCNM, and TCNM, were predominantly formed due to the highly reactive radical species. The mechanism analysis manifested that the CAP firstly underwent dehydration, the

C—N bond was broken and generated two separate intermediates, which further went through oxidation or chlorine-substitution and ring opening with the attack of radicals (i.e., $\bullet Cl$, $\bullet Cl_2$, $\bullet OH$). Eventually, the HNMs were formed simultaneously with the formation of TCM (Fig. 6). Chu et al. [83] also reported that the CAP and its analogs could be the precursors of DCAcAm and other *N*-DBPs in the chlorination process. Moreover, in research on DBPs formation by comparing CAP and other antibiotics like ciprofloxacin and sulfamerazine [85], the benzene ring of CAP was found to be less susceptible to chlorine electrophilic substitution because its electron density is decreased by the strong electron-withdrawing nitro group. Thus, during the chlorination of CAP, the side chain of CAP, rather than its benzene ring, was more likely to be attacked by chlorine to form DCAcAm.

3.1.2. Non-steroidal anti-inflammatory drugs

The NSAIDs have anti-inflammatory, antirheumatic, analgesic, antipyretic, and anticoagulant properties, and are widely applied to

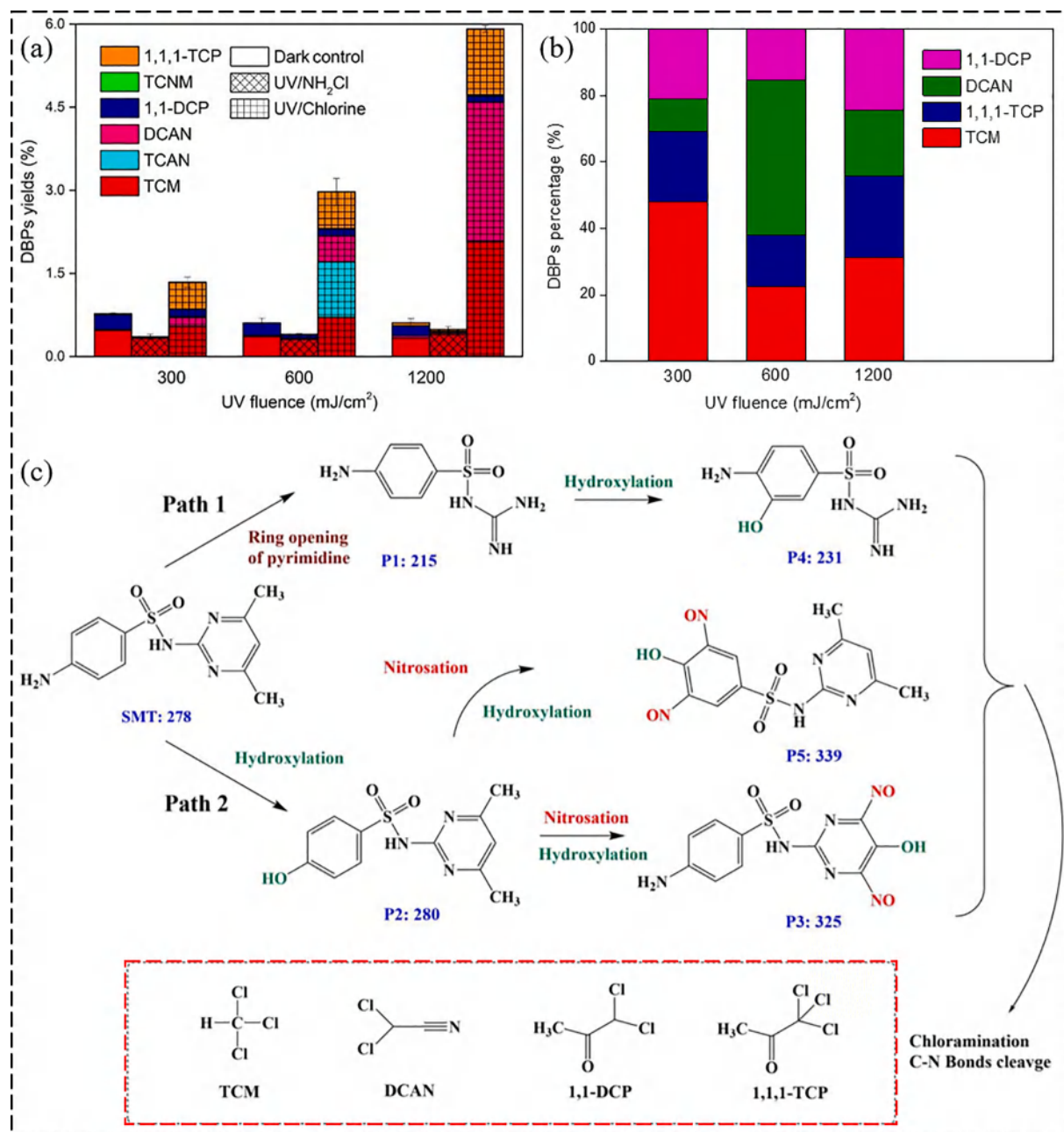


Fig. 4. DBPs yields from SMT during different disinfection processes (a) [86]; Proportion of formed DBPs during UV/NH₂Cl process (b) [86]; Proposed pathways of DBPs formation from SMT during UV/NH₂Cl process (c) [86]. Copyright 2022 Chemical Engineering Journal.

relieve arthritis, fever, and pain symptoms. Although the concentration of NSAIDs in water is usually low, they have attracted increasing concern because of their DBPs formation during the disinfection process [57,89,90]. Ibuprofen (IBP) is a typical and widely used NSAIDs, some studies have proved that IBP can be the precursor of DBPs during the Cl-DPs. For example, Xiang et al. [69] reported the IBP degradation and DBPs formation during the UV/chlorine process. The results demonstrated that the degradation was triggered by $\bullet\text{OH}$ -induced hydroxylation and $\bullet\text{Cl}$ -induced chlorine substitution, followed by decarboxylation, demethylation, chlorination, and ring cleavage to generate more stable products. During this process, many chlorinated DBPs like TCM, 1,1,1-TCP, CH, 1,1-DCP, DCAA, and TCAA were produced, and the known DBPs comprised 17.4 % of the total organic chlorine (Fig. 7). Similarly, Aghdam et al. [55] found that the same DBPs formed from the degradation of IBP by UV/chlorine process, and TCM, 1,1,1-TCP, and DCAA were the major DBPs. During the process, the

contribution portion of RCS and $\bullet\text{OH}$ to IBP decomposition were 75 % and 22 %, respectively. To be specific, RCS was highly reactive to the compounds with electron-rich moieties and could attack the aromatic moiety of IBP and its intermediates, thereby leading to the IBP degradation and DBPs formation. Li et al. also [57] studied the degradation of IBP in UV/NH₂Cl and UV/NaClO processes. Compared to the UV/NaClO process, the UV/NH₂Cl process was a more stable degrader and was effective in degrading IBP. Meanwhile, mechanism experiments showed that $\bullet\text{OH}$ was the major radical in degrading IBP via UV/NH₂Cl. As for the DBPs generation, TCM was the only THMs yielded in synthetic water, while BDCM was the major THMs formed in natural water; DCAA was the primary HAAs formed in synthetic water; DCAN was the main N-DBPs formed in synthetic water while there was additional TCNM formed in natural water [57]. What's more, the risk of DBPs formation (including THMs, HAAs, and N-DBPs) in the NH₂Cl system is smaller than that in the NaClO system.

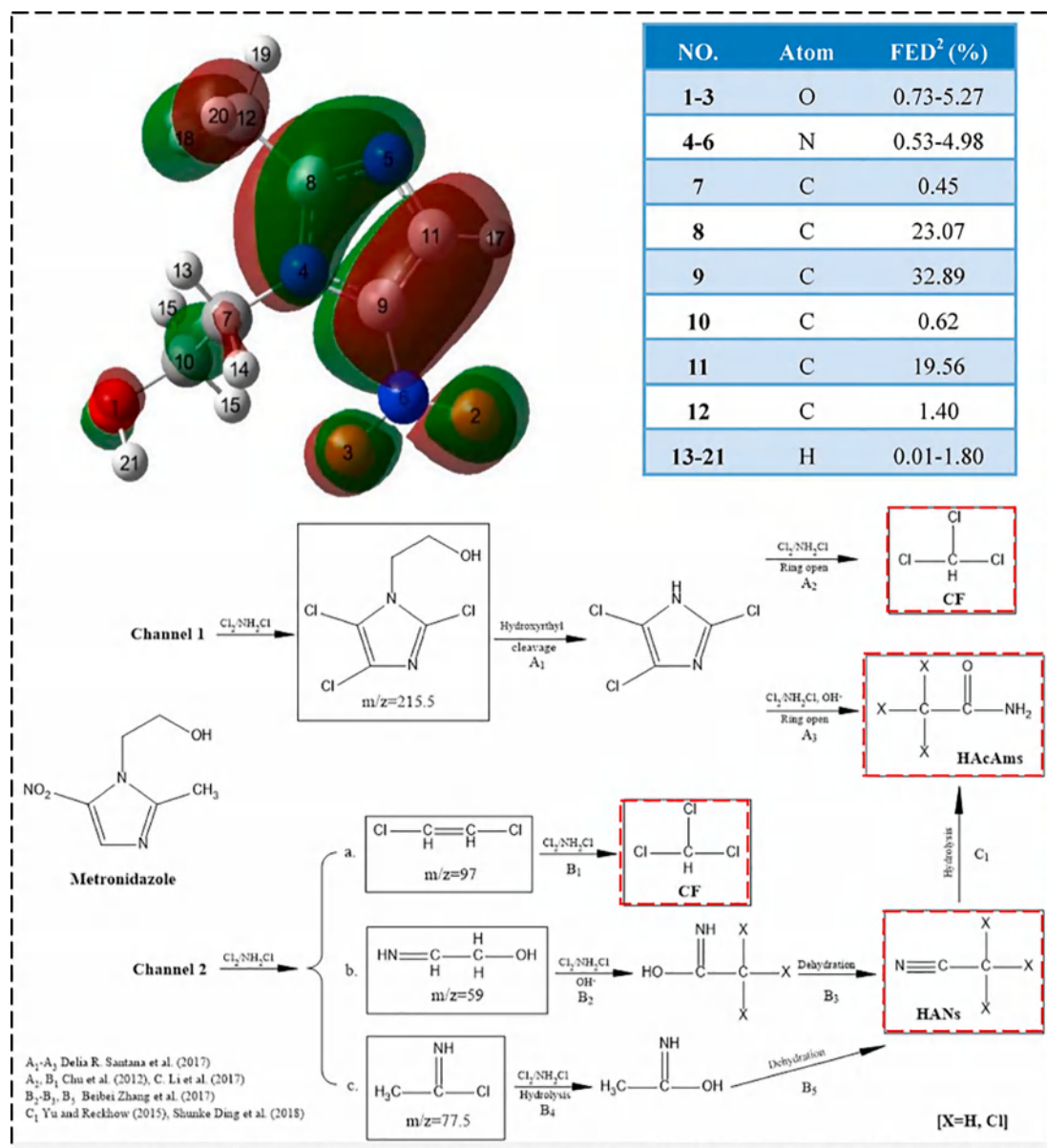


Fig. 5. Optimal structure and FED² in HOMO on atoms of MNZ, and the conversion pathways of MNZ to DBPs during chlor(am)ination [37]. Copyright 2019 Chemosphere.

In addition to IBP, the DBPs formation from other NSAIDs during Cl-DPs also have been studied. For instance, Qiu et al. [90] investigated the formation of DBPs from indole-derivative NSAIDs (including indomethacin and acemetacin) during chlorine disinfection. The analysis revealed that indomethacin and acemetacin would undergo five primary reactions (chlorine substitution, hydrolysis, decarboxylation, C—C coupling, and C—N cleavage) to generate various DBPs during chlorination, among which 19 DBPs were identified with structure. Zhu et al. [49] studied the degradation of phenacetin by the UV/chlorine process. Mechanism analysis indicated that the chlorination, $\bullet\text{OH}$, and RCS were responsible for the UV/chlorine oxidation of phenacetin with contributions of 26.33 %, 14.6 %, and 59.07 %, respectively. Six typical DBPs, including TCM, CH, 1,1-DCP, 1,1,1-TCP, TCNM, and DCAN, were detected. Ding et al. [36] surveyed the formation of THMs, HANs, and HAcAms from the chlor(am)ination of acetaminophen. The results displayed that acetaminophen could form CF, DCAN, DCaAm, and TCAcAm during chlor(am)ination, and the yields of all DBPs were higher during chlorination than that chloramination [36].

3.1.3. Antiepileptics

Antiepileptics are another classic PPCPs. They can be used to treat epilepsy, trigeminal neuralgia, and decrease excitatory neurotransmission. The degradation pathways, mechanisms, and DBPs formation of antiepileptics during Cl-DPs were mainly examined with the most common kinds of compounds, such as carbamazepine (CBZ), which has biological activity, lipophilicity and persistent physicochemical properties, and may do harm to human and non-target organisms. The degradation and DBPs formation of CBZ during Cl-DPs also have arouse much interest [91–94]. Just during the UV/chlorine process, the pathways of DBPs formation during CBZ degradation were proposed as follows [71]. Firstly, CBZ went through hydroxylation substitution and formed CBZ diols, followed by a ring contraction process. At the same time, the reaction could also start from hydroxylation and chlorine substitution. After intramolecular rearrangement, there was a loss of HCl, forming protonated epoxide or hydroxy compounds. The former would further generate CBZ epoxide or CBZ diols, while the latter further went through heterocyclic ring oxidation, and formed a new carbonyl group. Eventually, DBPs like TCM, DCAA, TCAA, DCAN, and

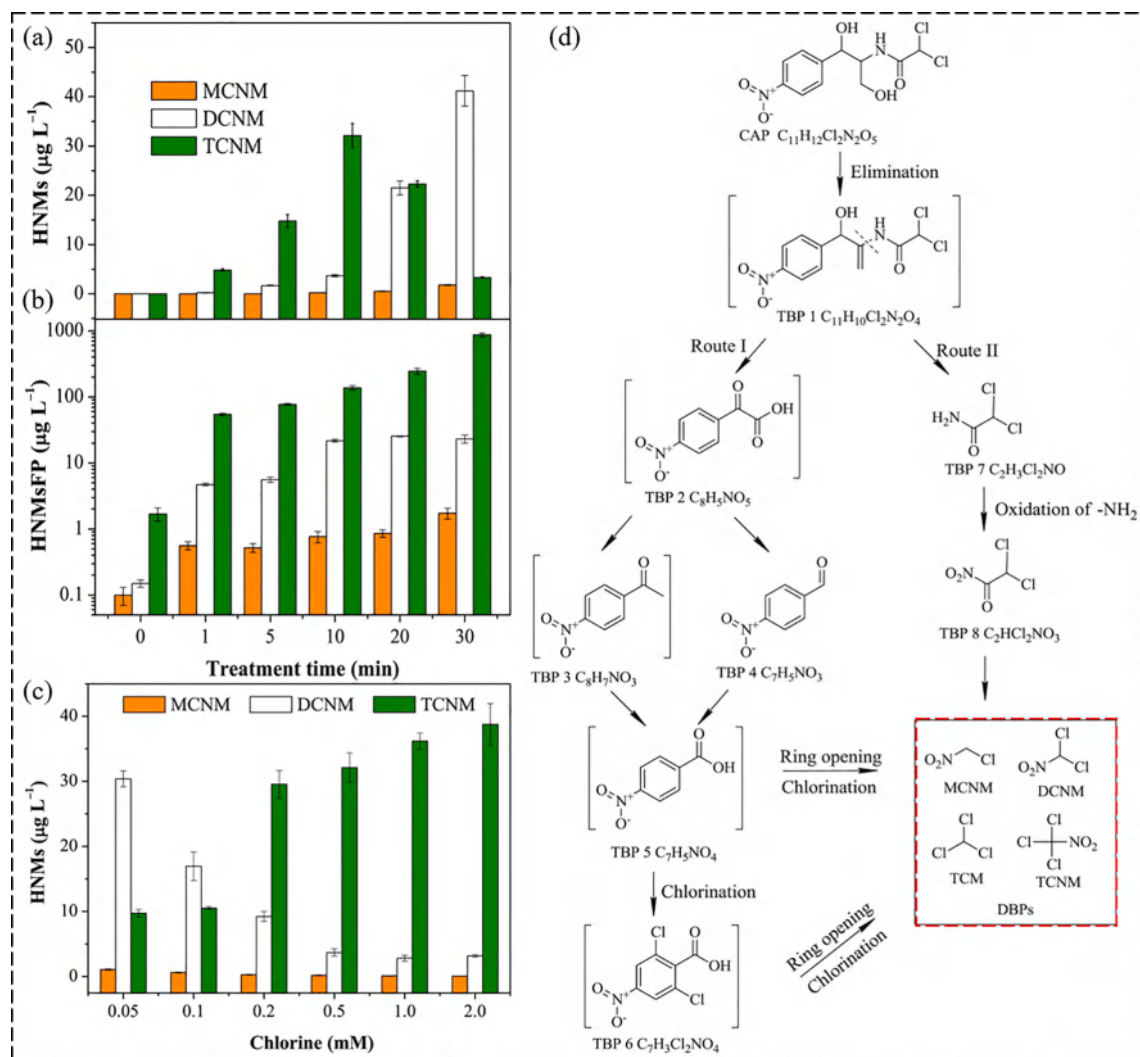


Fig. 6. The concentration (a-c) and the pathways (d) of HNMs formation from CAP during UV/chlorine process [54]. Copyright 2017 Water Research.

TCNM were formed with further oxidative ring-opening reactions. It was noteworthy that the detected DBPs could not represent all the DBPs formation during the CBZ degradation (Fig. 8a). Bu et al. [92] studied the degradation of CBZ in the UV/ NH_2Cl process. The results indicated that the degradation of CBZ was mainly caused by electron transfer, hydrogen abstraction, hydroxylation, and heterocyclic ring oxidation. DBPs, including TCM, TCAN, and TCNM, were found during both chloramination and UV/chloramination processes. The addition of the UV increased the generation potential of TCM, but decreased that of TCAN and TCNM. Furthermore, compared to deionized water, more DBPs were generated in actual waters (Fig. 8b-c). Qin et al. [93] reported that the formation of *N*-DBPs (i.e., DCAN and TCNM) in the abatement of CBZ was negligible, and the 1,1,3-TCP was the primary DBPs for CBZ degradation in the UV/chlorine and the vacuum UV/UV/chlorine processes. Compared with the UV/chlorine process, the vacuum UV/UV/chlorine process enhanced the formation of ClO_3^- and BrO_3^- but retarded the formation of DBPs.

3.2. Endocrine disrupting chemicals (EDCs)

EDCs can change the functions of the endocrine system, thus having adverse effects on organisms. EDCs have posed a severe threat to human health due to their wide distribution, long half-lives, high resistance to metabolic degradation, and lipophilic nature. Among the well-known exogenous EDCs, bisphenol A (BPA) has been largely produced and

utilized around the world, causing the concentration in the water to reach the $\mu\text{g/L}$ range. Besides the adverse health effects of normal EDCs, BPA also harms the immune system, mammary glands, prostate, brain function, and development [74,95]. Considering the fact that chlorination is the most common technique of disinfection, the occurrence of chlorinated derivatives of BPA ($\text{Cl} \times \text{BPAs}$) is within expectation. Moreover, with the electron-donating capacity of two hydroxyl groups, BPA is likely to have electrophilic substitution reactions, the order of which is *ortho*-substitution and *meta*-substitution, since *para*-substitution won't occur for the occupied *para* position of BPA. To be specific, BPA can react with chlorine and quickly disappear after 10 min of chlorination. The mechanism of the reaction between BPA and HOCl was the electrophilic attack on the phenoxide ion by HOCl and the generation of chlorinated DBPs, which were facilitated by a negative charge on BPA. Eventually, trichlorophenol would form during the chlorination process [96]. $\text{Cl} \times \text{BPAs}$ have been detected in an aqueous environment, which might exhibit higher estrogenic activity than its parent compound. To better understand the characteristics of $\text{Cl} \times \text{BPAs}$, Li et al. [97] took on a series of experiments. Since most $\text{Cl} \times \text{BPAs}$ have not been thoroughly studied yet, this research focused on 2,2',6,6'-tetrachlorobisphenol A and 2,4,6-trichlorophenol, whose formation were dependent on initial chlorine concentrations and reaction time. The activities of these byproducts were dependent on the endpoints of assays.

$\text{Cl} \times \text{BPAs}$ belong to halogenated BPA (HBPs), which are the

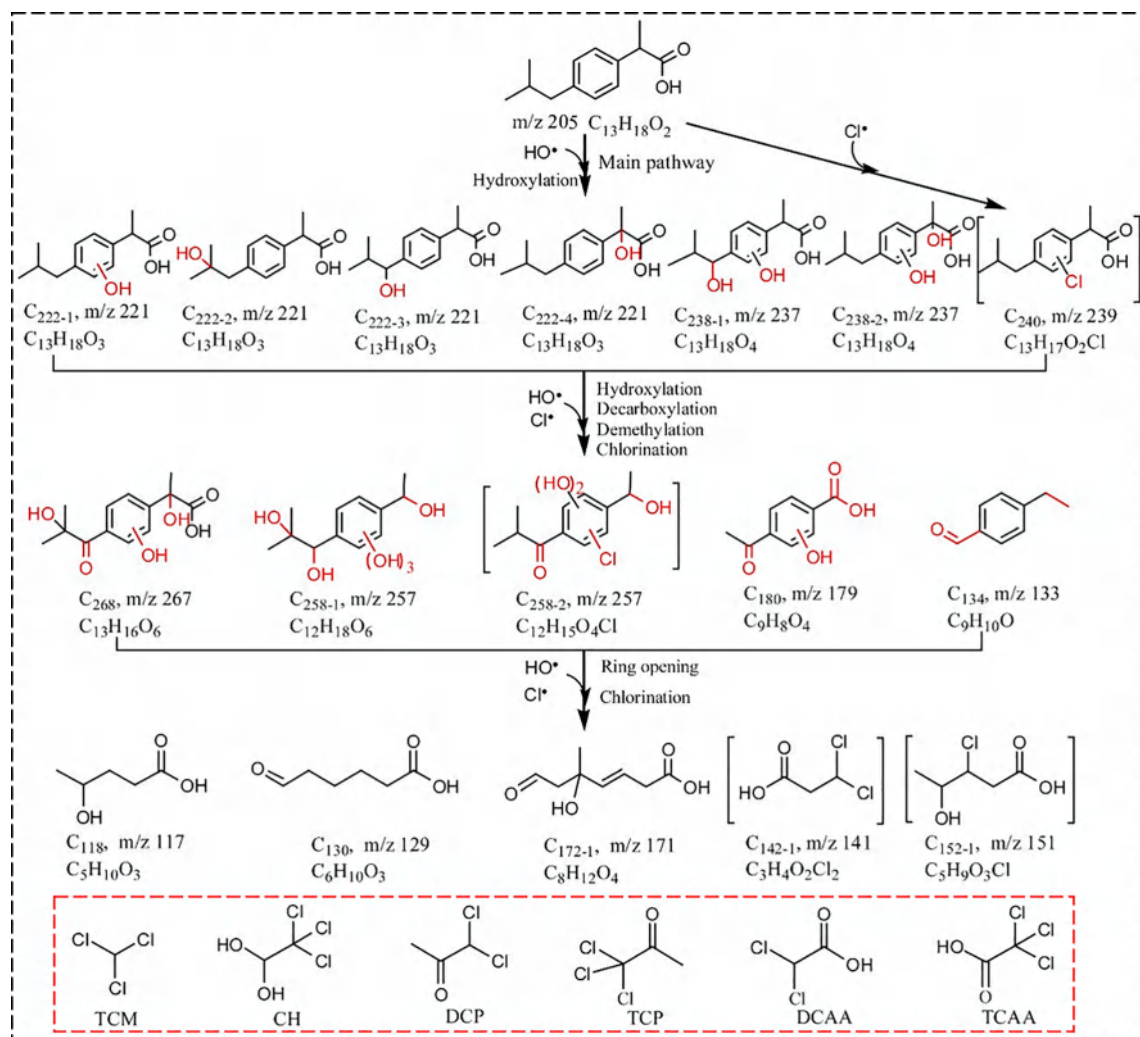


Fig. 7. Proposed pathways of DBPs formation from IBP during UV/chlorine process [69]. Copyright 2016 Water Research.

emerging DBPs. Although Cl \times BPAs have been gaining attention gradually, the study of HBPs still has a long way to go, especially considering that Br \times BPAs and I \times BPAs may be much more toxic than Cl \times BPAs [98]. Recently, Li et al. [74] investigated the formation of HBPs with Br⁻ and/or I⁻ during chlorination. The results showed that the Br⁻ could be easily oxidized to HOBr/BrO⁻ by HOCl/Clo⁻, followed by the formation of Br \times BPAs via electrophilic substitution between BPA and HOBr/BrO⁻. On the other hand, BPA might react with HOCl/Clo⁻ directly to form Cl \times BPAs, whose concentrations were lower than Br \times BPAs because of the lower reaction rate with HOCl/Clo⁻. I⁻ could also be easily oxidized to HOI/IO⁻ by HOCl/Clo⁻, followed by the formation of I \times BPAs or mono-Cl-mono-I-BPAs. Since the C—Cl bond is stronger than C—Br, and the C—I bond is the weakest [99], the generated I \times BPAs were likely to be substituted by HOCl/Clo⁻ and HOBr/BrO⁻, resulting in the yield of Cl \times BPAs in this reaction path. With the presence of both Br⁻ and I⁻, there were three reaction pathways, including the primary transformation of BPA into mono-I-BPA, mono-Br-BPA, and mono-Cl-BPA. Besides, the high reactivity of BPA transformation into HBPs with I⁻ showed that I⁻ could act as a catalyst, which would quickly transform into I \times BPAs and then become I⁻ again, with the formation of Cl \times BPAs and Br \times BPAs by HOCl/Clo⁻ and HOBr/BrO⁻ electrophilic substitution (Fig. 9a).

In addition to chlorine, the reaction between BPA and chloramine has also been studied. He et al. [75] investigated the generation and reaction pathways of DBPs from BPA during chloramination. The results displayed that twelve DBPs were identified, including seven chlorinated

BPAs, four brominated BPAs, and one nitrogenous BPA (Fig. 9b). Compared with chlorine, the oxidation of chloramine was much weaker, making the formation of DBPs via benzene ring cleavage difficult. The reaction between BPA and chlorine or chloramine was attributed to a negative charge on the nucleophilic substrate. In this study, the degradation pathways of BPA involved substitution reactions on the phenol moiety of BPA [75]. However, it remained unknown whether all the DBPs disappeared within 3 h or unidentified DBPs were formed. Moreover, by detecting THMs, HAAs, and HNMs in the presence and absence of BPA during chloramination, their concentrations were found to be almost the same, indicating that the degradation of BPA had little effect on the formation of these regulated DBPs [75].

Because of the toxicity of BPA on human and ecological environment, it has been listed on the contaminant list by many countries. Therefore, BPA analog, like bisphenol S (BPS), is becoming the alternative to BPA. However, they can leach from materials like BPA and may react with disinfectants to form various DBPs. For example, Zheng et al. [76] studied the chlorinated DBPs from BPS during chlorination. The mechanism analysis indicated that BPS would generate monochloro-, dichloro-, trichloro- and tetrachloro-BPS step-by-step, and 2,4,6-trichlorophenol was generated along with the attack of OCl⁻ to BPS's sulfur-oxygen bond. Over time, it was the oxidative coupling process between chlorinated phenoxy radicals and phenoxy that formed biphenyl ether dimers, which then generated trimers by oxidative coupling reactions with trichlorophenol. Ultimately, twenty-two newly chlorinated compounds were identified, and these byproducts are worth

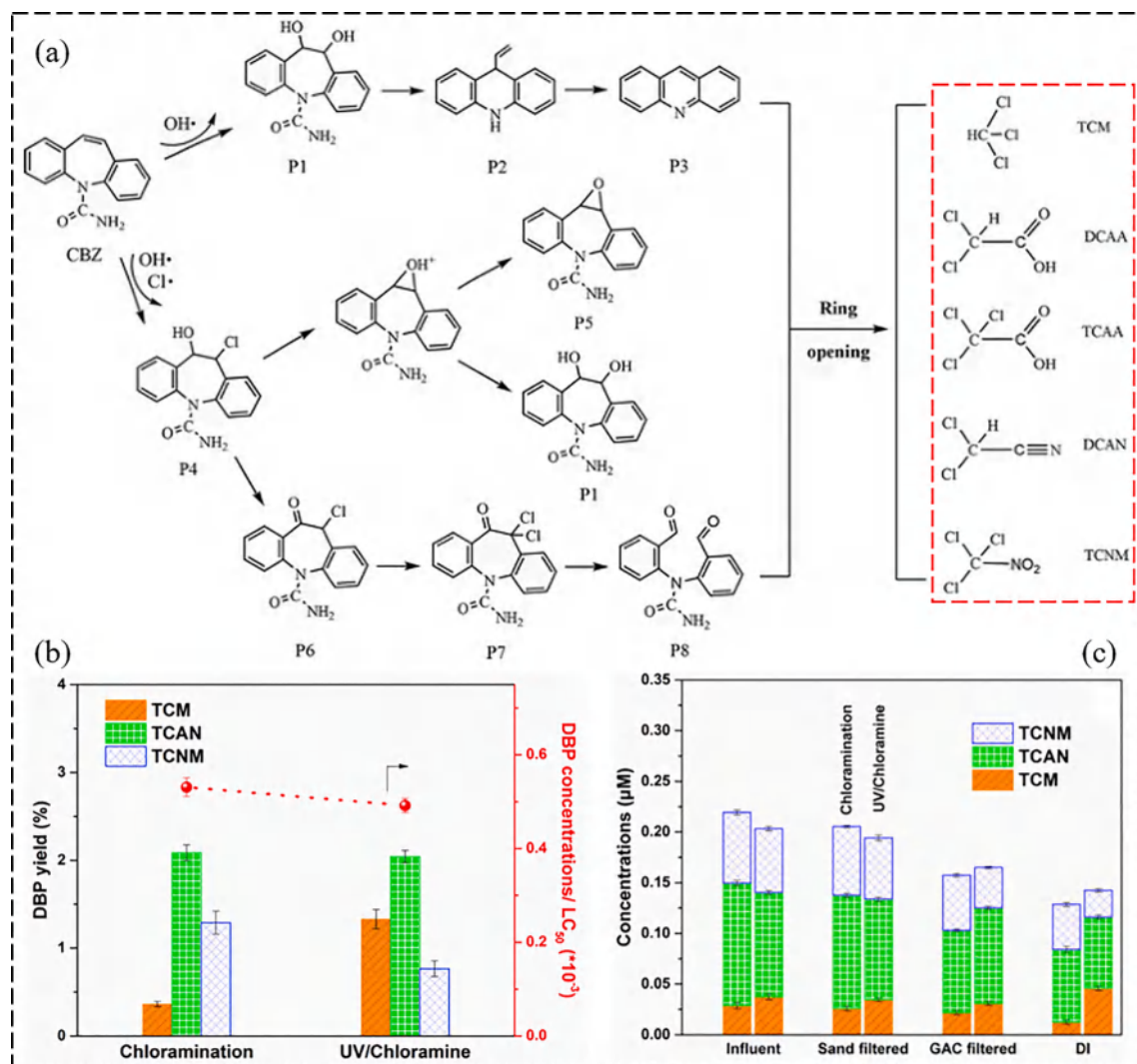


Fig. 8. Proposed pathways of DBPs formation from CBZ during UV/chlorine process (a) [71]. Copyright 2016 Environmental Science and Pollution Research; DBP yields of CBZ under chloramination and UV/chloramine in DI water and actual waters (b-c) [92]. Copyright 2018 Water Research.

noting for their potential risks.

3.3. Brominated flame retardants (BFRs)

BFRs are commonly added to polymeric components to enhance their fire resistance, and they are widely used in plastic, textiles, and electronic equipment products [13]. Among the BFRs, tetrabromobisphenol A (TBBPA) and polybrominated diphenyl ethers (PBDEs) are the most widely applied chemicals, and they are resistant to natural degradation, thus accumulating in aquatic systems and living organisms [100]. Recent studies have shown that the BFRs can be the precursors of DBPs during Cl-DBPs.

As mentioned before, the existence of Br⁻ can be easily transformed into HBrO/BrO⁻ during chlorination, followed by the formation of more cytotoxic and genotoxic BrOminated DBPs [74]. As a BrOminated flame retardant, TBBPA can release many Br⁻ via deBrOmination during oxidative treatment [101]. It was found that TBBPA had a similar structure to steroid estrogen, enabling it to exhibit thyroid hormonal activities and act as an endocrine disruptor. But it is different from EDCs like BPA because the DBPs formation during chlorination of TBBPA has nothing to do with that of BPA and Br⁻ mixture [77]. Therefore, it is important to investigate the relationship between TBBPA and DBPs generation during chlorination. As reported by Gao et al. [77], the transformation of TBBPA during chlorination has been studied.

Compared with BPA, which generates DBPs by electrophilic substitution with chlorine, electron transfer is the key to generate DBPs during the chlorination of TBBPA. This may be attributed to the unique chemical structure of TBBPA that BrOmine atoms occupy ortho and para positions on its aromatic rings, and meta positions are difficult to be substituted (considered as entire substituted compound). The pathways of TBBPA degradation were proposed in Fig. 10a. Firstly, chlorine attacked the phenol moiety of TBBPA, which then lost one electron and formed R₁. Secondly, R₁ released R₂ and R₃ by β-scission. Meanwhile, two R₁ radicals could eliminate R₂ and generate product VII by coupling. Afterward, more products were generated via substitution, oxidation, and exchange reactions. Thus, “fully substituted” phenolic compounds could be fully oxidized by chlorine and transformed into halobenzoquinones (HBQs) via electron transfer during the chlorination. Furthermore, during chlorination of TBBPA, DBPs like THMs, HAAs, HKs, HANs, and HNMs were all detected, among which TBM and DBCM were the primary species [101].

Similar to TBBPA, PBDEs are also widely used fire retardants, which contains 209 congeners, each of them possesses the same diphenyl ether skeleton but different amount of bromine atoms on different substitution position, making it possible to form brominated DBPs during chlorination [78]. As reported by Wang et al. [102], the DBPs formation from 2,2',4,4'-tetrabromodiphenyl ether (BDE-47) and 2,2',3,3',4,4',5,5',6,6'-decabromodiphenyl ether (BDE-209) were investigated during chlor

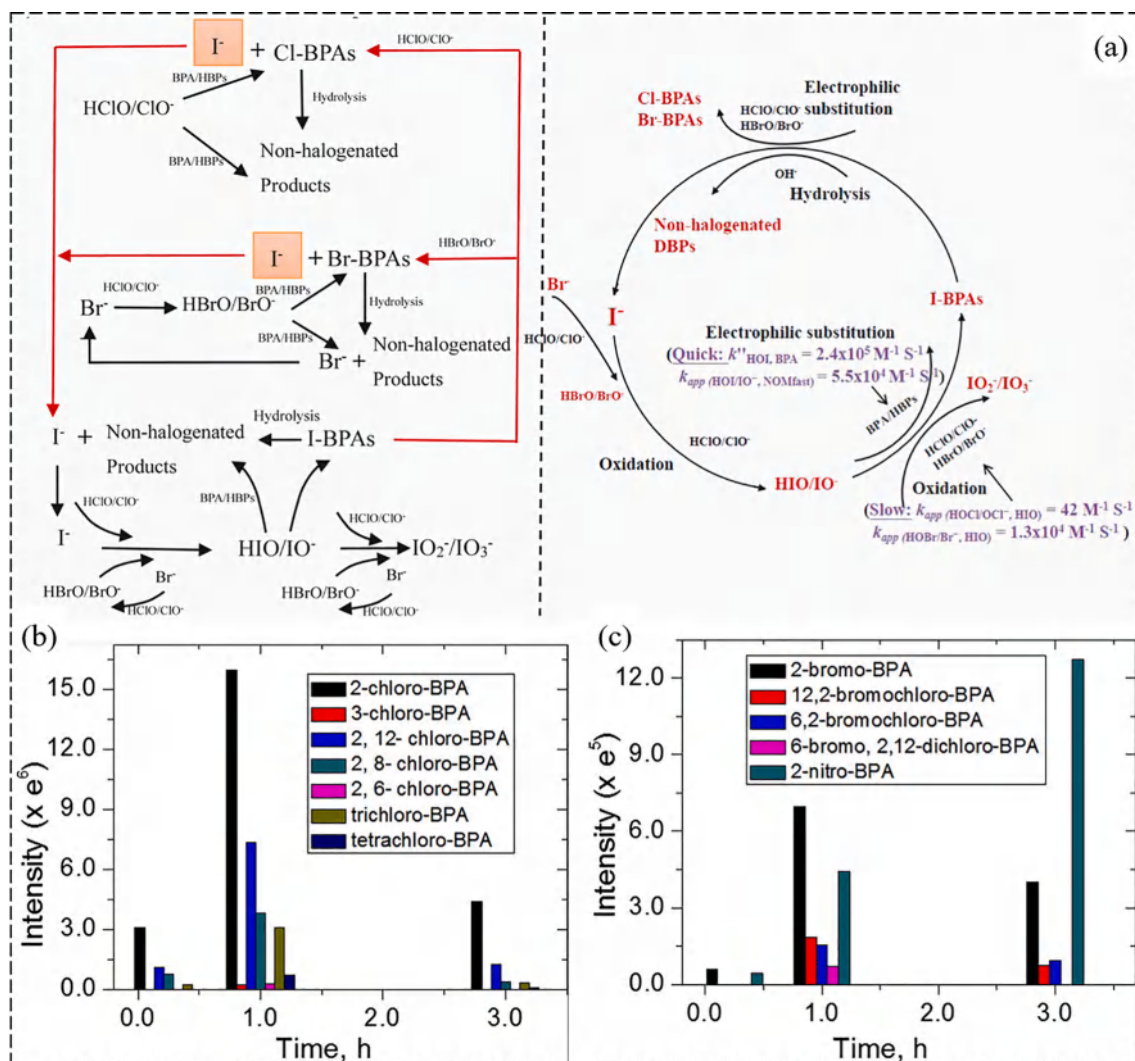


Fig. 9. The pathways of HBPs formation and I^- recycling during chlorination (a) [74]. Copyright 2021 Journal of Hazardous Materials; The intensities of seven chlorinated BPAs, four brominated BPAs and one nitrogenous BPA generated from BPA during chloramination (b) [75]. Copyright 2017 Chemical Engineering Journal.

(am)ination. The results showed that BDE-47 and BDE-209 could promote the generation of DBPs like TCM, BDCM, DCAN, 1,1-DCP, and 1,1,1-TCP, of which 1,1,1-TCP was determined to be the major species, during chlorination. Compared with chlorination, less TCM, DCNA, and 1,1-DCP formed in the presence of BDE-47, and less DCAN and 1,1-DCP formed in the presence of BDE-209 during chloramination. When it comes to the natural water, however, the influence of BDE-47 and BDE-209 on the DBPs generation was negligible due to the complicated composition of natural water. Zhang et al. [78] also studied the formation of DBPs from 2-bromodiphenyl ether (BDE-1) during the UV/chlorine process. The results showed that the BDE-1 has *ortho*-bromine substitution, enabling it to convert into dibenzofuran (DF)-type products (Fig. 10b). The formation mechanism of DF-type products was related to indirect photolysis during UV/chlorine treatment. The radical reactions of $\bullet Cl$ or $\bullet OH$ with *ortho*-carbon radicals could generate important intermediates of 2-chlorodiphenyl ether (2-Cl-DE) or 2-phenoxyphenol (2-OH-DE), which plays an important role in DF-type products formation. Wang et al. [102] also reported the DF yield in natural water decreased, which might be because of competitive light absorption and scavenging effects of the water matrix.

3.4. Effects of water quality parameters on DBPs formation

Many studies have shown that water quality parameters have an essential impact on DBPs formation from EOMPs during the Cl-DPs. The water quality parameters mainly include NOM, temperature, pH value, and the type of ions [11].

3.4.1. NOM content

DBPs are formed by the reaction of disinfectants with NOM or other water constituents. Therefore, the NOM content in water is the critical factor leading to the formation of DBPs. Due to the different quality of raw water, the content of NOM in water is not the same. Previous studies displayed that the NOM (e.g., humic acid, fulvic acid, and amino acid) has obvious effects on DBPs formation during Cl-DPs [92,103–105]. Generally, the content of NOM precursors in raw water is proportional to the generation amount of DBPs [106]. As reported by Chu et al. [83], a higher concentration of DCACAm would be generated during the treatment of CAP by chlorination in the presence of amino acid (i.e., asparagine). In addition, the molecular weight, structure, and hydrophobicity of NOM also influence the generation of DBPs. It has been reported that the THMs formation potential of hydrophobic NOM was twice than that hydrophilic component, because the THMs generation happened by the reaction of $HOCl/OCl^-$ with the humic-like matter. The low molecular

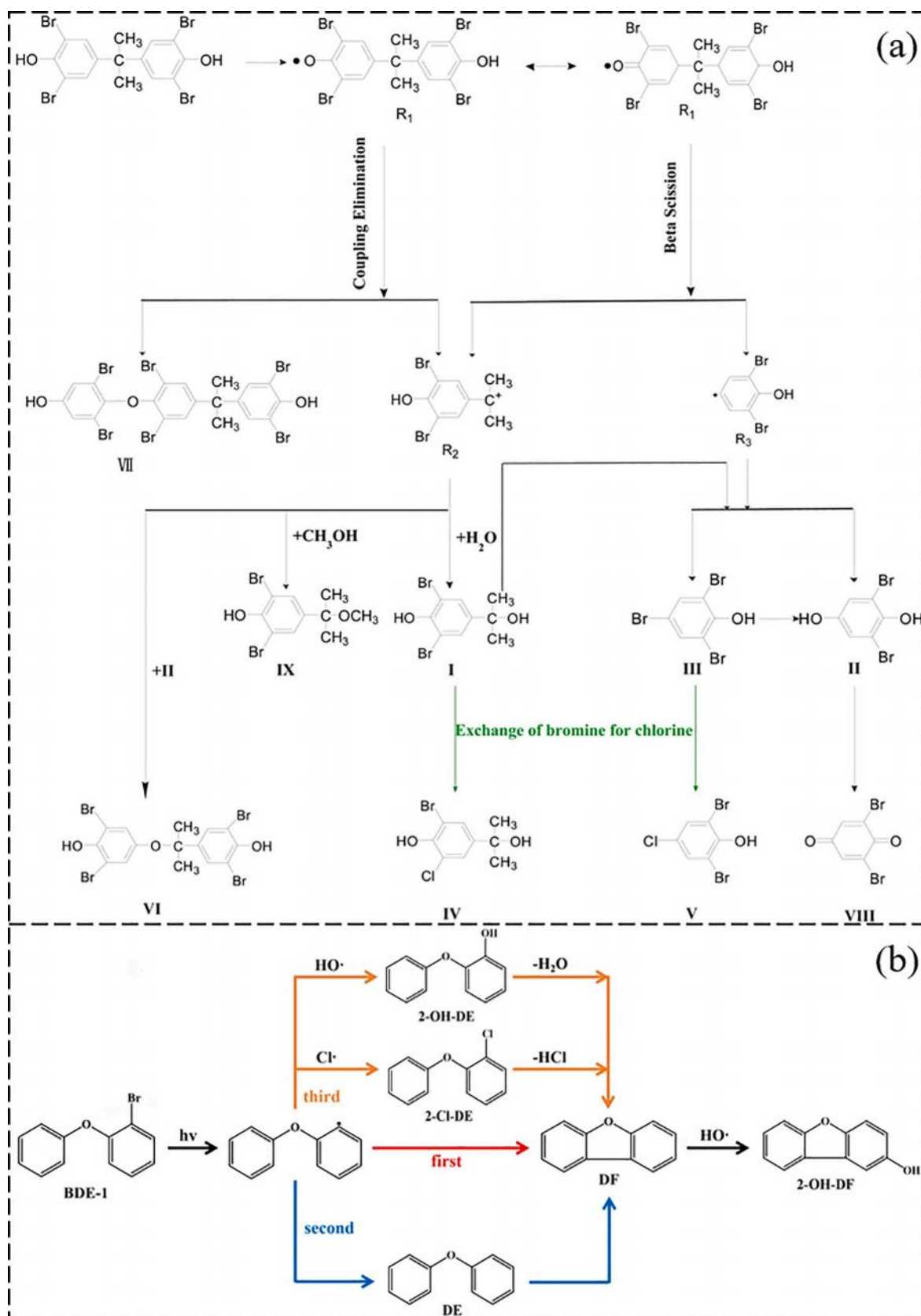


Fig. 10. (a) Proposed pathways of TBBPA degradation and DBPs generation during chlorination [77]. Copyright 2016 Environmental Science & Technology. (b) The pathways of DF-type products formation during UV/chlorine treatment [78]. Copyright 2021 Chemical Engineering Journal.

weight NOM accelerated the generation of brominated DBPs (e.g., DBCM and BDCM). However, no influence of hydrophobicity or hydrophilicity was observed on other types (such as HKs and HALs). Hydrophobic and high molecular weight NOM has more phenolic groups, thus enhancing the generation of aromatic DBPs [11,107]. Although some studies have been reported, the complex nature of NOM makes it challenging to understand the genuine mechanism and effect on DBPs formation, and more effort is needed [11,108].

3.4.2. Temperature

Substitution, addition, and redox reactions are the main pathways for EOMPs degradation and DBPs formation during Cl-DPs, and the reaction rate is positively correlates with the reaction temperature [45,49–52]. That is, as the increase of temperature, the reaction between disinfectant and precursors could be accelerated, it could result in more DBPs being generated. In addition, there is more NOM in the summer compared to the cooler months. Furthermore, the high temperature contributes to the volatilization of volatile DBPs (e.g., THMs) and would also lead to the decomposition of unstable DBPs (e.g., HANs, HKs, and HALs) to convert to more stable DBPs [45,49–52]. Such as Mompremier et al. [109] reported that the temperature increase from 17 to 37 °C could cause the reduction of HAAs during chlorination. Hong et al. [110] found that the HKs production increased when the temperature increased from 10 to 20 °C, and then began to decline with further enhancement of temperature. Therefore, the generation of DBPs can be reduced by controlling the reaction temperature appropriately [11,106,109,111].

3.4.3. Value of pH

The pH value also has an important influence on DBPs formation from EOMPs during Cl-DPs, and different kinds of DBPs can be produced at different pH values. Meanwhile, the influence of pH on DBPs generation is foreign for different EOMPs. Generally, when the pH value is 6–9, the production of TCAA reduces with the enhancement of pH value, and the production of THMs increases with the increase of pH value, during the chlorine disinfection process [11,36,106,111]. However, during the chloramine disinfection, the production of DCAA reduces with the increase of pH value, and the production of TCAA and THMs is tiny that can be neglected. Under alkaline conditions, the HANs can produce HACams and HAAs, the HALs easy to be degraded into THMs, and the HACams are accessible to hydrolysis, due to their unstable properties. Acidic conditions benefit the generation of *N*-DBPs (e.g., HANs), while alkaline conditions benefit the generation of stable *C*-DBPs (e.g., THMs) [11,36,106,111]. For example, Ye et al. [9] reported that the yield of TCM gradually enhanced as the pH enhanced from 5 to 9 during the chlorination of TC, while the DCACAm yield reduced from 23.58 % to 4.39 % as the pH enhanced. This was because the hydrolysis rate of DCACAm catalyzed by alkali is higher at higher pH values. Ding et al. [36] also found that the yield of CF steadily enhanced as the pH enhanced from 5 to 9 during the chlorination of acetaminophen, and it wasn't easy to detect during chloramination unless at pH 9, the production of DCAN was the highest at pH 6, and decreased with the increase of pH. During chloramination, the DCAN gradually reduced with the rise in pH to 8. The production of DCACAm and TCACAm showed the same tendency of falling with the enhancement of pH from 5 to 9 during both chlorination and chloramination.

3.4.4. Coexisting ions

The composition of actual water is very complex, and contains many anions and cations. In the last few years, many studies have shown that these ions have a noticeable influence on DBPs formation during Cl-DPs. For example, the most widely studied anion is Br^- , which commonly existed in the groundwater or surface water, especially in coastal cities because of the saltwater intrusion. Generally, Br^- conduces to the generation of brominated DBPs via its reaction with chlorine to form HOBr, subsequently reacting with NOM to generate brominated and mixed

chlorinated-brominated products. In addition to Br^- , the effect of I^- on DBPs formation has also received increasing attention due to the formation of more toxic iodinated DBPs [112]. Besides, when the concentration of inorganic nitrogen (i.e., NO_3^- , NO_2^- , etc.) is high, more *N*-DBPs are generated [113]. Furthermore, some coexisting anions (e.g., HCO_3^-) would scavenge radicals, including $\bullet\text{OH}$, $\bullet\text{Cl}$, and $\bullet\text{Cl}_2$, causing the decrease of formed DBPs. Zhang et al. [78] reported that the generation of DF-type products significantly decreased by 30.2 %, 44.8 %, and 55.1 % with HCO_3^- enhanced from 1 to 50 mM during the degradation of BDE-1 by UV/chlorine treatment. Compared with anions, the influence of cations on DBPs formation has received more attention. Such as the Ca^{2+} and Mg^{2+} , which are typical hardness ions in water. Previous studies have shown that the Ca^{2+} and Mg^{2+} can change the structure and charge distribution of NOM by complexation, thus affecting the formation and distribution of DBPs during the disinfection processes [108,113–115]. The Cu^{2+} , Fe^{3+} , and Al^{3+} are also widely present in surface water and the distribution system of drink water, due to the catalyst effect, the Cu^{2+} , Fe^{3+} , and Al^{3+} usually would improve the formation of THMs DBPs [94,108,113–115]. Cu^{2+} , Fe^{3+} , and Al^{3+} promote THMs generation because they can bond with humic acid, Cl^- , and Br^- in water. The formation of intermediates, such as metal–Cl–humic acid, weakens the original bonds of humic acid and are easily destroyed by disinfectants [11,113,114]. As for NH_4^+ , which could react with disinfectant, thus reducing the generation of THMs. The results showed that NH_4^+ could react with ClO^- to form NH_2Cl . As a result, the availability of disinfectants is decreased, ultimately causing the reduction of THMs formation. However, NH_4^+ benefits the generation of *N*-DBPs [11,113,114]. Just reported by Ta et al. [114], the generation of THMs was mainly affected by the ions, but the degree and mechanism of the influence mainly depend on the type of ions. Ca^{2+} , Mg^{2+} , and NH_4^+ obviously reduced THMs formation, while Cu^{2+} , Fe^{3+} , and Al^{3+} promoted THMs formation. The effects of the above ions on DBPs formation are largely attributed to complexation, consumption, and catalysis. Sheng et al. [94] reported that the total DBPs concentration (including TCM, DCAN, DCP, TCNM, and TCP) enhanced from 1.76 to 7.70 $\mu\text{g/L}$ with Cu^{2+} concentration enhanced from 0 to 50 μM during CBZ degradation in chloramine system. Although it can be confirmed that the ions will affect the formation of DBPs, the results obtained for different systems are also different, no unified conclusion has been formed, so the specific influencing process and mechanism need to be further studied.

4. DBPs detection and control

4.1. Detection of DBPs

The accurate detection and identification of generated DBPs are essential for further research on DBPs. The structure and chemical properties of different DBPs are different, in order to better characterize and quantify DBPs in drinking water, the different analytical methods should be selected according to their properties. To date, the detection and characterization of DBPs are mainly performed by chromatography technologies, including gas chromatography (GC)/GC-mass spectrometry (MS), liquid chromatography (LC)/LC-MS, and ion chromatography (IC)/IC-MS technologies, due to their high separation efficiency, fast analysis speed, and wide application range. Due to the low concentration of DBPs in water (usually ng/L to $\mu\text{g/L}$ level), the DBPs generally undergo concentration and enrichment before detection. In addition, some non-volatile DBPs with high boiling points and strong polarity cannot be directly analyzed by the chromatography method due to their strong adsorption effect on chromatographic columns and long retention time, so it is necessary to use derivatization technology to convert them into easy-to-analyze compounds (e.g., some HAAs) [116–120]. Although more than 700 DBPs have been detected and identified to date, this is just the tip of the iceberg, and more effort is needed.

The GC method is suitable for the analysis of volatile/semi-volatile, low molecular weight, and good thermal stability of DBPs, such as

THMs, HANs, CH and some emerging DBPs (e.g., HACams), and the electron capture detector is the main detector for DBPs detection [116,117]. Although the electron capture detector has a high sensitivity for detecting halogenated DBPs, it lacks selectivity and is susceptible to interference from unknown components, so it cannot be used for qualitative analysis of unknown DBPs. The GC-MS technology has high sensitivity and selectivity, which can meet both quantitative and qualitative requirements for DBPs detection. For example, Zhang et al. [121] used GC-MS to identify and quantify eight emerging *N*-DBPs (i.e., chlorophenylacetoneitriles), the results showed that this method had method detection limit, method quantification limit, and precision ranging from 0.15 to 0.37 ng/L, 0.50–0.95 ng/L, and 5.8 %–11 %, respectively, under optimized conditions. The recoveries of the eight chlorophenylacetoneitriles ranged from 92 % to 102 %. Furthermore, the GC-MS technology has also been proven to be promising in the detection of some HBQs, but it is limited to the detection of volatile, heat-stable, non-ionic, and non-polar HBQs. As reported that three new iodinated HBQs, including 2-chloro-6-iodo-1,4-benzoquinone, 2-bromo-6-iodo-1,4-benzoquinone, and 2,6-diiodo-1,4-benzoquinone, were detected and identified by the HPLC-MS technology.

The LC method is another separation technique that can make up for shortcomings of GC, it is widely applied to analyze the polar, high molecular weight, and thermally unstable DBPs (e.g., aromatic DBPs, iodinated DBPs) [116,117,122]. Different from GC-MS, the reverse phase column, electrospray ionization, and atmospheric pressure chemical ionization are the most commonly used column and ionization techniques for LC-MS detection, which may be not helpful for ionizing significant or nonpolar substances but is effective for small polar molecules [118,119]. As reported by Hu et al. [123], the high performance LC (HPLC)-MS/MS method was developed for the simultaneous determination of iodinated HAAs and aromatic iodinated DBPs. This HPLC-MS/MS method was demonstrated to be sensitive and accurate with detection limits of 0.06–0.15 ng/L and recoveries of 70 %–110 %. In addition, LC-MS can also be used to screen non-target compounds, detect and identify new DBPs. Just as Han et al. [124] reported that a new group of polar halogenated DBPs, trihalomethanols, had been characterized and identified by the HPLC-MS method.

The IC method is developed based on the ion exchange principle. Compared with other methods, the IC method could determine the DBPs with less interference, simply, quickly, and sensitively advantages. When combined with MS, the sensitivity would be significantly increased, but the complexity and cost of the analysis would also be increased. Previous studies indicated that the ClO_2^- and ClO_3^- formed during the ClO_2 disinfection could be well detected by IC/IC-MS [120]. Besides, the IC method has also been proven to be able to detect HAAs. As found by Yang et al. [125], a one-pump column-switching IC method was designed and used to detect trace HAAs. This IC method can enrich HAAs online and meanwhile dramatically removes anions, and it can achieve comparable recoveries as the GC method but uses no solvent.

In addition to the above precise techniques, researchers have proposed some estimation methods for DBPs analysis, such as the UV differential optical absorption method. Although a variety of efficient methods have been used for the detection and identification of DBPs, a large number of DBPs have not yet been detected and identified. Therefore, more selective and sensitive analytical methods should be paid more effort for identifying more emerging DBPs.

4.2. Advanced technologies for DBPs abatement or minimization

The control strategies for DBPs can be divided into three categories: source control, process control, and end control. Source control means to reduce the concentration of DBPs precursors by water resource protection or treatment processes before the addition of disinfectants. Process control means reducing the generation of DBPs or changing the generation type of DBPs by changing the disinfection method and optimizing the disinfection process. End control means removing the generated

DBPs by some physical or chemical methods. Each method has its advantages and disadvantages, and its application should depend on the actual conditions.

4.2.1. Removing DBPs precursors to reduce DBPs formation

Water source protection is an effective strategy to control the concentration of DBPs precursors (including NOM and halogen ions) in water. In terms of controlling NOM, the growth of algae can be restricted by controlling the trophic degree of source water and the cycling process of nutrients, so as to control the NOM in raw water. As for the halogen ions, it is necessary to avoid seawater or brackish water from entering the drinking water source. Meanwhile, some attention should also be paid to the local aquaculture industry to prevent large amounts of halogens from entering the water [7,22,25]. Furthermore, it is strictly prohibited to discharge untreated wastewater (e.g., industrial wastewater, medical wastewater, etc.) directly into the water body, which contains a large number of organic compounds and halogens.

In addition to the water source protection strategy, the pretreatment processes also have a significant effect on the removal of DBP precursors. Among the technologies, the coagulation process as a conventional technology can effectively remove the precursors of DBPs, especially for the high molecular weight organic matter. Meanwhile, the removal efficiency of the C-DBPs precursor is generally better than that of the *N*-DBPs precursor [7,126–128]. However, the coagulation process cannot effectively remove small molecules and hydrophilic organic matter. Therefore, to further improve the removal of DBPs precursors, some strengthening pretreatment processes are often implemented before coagulation, including pre-oxidation, activated carbon adsorption, membrane filtration, ion exchange, and so on. These processes can reduce the DBP precursors to some extent, thus reducing the formation of DBPs [22,25,129]. For example, Liu et al. [130] used ferrate (Fe(VI)) to pre-oxidize NOM in the source water to control DBPs generation in subsequent chlorine or chloramine disinfection. It was validated that Fe(VI) pretreatment followed by chlorination (or chloramination) resulted in generated DBPs containing less unsaturated, halogenated, and aromatic moieties. He et al. [131] also reported that $\text{Fe(VI)}/\text{FeCl}_3$ /ultrafiltration system could remove more than 10 % ~ 34 % of the dissolved organic matter and 6 % ~ 17 % of the total nitrogen compared with FeCl_3 /ultrafiltration system for algae-laden source water. The generation potentials of 12 kinds of C-DBPs and seven kinds of *N*-DBPs were reduced by 32.5 % and 22.5 %, respectively, due to the increased elimination of dissolved organic matter and total nitrogen. Wang et al. [132] studied DBPs generation through chlorination of alachlor pre-oxidized by a zero-valent iron/persulfate (ZVI/PS) system. The results showed that the application of ZVI/PS in actual water containing alachlor decreased DBPs formation by increasing PS dosage. Ersan et al. [133,134] found that the ion exchange and nanofiltration pretreatment could enhance the removal of Br in potable reuse, thus decreasing the formation potential THMs and HAAs DBPs. These studies have indicated that pretreatment processes are effective in alleviating DBPs precursors, thus reducing the formation of DBPs.

4.2.2. Optimizing the disinfection process to reduce DBP formation

Changing the disinfection method is an effective means to control the generation of DBPs. Chlorine is commonly used in disinfection, which will cause the formation of many THMs and HAAs DBPs. To control the formation of these DBPs, several new processes have been used to replace chlorine disinfection, including chloramine, UV, ozone, ClO_2 , and the combined disinfection processes. The alternative disinfectants usually result in less formation of some conventional DBPs (e.g., THMs and HAAs), but some specific DBPs would be generated [22,25,35]. For example, the use of chloramine would result in the formation of HANs, NDMA, and some *N*-DBPs, while the use of ClO_2 usually results in the formation of ClO_3^- and ClO_2^- . Meanwhile, the chloramine and ClO_2 would cause the generation of more toxic iodinated DBPs. As for the ozone, which could cause the generation of aldehydes and brominated

DBPs. Therefore, various factors should be fully considered when changing the disinfection method to control the generation of DBPs, not only to ensure a good disinfection effect, but also to minimize the formation of DBPs [22,25,35].

Compared with seeking a disinfectant that does not generate DBPs, optimizing disinfection parameters should be a more efficient way to reduce DBPs formation. Section 3.4 has discussed that the water quality parameters have an important influence on the formation of DBPs, thus the formation of DBPs can be reduced by regulating and optimizing these water quality conditions. Besides, the operating conditions, including the disinfectant dosage, contact time, injection position, and mode of disinfectant, will all affect the formation of DBPs [22,25]. As Ye et al. [9] reported, with the increase of chlorine dose from 0.25 mM to 1.25 mM, the yield of TCM, CH, and TCACAm steadily increased after chlorination of TC for 2 h, and the DCAN yield first enhanced and then declined, while the DCACAm yield gradually reduced. The reduction of DCAN and DCACAm yield might be due to the acceleration of the decomposition of DCAN and DCACAm by excess chlorine [135]. The chlorination time had little influence on the amount of the produced DBPs during chlorination, while DBPs yields steadily enhanced with the increase of contact time and chloramine dose during chloramination. This result was related to the relative stability of the DBPs (including DCACAm and DCAN) in the presence of NH_2Cl . Ding et al. [36] reported the formation of THMs, HANs, and HACams from the chlor(am)ination of acetaminophen. The results showed that the yield of CF steadily increased as chlorine dose enhanced from 0.05 to 1.0 mM, while the yield of DCAN, DCACAm, and TCACAm showed the same tendency of enhancing first and then declining. However, the yield of DCAN, DCACAm, and TCACAm all exhibited a tendency of enhancing with the enhancement of NH_2Cl dose. For the reaction time, the CF and TCACAm yield steadily increased as the time enhanced from 1 to 48 h during chlorination. DCAN and DCACAm yield showed a tendency of enhancing first (1 h to 20 h) and then decreasing (24 h to 48 h). However, the yields of DCACAm and TCACAm both were enhanced from 1 h to 48 h during the chloramination. These results indicated that the effects of disinfectant dosage and reaction time on DBPs formation not only depends on the disinfectant itself, but also depends on the disinfection processes, the types of EOMPs and DBPs. As for the injection position of disinfectant, Jiang et al. [136,137] proposed replacing the position of the granular activated carbon (GAC) process with a disinfection process during chlorination, which could use the GAC to remove some produced DBPs by adsorption, thus reducing the concentration of DBPs in the effluent water. As for the adding mode of disinfectant, Li et al. [138] found that the sequential chlorination process can effectively control the formation of NDMA compared to the normal chloramination process. The controlling mechanism of NDMA in the sequential chlorination process was that rapid oxidation of NDMA precursors by free chlorine, which causes less or no formation of NDMA in subsequent chloramination. Additionally, the adding way of chloramine (in situ generation or preformed chloramine) and the adding order and ratio of Cl_2 and NH_3 in chloramine disinfection also affect the generation of DBPs. Fang et al. [139] found that in-situ chloramination could effectively mitigate the formation of diiodoacetamide. Breakpoint chlorination is also an efficient disinfection mode for controlling DBPs formation, especially for NDMA and iodinated DBPs [140]. The above discussion manifested that the operating conditions have a great influence on DBPs formation, thus the formation of DBPs could be reduced by adjusting and optimizing the relevant operating conditions.

4.2.3. Removing the generated DBPs by some advanced technologies

The end control is to remove the generated DBPs by some physical or chemical methods, and is the last barrier to safe drinking water. The physical methods mainly include adsorption, membrane filtration, and heating. As for adsorption, the activated carbon has shown high adsorption removal efficiency for various DBPs, and the removal efficiency even reached 100 % for some DBPs, but it is difficult to remove

the high hydrophilic DBPs by adsorption [22,25,136]. Air stripping is also a cost and effective technique for the removal of volatile DBPs, especially in small water treatment systems. However, compared to activated carbon adsorption, air stripping is less effective in removing DBPs [24,141]. Membrane filtration technology is an effective means of purifying treatment for water, and is widely used in a household water purifier. According to the different selectivity of membrane, it can be divided into reverse osmosis (RO), nanofiltration (NF), ultrafiltration (UF), and microfiltration (MF). Due to the lower relative molecular weight of most DBPs, the RO, NF, and UF processes can remove most DBPs by size screening and charge exclusion mechanisms. However, it should be noted that the regular cleaning or replacement of the membrane is the key to maintain high efficiency of membrane filtration, which will greatly increase the cost of use. Heating is an ancient water purification technique, especially in China. In the heating of water, the concentration of volatile DBPs will be reduced by volatilization, and some refractory DBPs can also be decreased by hydrolysis or decarboxylation reaction [22,25].

The chemical methods mainly include oxidation and reduction technologies, including advanced oxidation processes (AOPs), advanced reduction processes (ARPs), and electrochemical methods, etc., which could remove the generated DBPs by dehalogenation, decarboxylation, mineralization, and other approaches [142]. As reported by Hou et al. [143], the UV/persulfate process showed a high degradation efficiency for HANs DBPs, and the degradation kinetics of monochloroacetonitrile (MCAN), DCAN and TCAN by $\text{SO}_4^{\cdot-}$ followed second order kinetics at the rate constants of $7.48 (\pm 0.58) \times 10^7$, $6.36 (\pm 0.16) \times 10^7$ and $2.43 (\pm 0.15) \times 10^7 \text{ M}^{-1} \cdot \text{s}^{-1}$, respectively, which were ten times higher than those by $\bullet\text{OH}$. The degradation of chlorinated HANs in the UV/persulfate system was started through hydrogen abstraction and C—C bond breaking by $\text{SO}_4^{\cdot-}$ instead of C—Cl bond cleavage, followed by oxidation and hydrolysis processes to generate Cl^- , NO_3^- , CO_2 and H_2O . This study indicated that $\text{SO}_4^{\cdot-}$ was more appropriate for chlorinated HANs degradation than $\bullet\text{OH}$. Chen et al. [144] used a weak magnetic field (WMF) to accelerate trichloroacetamide (TCAM) removal by ZVI, in which the ZVI has strong reducibility. The results showed that WMF could strengthen TCAM removal by ZVI, particularly at low ZVI doses and high pH, and the dechlorination was dominant and hydrolysis was secondary for TCAM removal by WMF-ZVI system. Besides, the sulfite also possesses strong reducibility, many studies have verified that HANs, HNMs, HACams, and some other DBPs could be removed by sulfite undergoing reductive dehalogenation reaction. As reported by Ding et al. [145], the sodium sulfite (S(IV)) could rapidly decompose various brominated and iodinated HACams, and the order of the reductive dehalogenation rates of HACams versus the substitution of halogen atoms was iodo- > bromo- > chloro-. The mechanism analysis affirmed that the S(IV) reactions with HACams mainly rest on sulfite replace bisulfite, and HACams decomposition by S(IV) primarily generated HACams sulfonate via nucleophilic substitution. Furthermore, the electrochemical methods also are attractive and promising techniques for DBPs degradation. As Bromberg et al. [146] reported that the phosphomolybdate-bipyridylpropane complex (FePM-BPP) could reduce a variety of carcinogenic DBPs (including CF, NDMA, and BrO_3^-) by the electrocatalytic reduction process. Although these chemical methods can efficiently remove DBPs, they still have problems such as high energy consumption and easy to produce secondary pollution, so more studies are urgent needed for the actual application.

5. Conclusions and prospects

The harm of DBPs to human health has attracted extensive attention, and the EOMPs have been confirmed to be the precursors of DBPs during the Cl-DBPs. Therefore, how to effectively and economically control the formation of DBPs from EOMPs during the Cl-DBPs has become one of the hotspots and difficult points in the environmental field. This review has systematically discussed the formation of DBPs from EOMPs during the

Cl-DPs, including the pathways, mechanisms, and influencing factors, etc. Although some achievements have been made, more efforts must be paid to solve the related fundamental and technical gaps and challenges. In future research, we can make more exploration in the following aspects:

- (1) Optimizing the disinfection process. The above discussion has indicated that the disinfection processes, including the disinfectant type, disinfection parameters, and operating conditions, have an essential influence on the formation of DBPs. For example, the EOMPs can react with chlorine to produce a large number of DBPs, but the generated DBPs are significantly reduced when using chloramine as the disinfectant. The acidic conditions favor the reaction between EOMPs and chlorine to form N-DBPs, while alkaline conditions favor the formation of stable C-DBPs. Therefore, the DBPs formation can be reduced by optimizing the disinfection process. Furthermore, the pretreatment processes like ferrate(VI) pretreatment and ozone pretreatment can be added before disinfection, which could remove EOMPs or alter the properties of EOMPs in the source water. In this case, the potential adverse effects caused by DBPs precursors can be minimized.
- (2) Developing more advanced disinfection techniques. Cl-DPs are now the mainstream disinfection technologies, but the formation of DBPs is inevitable during the disinfection processes. Many researchers are working to find more advanced disinfection techniques, which could significantly reduce or even not produce DBPs. The combination of Cl-DPs and photocatalysts has shown a great application prospect. For example, when combined TiO₂ with UV/chlor(am)ine processes, it can significantly increase the production of active radicals (e.g., •OH and •Cl), promote the degradation of EOMPs, and reduce the generation of DBPs. This is because the electron (e⁻) and hole (h⁺) would be formed when TiO₂ was illuminated under UV light, which promotes the production of active radicals, thus increasing the oxidation of the disinfection system. Meanwhile, the TiO₂ could shorten the contact time of chlorine with DBPs precursors and reduce the chlorine concentration in the UV/chlorine/TiO₂ process, thereby significantly reducing the formation of DBPs. In addition to TiO₂, many other metal oxides (e.g., ZnO, WO₃) and new photocatalysts (e.g., g-C₃N₄, MOFs) could also be integrated into the disinfection process.
- (3) Studying the mechanisms in depth. Although the overall mechanism and the corresponding DBPs formation during the transformation of EOMPs discussed in this paper were generally understood, the specific mechanism and detailed pathways of some EOMPs (e.g., tetracyclines, BPA) remain unclear. If fully understood, there could be effective ways to predict the formation potential of some DBPs by monitoring the occurrence of intermediates or to prevent the formation of DBPs by interfering with the generation of intermediates. Besides, in addition to the EOMPs mentioned in this paper, there are other EOMPs cannot be effectively removed by the disinfection techniques discussed in this paper. For instance, perfluoroalkyl and polyfluoroalkyl substances can serve as not only EOMPs but also DBPs generated from more complex compounds during Cl-DPs. In this case, perfluoroalkyl and polyfluoroalkyl substances seem to be the final products during Cl-DPs, which must be further degraded. Another example is about microplastics. Previous studies have found that disinfectants might degrade microplastics or break them into smaller sizes, and even nanoplastics. However, little study has focused on the fate of microplastics before and after disinfection. During the Cl-DPs, the microplastics are more prone to reactions in chlorination due to the large surface-to-volume ratios, and the chemical interactions between microplastics and chlorination can lead to the formation of new bonds and structures (e.g., chlorine-

carbon bond), which will alter the adsorption processes between microplastics and other organic pollutants, thus increasing the environmental persistence and ecotoxicity of microplastics. Meanwhile, the microplastics contain many halogen elements (e.g., Cl and Br), which could be exposed or released during the interaction between microplastics and disinfectants, thus promoting the formation of more DBPs, even the more toxic DBPs. Therefore, more studies are needed to fully understand the fate of these emerging EOMPs during the disinfection processes and to reduce their harmfulness toward human beings and the environment.

- (4) Establishing a database. To facilitate simultaneous control of various EOMPs and DBPs in an aqueous system, it is necessary to establish a “big database” on DBPs generation from EOMPs. Meanwhile, most of the unregulated emerging DBPs generated from EOMPs should be clarified in future studies regarding their potential precursor, formation mechanism, and health risk. In these cases, the impact of EOMPs can be minimized and the DBPs formation can be predicted and well controlled.
- (5) Investigating the persistence of DBPs. DBPs include volatile DBPs (e.g., THMs, HKs, HNMs, HANs) and non-volatile DBPs (e.g., HBQs, aromatic halogenated DBPs), compared with volatile DBPs, non-volatile DBPs is more persistent in water. However, there has been a long-standing contradiction in DBPs research that chemical analysis and regulations focus more on volatile DBPs while toxicity assays usually evaluate the non-volatile DBPs. This is because the in vitro DBPs toxicity assays contain the enrichment of DBPs by executing a pretreatment (e.g., solid-phase extraction or liquid-liquid extraction), while these pretreatment processes only keep non-volatile DBPs, the volatile DBPs are inevitably lost when the organic solvents (e.g., acetone, methanol) used in the pretreatment are removed. The limitations of currently used pretreatment methods mean volatile DBPs toxicities are not understood and are of concern. Moreover, the loss of volatile DBPs might lead to the underestimation of the overall toxicities. Therefore, it is worth digging into the persistence of various DBPs, which would help to point out the contribution rate of each DBPs in the toxicological research of DBPs, thus providing the targeted guidance for controlling DBPs formation.
- (6) Assessing the risk of DBPs. On the one hand, it is of great significance to conduct an entire risk analysis containing toxicokinetic studies and sets of different bioassays that are closer to human health so as to gain a comprehensive estimation of the potential toxic risk of DBPs and to avoid the false negative conclusion affected by inherent problems like methodological drawbacks and exposure assessment limitations. On the other hand, more research to assess the health risks of DBPs, like the route of exposure, the role of genotype, and the effect in vulnerable populations, is needed. For instance, there could be a longitudinal study developed to follow exposure in utero through to the development of health problems in adulthood, associating DBPs exposure with the potential disease.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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