Impact on Disinfection Byproducts Using Advanced Oxidation Processes for Drinking Water Treatment

Brooke K. Mayer and Donald R. Ryan

Abstract Since the inception of drinking water treatment systems, ensuring the production of microbiologically safe drinking water has been a primary objective. While chemical oxidants are often successfully employed to mitigate microbial risks, the chemical reactions that occur between oxidants and the dissolved or particulate constituents present in source waters, e.g., natural organic matter (NOM), can produce byproducts associated with unintended health consequences. These disinfection byproducts (DBPs) are potentially carcinogenic, mutagenic, genotoxic, and/or teratogenic. Since the discovery of DBPs in the early 1970s, considerable effort has been afforded to develop regulations or guidelines striving to simultaneously control microbial pathogens and DBPs. As advanced oxidation processes (AOPs) gain traction as an integral part of advanced treatment trains in water, wastewater, and water reuse scenarios, their impact on DBPs, in terms of both formation and destruction, is an increasingly important consideration and is the focus of this chapter.

This chapter begins with a brief overview of major drinking water disinfection processes, followed by an introduction to common classes of disinfection byproducts (DBPs) and their precursors, and concludes with discussion of the influence of AOPs on DBP formation, formation potential, and removal.

Keywords Disinfection byproducts (DBP), Haloacetic acids (HAA), Natural organic matter (NOM), Oxidation, Trihalomethanes (THM)

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1 Brief Introduction to Disinfection

The five most commonly used drinking water disinfection strategies are free chlorine, combined chlorine, chlorine dioxide, ozone, and ultraviolet (UV) light. Figure 1 shows the relative distribution of the use of these disinfectants in the United States based on surveys conducted by the American Water Works Association (AWWA).

UV inactivates microorganisms on the basis of electromagnetic radiation, which primarily disrupts nucleic acids. Each of the other four common disinfection processes involves additions of oxidizing chemicals. These oxidizers damage microbial proteins (amino acids) and genomes (nucleic acids) [3], thereby preventing microbial replication, i.e., causing inactivation. However, these oxidants are relatively nonselective, so they also react with other materials in the water (such as natural organic matter, NOM), and can produce disinfection byproducts (DBPs), which are potentially carcinogenic, mutagenic, genotoxic, and/or teratogenic. This is represented by the generalized reaction:

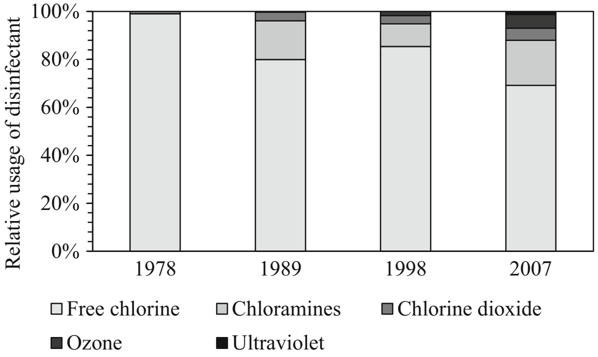


Fig. 1 Temporal summary of relative disinfectant use in municipal drinking water treatment in the United States. Adapted from [1, 2]. The cited surveys reported the use of multiple types of disinfectants for some systems (yielding totals in excess of 100% of the number of systems surveyed); here the relative distribution of type of disinfectant used is shown, resulting in a maximum of 100%

$$\text{Oxidant (e.g., HOCl)} + \text{Precursor (e.g., NOM)} \rightarrow \text{DBP (e.g., } CHCl_3\text{)}$$

The extent of DBP formation is a function of the type of disinfectant used, disinfectant dose, system parameters (e.g., contact time), and water quality (e.g., quantity and character of NOM, pH, and temperature).

1.1 Common Disinfectants

Free chlorine (primarily in the form of HOCl and OCl^- [$E^o = 1.49$ V for $HOCl/Cl^-$]) is typically added as gaseous Cl_2 or NaOCl. It is the most commonly used disinfectant for water treatment as it is broadly effective against microbial pathogens and is comparatively inexpensive. Although free chlorine remains the dominant drinking water disinfectant, concerns over chlorine-resistant microbes (e.g., *Cryptosporidium* and *Giardia*) and formation of halogenated DBPs have increased interest in alternative disinfection strategies. Free chlorine is associated with the production of classically regulated DBPs such as trihalomethanes (THMs) and haloacetic acids (HAAs), as well as emerging DBPs, including chloral hydrate, chlorophenols, formaldehyde, haloketones, halogenated furanones, and haloacetonitriles. In general, the production of organochlorine compounds during chlorination is caused by reactions between chlorine and humic substances [4]. There are three general pathways through which free chlorine reacts with water constituents: oxidation, addition, and substitution [5]. When organic compounds have double bonds, the chlorine can undergo an addition reaction, but this reaction is often too slow to be of importance in water treatment. Thus, most chlorinated DBPs are formed via oxidation and substitution reactions, with reactions occurring much more rapidly at high pH than at low pH [4].

Combined chlorine is the sum of the species formed through the reaction of chlorine and ammonia: monochloramine (NH_2Cl), dichloramine ($NHCl_2$), and trichloramine (NCl_3). Combined chlorine, or chloramines, is not as effective as free chlorine for inactivation of pathogens and is thus not commonly used as a primary disinfectant. However, its longer residual makes it a common choice for secondary disinfection to avoid biological regrowth in the distribution system. Chloramines reduce the amount of THMs and HAAs formed in comparison to free chlorine; however, they introduce concerns for nitrosamine and cyanogen chloride DBP formation. Reactions of chloramines with humic materials and amino acids produce haloacetonitriles and non-halogenated acetonitriles, following a pathway similar to that for chlorine [4].

Chlorine dioxide (ClO_2) is a powerful disinfecting agent ($E^o = 0.95$ V for ClO_2/ClO_2^-) but is volatile, typically requiring onsite generation. It is widely used as a disinfectant in continental Europe but is not as commonly used in the United States. At the dosages typically used in drinking water treatment, ClO_2 (which is more selective than free chlorine) does not react with NOM, so it avoids formation of THMs and HAAs, and produces almost no identifiable organic byproducts (although low levels of some aldehydes and ketones can result) [6]. Chlorine dioxide reacts only by oxidation, which explains the lack of organochlorine compound formation [4]. Although stable in pure water, ClO_2 decomposes in drinking water as it is photoreactive and can also undergo disproportionation to produce the inorganic DBPs chlorite (ClO_2^-) and chlorate (ClO_3^-), the kinetics and degree of which depend on ambient water quality parameters [7].

Of the common chemical disinfectants, ozone (O_3, $E^o = 2.07$ V for O_3/O_2) is the strongest oxidizing agent and must be generated on-site as it is unstable. Ozone provides effective oxidation of many chemical contaminants as well as inactivation of microbial pathogens. Ozonation itself does not produce halogenated DBPs and has thus become increasingly common. However, when bromide is present in waters, ozone can produce brominated DBPs such as bromate (BrO_3^-). In general, bromate forms through a combination of molecular ozone attack and reactions of bromide with free radicals, which are formed as ozone decomposes during water treatment [4]. The radical pathway may play a more important role than the molecular ozone pathway [4]. Ozone can also react with bromide to form brominated organics such as bromoform, dibromoacetonitrile, and dibromoacetone [4, 8]. As ozone progressively degrades complex organics, non-halogenated DBPs such as formaldehyde (CH_2O) may also result.

In the case of UV disinfection, microorganisms are inactivated via disruption of their genetic material (DNA or RNA) rather than via chemical oxidation. For the fluences (i.e., UV dose, which is a function of intensity and exposure time) typically used in drinking water treatment (<200 mJ/cm^2), there is no evidence of DBP formation, nor are DBP levels exacerbated using post-UV disinfection [9].

1.2 Advanced Oxidation Process-Based Disinfection

Recalcitrant contaminants, such as endocrine-disrupting compounds (EDCs), pharmaceuticals and personal care products (PPCPs), pesticides, etc., are typically the primary targets for AOPs, and there are numerous reports of this application. However, the hydroxyl radicals (HO•, $E^{\text{o}} = 2.70$ V) or sulfate radicals ($SO_4{\bullet}^-$, $E^{\text{o}} = 2.5\text{–}3.1$ V) generated from AOPs or sulfate-radical-based AOPs (SR-AOPs), respectively, may also provide some degree of disinfection [10]. The use of AOPs for disinfection is far less frequently reported in comparison to chemical degradation (e.g., for UV/TiO_2 [11–14]) but may be realized as a secondary outcome of the use of AOP treatments in drinking water. Disinfection using solar irradiation-based AOPs may be of particular interest for use in developing countries [15]. Hydroxyl radicals may oxidize and disrupt cell walls and membranes, thereby lysing the cell, or they may diffuse into the cells and react with intracellular components. AOP-based disinfection may be limited by mass transfer through the cell walls or membranes as HO• reacts with most biological molecules at diffusion-controlled rates. Although there may be some oxidative enhancement in virus inactivation due to HO•, UV appears to be primarily responsible for microbial inactivation using UV-based AOPs [10].

Since the oxidation pathway in AOPs relies on radicals rather than halogens, halogenated DBP production during AOP treatments is generally less of a concern in comparison to traditional oxidative disinfectants. However, ozone-associated DBPs may be generated during ozone-based AOPs, and non-halogenated organic DBPs can occur as complex organic matter is degraded. DBP formation during AOP treatments is discussed in greater detail in Sect. 4.1.

2 Disinfection Byproducts

Reactions between oxidizing disinfectants and the organic or inorganic precursor material found in water can lead to the generation of potentially harmful DBPs, as depicted in the generalized illustration in Fig. 2.

The range of DBPs produced via reactions between oxidants and organic precursors (NOM or anthropogenic organic pollutants) or inorganic precursors (i.e., bromide or iodide) include halogenated organics, organic oxidation byproducts, and inorganics. Table 1 lists several important classes of DBPs, their main causative agents, and examples of established drinking water regulations.

The formation of DBPs during drinking water disinfection has been recognized since the 1970s [23, 24], but advances in analytical techniques and risk assessment continue to facilitate discovery and better characterization of the more than 600 currently identified DBPs. Of note, the number of DBPs identified and quantified in water to date is only a small fraction of those potentially formed. As illustrated for

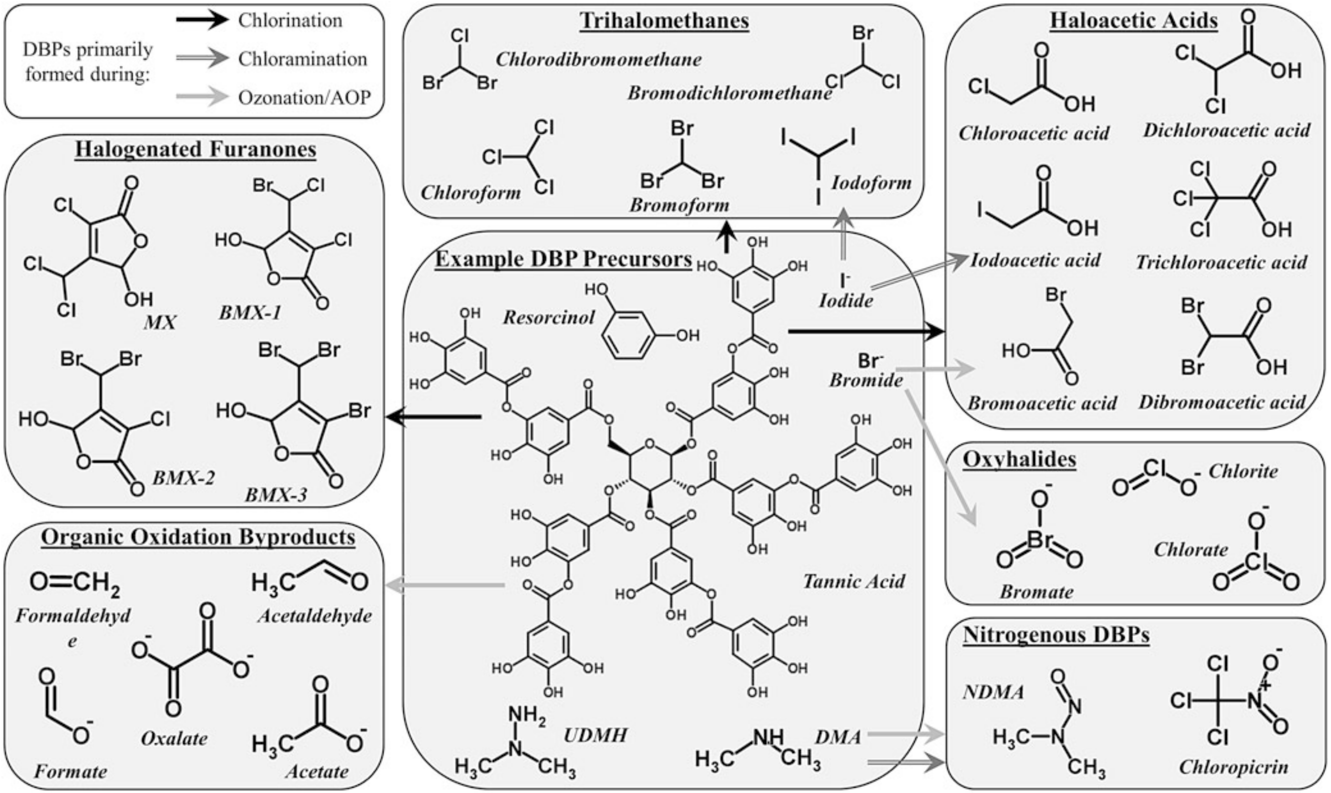


Fig. 2 Examples of disinfection byproducts (DBPs) produced from reactions between oxidizing disinfectants and precursor material, in accordance with the general reaction: Oxidant + Precursor → DBP. All chemical structures are from the ChemSpider website (http://www.chemspider.com/)

Table 1 Examples of classical and emerging drinking water disinfection byproducts (DBPs) produced by conventional oxidative disinfection processes and advanced oxidation processes (AOPs) (all concentrations in μg/L)

		Primarily a byproduct of						Selected drinking water regulations				
Species	Chemical formula	Free chlorine	Chloramines	ClO_2	O_3	O_3-based AOP	Non-O_3-based AOP	Australia[a]	European Union (EU)[b]	Health Canada (HC)[c]	US Environmental Protection Agency (USEPA)[d]	World Health Organization (WHO)[e]
Trihalomethanes (THM)	TTHM[f]							250	100	100	80	[g]
Chloroform	$CHCl_3$	X	X									300
Bromodichloromethane	$CHBrCl_2$	X	X									60
Dibromochloromethane	$CHBr_2Cl$	X	X									100
Bromoform	$CHBr_3$	X	X		X	X						100
Dichloroiodomethane	$CHICl_2$	X	X									
Chlorodiiodomethane	CHI_2Cl	X	X									
Bromochloroiodomethane	$CHBrICl$	X	X									
Dibromoiodomethane	$CHBr_2I$		X									
Bromodiiodomethane	$CHBrI_2$		X									
Triiodomethane	CHI_3		X									
Haloacetic acids (HAA)	HAA5[h]									80	60	
Monochloroacetic acid	$C_2H_3ClO_2$	X	X					150				20
Dichloroacetic acid	$C_2H_2Cl_2O_2$	X	X					100				50
Trichloroacetic acid	$C_2HCl_3O_2$	X	X					100				200
Monobromoacetic acid	$C_2H_3BrO_2$	X	X									--
Dibromoacetic acid	$C_2H_2Br_2O_2$	X	X									
Bromochloroacetic acid	$C_2H_2BrClO_2$	X	X									
Dibromochloroacetic acid	$C_2HBr_2ClO_2$	X	X									
Bromodichloroacetic acid	$C_2HCl_3O_2$	X	X									
Tribromoacetic acid	$C_2HBr_3O_2$	X	X									
Oxyhalides												
Bromate	BrO_3^-				X	X		20	10	10	10	10
Chlorite	ClO_2^-			X				800		1,000	1,000	700
Chlorate	ClO_3^-			X						1,000		700
Haloketones (HK)												
1,1-Dichloro-2-propanone	$C_3H_4Cl_2O$	X	X									

(continued)

Table 1 (continued)

		Primarily a byproduct of						Selected drinking water regulations				
Species	Chemical formula	Free chlorine	Chloramines	ClO_2	O_3	O_3-based AOP	Non-O_3-based AOP	Australia[a]	European Union (EU)[b]	Health Canada (HC)[c]	US Environmental Protection Agency (USEPA)[d]	World Health Organization (WHO)[e]
1,1,1-Trichloro-2-propanone	$C_3H_3Cl_3O$	X	X									
Chlorophenols												
2-Chlorophenol	C_6H_5ClO	X	X					300				
2,4-Dichlorophenol	$C_6H_4Cl_2O$	X	X					200				
2,4,6-Trichlorophenol	$C_6H_3Cl_3O$	X	X					20		5		200
Chloral hydrate (trichloroacetaldehyde)	$C_2H_3Cl_3O_2$	X	X					100				
Haloacetonitriles (HANs)		X	X									
Dichloroacetonitrile	C_2HCl_2N	X	X									20
Dibromoacetonitrile	C_2HBr_2N	X	X									70
Trichloroacetonitrile	C_2Cl_3N	X	X									
Bromochloroacetonitrile	$C_2HBrClN$	X	X									
Nitrosamines												
N-Nitrosodimethylamine (NDMA)	$C_2H_6N_2O$		X		X	X		0.1		0.04		0.1
Trihalonitromethanes												
Trichloronitromethane (chloropicrin)	CCl_3NO_2	X	X									
Bromodichloronitromethane	$CBrCl_2NO_2$	X	X									
Dibromochloronitromethane	$C_2Br_2ClNO_2$	X	X									
Tribromonitromethane	CBr_3NO_2	X	X									
Cyanogen halides (CNX)												
Cyanogen chloride (as cyanogen)	CNCl		X					80				70
Cyanogen bromide	CNBr	X	X									
Aldehydes												
Formaldehyde	CH_2O	X	X		X	X	X	500				
Acetaldehyde	C_2H_4O	X	X		X	X	X					
Glyoxal	$C_2H_2O_2$	X	X		X	X	X					

Methylglyoxal	$C_3H_4O_2$	X	X		X	X	X					
Carboxylates												
Formate	CHO_2^-				X	X	X					
Acetate	$C_2H_3O_2^-$				X	X	X					
Oxalate	$C_2O_4^{2-}$				X	X	X					
Keto acids												
Glyoxylic acid	$C_2H_2O_3$				X	X	X					
Pyruvic acid	$C_3H_4O_3$				X	X	X					
Ketomalonic acid	$C_3H_2O_5$				X	X	X					

Updated and adapted from [16, 17]

[a] [18]

[b] [19]

[c] [20]

[d] [21]

[e] [22]

[f] TTHM = sum of four THMs: chloroform, bromodichloromethane, dibromochloromethane, and bromoform

[g] The sum of the ratio of the concentration of each to its respective guideline value should not exceed 1

[h] HAA5 = sum of five HAAs: monochloroacetic acid, dichloroacetic acid, trichloroacetic acid, monobromoacetic acid, and dibromoacetic acid

chlorinated drinking water in Fig. 3, more than half of the total organic halide (TOX) formed during chlorination has yet to be chemically identified [25, 26].

2.1 Disinfection Byproduct Regulations

Since their discovery in the 1970s, DBPs have been widely regulated as drinking water contaminants, as demonstrated by the list of select DBPs and applicable regulations/guidelines shown in Table 1. For historical context, a brief description of the regulatory basis for DBPs in the United States is provided here. Next, the most commonly regulated, or classical, DBPs are introduced, including trihalomethanes, haloacetic acids, chlorate, chlorite, and bromate. This section concludes with brief descriptions of several classes of emerging DBPs.

In the United States, DBPs were first regulated in 1979, beginning with the TTHM (total trihalomethanes) Rule, which set a maximum contaminant level (MCL) of 100 μg/L TTHM based on a running annual average of distribution system samples. In 1986, amendments to the Safe Drinking Water Act (SDWA) noted that disinfectants and DBPs should be regulated [28]. Thus, to simultaneously control microbial pathogens, residual disinfectants, and DBPs, three related rules were developed: the Information Collection Rule (ICR), the Disinfectants/DBP Rule (D/DBPR, implemented in two stages), and the Enhanced Surface Water Treatment Rule (ESWTR, implemented in stages, e.g., Long-Term 2 Enhanced Surface Water Treatment Rule or LT2). In Stage 1 of the D/DBPR, the USEPA reduced the existing TTHM standard to 80 μg/L and expanded regulations to include haloacetic acids (HAA5s = 60 μg/L), bromate (BrO_3^- = 10 μg/L), and chlorite (ClO_2^- = 1,000 μg/L). In Stage 2 of the D/DBPR, the DBP MCLs were maintained, but compliance was amended to a locational running annual average basis (rather than the previous approach of averaging concentrations across distribution system sampling points).

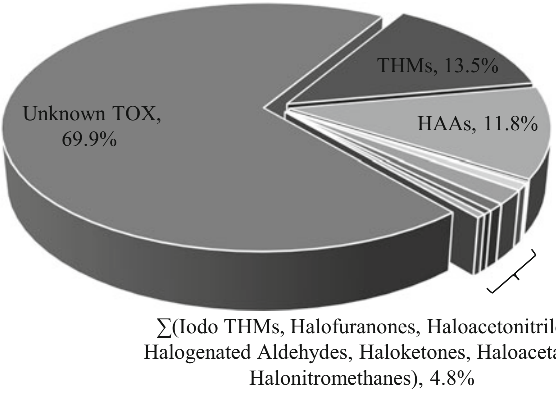


Fig. 3 Distribution of characterized total organic halides (TOX) in chlorinated drinking water, including unknown TOX, trihalomethanes (THMs), haloacetic acids (HAAs), and several classes of emerging halogenated disinfection byproducts (DBPs) which account for <5% of the total DBPs. Adapted from [27]

In addition to these established federal regulations, the USEPA also periodically reviews the status of unregulated DBPs (and other drinking water contaminants) as part of the Contaminant Candidate List (CCL) and Unregulated Contaminant Monitoring Rule (UCMR). The CCL is a list of currently unregulated contaminants that are known or believed to occur in public water systems and are thus identified as research priorities in order to better inform determinations of risks and regulations. The USEPA's 4th version of the CCL (CCL4, announced in 2016) includes several additional DBPs: acetaldehyde (an O_3-DBP), chlorate (formed during ClO_2 and hypochlorite disinfection), formaldehyde (O_3 based), bromochloromethane, *N*-nitrosodiethylamine (NDEA), *N*-nitrosodimethylamine (NDMA), *N*-nitrosodi-*n*-propylamine (NDPA), *N*-nitrosodiphenylamine (NDPhA), and *N*-nitrosopyrrolidine (NPYR) [29]. The state of California's Department of Public Health has already set a notification level of 10 ng/L for NDEA, NDMA, and NDPA and a public health goal for NDMA of 3 ng/L [30]. Monitoring results from public water systems collected as part of the USEPA's UCMR program suggest that more than 10% of the US' chloraminated systems could be affected if a NDMA MCL was introduced at the California action level of 10 ng/L [31].

2.2 Conventional Disinfection Byproducts: Trihalomethanes, Haloacetic Acids, and Oxyhalides

The trihalomethanes (THMs) were the first DBPs to be discovered and are one of the most prevalent classes of DBPs resulting from chlorine disinfection [25]. Together with haloacetic acids, THMs account for approximately 25% of the halogenated DBPs from chlorination [32]. Chloramination can also generate THMs, albeit typically to a much lesser extent, as can ozone through production of bromoform. Many DBP regulations are based on total trihalomethanes (TTHMs), which are calculated as the sum of four THMs: chloroform, bromoform, bromodichloromethane, and chlorodibromomethane, of which chloroform is often found at the highest concentrations [25]. All of the TTHM species demonstrate carcinogenicity in rodents [25].

Surface water typically contains higher concentrations of precursor NOM and, as such, is associated with higher DBP production, as shown in Fig. 4. Other commonly used indicators of THM formation include chlorine dose, pH, temperature, bromide concentration, and disinfection contact time. In general, as these parameters increase, so does DBP formation (although DBP responses to increasing pH are mixed). A number of empirical and semi-mechanistic DBP formation models have been used to predict DBP concentrations based on these and other parameters, often using a multiple linear or nonlinear regression approach. When applied to the treatment scenarios for which they were specifically developed, these models can be helpful indicators of operation, risk assessment, etc. [33], although they tend to overpredict DBPs for conditions least conducive to formation while

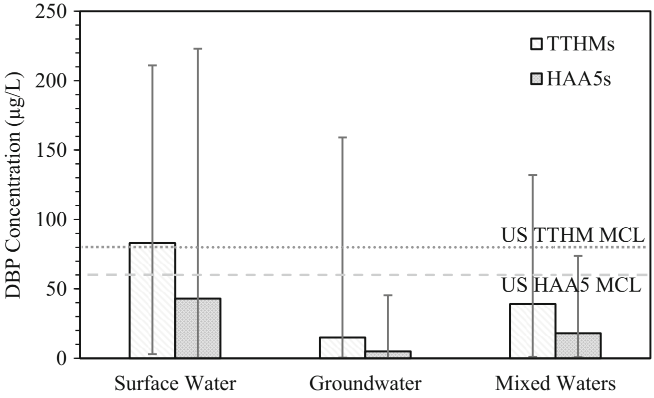


Fig. 4 Formation of TTHMs and HAA5s in finished water surveyed in 1992 at more than 100 US drinking water treatment plants with varying source waters. The bars represent average values, while the error bars illustrate the range in values reported, and the lines denote regulatory maximum contaminant levels (MCLs) in the US. Data from [36]

underpredicting for the conditions most conducive for DBPs [8, 16, 34, 35]. However, Mayer et al. [16] reported that TTHM and HAA5 models generally performed poorly when applied to DBP data not used to directly develop the model, regardless of the use and extent of AOP treatment and type of source water. This suggests that bulk indicators and/or models should be used cautiously as metrics for AOP mitigation of DBP formation potential.

The main haloacetic acids (HAAs) include nine different halogenated compounds, as shown in Table 1. When regulated, the HAAs are sometimes dealt with on the basis of individual compounds but are sometimes grouped together, for example, as HAA5, or the sum of five of the HAAs: bromoacetic acid, dibromoacetic acid, chloroacetic acid, dichloroacetic acid, and trichloroacetic acid, all five of which are mutagenic [25]. The remaining four main HAAs were more difficult to quantify when the US regulation was promulgated and so were excluded from regulation. Like THMs, chlorination generally produces the highest levels of HAAs, although lower levels can result from chloramination, ClO_2, and O_3 [37].

The oxyhalides chlorite (ClO_2^-) and chlorate (ClO_3^-) are the inorganic DBPs produced through reactions of NOM with ClO_2. Chlorine dioxide rapidly reacts with NOM and inorganic matter, degrading to chlorite, chlorate, and chloride [25].

When bromide is present in source water, brominated DBPs including inorganic bromate (BrO_3^-) and organic brominated DBPs may pose a concern. Bromate is of particular concern for ozonation processes when bromide is present in source waters at high levels (>50–100 μg/L) [25, 38]. Bromate is both genotoxic and carcinogenic, and of the DBPs regulated in the United States, it is the most potent carcinogen in laboratory animals [25]. It is formed by a series of oxidations mediated by O_3 or a combination of O_3 and HO• reacting with natural bromide, where O_3 sequentially oxidizes bromide to hypobromite (BrO^-), followed by bromite (BrO_2^-), and finally to bromate [39]. The HO• produced as part of the ozonation process also participates in the intermediate reactions [39].

2.3 Emerging Disinfection Byproducts, Including Brominated, Iodinated, and Nitrogenous Species

To date, the greatest emphasis in DBP research and mitigation has been on a subset of more conventionally regulated DBPs including THMs, HAAs, and BrO_3^-. However, there are a large number of "emerging" DBPs, including those not currently widely regulated. As the majority of TOX often consists of unidentified compounds (see Fig. 3), developing a better understanding of emerging DBPs is an important area of research. In this section, several major classes of emerging DBPs are introduced.

2.3.1 Organic Brominated and Iodinated Disinfection Byproducts

Bromide and iodide are naturally occurring inorganic DBP precursors for a variety of DBPs. These ions may be present, and of concern, in source waters impacted by seawater intrusion and natural salt deposits, e.g., coastal cities or areas affected by oil and gas brines. When bromide is present, organic brominated DBPs (B-DBPs) are primarily produced by chlorination in the same manner as the classical DBPs. In contrast, iodinated DBPs (I-DBPs) are primarily produced by chloramination of iodide-containing waters. Both B-DBPs and I-DBPs are more toxic and carcinogenic than their chlorine analogs, in order of greatest health risk: chlorinated $<$ brominated $<$ iodinated [40].

Although iodo-THMs and iodo-HAAs are among the most toxic unregulated DBPs, iodate (IO_3^-) is generally not problematic and is readily reduced to iodide (I^-) after consumption [41]. In processes that use strong oxidizing disinfectants, e.g., ozone or chlorine, I^- is readily oxidized to IO_3^- (as shown below), which results in very low amounts of organic I-DBPs remaining in solution.

$$I^- \rightarrow IO^-/HIO \rightarrow IO_2^- \rightarrow IO_3^-$$

For example, 90% of naturally occurring I^- was converted to IO_3^- during ozonation [42]. This stems from the higher activity of hypoiodous acid (HIO) with strong oxidizing disinfectants in comparison to reactivity with NOM. Thus, the oxidation reactions can be optimized as a sink to form IO_3^- rather than organic I-DBPs when I^- reacts with NOM [43].

The smaller oxidative potential of chloramines yields ineffective oxidation of HIO to IO_3^-, which can increase formation of I-DBPs during chloramination [42]. Iodide can be oxidized prior to ammonia additions during chloramination using prechlorination or preozonation; however, this approach could increase the formation of B-DBPs and chlorinated DBPs [40, 42].

2.3.2 Halogenated Furanones

Halogenated furanones, including MX (3-chloro-4-(dichloromethyl)-5-hydroxy-2 (5H)-furanone) and its brominated analogues (BMX), are highly mutagenic DBPs. Weinberg et al. [26] found that MX and BMX analogues are generally found at concentrations of 60 ng/L or less, but they have also been found at concentrations as high as 80 ng/L [44]. These species can account for more than 50% of the mutagenicity in bioassays of chlorinated drinking waters [45, 46]. The formation pathway for MX may be similar to that for THMs and HAAs as occurrence of MX analogues is positively correlated with occurrence of chloroform, and MX analogues have been found in effluent from chlorine and chlorine dioxide disinfection processes which also contained THMs and HAAs [47]. Chloramine disinfection processes yield comparatively smaller concentrations of MX and BMX analogues [47].

2.3.3 Nitrogenous Disinfection Byproducts

Nitrogenous DBPs (N-DBPs) are a subset of the classical carbonaceous DBPs (C-DBPs) [27]. They may result when sufficient levels of nitrogen are present for DBP incorporation, e.g., using source waters impaired by algal blooms, during chloramination, in the presence of certain polymers, or at water reuse facilities.

Nitrosamines are one of the most widely studied N-DBPs. They are a family of emerging DBPs often found at ng/L concentrations but associated with serious health risks as they have been reported to be carcinogenic, mutagenic, and/or teratogenic [48, 49]. *N*-Nitrosodimethylamine (NDMA) is the most common nitrosamine and is a probable human carcinogen, with 0.7 ng/L NDMA correlating to a lifetime cancer risk of 10^{-6} [50].

The NDMA formation potential varies as a function of source water and treatment process. It is primarily produced during chloramination of water [51], which directly adds nitrogen during disinfection. Low molar yields of NDMA may be generated by reacting precursors with either chloramines or ozone, but most precursors are more reactive with just one of the disinfectants (i.e., chlorine- or ozone-reactive NDMA precursors) [52]. Some studies have shown that preozonation increases NDMA formation potential in water [53], but others have found decreased NDMA formation potential [54].

In general, NDMA precursors comprise secondary, tertiary, or quaternary amines, with sources including PPCPs, pesticides, water or wastewater treatment chemicals, and industrial chemicals [52]. As wastewater effluent may contain more of these N-rich compounds in comparison to many drinking water sources, NDMA is of particular concern in wastewater effluent and water reuse scenarios. Naturally occurring bromide can also contribute to NDMA formation by catalyzing reactions with precursors [55]. Padhye et al. [56] found that NDMA formation tripled in the presence of 100 μM bromide.

In addition to NOM, polymers may serve as NDMA precursors. As shown in Fig. 5, cationic amine-based polymers, such as polyamine and poly-DADMAC, used to enhance coagulation and dewatering can contain dimethylamine (DMA) and other small amine moieties which serve as significant NDMA precursors [48, 51, 57]. When dosed at optimal levels, minimal polymer residual remains in solution following physicochemical treatment. Accordingly, it is unlikely that sufficient concentrations of polymer will be present to react with chloramines to form NDMA. Rather, the primary concern lies in degradation of the polymers and release of NDMA precursors. Polyamine is generally more susceptible to degradation and DMA release than poly-DADMAC and therefore is more closely linked to DBP formation [57]. Alternative polymers produced from natural products may perform as well as poly-DADMAC while limiting nitrosamine formation potential [58].

2.4 Non-halogenated Organic Disinfection Byproducts

When condensed aromatic compounds are oxidized, low molecular weight, non-halogenated organic DBPs may result. These products may include aldehydes, carboxylic acids, and keto acids, all of which can enhance biodegradability and can even be toxic. The most commonly observed organic byproducts are aldehydes such as formaldehyde and acetaldehyde [59]. Other common organic byproducts include formate, acetate, and oxalate [17].

3 Disinfection Byproduct Precursors

DBP precursors include both organic matter (e.g., NOM) and inorganic compounds (e.g., bromide and iodide). Increases in the ratio of bromide ion relative to chlorine or organic matter can shift speciation of THMs and HAAs toward more bromine-

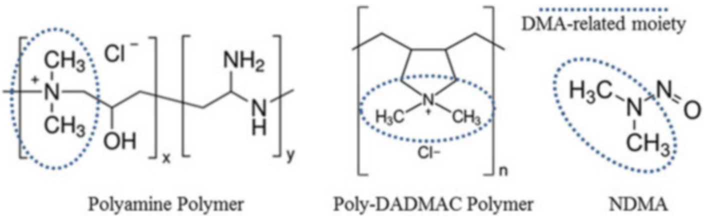


Fig. 5 *N*-Nitrosodimethylamine (NDMA) and common polymers acting as NDMA disinfection byproduct (DBP) precursors, with the dimethylamine (DMA)-related moiety (primary component serving as NDMA precursor) highlighted in each molecule

substituted species, which are associated with more significant health risks compared to chlorinated DBPs [60].

Natural organic matter is ubiquitous in drinking water sources and serves as the primary organic DBP precursor. Its enigmatic character derives from a complex mixture of numerous compounds ranging from aromatic phenolic compounds and aliphatic carboxylic acids to nitrogenous compounds such as proteins, sugars, amino acids, and large biopolymers, e.g., lignin [61]. Understanding the quantity and character of NOM is essential for water treatment design to effectively mitigate NOM-related problems such as DBP formation; greater coagulant dose requirements; increased bioavailability of organics in the water; and aesthetic concerns such as color, taste, and odor [62]. Multiple approaches can be used to provide indications of the quantity and quality of complex mixtures of NOM, including bulk organic measurements and fractionation on the basis of fluorescence excitation/emissions, size, or operational behavior (e.g., hydrophilic, acid, etc.).

3.1 Bulk Organic Measurements

Total organic carbon (TOC), dissolved organic carbon (DOC), ultraviolet absorbance at a wavelength of 254 nm (UV_{254}), and specific ultraviolet absorbance (SUVA) are bulk parameters often used as indicators of NOM quantity and general character. These parameters are also commonly used as surrogates for estimating DBP formation potential, although they do have limitations. They do not always correlate to DBP concentrations in finished drinking water since other factors such as disinfectant type and dose, as well as water pH, temperature, bromide concentrations, etc. all strongly influence DBP formation [16, 36]. However, bulk organic parameters are still commonly used as they offer an easy, rapid, and inexpensive approach to gauging NOM.

Natural waters used as drinking water sources typically contain low levels of synthetic organic contaminants, so TOC is often considered synonymous with NOM [61]. The DOC fraction is classified as the organic carbon that passes through a 0.45 μm filter, whereas the fraction that is retained is the particulate organic matter (POM, often accounting for $<10\%$ of TOC) [63, 64].

Spectrophotometric analysis in the wavelength range of 220–280 nm is also commonly used as an indicator of the presence of organics. Molar absorptivities vary widely due to the diversity of chromophores present in NOM; for example, carboxylic acids and aromatic compounds are associated with a wavelength of 220 nm [65], with maximum absorption at 254 nm for most aromatic groups. Accordingly, absorbance at 254 nm (UV_{254}) is primarily used to indicate the presence of the dense, aromatic, hydrophobic portion of NOM [66] and is also used as a rough indicator of overall NOM content [61].

SUVA is another helpful correlation parameter for DBP formation potential [67] as it is indicative of the relative aromaticity of the NOM. The SUVA value normalizes UV_{254} relative to the DOC concentration.

$$\mathrm{SUVA} = \frac{\mathrm{UV}_{254}}{\mathrm{DOC}}, (\mathrm{L/mg\ m})$$

High SUVA values (>4) indicate largely aromatic, hydrophobic, high molecular weight compounds, whereas low SUVA values (<4) represent small molecular weight, hydrophilic compounds [68].

These bulk organic parameters are useful in describing the quantity of NOM and providing an indication of its character, which can provide an indication of water quality through treatment stages as well as DBP formation potential (as bulk organic matter parameters increase, DBP formation potential generally increases). However, bulk parameters do not always correlate to DBPs, nor do they provide information regarding specific NOM constituents such as amino acids, sugars, and carbohydrates.

3.2 Natural Organic Matter Fractionation

To better characterize the array of diverse compounds present in NOM, fractionation techniques based on parameters such as absorbance, size, hydrophobicity, etc. may be employed.

3.2.1 Fluorescence Absorption and Emission-Based Fractionation

Analysis using a 3-D fluorescence excitation emission matrix (EEM) can be useful for understanding NOM fractions [69]. In water, fluorophores are generally divided into humic-like fluorophores and protein-like fluorophores [70, 71]. The NOM can be fractionated prior to analysis in order to express characteristic peaks, locations of which are illustrated in the EEM matrix in Fig. 6 [72–75]. Each fraction is characterized by its own potential for DBP production. The humic-like peak correlates strongly with TTHM formation potential, and the tryptophan-like peak correlates well with NDMA formation potential [76]. EEM analysis may provide better correlation to NDMA formation potential compared to UV_{254} and SUVA indicators [76–78].

3.2.2 Size-Based Fractionation

Size exclusion chromatography (SEC) and high-performance liquid chromatography-SEC (HPLC-SEC) can be used to characterize NOM samples on the basis of molecular size. Although molecular size can provide an indication of DBP formation potential, there is a great deal of variation in observed correlations between size of precursor NOM and resulting DBP formation. While some studies have found the hydrophobic NOM fraction with an apparent molecular weight (AMW) of 1–10 kDa

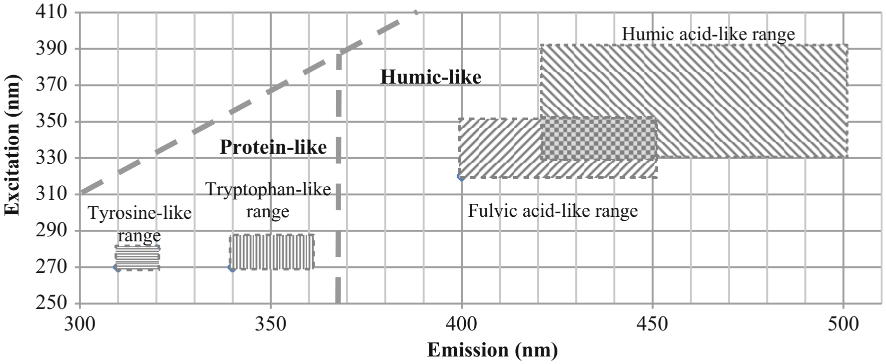


Fig. 6 Excitation emission matrix (EEM) wavelengths associated with natural organic matter (NOM) fractions. Adapted from [79, 80]

to be the primary DBP precursor [81], hydrophilic and lower molecular weight fractions may also generate significant DBPs [16, 82–84]. For example, the bulk portion of NDMA precursors consists of small molecular weight compounds (<3,000 Da) [85, 86]. Similarly, Zhao et al. [87] found that low molecular weight dissolved organic matter serves as a significant THM precursor.

Figure 7 shows several example datasets from disinfected surface waters illustrating the relative contribution of different NOM size fractions to C-DBP, N-DBP, and I-DBP formation potential. As exemplified here, there is no clear trend between NOM molecular weight fractions and DBP formation; therefore, size fractionation by itself is a less important predictor for DBP formation compared to chemical composition of the NOM and water quality parameters [88, 89].

Thus, while using UV detectors for HPLC-SEC provides helpful information for evaluating the potential for removal of high molecular weight organic matter via coagulation or other processes, their use for understanding DBP formation potential may still be limited. Alternatively, coupling UV detectors in tandem with DOC analyzers or fluorospectrometers can be used to provide more informative datasets by detecting aromatic and nonaromatic datasets as a function of molecular weight, both of which parameters are important for predicting DBP formation potential [90, 91]. Compound classes and their respective apparent molecular weights are shown in Table 2.

3.2.3 Resin Fractionation

To better understand complex organic matter, resin fractionation methods can be used to classify NOM in accordance with behavior during different water treatment processes. The predominant properties of organic matter can be characterized as hydrophobic, hydrophilic, acidic, basic, and neutral (although distinctions are not always clear, e.g., a great deal of dissolved organic matter is recognized as both

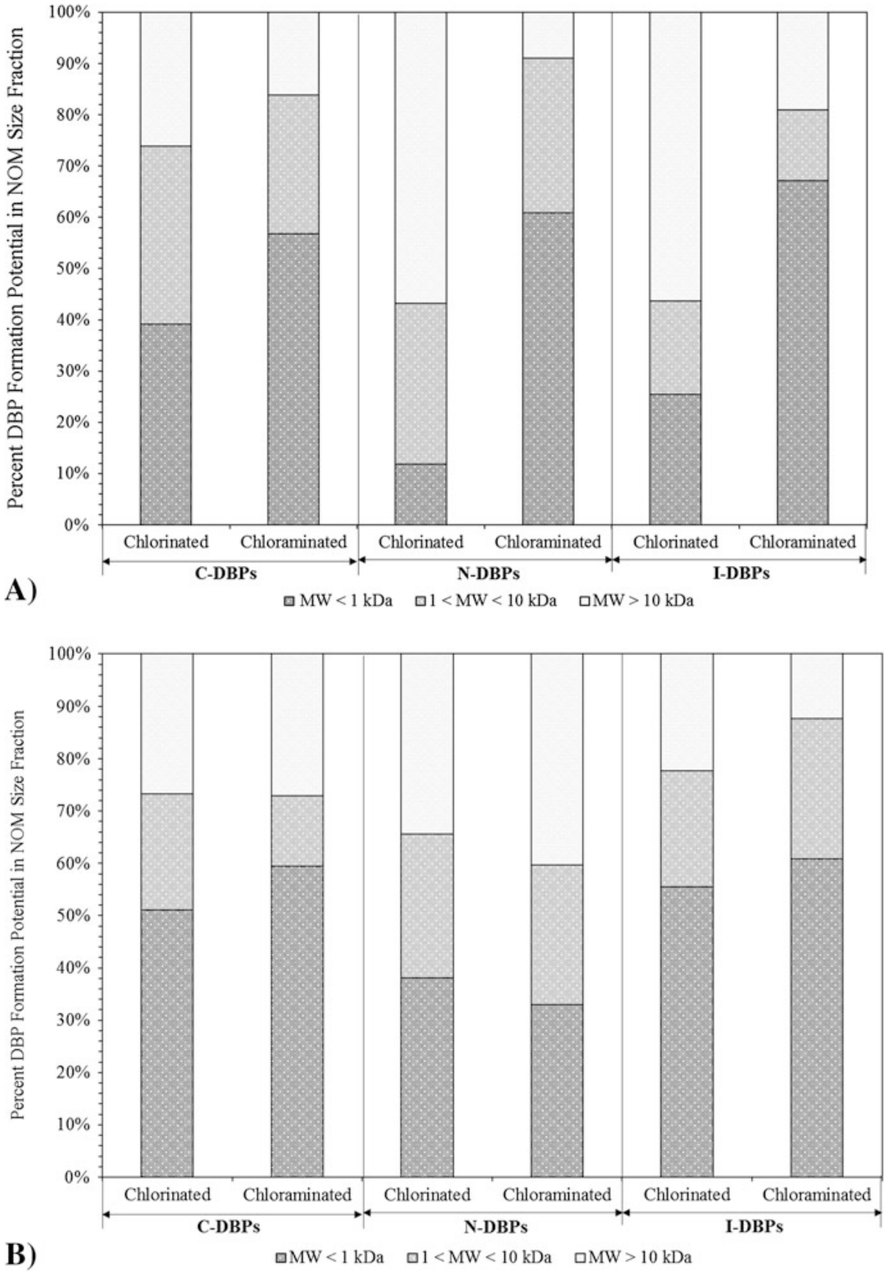


Fig. 7 Disinfection byproduct formation relative to natural organic matter (NOM) molecular weight (MW) size fraction for C-DBPs, N-DBPs, and I-DBPs in chlorinated and chloraminated water from the (**a**) Huangpu River, China, and (**b**) the Yangtze River, China. Data from [89]

Table 2 Size characterization using a combination of high-performance liquid chromatography-size exclusion chromatography (HPLC-SEC) with (ultraviolet) UV and online dissolved organic carbon (DOC) detectors to characterize natural organic matter (NOM) by apparent molecular weight (AMW)

Compound class	Apparent molecular weight (AMW)
Polysaccharide- and protein-like substances	High (>10,000 g/mol)
Highly aromatic and fulvic substances	Medium (1,000–5,000 g/mol)
Aliphatic-like substances	Low (<680 g/mol)

Adapted from [92]

amphiphilic and amphoteric) [61]. Each of these fractions, or subsets thereof, can be isolated using sequential resin-based separation.

The hydrophobic portion of NOM is composed of densely aromatic structures, conjugated double bonds, and high molecular weight compounds. The hydrophobic fraction is also characterized by a high specific surface charge, making it more amenable to removal via coagulation [93]. The hydrophobic fraction can account for more than half of the DOC in water [64, 93, 94], although there is great variation in fractionation among different source waters. This can be problematic for drinking water treatment since the hydrophobic portions of NOM serve as significant precursors for DBPs and produce greater amounts of unidentified total organic halogen products (TOX) [95–97].

The hydrophilic fraction of NOM contains low molecular weight polar compounds such as carboxylic acids, as well as nitrogenous compounds including sugars, peptides, and amino acids [61]. The hydrophilic NOM fraction is also a significant precursor for DBPs and generally forms more NDMA than the hydrophobic fractions [98]. The hydrophilic fraction has been observed to be more reactive with bromine and iodine than the hydrophobic NOM fraction [95], as illustrated in Fig. 8a, b, which shows DBP formation potential from different NOM fractions in several waters.

As shown in Fig. 8, although the presence of different fractions can provide an indication of DBP formation potential, actual DBP production can vary widely with source water and operational parameters in the disinfection process.

3.3 Structure and Reactivity of Natural Organic Matter (NOM) Fractions

The physicochemical properties (K_{ow}, pK_a, and molecular weight) of individual NOM species do not correlate well to DBP formation potential [101]. However, halogen substitution efficiency is an effective indicator of DBP formation potential. As shown in Fig. 9, compounds exhibiting high halogen substitution efficiency, and which produce substantial THMs and HAAs, include ferulic acid, L-tryptophan, and resorcinol [101]. These compounds are considered activated aromatics because the

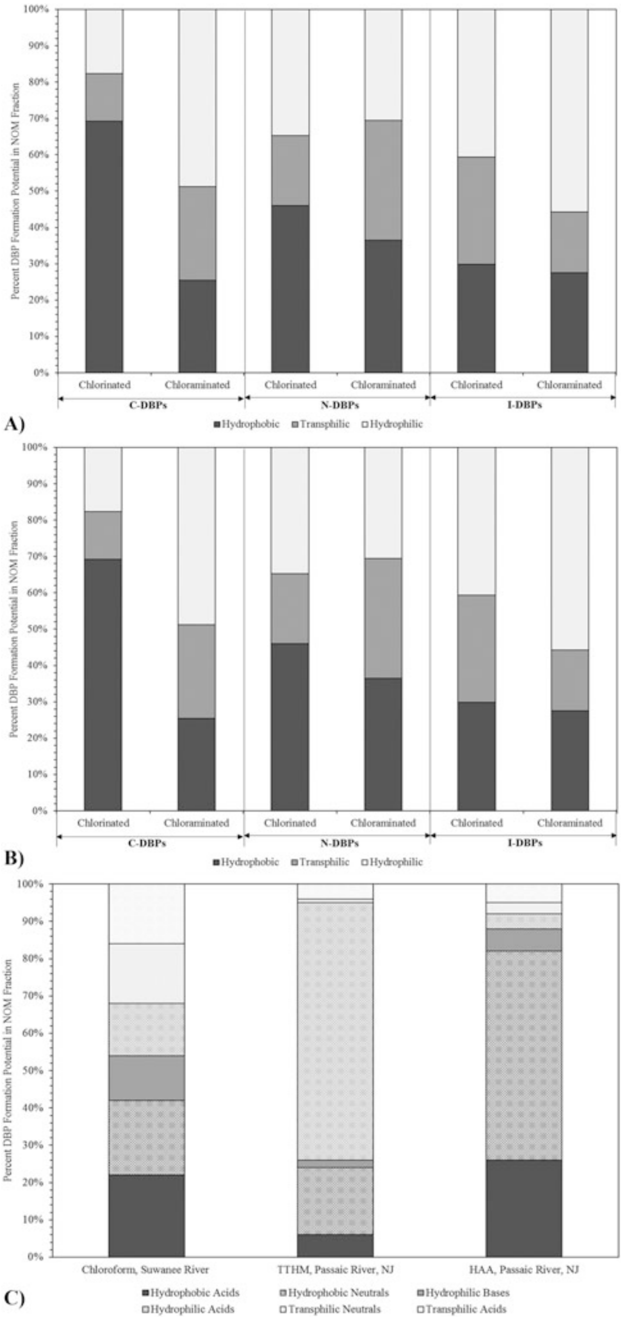
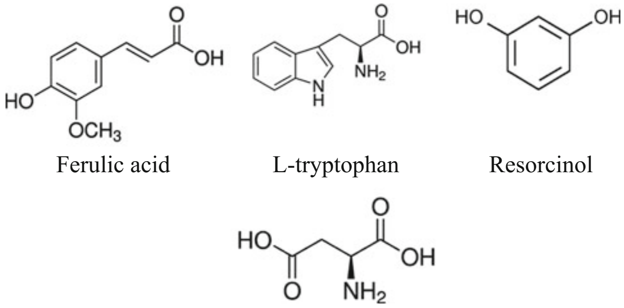


Fig. 8 Disinfection byproduct (DBP) formation potential associated with natural organic matter (NOM) fractions in variable source waters. C-DBPs, N-DBPs, and I-DBPs formed during chlorination or chloramination of water from (**a**) the Huangpu River, China, and (**b**) the Yangtze River, China [89]. (**c**) Shows chloroform [99], total trihalomethane (TTHM), and haloacetic acid (HAA) formation following chlorination [100]



Ferulic acid L-tryptophan Resorcinol

L-aspartic acid

Fig. 9 Compounds exhibiting high halogen substitution efficiency and which produce substantial trihalomethanes (THMs) and/or haloacetic acids (HAAs)

constituents on the ring are electron donors. Although not an activated aromatic species, L-aspartic acid also has many electron donating functional groups, has a high substitution efficiency, and serves as a significant precursor for HAA species.

3.4 Synthetic Organic Disinfection Byproduct Precursors

In addition to NOM, synthetic organic compounds can serve as precursor material for DBP formation. For example, the active compounds in sunscreens can be transformed to halogenated DBPs when swimming pools are disinfected with chlorine [102]. Understanding of DBPs produced by oxidation of the activated aromatic rings in synthetic compounds is a relatively new undertaking in comparison to their NOM-derived relatives. However, research is progressing, often stemming from studies of oxidative degradation of compounds such as pesticides (e.g., S-triazine herbicides and isoproturon), pharmaceuticals (e.g., carbamazepine and acetaminophen), antibacterial agents (e.g., triclosan and carbadox), textile dyes (e.g., azo), bisphenol A, alkylphenol ethoxylate surfactants, etc. [25].

4 Disinfection Byproduct Formation in Relation to Advanced Oxidation Processes

Advanced oxidation processes primarily impact DBP formation in two different ways: directly through in situ DBP formation and indirectly by influencing the DBP formation potential of the organics in the water matrix. In the first case, DBPs may be generated during the operation of AOPs themselves, particularly when using AOPs with direct inputs of chemical oxidants, e.g., ozone or hydrogen peroxide.

Additionally, organic oxidation byproducts may result during AOPs as complex organics are progressively degraded. In addition to direct formation during AOP treatments, AOPs may influence subsequent DBP formation potential as the DBP precursor organic material undergoes dramatic transformations during AOPs, which can serve to either decrease or increase DBP formation during subsequent disinfection processes.

4.1 Disinfection Byproduct Formation in Advanced Oxidation Processes

Hydroxyl radicals can attack organic molecules by radical addition, hydrogen abstraction, electron transfer, and radical combination. Select kinetic rate constants for reactions of HO• with organic matter, with and without radical scavengers (i.e., dissolved organic matter [DOM]), are shown in Table 3. The rate constants are generally greater for benzene-based compounds (44–120 × 10^8/M s) in comparison to carboxylic acid-based compounds (1–120 × 10^8/M s; at 190/M s, cysteine appears to be an outlier, perhaps based on its thiol properties). However, there are no distinct correlations between structure, molecular weight, and reactivity [103].

Westerhoff et al. [105] analyzed the reactivity of ozone and HO• with hydrophobic organic acids isolated from a variety of source waters. Although NOM characteristics varied among samples, there were strong correlations between SUVA values and the rate constants for O_3 and HO• interactions, as shown in Fig. 10. The data demonstrate ozone's strong preference for densely conjugated aromatic NOM, whereas HO• reactions with NOM were rapid and nonselective.

The general progression of oxidation using AOPs follows the pathway:

$$\begin{aligned}\text{organic pollutant} &\rightarrow \text{aldehydes} \rightarrow \text{carboxylic acids}\\ &\rightarrow \text{carbon dioxide and mineral acids}\end{aligned}$$

Accordingly, although AOPs can effectively mitigate organic precursors to limit downstream formation of DBPs, they can also directly generate their own suite of DBPs in the event of incomplete oxidation, wherein the products do not completely mineralize due to insufficient chemical and/or energy inputs. DBPs produced during AOP treatments may include BrO_3^-, NDMA, and small molecular weight organic compounds, e.g., acetaldehyde and formaldehyde [59, 106].

Table 3 Hydroxyl radical (HO•) kinetic rate constants with various organic compounds, with and without dissolved organic matter (DOM)

Compound	Chemical formula	Compound class	$k_{HO\bullet}$ ($\times 10^8$/M s)	$k_{HO\bullet, DOM}$ ($\times 10^8$/M_{carbon} s)
Benzaldehyde	C_7H_6O	Benzene-based	44	6
Hydroquinone	$C_6H_6O_2$	Benzene-based	52	9
Catechol	$C_6H_6O_2$	Benzene-based	110	18
Phthalic acid	$C_8H_6O_4$	Benzene-based, carboxylic acid	59	7
Salicylic acid	$C_7H_6O_3$	Benzene-based, carboxylic acid	120	17
Oxalic acid	$C_2H_2O_4$	Carboxylic acid	1	0.2
Citric acid	$C_6H_8O_7$	Carboxylic acid	3	1
Tartaric acid	$C_4H_6O_6$	Carboxylic acid	14	4
Cysteine	$C_3H_7NO_2S$	Carboxylic acid, thiol	190	63
Mean value for hydrophobic organic acids isolated from a variety of sources		Organic acids		3.6

Data from [103–105]

4.1.1 Bromate and Organic Brominated Disinfection Byproducts

Bromate (BrO_3^-) formation stems from ozonation, wherein O_3 directly oxidizes Br^- to BrO_3^-:

$$Br^- \rightarrow BrO^-/HBrO \rightarrow BrO_2^- \rightarrow BrO_3^-$$

Consequently, O_3-based AOPs such as O_3/UV and O_3/H_2O_2 can directly generate BrO_3^-, the extent of which depends on water quality and process operation. During O_3-based AOPs, the synergistic effect of O_3 and HO• may oxidize Br^- to BrO_3^- as HO• can participate in intermediate steps by producing radical species (e.g., Br•, BrO•) [107]. Relative to O_3-only processes, O_3/UV may produce similar amounts of BrO_3^- [108]. However, O_3/H_2O_2 can produce less BrO_3^- than O_3/UV, and O_3-only processes since H_2O_2 can reduce BrO^- to Br^-; hence optimized H_2O_2 doses can mitigate BrO_3^- formation [109, 110]. Although HO• is involved in BrO_3^- formation during ozonation processes, non-O_3-based AOPs such as UV/H_2O_2 and TiO_2 photocatalysis (UV/TiO_2), which rely on the production of HO• radicals, have not been shown to form significant amounts of BrO_3^- [109].

The production of organic B-DBPs can be much less prominent than BrO_3^- during ozonation and AOPs due to competing kinetics between HBrO and HO•.

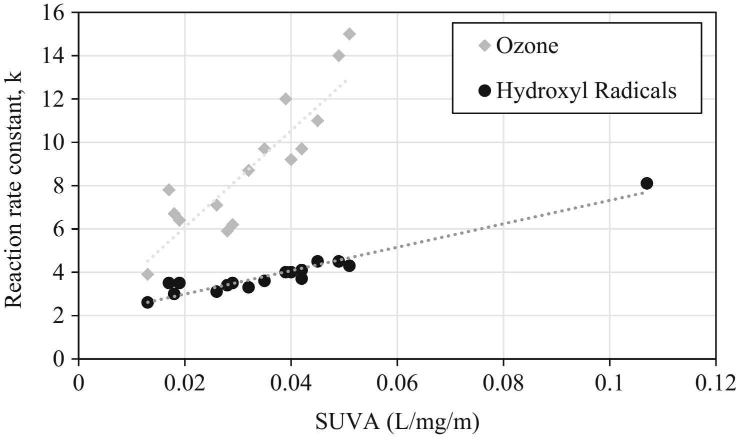


Fig. 10 Reactivity of natural waters with ozone (*k* in units of $\times 10^3$ per second) and hydroxyl radicals (*k* in units of $\times 10^{-8}$ L/mol C s). Data from [105]

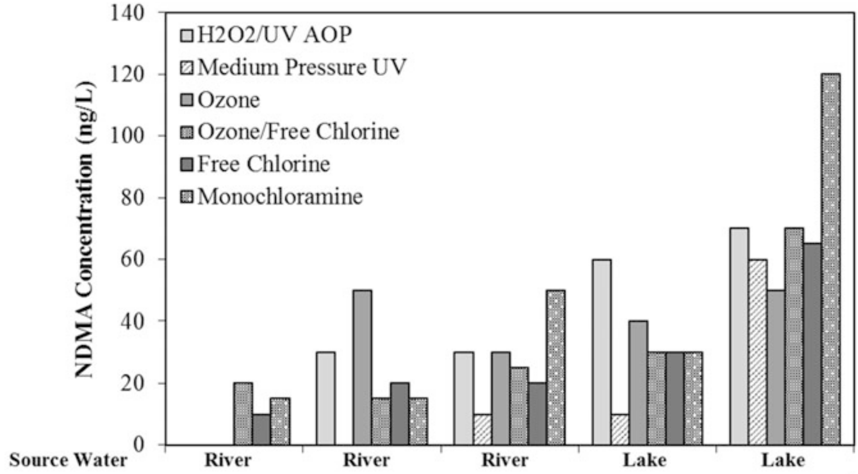
Hypobromous acid reacts more readily with O_3 and HO• compared to the precursor NOM necessary to form B-DBP haloorganics [111].

4.1.2 *N*-Nitrosodimethylamine (NDMA)

The use of AOP treatments can have variable results in terms of NDMA formation, as a function of influent water quality parameters. This is demonstrated in Fig. 11, where Zhao et al. [112] analyzed seven different source waters and found that UV/H_2O_2 yielded the highest amount of NDMA for some waters but lower NDMA for other waters. Interestingly, there was no correlation with bulk organic precursors (DOC, UV_{254}, SUVA), although the two waters yielding the most nitrosamines using UV/H_2O_2 had high UV_{254} values. In contrast, the water with the highest TOC and UV_{254} yielded small amounts of NDMA relative to others [112].

4.1.3 Non-halogenated Organic Disinfection Byproducts

AOPs can produce non-halogenated organic DBPs, primarily due to oxidation of condensed aromatic compounds, which produces low molecular weight organics. These byproducts can enhance biodegradability and can even be toxic. Wert et al. [113] compared organic byproduct formation during O_3 treatment to O_3/H_2O_2 AOP treatment and showed that O_3/H_2O_2 produced more organic byproducts than ozonation alone. This indicated greater organic degradation using the AOP, leading to incomplete oxidation. Incomplete oxidation can be problematic in distribution systems as it increases assimilable organic carbon (AOC), which can enhance downstream biological growth. Moreover, incomplete oxidation can actually increase DBP formation potential, as described in the following section.



Source Water	River	River	River	Lake	Lake
TOC (mg/L)	7.3	23.9	5.9	5.7	15.9
UV_{254} (cm^{-1})	0.223	0.933	0.127	0.329	0.464
pH	7.7	7.4	8.0	7.3	8.8
Turbidity (NTU)	0.84	4.68	0.75	6.1	30

Fig. 11 Comparison of *N*-nitrosodimethylamine (NDMA) formation during disinfection of variable quality untreated source water. The disinfection strategies tested include conventional approaches as well as advanced treatments such as the UV/H_2O_2 advanced oxidation process (AOP). Data from [112]

4.2 The Impact of Advanced Oxidation Processes on Disinfection Byproduct (DBP) Formation Potential: Influence of Oxidation on Precursor Organic Matter and Subsequent DBP Formation

Although AOPs have the ability to mineralize NOM and recalcitrant synthetic organic compounds, variations in chemical and energy inputs as well as process configuration can lead to incomplete oxidation. Incomplete oxidation products can include small organics such as carboxylates, ketones, and aldehydes. These compounds are formed when HO• oxidizes the hydrophobic, densely conjugated portions of NOM, thus opening ring structures and decreasing aromaticity. This is illustrated for the photo(electro)catalytic degradation pathways of phenol shown in Fig. 12. As the ring structures open, the NOM becomes more hydrophilic, and the exposed ring structure can exhibit greater halogen substitution efficiency, thereby serving as an active site for halogenated DBP formation [114].

In many drinking water systems, an oxidizing disinfectant such as free or combined chlorine is added prior to releasing the water to the distribution system to provide residual disinfectant to inactivate pathogens, maintain water quality, and protect against biological regrowth. The use of this type of secondary disinfection

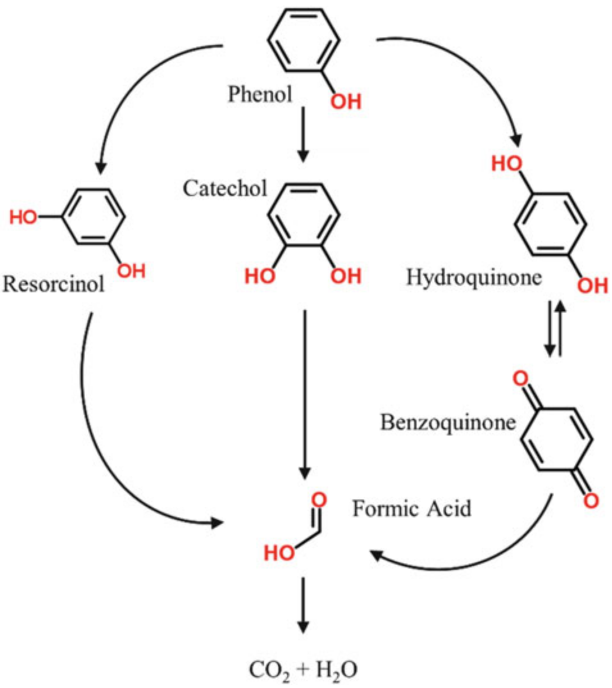


Fig. 12 Photo(electro)catalytic degradation pathways of phenol mineralization using $BiVO_4$ as the catalyst with visible light irradiation. Based on [115]

after AOP treatments wherein incomplete oxidation occurs can potentially exacerbate DBP production, depending on the type and dose of residual disinfectant. Incomplete oxidation leads to conversion of the humic fraction toward the fulvic fraction, which can increase THM and HAA formation potential as the structural properties of NOM change to resemble significant precursors, such as resorcinol. Structural changes in NOM due to reactions with HO• can particularly affect the formation of B-DBPs and I-DBPs because, in comparison to chlorine, bromine and iodine are more reactive with hydrophilic fractions of NOM produced by HO• [95].

AOP-derived chemical changes in NOM can also significantly impact NDMA formation as the hydrophilic NOM fraction produced during incomplete oxidation generally forms more NDMA than the hydrophobic fraction [98]. Additionally, AOPs can degrade residual polymer, which can potentially exacerbate the release of NDMA precursors, thereby greatly increasing NDMA formation when downstream chloramines are used as the residual disinfectant [56].

The extent to which DBP formation potential increases or decreases following AOP treatment is a function of numerous parameters and can thus vary widely across systems as well as within systems. The variation in AOPs' impact on DBP formation potential for selected studies is shown in Table 4.

As oxidation progresses toward NOM mineralization using greater energy and/or chemical AOP inputs, DBP formation potential decreases, as illustrated in Fig. 13, for TiO_2 photocatalysis AOP treatment followed by free chlorine addition.

Complete mineralization, and the resultant reduction in DBP formation potential, is energy and/or chemically intensive, perhaps making combinations of AOP treatment together with processes such as filtration more feasible for implementation in multi-barrier drinking water treatment trains. For example, dual barriers using AOPs followed by biological activated carbon (BAC) filtration can be used to more effectively mitigate DBP concerns using more feasible energy inputs. Toor and Mohseni [120] showed that using UV/H_2O_2 AOP followed by BAC significantly reduced DBP formation potential, whereas using the AOP as a stand-alone treatment required extremely high initial H_2O_2 concentrations and UV fluences to effectively reduce DBP formation ($>$23 mg/L H_2O_2 and $>$1,000 mJ/cm^2; for perspective, $<$200 mJ/cm^2 is typical for drinking water treatment).

5 Mitigation of Disinfection Byproducts

To mitigate DBPs, the recommended course of action is to prevent DBP formation in the first place. Several strategies are employed for this purpose, including employing alternative disinfectants and removing precursor material prior to disinfection. An additional option is to remove/destroy DBPs after they have formed.

5.1 Alternative Disinfectants

Free chlorine remains the most commonly used disinfectant, but concerns over DBP production have led to implementation of alternative disinfectants, including other chemical oxidants such as chloramines, chlorine dioxide, and ozone, as well as non-oxidant-based strategies. It is also possible to move the point of chlorination further downstream in the treatment process to allow reductions in NOM precursor material prior to disinfection [124].

As described in Sect. 2.1, each of the oxidizing disinfectants is characterized by varying degrees of effectiveness against different microbial pathogens and also has potential to produce DBPs, although they may impact the magnitude of DBP formation or the type of DBP produced. For example, monochloramine reduces production of THMs and HAAs; however, it can increase formation of iodo-acids, which are considered one of the most toxic DBPs [40]. Likewise, chlorine dioxide introduces concerns for chlorite and chlorate production, while ozonation can increase bromate formation.

Heat (e.g., boiling or pasteurization) and electromagnetic radiation (e.g., gamma and UV radiation) offer non-oxidant-based disinfection strategies. For water disinfection, the only one of these approaches in routine practice is UV radiation [17]. A

Table 4 Impact of advanced oxidation processes (AOPs) on disinfection byproduct (DBP) formation potential reported in select studies

AOP	Source water	Process description	Trend in DBP formation potential (FP) following AOP treatment	Reference
O_3	River Ruhr, Germany	1.5 mg O_3/mg DOC	↓ TTHMFP and AOXFP[a]	[116]
O_3	Indoor swimming pool	6 mg/L O_3	↓ TTHMFP, AOXFP, TOC, AOX	[117]
O_3/H_2O_2	Indoor swimming pool	6 mg/L O_3, 1.5 mg/L H_2O_2	↑ TTHMFP	[117]
			↓ AOXFP, TOC, AOX	
O_3/UV	Indoor swimming pool	6 mg/L O_3, 2.93 W low-pressure UV lamp	↑ TTHMFP	[117]
			↓ AOXFP, TOC, AOX	
O_3/UV	Seymour reservoir, Canada	0.62±0.019 mg O_3/mL, UV fluence = 1.61 J/cm^2	↓ TTHMFP and HAA5FP	[118]
UV/H_2O_2	Ohio river sample from water treatment plant	5–10 mg/L H_2O_2, medium- and high-pressure UV lamps	↑ TTHM yield following post-chlorination	[119]
UV/H_2O_2	River Ruhr, Germany	15 W low-pressure UV lamp, 8 mg/L H_2O_2 initially	↑ TTHMFP prior to 1,050 min of irradiation	[116]
			↓ TTHMFP after 1,050 min of irradiation and 5.6 mg/L H_2O_2 consumed	
UV/H_2O_2	Vancouver reservoir	5–15 mg/L H_2O_2, low-pressure high-output UV lamp	↓ TTHMFP for fluences $>1{,}500\ mJ/cm^2$	[114]
UV/H_2O_2	Raw surface water	0–23 mg/L H_2O_2, low-pressure UV fluence = 0–3,500 mJ/cm^2	↓ DBP formation potential for $>1{,}000\ mJ/cm^2$ and initial H_2O_2 concentrations >23 mg/L	[120]
UV	Indoor swimming pool	2.93 W low-pressure UV lamp	↑ TTHMFP	[117]
			↓ AOXFP, TOC, AOX	
UV/TiO_2	Arizona surface water	7 mW/cm^2 low-pressure UV, 400 mg/L TiO_2	↑ TTHMFP using 5–20 kWh/m^3	[121]
			↓ TTHMFP for energy inputs $>20\ kWh/m^3$	
UV/TiO_2	Myponga reservoir, Australia	Blacklight blue fluorescent UV lamp, 0.1 g/L TiO_2	↓ TTHMFP	[122]
			↑ HAA5FP before 30 min of irradiation	
			↓ HAA5FP after 30 min of irradiation	

(continued)

Table 4 (continued)

AOP	Source water	Process description	Trend in DBP formation potential (FP) following AOP treatment	Reference
UV/ TiO_2	Hillsborough river water, Florida; Sacramento-San Joaquin Estuary, California	450–1,200 W high-pressure UV lamps, 1.0 g/L TiO_2	↓ THMFP	[123]

[a] AOX represents the organically bound halogens adsorbable on activated carbon

major advantage of UV disinfection is that at the fluences typically used in drinking water treatment (<200 mJ/cm^2), there is no evidence of DBP formation, nor are DBP levels exacerbated using post-UV disinfection [9]. However, UV provides no residual disinfection, so an oxidant such as chlorine or chloramines is typically applied prior to release of the water in the drinking water distribution system to protect against pathogen regrowth.

While AOPs can provide some degree of disinfection, they are unlikely to be used explicitly for this purpose. Moreover, increased reactivity of the NOM due to the production of small organic compounds during AOP-based incomplete oxidation can exacerbate DBP formation and also lead to challenges in the distribution system. Enhanced biodegradability of the small organics in the effluent can lead to increased corrosion, nitrification, taste and odor compound formation, and enhanced microbial growth that can impair the microbial safety of the drinking water [62, 114, 125].

To simultaneously mitigate concerns related to a wide spectrum of microbial pathogens, DBPs, and contaminants of emerging concern, water treatment plants may use dual barriers including an alternative disinfectant such as ozone or chloramination alongside advanced treatment (e.g., AOP-BAC) [126].

5.2 Removal of Precursor Natural Organic Matter Prior to Disinfection

Given the trade-offs associated with the use of alternative disinfectants, the most common strategy to mitigate DBPs is to avoid formation by removing precursor NOM prior to disinfection [127].

Physicochemical unit operations including enhanced coagulation or softening, granular activated carbon adsorption, and membrane processes are considered best available techniques for physical removal of NOM from water [83, 128]. These processes are often sufficient to control DBP formation, but alternatives such as ozonation or AOP treatments have also been investigated [16, 84, 121, 129].

Coagulation processes preferentially remove the humic and higher molecular weight portions of NOM. Removal of 15–50% TOC is commonly achieved using

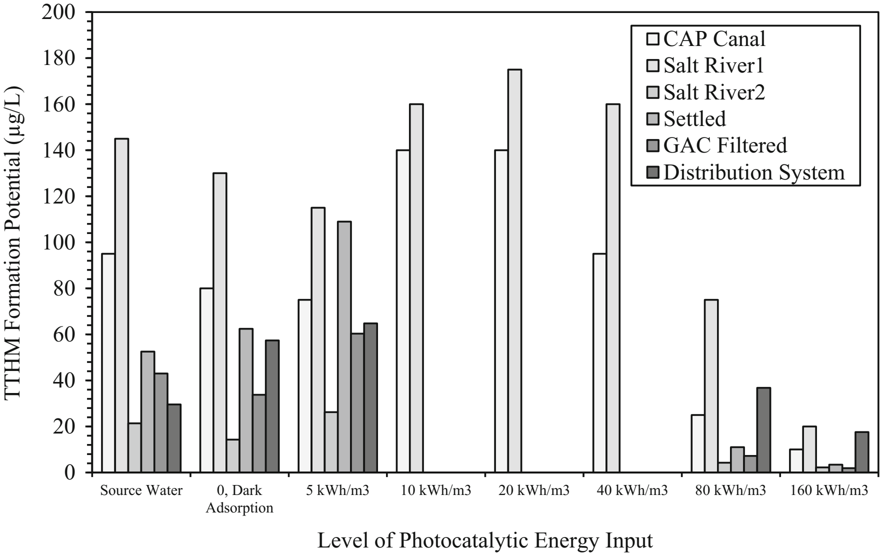


Fig. 13 Total trihalomethane (THM) formation potential in various source waters resulting from UV/TiO_2 advanced oxidation process (AOP) treatment followed by free chlorine addition. The data show that TTHM formation potentials increase in some source waters following incomplete oxidation with relatively low-energy inputs ($\leq$5 kWh/m^3). In all waters tested, high-energy inputs approached more complete natural organic matter (NOM) mineralization, and TTHM formation potential decreased. Adapted from [84, 121]

enhanced coagulation (which relies on the use of higher coagulant doses and/or pH adjustment to target NOM removal) or enhanced softening [17]. Since the hydrophobic portion of NOM, which generally consists of humic substances, is primarily removed by coagulation, further treatment may be necessary to remove the hydrophilic, fulvic portion of NOM, which can also contribute to DBP formation.

Adsorption of NOM is possible using activated carbon (granular [GAC] or powdered [PAC]) or ion-exchange resins. However, the use of activated carbon for NOM can be costly as a significant fraction of the NOM, comprised of large molecular weight organics, is poorly adsorbed, meaning that large amounts of activated carbon are used to remove relatively small amounts of NOM. With more selective ion-exchange media, e.g., MIEX resin, much greater NOM removal can be achieved more quickly [17].

In some cases, membrane filtration can effectively remove DBP precursors, although results vary for different types of membranes. For example, ultrafiltration with a molecular weight cutoff (MWCO) of 100,000 Da was not effective for controlling DBP formation in pilot studies, whereas nanofiltration with a MWCO of 400–800 Da was effective when little-to-no bromide was present [130]. Microfiltration and ultrafiltration are not effective at removing NDMA precursors, but 57–98% of precursors were removed using nanofiltration and reverse osmosis [131]. Reverse osmosis has been effectively used for NOM removal, rejecting >90% NOM and DBP precursors [132].

The use of O_3 or AOP treatments in combination with BAC filtration can provide an effective means for removing NOM to both reduce DBP formation potential and decrease AOC in the distribution system. Using AOPs or ozonation can break carbon-carbon double bonds in NOM, which transforms the NOM into more readily biodegradable organic matter (higher AOC or biodegradable dissolved organic carbon – BDOC), which is particularly amenable to biofiltration. By combining ozonation with biologically active filtration, 35–40% DOC removal can be achieved [17]. This sequential AOP-biological process treatment train concept is depicted in Fig. 14.

5.3 *Mitigation of Preformed Disinfection Byproducts Using Advanced Oxidation Processes*

Another strategy to mitigate DBPs is to remove them from water following DBP generation during disinfection processes. While the use of phase-transfer processes or redox chemistry may offer options to accomplish this, DBP removal is typically a less effective and economical approach compared to avoiding DBP formation in the first place via removal of precursors prior to disinfection processes, as described in Sect. 5.2.

Phase-transfer processes such as activated carbon adsorption and air stripping can be used to remove DBPs from water. However, these approaches may introduce elevated operation and maintenance costs that limit feasibility of implementation. For example, GAC is characterized by low THM adsorption capacity, meaning that large amounts of GAC would be required for adequate DBP removal [134, 135]. Additionally, while volatile THMs will readily be removed by air stripping, HAAs will remain [136].

The hydroxyl radicals produced during AOPs can degrade organic DBPs, as illustrated by the kinetic rate constants of several different types of DBPs shown in Table 5.

AOPs have been used to mitigate DBPs in swimming pool water, where O_3/UV and O_3/H_2O_2 generally improved removal of TOC precursors and DBPs (quantified as AOX) beyond levels achieved by O_3 alone. For THM formation potential, O_3 provided a slight advantage over the AOPs due to O_3 oxidation selectivity in comparison to the small reactive molecules produced via HO• reactions, which are more easily transformed to THMs [117].

NDMA readily penetrates reverse osmosis membranes and is poorly adsorbed and stripped, so UV-AOPs have been used to meet regulatory guidelines for potable water reuse [137, 141]. Notably, NDMA is photodegradable using direct UV irradiation ($\lambda < 260$ nm), so additions of H_2O_2, O_3, or TiO_2 to provide advanced oxidation would not be necessary if other recalcitrant compounds were not also

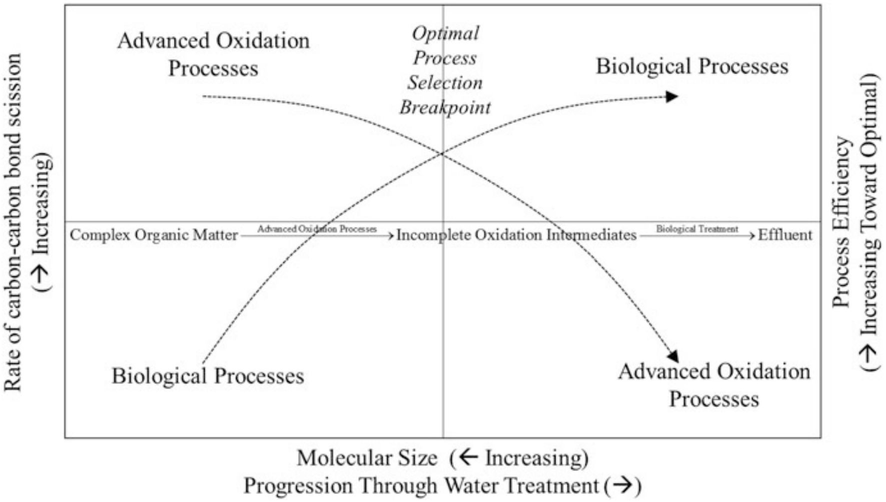


Fig. 14 Conceptual sequential advanced oxidation process (AOP)/biological process (e.g., BAC) approach to treatment, taking advantage of the efficiency of each process for degrading organic matter. The breakpoint between AOPs and biological processes is illustrated, where biological treatment becomes more attractive in terms of rate and efficiency as incomplete oxidation byproducts can be easily biodegraded. Modified after [133]

being targeted, e.g., 1,4-dioxane [141]. Degradation of NDMA during UV treatments can proceed via three pathways: hemolytic cleavage of N-NO bonds, heterolytic cleavage of N-NO bonds, and photooxidation [142]. During UV/H_2O_2 AOP treatment, HO•-based degradation of NDMA occurs by hydrogen atom abstraction from the methyl groups in NDMA [137, 143].

Using a UV dose of $\geq$1,000 mJ/cm^2 together with 3 mg/L H_2O_2, 1 log removal of NDMA can typically be achieved [141]. As noted previously, additions of H_2O_2 do not substantially improve NDMA degradation beyond UV alone. However, direct photolysis of NDMA can produce DMA as a major byproduct, and as DMA reacts with chloramines to produce NDMA, care must be taken to avoid regeneration of NDMA [141].

The electrical energy per order (EEO) of reduction is a metric used to evaluate electrical efficiency of processes, e.g., UV-AOPs. For one log reduction of NDMA using UV/H_2O_2, the EEO is approximately 21–265 kWh/m^3 using doses of 5–6 mg/L H_2O_2 (although this can vary greatly across different waters) [144]. The EEO for destruction of THMs using TiO_2 photocatalysis has been reported at 19–64 kWh/m^3 in several surface waters [121]. For perspective, EEO values less than 0.265 kWh/m^3 are considered favorable for water treatment [145], which demonstrates that AOPs are not an efficient means of destroying preformed DBPs.

Table 5 Hydroxyl radical (HO•) rate constants with various disinfection byproducts (DBPs)

DBP	Chemical formula	DBP class	$k_{HO\bullet}$ (×10^8/M s)
Chloroform	$CHCl_3$	Trihalomethane	0.11
Dichloromethane	CH_2Cl_2	Halomethane	0.22
Bromoform	$CHBr_3$	Trihalomethane	1.5
Dibromomethane	CH_2Br_2	Halomethane	0.99
Bromodichloromethane	$CHBrCl_2$	Trihalomethane	0.711
Chlorodibromomethane	$CHBr_2Cl$	Trihalomethane	0.831
N-Nitrosodimethylamine (NDMA)	$C_2H_6N_2O$	Nitrosamines	4.3
Chloronitromethane	CH_2ClNO_2	Halonitromethane	1.94
Dichloronitromethane	$CHCl_2NO_2$	Halonitromethane	5.12
Trichloronitromethane (chloropicrin)	CCl_3NO_2	Halonitromethane	0.497
Bromonitromethane	CH_2BrNO_2	Halonitromethane	0.836
Dibromonitromethane	$CHBr_2NO_2$	Halonitromethane	4.75
Tribromonitromethane	CBr_3NO_2	Halonitromethane	3.25
Bromochloronitromethane	$CHBrClNO_2$	Halonitromethane	4.2
Bromodichloronitromethane	$CBrCl_2NO_2$	Halonitromethane	1.02
Dibromochloronitromethane	CBr_2ClNO_2	Halonitromethane	1.80

Values from [137–140]

6 Summary

Although the premise of disinfection is easily understood, interactions between disinfectants and the target and nontarget constituents in complex drinking water matrices are incredibly complex. Accordingly, there is not a one-size-fits-all approach to minimizing the risks posed by microbial pathogens against those posed by chemical contaminants, e.g., DBPs. While a given disinfection process may significantly reduce one DBP, it may lead to substantial increases in another DBP (e.g., chloramination may reduce THMs and HAAs but increase NDMA). Likewise, shifts in precursor NOM composition during unit operations prior to disinfection can have variable impacts on subsequent DBP formation during disinfection processes. Overall, removal of this precursor material prior to disinfection offers the most effective strategy to mitigate DBPs.

The use of AOPs in drinking water treatment trains may impact DBPs via three different pathways: (1) direct formation during AOP treatment, (2) indirect influences on DBP formation potential in downstream disinfection, and (3) destruction of preformed DBPs. High AOP energy and/or chemical inputs are needed to destroy preformed DBPs, making it much more efficient to avoid DBP production in the first place.

The direct generation of DBPs during AOP treatments is generally less of a concern in comparison to disinfection strategies based on additions of halogenated oxidants such as chlorine since AOPs do not directly form halogenated DBPs. However, direct inputs of chemical oxidants, e.g., O_3 or H_2O_2, during AOPs can generate DBPs such as BrO_3^- or NDMA. Moreover, as complex organics are progressively degraded, AOPs can also directly generate their own suite of DBPs in the event of incomplete oxidation, which produces small molecular weight organic compounds, e.g., acetaldehyde and formaldehyde. These non-halogenated organic DBPs can be toxic or can lead to subsequent issues such as enhanced DBP formation potential, higher biodegradability (AOC or BDOC) in the distribution system, etc.

In addition to direct DBP formation, AOPs may also strongly influence subsequent DBP formation potential as DBP precursor organic material undergoes dramatic transformations during AOPs. Although AOPs can effectively mitigate organic precursors to limit downstream formation of DBPs given sufficient energy and/or chemical inputs to yield complete mineralization, lower inputs lead to incomplete oxidation, which can exacerbate DBP formation. Thus, AOPs may either decrease or increase DBP yields during subsequent disinfection processes depending on the water matrix and process operation.

To simultaneously mitigate concerns related to a wide spectrum of microbial pathogens, DBPs, and contaminants of emerging concern, drinking water treatment plants may use dual barriers including an alternative disinfectant such as ozone or chloramination alongside advanced treatment (e.g., AOP-BAC). The impact of these processes on DBP formation potential must be evaluated for each individual source water using selected operational parameters as changes in DBP precursors during treatment processes can have widely variable impacts on DBP formation, and care must be taken to avoid increasing DBP formation via incomplete oxidation during AOP treatments.

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