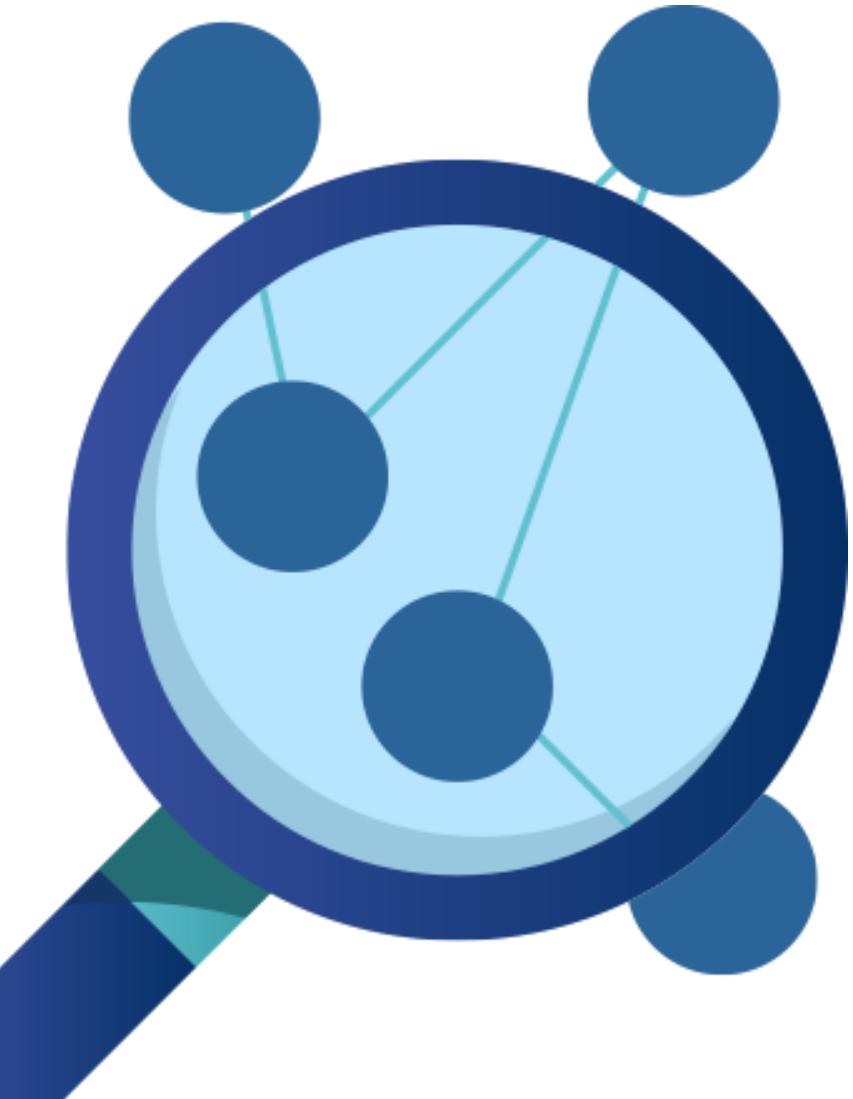
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Strategies for DBP minimization

Deliverable D4.1

WP 4



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ABSTRACT	This report summarizes the strategies for DBPs minimization reviewed based on the recent literature, with particular attention to the DBPs regulated by the new European Drinking Water Directive and to the emerging DBPs (e.g., NDMA). The identified approaches for DBPs control include (1) source water quality control, (2) disinfection strategy selection, (3) removal of already formed DBPs, and (4) removal of DBPs precursors. Emphasis is also given to the use of alternative pre-oxidation processes that may be easily implemented for the upgrade of water treatment plants and to advanced treatment processes to remove DBPs and/or their precursors.		

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SUMMARY

This report summarizes the strategies for minimization of DBPs formation reviewed based on the recent literature, with particular attention to the DBPs regulated by the new European Drinking Water Directive and to the emerging DBPs (e.g., NDMA). The identified approaches for DBPs control include (1) source water quality control, (2) disinfection strategy selection, (3) removal of already formed DBPs, and (4) removal of DBPs precursors. Emphasis is also given to the use of alternative pre-oxidation processes that may be easily implemented for the upgrade of water treatment plants and to advanced treatment processes to remove DBPs and/or their precursors.

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1.0 INTRODUCTION

The importance of water availability for establishing civilizations has been recurrent through history. And so does the need for water treatment systems. Some ancient documents from the Sanskrit and Greek (4000 B.C.) already report some treatment methods like sunlight exposure or charcoal filtering. However, on those early stages the main focus was turbidity reduction. It was not until the late 1800s when drinking water contaminants started to gain concern and during the beginning of 1900s when the goal of water treatment completely moved into disease-causing microbes (US EPA, 1999). This advance turned into an increased life expectancy because of the massive reduction of the water-borne illness, and the main player can be attributed to the development of disinfection processes.

Unfortunately, the undesired consequence of disinfection is the generation of disinfection by products (DBPs). For instance, several DBPs are formed from the reaction between chlorine and DBP precursors like natural organic matter (NOM), effluent organic matter (EfOM) or other anthropogenic trace contaminants (pesticides, pharmaceuticals, etc.) that are present in discharged treated wastewater, ammonium, bromide and iodide. The first studied DBPs were trihalomethanes (THMs) in the early 1970s. The major concern of these compounds was associated to their potential health risks and thus, the US Environmental Protection Agency (EPA, 1979) started regulating THMs after many toxicological studies investigating their mutagenic and carcinogenic properties. Later, haloacetic acids (HAAs), bromate and chlorite followed THMs and also entered in the Stage 1 and Stage 2 Disinfectants/DBP Rules in the 1990s (EPA, 2001; 2004; 2005). At the same time, the European Union published the first European Directive on the quality of water intended for human consumption, where only THMs and bromate were listed as concerning pollutants. Recently the European Union has been updated by including, among other concerning pollutants, HAAs, chlorite and chlorate (Directive (EU) 2020/2184).

To that extent, the pressure to meet legislation requirements moved drinking water treatment plants to explore distinct ways to perform disinfection so concentrations of this target contaminants could be lowered. This involved strategies such as using alternative disinfectants like chloramine, chlorine dioxide, ozone and UV irradiation. While these disinfection processes result to be effective measures to reach the goal, on the flip side, DBP generation is shifted into other emerging species like nitrogenous DBPs (N-DBPs), iodo-DBPs (I-DBPs), haloaldehydes, haloketones or haloacids. This, hand in hand with all the improvements in methodologies for detection and monitoring DBPs, have led to an increasing number of reported emerging compounds. So, from those early stages where THMs were firstly reported to nowadays, up to more than 700 DBPs have been lately identified.

The fact that toxicity of those emerging species (specially of N-DBPs and I-DBPs) is known to be worse than their chlorinated analogous, and that their occurrence in several waters has been reported globally (Gilca et al., 2020; MacKeown et al., 2022a; Postigo

& Zonja, 2019a; Richardson et al., 2007; Richardson & Plewa, 2020; Wagner & Plewa, 2017) seem to be a compelling argument to reconsider regulations. Unfortunately, their effects in human beings remain unclear and, with few studies and inconclusive data, there is still a long way to go to promote significant modifications. So far, in the eyes of legislation, THMs and HAAs are still regarded as representative DBPs acting as surrogates for the other chlorinated species. Meanwhile clear studies on the dose-exposure relationship and toxicity effects on human should be carried out (World Health Organization, 2022) specially for all those new DBPs.

In view of the current global situation where we are constantly moving from one to another scenario, driven by factors such as population growth, climate change effects, or energetical crisis, water treatments need an imminent rethinking, probably shifting into more water reuse technologies. Imperatively, the evaluation of DBPs formation and fate should not be put aside during this reassessment, particularly when minimizing their formation becomes one of the main preventive actions to adopt while their regulations remain controversial.

The scope of this report is to recap the latest information about the main DBPs of concern, the principal factors promoting their formation, and evaluating the principal strategies for reducing their occurrence in disinfected water. The ultimate goal is to identify alternative processes and technologies to upgrade water treatment plants, as the ones that will be developed within intoDBP project.

2.0 CLASSIFICATION, FORMATION, OCCURRENCE AND TOXICITY OF DBPs

2.1 Classification and formation

DBPs can be classified based on their structure, properties, occurrence, etc. In general, DBPs are recognized in organic DBPs and inorganic DBPs. Since, some DBPs are regulated, while a large part are unregulated/emerging compounds, in the following sections the classification of DBPs distinguishes firstly regulated and emerging (often unregulated) DBPs and secondly organic and inorganic DBPs.

2.1.1 Organic DBPs

DBPs comprise a broad family of organic compounds, which can be grouped in aliphatic, alicyclic and aromatic, as shown in Figure 1.

Trihalomethanes (THMs) and haloacetic acids (HAAs) are the most prevalent DBPs in chlorinated drinking waters so they are considered as representative of other and are regulated under the Stage 1 and Stage 2 D-DBP Rule in the US (EPA, 2001; 2004) and listed in the European Directive (EU) 2020/2184 that stablishes the framework from which the Member States must transpose into national legislations. In Europe, the latest recast of the Directive, on 16th December 2020 introduces for the first time HAAs, and from 12th January 2023, concentrations of 100 µg/L of the sum of THM4 (trichloromethane, bromodichloromethane, dibromochloromethane and tribromomethane) and 60 µg/L of the sum HAA5 (monochloroacetic acid, dichloroacetic acid, trichloroacetic acid, monodibromoacetic acid and dibromoacetic acid) must not be exceeded in disinfected waters for human consumption.

THMs structurally derive from a methane molecule where hydrogen atoms have been substituted with halogens (chlorine, bromine or iodine). This rises to a total combination of 27 THMs, given the formation of the four following species the most relevant due to their occurrence: trichloromethane or chloroform ($CHCl_3$), bromodicloromehtane ($CHBrCl_2$), bromodichloromethane ($CHBr_2Cl$) and tribromomethane or bromoform ($CHBr_3$), and all possible combinations with iodide and bromide. In contrast to what might seem, formation of THMs in chlorinated waters does not derive from reaction of chlorine with methane but it is a complex reaction between disinfectants and natural organic matter (NOM) like humic and fulvic substances.

HAAs are the second major group of DBPs formed in chlorinated drinking water. Structurally, this family of DBPs derive from a substituted acetic acid molecule that depending on the degree of substitution lead to the formation of three groups: monohaloacetic acids (CH_2XCOOH), dihaloacetic acids (CHX_2COOH) and trihaloacetic acids (CX_3COOH) which differ both in formation mechanisms and in chemical and biological properties. There are nine common HAAs: monochloroacetic acid

(CH_2ClOOH), monobromoacetic acid ($CH_2BrCOOH$), dichloroacetic acid ($CHCl_2COOH$), bromochloroacetic acid ($CHBrClCOOH$), dibromoacetic acid ($CHBr_2COOH$), trichloroacetic acid (CCl_3COOH), bromodichloroacetic acid ($CBrCl_2COOH$), chlorodibromoacetic acid ($CBr_2ClCOOH$) and tribromoacetic acid (CBr_3COOH), apart from the possible combinations with iodide. As with THMs, formation of HAAs derive from complex reactions between chlorine, bromine and NOM.

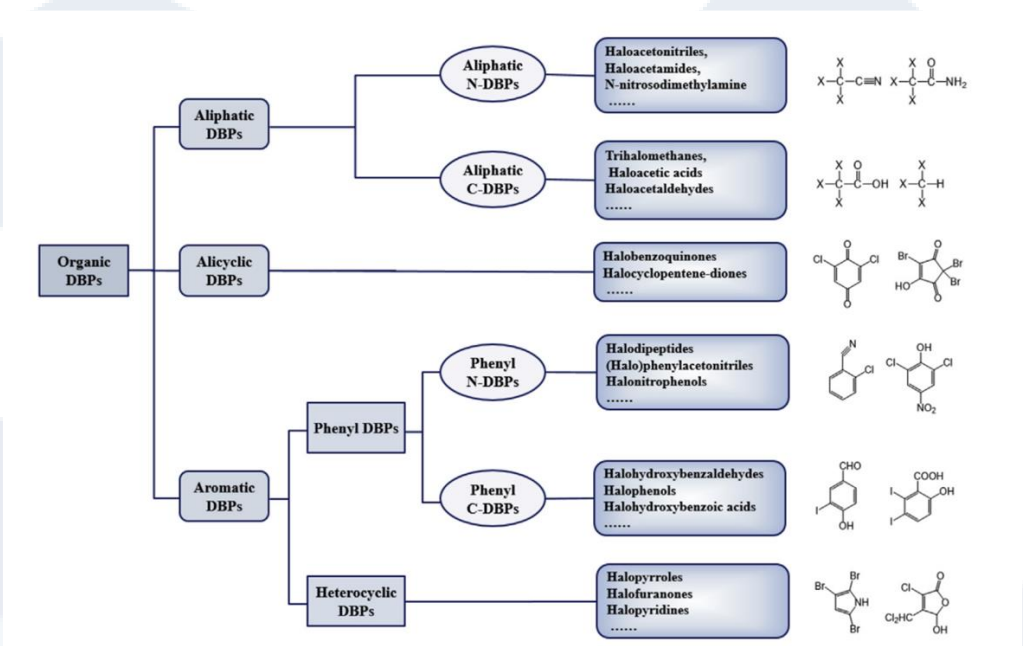


Figure 1. Classification of organic DBPs (Liu et al., 2020)

Brominated species such as bromoform, dibromochloromethane, bromodichloromethane, monobromo- and dibromo- acetic acids or dibromoacetone can also originate in source waters containing higher levels of bromide. Other less abundant halogenated DBPs can include haloacetaldehydes (mainly chloral hydrate) and haloketones. Those, with their brominated analogues conform two DBPs subfamilies that can also lead to the formation of THMs and HAAs through several reactions. However, one of the major drawbacks involving their study is the lack of commercial standards and their instability, factors hindering their systematic analysis (Xie, 2004). Other DBPs that will be also discussed later are haloacetonitriles (HANs) and halonitromethanes (HNMs).

Some non-halogenated organic DBPs can be generated as an outcome of disinfection with chlorine or chloramines as well as from oxidation processes with strong reagents such as ozone or advanced oxidation processes used as secondary disinfectants. Those include aldehydes, ketoacids, and carboxylic acids and cyanuric acid (World Health Organization, 2022; Xie, 2004). Formaldehyde and acetaldehyde are the most common aldehydes. Concentrations of ketoacids tend to be five to ten times higher than the total aldehydes, being glyoxylic acid, pyruvic acid and ketomalonic acid the most abundant.

Formic acid, acetic acid and oxalic acid are the most common and simplest carboxylic acids reported in ozonated drinking waters (Xie, 2004). Few information about those DBPs is still available and although they are not end by-products, can act as intermediates to the formation of other DBPs such as THMs or HAAs.

2.1.2 Inorganic DBPs

Bromate (BrO_3^-) and chlorite (ClO_2^-) are two inorganic DBPs regulated in US under the Stage 1 D-DBP Rule. The European Directive (EU) 2020/2184 stablishes limits of 10 µg/L for bromate and 0.25 mg/L for chlorite and also includes chlorate (ClO_3^-) at same level (permitting up to 0.7 mg/L in the case of disinfection with ClO_2).

Hypochlorite ion (OCl^-) from hypochlorite stock solutions is unstable and decomposes in chloride and chlorate simultaneously. Chlorite is an intermediate of the reaction of hypochlorite and chlorate. Also, when hypochlorite is present in processes involving chlorine dioxide, a disproportionation reaction undergoes to form chlorate (Gilca et al., 2020). Chlorate can be produced during the generation of chlorine dioxide from sodium chlorite and free chlorine, from photodecomposition of chlorine dioxide and from conversion of chlorine dioxide under high pH conditions (pH >9) to chlorite and chlorate. Chlorate can be also produced through the reaction of residual chlorite and free chlorine during secondary disinfection.

Bromate is formed mainly from the oxidation of bromide during ozonation processes via different mechanisms including the reaction with direct ozone, hydroxyl radicals, as well as other direct/indirect pathways involving combinations of them (Xie, 2004). The main formation mechanism involves two pathways: 1) the oxidation of Br^- transformed to a decisive intermediate hypobromous acid/hypobromite (HOBr/ OBr^-) and further to BrO_3^- by O_3 or $OH^\bullet$ and 2) the formation of bromine radicals ($Br^\bullet$) by the reaction of $OH^\bullet$ and Br^-; where $Br^\bullet$ is directly oxidized by O_3 to form bromine oxide radical ($BrO^\bullet$) and then to BrO_3^-. Furthermore, it has been reported controlling HOBr/OBr^- would partially suppress BrO_3^- formation, whereas the formation could be fully inhibited if the reaction from $Br^\bullet$ to $BrO^\bullet$ is controlled with no formation of $Br^\bullet$ (Jahan et al., 2021).

2.1.3 Emerging DBPs (N-DBPs, I-DBPs and HMW-DBPs)

As analytical methods for screening and analysing DBPs progress by lowering detection limits, the number of reported DBPs increases. Some of those new described species, detected at very low concentrations in some disinfected waters (Gilca et al., 2020), can be named as emerging DBPs. They appear to have worst impacts on human health due to their cytotoxicity, genotoxicity, endocrine disruption effect and carcinogenicity (MacKeown et al., 2022a; Postigo & Zonja, 2019a; Richardson et al., 2007; Wagner & Plewa, 2017) meanwhile conclusive studies on their occurrence, formation and toxicity are still limited and they remain unregulated. Some of the most reported emerging DBPs are described in the following sections.

When introducing N-DBPs, there is a straight tendency on associating generation of those pollutants with the direct use of chloramines as disinfectants. However, the presence of nitrogen as a precursor for these by-products can also proceed from the main source waters, like in the case of wastewater effluent discharges (EfOM) that can contain considerable concentrations of ammonia, or waters with high amounts of algal organic matter (AOM), where levels of dissolved organic nitrogen (DON) can be significant enough to enhance formation of those DBPs (Bond et al., 2011). N-DBPs includes the formation of haloacetonitriles (HANs), which are the most abundant N-DBPs, being dichloroacetonitrile (DCAN) the prevalent specie in the absence of bromide; haloacetamides (HacAms) that are frequently detected in waters treated with ClO_2 as a primary disinfectant prior to final treatment with chloramines (Bond et al., 2011; Gilca et al., 2020); halonitromethanes (HNMs), and cyanogen halides as organohalogenated products. Nitrosamines are the main family of N-non-halogenated products, especially N-nitrosodimethylamine (NDMA), typically detected at levels of ng/L. Nitrogenated inorganic DBPs can also be detected in drinking waters such as nitrites, nitrates and hydrazine (Bond et al., 2011).

Another emerging family of DBPs are I-DBPs. They result from the chemical disinfection of waters containing iodide. Specially chlorination and chloramination may lead to the formation of those compounds, but also other oxidants such as permanganate, peracetic acid, ferrate or ozonation can increase concentrations of I-DBPs (Bichsel & von Gunten, 2000; Liu et al., 2017; MacKeown et al., 2022b; Postigo & Zonja, 2019b). On a first stage of the disinfection process, iodide is oxidized to hypochlorous acid (HOI), which subsequently can react with NOM to form I-DBPs or be oxidized into iodate (IO_3^-), which is considered to be a stable and safe end product. Some disinfectants with strong oxidizing power such as ozone or ferrate can mitigate formation of I-DBPs as they rapidly turn iodide into iodate. Bischsel (Bichsel & von Gunten, 2000) reported than more than 90% of iodide was oxidized to iodate with ozonation thus not generating detectable I-DBPs compared to chlorination or chloramination processes. So apparently, peroxidation could be a critical step in terms of mitigation of I-DBPs (Bichsel & von Gunten, 2000; Liu et al., 2017; MacKeown et al., 2022b; Postigo & Zonja, 2019b). On the contrary, disinfectants with lower oxidizing capacity such as chloramines are expected to enhance formation of I-DBPs (Yang et al., 2014). Iodomethanes (I-THMs) were the first reported I-DBPs and as a result had become the most studied ones acting as surrogates of the rest, specifically dichloroiodomethane ($CHCl_2I$) and bromochloroiodomehtane (CHBrClI) which have also been the most detected (Allard et al., 2015; Bichsel & von Gunten, 2000; Dong et al., 2019; Liu et al., 2017; Postigo & Zonja, 2019b). In fact, I-DBPs can be grouped into six big families: I-THMs, iodo-haloacetic acids (I-HAAs); iodo-haloacetamiedes (I-HAMs) and iodo-haloacetonitriles (I-HANs) that are nitrogenated; iodo-haldehydes (I-HALs) like iodobutanal and iodoacetaldehyde; and iodo-phenols (I-phenols), including hydroxybenzaldehydes, iodinated hydroxybenzoic acids and iodinated nitrophenols (Dong et al., 2019). Though I-DBPs usually range in low concentrations levels (around ng/L to low µg/L), their occurrence has been reported worldwide (Dong et al., 2019; MacKeown et al., 2022b). Both their cytotoxic and genotoxic effects are supposed to be worse than their brominated and chlorinated analogous (Krasner et al., 2006; Yang et al., 2014), specially iodoacetic acid, the most

genotoxic, and diiodoacetamide and iodoacetamide as the most cytotoxics (Dong et al., 2019). However, still nowadays, I-DBPs are the only known group of DBPs that are not regulated in any country. One of the major concerns of those DBPs could be gaining ground when moving into upcycling water technologies, particularly the ones involving blending waters from conventional treatments and waters from desalination processes, where concentrations of iodide could be relevant to the formation of those species when reacting with incoming NOM at the time of mixing. Unfortunately, there is still little information about these emerging contaminants. Partly because of a lack of systematic measurements, mostly driven by the absence of quantification standards (MacKeown et al., 2022b; Postigo & Zonja, 2019b) as well as the need to develop analytical methods capable to reach lower detection limits (Dong et al., 2019; Postigo & Zonja, 2019b). Also, despite the knowledge about their potential toxicological activity, it is a must to obtain more conclusive studies about their human-health effects (Postigo & Zonja, 2019b) in order to push them into legislations. Overall, there is yet plenty of room to cover when it comes to understanding the fate and effects of DBPs, particularly to those of emerging concern, including the unknown DBPs, which call for new and advanced analytical techniques and collaborative research to face all the challenges associated.

For example, there is a big fraction of higher-molecular-weight, non-volatile DBPs (HMW-DBPs) that are amenable to analysis by liquid chromatography mass spectrometry (LC–MS). As such there has been a lot of recent attention onto unravelling this fraction with high resolution mass spectrometry techniques. Mitch and co-authors (2023) reviewed the recent findings on this topic. They report that over 1,000 distinct elemental formulae were discovered in chlorine-treated drinking water supplies in China (Zhang et al., 2012). In a Chinese drinking water supply that underwent chlorination, 556 chlorinated DBP features were detected. Similarly, a chlorine-disinfected Swedish drinking water contained approximately 800 DBP features that had one to three chlorine atoms (Gonsior et al., 2014), while a disinfected Spanish river water had 495 halogenated DBP features, and its associated finished drinking water had 131 halogenated features (Sanchis et al., 2022). Efforts are currently undertaken to investigate this subset of DBPs of potential health relevance.

2.2 *Occurrence and toxicity*

Table 1 shows the major DBPs, their main related disinfectants, their occurrence, cytotoxicity, genotoxicity, and carcinogenicity. As shown in Table 1, bromate, chlorite and chlorate are the major inorganic by products. The occurrence of bromate and iodate is related to ozonated bromide- and iodide-containing waters (Allard et al., 2013). Chlorate and chlorite are often found in water during oxidation by ClO_2.

Among the organic DBPs, THMs and HAAs are generally present at the highest levels (up to several hundred ppb) in chlorinated water, with chloroform generally being the dominant THM and dichloroacetic acid and trichloroacetic acid being the dominant HAAs. Other DBPs that occur at the highest levels include trichloronitromethane (chloropicrin), and trichloroacetaldehyde (chloral hydrate), while HNMs, I-THMs, iodo-acids, halo-amides, and aldehydes (including haloaldehydes) form the next tier of DBPs, which are

generally present at sub-ppb to low-ppb levels. The lowest tier included those DBPs found at low-ng/L levels, such as halofuranones (MX analogues) and N-nitrosamines (Richardson et al., 2007; Dong et al., 2023). The formation of DBPs is not limited to chlorine disinfection. For instance, all DBPs mentioned above can be formed also during chloramination.

Although more than 500 DBPs have been reported in the literature (Richardson, 1998), more than 50% of the total organic halides (TOX) formed during the chlorination of drinking water (Krasner et al., 2006) and approximately 75% of the TOX in water treated with alternative disinfectants are not identified. Furthermore, approximately 60% of the assimilable organic carbon (AOC) measured in ozonated drinking water is unaccounted for (Stevens et al., 1989).

It is to be recognized that TOX and AOC represent only a portion of the types of DBPs formed, because they do not include non-halogenated DBPs, such as formaldehyde or carboxylic acids. As a consequence, the potential toxicity of several individual and total species of DBPs is still unknown and there is much that is still not known about the DBPs formed during disinfection (Richardson et al., 2007).

Table 1. Summary of occurrence, cytotoxicity, genotoxicity, carcinogenicity of major DBPs and related disinfectants (a 1 = low ng/L; 2 = ng/L to sub-µg/L; 3 = sub- to low-µg/L; 4 = low-µg/L; 5 = low- to mid-µg/L; 6 = high µg/L; nd = non detected; nda = no data available. b y = yes; n = no; na = no applicable or no data available) (adapted, from Richardson et al., 2007; Gilca et al., 2020; Dong et al., 2023)

CLASS	BY-PRODUCT	MAIN RELATED DISINFECTANTS	OCCURRENCE [a]	CYTOTOXICITY [b] LC_{50}(M)	GENOTOXICITY [b] 50% TDNA (M)	CARCINOGENICITY [b]
Inorganic byproducts	Chlorate	Hypochlorite, chlorine dioxide	6	y	y	y
	Chlorite	Chlorine dioxide	6	na	na	n
	Bromate	Ozone, chlorine dioxide, chlorine	3	y 9.63×10^{-4}	y 7.19×10^{-3}	y
Trihalomethanes	Chloroform	Chlorine chloramines	5	y 9.62×10^{-3}	na	y
	Bromodichloromethane	Chlorine chloramines	5	y 1.15×10^{-2}	na	y
	Dibromochloromethane	Chlorine chloramines	5	Y 5.36×10^{-3}	na	y
	Bromoform	Chlorine chloramines	5	Y 3.96×10^{-3}	na	y

	Dichloroiodomethane	Chlorine, chloramines	3	y 4.13×10^{-3}	na	na
	Chlorodiiodomethane	Chlorine, chloramines	3	y 2.41×10^{-3}	y 3 2.95×10^{-3}	na
	Bromochloroiodomethane	Chlorine, chloramines	3	y 2.42×10^{-3}	na	na
	Dibromoiodomethane	Chlorine, ozone, chlorine dioxide, chloramines	3	y 1.91×10^{-3}	na	na
	Bromodiiodomethane	Chlorine, ozone, chlorine dioxide, chloramines	3	y 1.40×10^{-3}	na	na
	Iodoform	Chlorine, ozone, chlorine dioxide, chloramines	3	y 6.60×10^{-5}	na	na
Haloacetic acids	Monochloroacetic acid	Chlorine, chloramines, chlorine dioxide	3	y 8.10×10^{-4}	y 4.11×10^{-4}	n
	Dichloroacetic acid	Chlorine, chloramines, chlorine dioxide	5	y 7.30×10^{-3}	na	Y
	Trichloroacetic acid	Chlorine, chloramines, chlorine dioxide	5	y 2.40×10^{-3}	na	Y
	Bromochloroacetic acid	Chlorine, chloramines, chlorine dioxide	4	y 7.78×10^{-4}	y 3.64×10^{-3}	y
	Bromodichloroacetic acid	Chlorine, chloramines, chlorine dioxide	4	y 6.85×10^{-4}	na	y
	Dibromochloroacetic acid	Chlorine, chloramines, chlorine dioxide	4	y 2.02×10^{-4}	y 1.36×10^{-2}	y
	Monobromoacetic acid	Chlorine, chlorine dioxide, chloramines, ozone	3	y 9.60×10^{-6}	y 1.70×10^{-5}	na
	Dibromoacetic acid	Chlorine, chlorine dioxide, chloramines, ozone	5	y 5.90×10^{-4}	y 1.76×10^{-3}	na
	Tribromoacetic acid	Chlorine, chloramines, chlorine dioxide	4	y 8.50×10^{-5}	y 2.46×10^{-3}	na
	Iodoacetic acid	Ozone, chloramines, chlorine dioxide	3	y 2.95×10^{-6}	y 8.70×10^{-6}	na
	Bromoiodoacetic acid	Ozone, chloramines, chlorine dioxide	3	y 8.97×10^{-4}	y 3.16×10^{-3}	na

Haloaldehydes	Chloroacetaldehyde	Chlorine, chlorine dioxide	3	y 3.51×10^{-6}	y 1.43×10^{-4}	y
	Dichloroacetaldehyde	Chlorine, chlorine dioxide	3	y 2.92×10^{-5}	y 7.95×10^{-4}	y
	Bromochloroacetaldehyde	Ozone, chlorine, chlorine dioxide	3	y 5.34×10^{-6}	y 6.21×10^{-4}	y
	Trichloroacetaldehyde (chloral hydrate)	Chlorine, chloramines, chlorine dioxide	4	y 1.16×10^{-3}	na	y
	Tribromoacetaldehyde	Ozone, chlorine, chlorine dioxide	3	y 3.58×10^{-6}	y 3.40×10^{-4}	na
Haloacetonitriles	Trichloroacetonitrile	Chlorine, Chloramines	3	y 1.60×10^{-4}	y 1.01×10^{-3}	na
	Dichloroacetonitrile	Chlorine, Chloramines	3	y 5.73×10^{-5}	y 2.75×10^{-3}	na
	Bromochloroacetonitrile	Chlorine, Chloramines	3	y 8.46×10^{-6}	y 3.24×10^{-4}	na
	Dibromoacetonitrile	Chlorine, Chloramines, ozone	3	y 2.85×10^{-6}	y 4.71×10^{-5}	na
	Chloroacetonitrile	Chlorine, Chloramines	3	y 6.83×10^{-5}	y 6.01×10^{-4}	na
	Bromoacetonitrile	Chlorine, Chloramines, ozone	3	y 3.21×10^{-6}	y 3.85×10^{-5}	na
	Iodoacetonitrile	Chlorine, Chloramines, ozone	na	y 3.30×10^{-6}	y 3.71×10^{-5}	na
	Bromodichloroacetonitrile	Chlorine, Chloramines	3	na	na	na
	Dibromochloroacetonitrile	Chlorine, Chloramines	3	na	na	na
	Tribromoacetonitrile	Chlorine, Chloramines, ozone	3	na	na	na
Haloacetamides	Chloroacetamide	Chloramines	3	y 1.48×10^{-4}	y 1.38×10^{-3}	na
	Bromoacetamide	Chloramines	3	y 1.89×10^{-6}	y 3.68×10^{-5}	na
	Iodoacetamide	Chloramines		y 1.42×10^{-6}	y 3.41×10^{-5}	na
	Dichloroacetamide	Chloramines	3	y 1.92×10^{-3}	na	na

	Bromochloroacetamide	Chloramines	3	y 1.71×10^{-5}	y 5.83×10^{-4}	na
	Dibromoacetamide	Chloramines	3	y 1.22×10^{-5}	y 7.44×10^{-4}	na
	Bromoiodoacetamide	Chloramines	3	y 3.81×10^{-6}	y 7.21×10^{-5}	na
	Trichloroacetamide	Chloramines	3	y 2.05×10^{-3}	y 6.54×10^{-3}	na
	Bromodichloroacetamide	Chloramines	3	y 8.68×10^{-6}	y 1.46×10^{-4}	na
	Dibromochloroacetamide	Chloramines	3	y 4.75×10^{-6}	y 6.94×10^{-5}	na
	Tribromoacetamide	Chloramines	3	y 3.14×10^{-6}	y 3.25×10^{-5}	na
	Diiodoacetamide	Chloramines	na	y 6.78×10^{-7}	y 3.39×10^{-5}	na
	Chloroiodoacetamide	Chloramines	na	y 5.97×10^{-6}	y 3.02×10^{-4}	na
Nitrosamines	N-Nitrosodimethylamine (NDMA)	Chloramines, Chlorine	2	na	y 2.39×10^{-3}	y
	N-Nitrosopyrrolidine	Chloramines, Chlorine	1	na	na	y
	N-Nitrosomorpholine	Chloramines, Chlorine	1	y 1.11×10^{-2}	y 5.22×10^{-2}	y
	N-Nitrosopiperidine	Chloramines, Chlorine	1	na	na	y
	N-Nitrosodiphenylamine	Chloramines, Chlorine	1	na	na	y
Halonitromethanes	Chloronitromethane	Chlorine	2	y 5.29×10^{-4}	y 2.15×10^{-3}	Na
	Bromonitromethane	Chlorine, ozone	2	y 7.08×10^{-6}	y 1.36×10^{-4}	na
	Dichloronitromethane	Chlorine	2	y 3.73×10^{-4}	y 4.21×10^{-4}	Na
	Dibromonitromethane	Chlorine, ozone	3	y 6.09×10^{-6}	y 2.62×10^{-5}	na
	Bromochloronitromethane	Chlorine	2	y 4.05×10^{-5}	y 1.65×10^{-4}	na

	Trichloronitromethane (chloropicrin)	Chlorine	4	y 5.36×10^{-4}	y 9.34×10^{-5}	na
	Bromodichloronitromethane	Chlorine	3	y 1.32×10^{-5}	y 6.32×10^{-5}	na
	Dibromochloronitromethane	Chlorine	3	y 6.88×10^{-6}	y 1.43×10^{-4}	na
	Tribromonitromethane (bromopicrin)	Chlorine, ozone	3	Y 8.57×10^{-6}	y 6.99×10^{-5}	na
MX compounds	MX	Chlorine, chlorine dioxide	2	y 3.35×10^{-5}	na	y
Cyanogen halides	Cyanogen chloride	Chloramines	na	y 3.25×10^{-3}	na	na
	Cyanogen bromide	Chloramines, Ozone	na	y 2.09×10^{-5}	y 5.0×10^{-4}	na

As seen many DBPs are cytotoxic, neurotoxic, mutagenic, genotoxic, carcinogenic and teratogenic. In general, unregulated DBPs are more toxic than regulated DBPs. I-DBPs are more toxic than brominated analogues and those more than chlorinated DBPs. Also, it is accepted that nitrogen containing DBPs, such as HANs, are more toxic than carbon based DBPs (Richardson 2007). Indeed, cytotoxicity and genotoxicity effects of N-DBPs are reported to be worse than the regulated C-DBPs according to studies in in vitro mammalian cells (Richardson et al., 2007; Wagner & Plewa, 2017). Despite, threshold concentration values based on health effects are not yet stablished for some of the most occurrent N-DBPs (such as bromochloroacetonitrile, cyanogen chloride or trichloroacetonitrile,) mainly because of the lack of adequate data to stablish a health-based value or because concentrations in drinking water are well below those of health concern, dichloroacetonitrile has a provisional guideline value though its uncertain health effects, and only dibromoacetonitrile and NDMA have associated values that can proof evidence of their health effects (World Health Organization, 2022). However, N-DBPs still remain outside the scope of legislation. Halogenated aromatic DBPs are mostly more toxic than aliphatic ones (Liu and Zhang, 2014; Yang and Zhang, 2013). The last comprehensive review on CHO cell cytotoxicity and genotoxicity of DBPs was conducted in 2017 by Wagner and Plewa (Wagner & Plewa., 2017) who review the toxicology of over 100 DBPs using the same analytical biological platform and endpoints. The conclusion of this study was that attention should be placed on nitrogen-containing DBPs and on I-DBPs. The authors also stated that new classes of DBPs such as the haloketones and halophenolics need to be evaluated for their toxicity. In particular, the most genotoxic DBPs listed in this review are iodoacetic acid, bromoacetic acid, bromoacetonitrile, iodoacetonitrile, dibromoacetonitrile, dibromonitromethane, tribromonitromethane, trichloronitromethane, bromodichloronitromethane, bromoacetamide, iodoacetamide, diiodoacetamide, bromoiodoacetamide and

bromochloroacetamide all with values of 50% TDNA or midpoint of Tail moment of the order of 10^{-5} M or below (Wagner & Plewa, 2017). Regarding cytotoxicity, the review listed iodoacetic acid, iodoacetonitrile, chloroacetaldehyde, bromoacetamide, iodoacetamide, diiodoacetamide as the most toxic ones with a cytotoxic concentration of 10^{-7} M or below (Wagner & Plewa., 2017). Although less relevant in drinking water, NAs are also highly toxic, and in particular NDMA and N-nitrosodiethylamine (NDEA). Stalter et al (2020) investigated the mixture effects of DBPs and found that HANs, haloketones, and monohaloacetic acids contributed the most to the total effect indicating a higher health relevance of these DBP groups. Mian et al (2018) review different endpoints and proposed a prioritization of unregulated DBPs. They again presented HANs as the most important group to consider when evaluating oral, inhalation, mutagenicity, carcinogenicity, cytotoxicity and genotoxicity. Based on three criteria, including concentration level, reported frequency, and toxicity they ranked the unregulated DBPs to be prioritized as dichloroacetonitrile > trichloroacetaldehyde > trichloronitromethane > formaldehyde > trichloropropanone > dibromoacetonitrile > dichloropropanone > acetaldehyde > bromochloroacetonitrile > NDMA. Bull et al (2011) used predictive chemical tools and found that haloquinones and halo-cyclopentene and cyclohexene derivatives appeared likely to be of health concern and were predicted to have chronic lowest observed adverse effect levels in the low µg/kg day range. Finally, recent research suggests that the HMW-DBPs dominates cytotoxicity, developmental toxicity, genotoxicity and oxidative stress (Mitch et al., 2023).

3.0 FACTORS AFFECTING DBPs FORMATION

3.1 Disinfectants and related DBPs

DBP concentrations are dramatically affected by the type and dose of disinfectant, the organic precursor's (NOM) content and reactivity, concentrations of inorganic precursors (bromide and iodide) and other water quality parameter (e.g. pH and temperature). DBP speciation is also related to the different kinetics of disinfectants.

As reported in Table 1, free chlorine produces several DBP species. In general, it generates a much higher level of total organic chlorine (TOCl) and bromine (TOBr) than chloramines and chlorine dioxide in the presence of bromide (Hua and Reckhow, 2007).

Chloramines form fewer halogenated DBPs as compared to chlorine, reducing the formation of THMs and other DBPs by about 80 percent, with a few notable exceptions. However, chloramination produces higher percentage of unknown TOX (UTOX) than free chlorine. Chloramination also forms more iodoform and total organic iodine (TOI) than free chlorine in the presence of iodide (Hua and Reckhow, 2007). NDMA (N-nitrosodimethylamine) was identified to be one of the disinfection by-products formed during chloramination (Choi and Valentine, 2002; Mitch and Sedlak, 2002).

Chlorine dioxide tends to form fewer THMs than chlorine, but it also generates a higher percentage of unknown TOX (UTOX) and more iodoform and total organic iodine (TOI) than free chlorine in the presence of iodide (Hua and Reckhow, 2007). Chlorine dioxide also produces several other organic by products, such as monocarboxylic acids, aldehydes, dicarboxylic acids, aromatic acids, halogenated ketone, ketones, aromatics, as results of NOM oxidation. The main DBPs formed by ClO_2 disinfection are chlorite and chlorate. Indeed, chlorine dioxide also disproportionate in alkaline waters generating chlorite and chlorate ions. Based on a 50 to 70 percent conversion of chlorine dioxide to chlorite, the maximum dose is limited to 1.4 to 2.0 mg/L unless the chlorite is removed through subsequent treatment processes. Thus, chlorite and chlorate are found at the highest concentration of any regulated DBP (up to 1 mg/L).

Numerous organic and inorganic ozonation disinfection/oxidation DBPs have been identified. The organic by-products of ozonation contain oxygen in their chemical structure (aldehydes, ketones, carboxylic acids and ketoacids, bromoform, bromoacetic acids, bromoacetone, dibromoacetonitrile, bromoalkanes, bromopicryn and bromohydrins and iodo-organic DBPs) (Richardson et al., 1999). However, most of these organic by products are readily biodegradable. Therefore, drinking water treatment plants in which ozonation is used for disinfection and taste and odour control typically include a biological filtration step downstream of ozonation to remove the organics and avoid fouling in the distribution system. Bromate is the main DBP formed during ozonation of bromide-containing waters (von Gunten, 2003a). Ozone reacts with bromide to form hypobromite anion (OBr^-), which quickly establishes acid-base equilibrium with hypobromous acid, HOBr (pKa = 8.8). HOBr may interact with natural organic matter to

form brominated organic byproducts, including bromoform, brominated acetic acids, acetonitriles, bromopicrin, and (if ammonia is present) cyanogens bromide. However, von Gunten (2003b) noted that O_3 and HOBr react with similar functional groups and, given that the concentration of O_3 is always much higher than that of HOBr, concluded that formation of bromo-organic compounds during ozonation is likely to be of minor importance. While HOBr is stable to further attack by ozone, OBr^- is oxidized slowly, via BrO_2^-, to bromate (BrO_3^-). Song et al. (1997) suggested that bromate ion formation may be problematic in waters containing more than 0.1 mg/L bromide. Low molecular weight (LMW) compounds from NOM ozonation were also found and organic acids constitute a large fraction of newly formed AOC after ozonation. Both the individual acids and total AOC form extremely rapidly upon ozone exposure (Hammes et al., 2006).

UV irradiation alone at doses commonly used for disinfection does not generate DBPs, as only low concentrations of formaldehyde have been reported in UV-irradiated ground and surface water (Malley et al., 1995). However, the concentration and the speciation of DBPs, could be affected by UV radiation when chlorine or chloramines were used as the post-disinfectant (Magnuson et al., 2002; Gallard and von Gunten, 2002; Buchanan et al., 2005; 2006; Liu et al., 2006).

The combined use of disinfectants can also influence the levels of DBPs formed. For example, pre-ozonation can decrease the formation of trihalomethanes (THMs), haloacetic acids (HAAs) and total organic halogen (TOX) for most waters during post-chlorination. Pre-ozonation before post-disinfection with chlorine or chloramines can also dramatically increase the levels of halonitromethanes compared to chlorination or chloramination alone (Hua and Reckhow, 2007).

3.2 Organic and inorganic precursors

3.2.1 Organic precursors

Organic precursors of DBPs can be generally divided between those of natural or anthropogenic origin. The content of NOM occurring in terrestrial environments and aquatic systems is defined by withering processes that involve biomass produced by plants and animals as well as their degradation products. NOM is a complex site-specific entity whose properties are defined by contributions of several classes of compounds, including amino acids, proteins, carbohydrates, amino sugars, and carboxylic acid (Croue et al., 2000). The nature of organic DBP precursors varies with season (Singer, 1992). NOM sources can be distinguished in allochthonous (terrestrial watershed, containing high humic species, probably as a result of lignin degradation) and autochthonous, derived from biota (e.g., algae, bacteria, macrophytes) growing in the water body. The autochthonous (non humic materials) mainly consists of algolgenic organic matter (AOM), which have relatively larger nitrogen and carboxyl contents and lower aromatic C and phenolic contents. The precursor for most DBPs are thought to be humic species (mainly humic and fulvic acids), whose major reactive sites are referred as polyhydroxyphenolic acid (PHA) moieties (Reckhow et al., 1990; Korshin et al., 1997b; 1997c; 1999a; Crouè et al., 2000), however also hydrophilic fractions (i.e., nonhumic

substances) play an important role for the production of DBPs during chlorination processes (Crouè et al., 2000; Kitis et al., 2002). For instance, hydrophilic acid plus neutral fraction resulted in higher THMs yield compared with the hydrophobic one (Hwang et al., 2000) and the hydrophilic and hydrophobic neutral fractions can be DBPs precursors (Li et al., 2002).

Total organic carbon (TOC) is the most comprehensive measurement used to quantify the presence of organic matter (OM) in aquatic systems. NOM can be into operationally defined fractions such as dissolved organic carbon (DOC) and particulate organic carbon (POC). POC, which is the fraction of the TOC that is retained on a 0.45 μm filter, generally represents a minor fraction (below 10%) of the TOC.

Due to the complexity and heterogeneity of NOM, isolation and fractionation into more homogenous components has been the most common approach to study NOM properties and reactivity. The most frequently applied procedures for NOM isolation and/or fractionation are based on sorption techniques and separation (based on size) by membranes. A protocol with XAD-8 resin has been widely used to isolate humic substances (Thurman and Malcolm, 1981) and the International Humic Substance Society (IHSS) created their standards as reference samples containing the hydrophobic fraction (i.e., humic plus fulvic acids). Another fractionation approach is used, employing XAD-8 and XAD-4 resins in succession (Aiken et al., 1985; 1992), in order to extract hydrophobic, transphilic (transphilic means fraction of intermediate polarity isolated from the XAD-4 resin) and hydrophilic fractions. Size exclusion chromatography (SEC) and high pressure SEC (HPSEC) are techniques that have been typically used to determine the molecular weight (MW) and molecular weight distribution (MWD) of NOM from a variety of aquatic and terrestrial environments. Although questions have been raised about whether isolation and fractionation processes can change and alter the structure and/or reactivity of NOM components, it was demonstrated that isolation and/or fractionation procedures, using XAD-8 adsorption and UF, do not alter either the SUVA or the reactivity of DOM for DBP formation. Furthermore, aromaticity of NOM components was found to be more important than the size for predicting DBP formation (Kitis at al., 2002). Multidetector systems, such as HPSEC-UV- fluorescence-DOC have been employed to characterize NOM from different origin as well as the selection of water treatment processes (Her et al., 2003; Allpike et al., 2005). Other techniques, such as pyrolysis GC/MS, 13C-NMR, H-NMR, IR/FTIR, UV/VIS and Fluorescence spectroscopy are used to provide information about the structural characteristics of NOM components (Crouè et al., 2000).

Due to the complexity of either NOM or halogenation process, several surrogate parameters (TOC, DOC, UVA, SUVA, Fluorescence and THMFP) have been used to quantify its reactivity in halogenation reaction and DBPs formation. In general, the concentrations of DBPs increase with the concentration of NOM (usually expressed as DOC) in waters with similar conditions of halogenation process, however DOC per se is not a good parameter to predict DBPs formation. NOM absorption of both visible and UV light is widely attributed to the aromatic chromophores (light absorbing) present in NOM molecules (primarily humics) dissolved in the water. Although nitrate content in low DOC

waters may interfere with UV absorbance measurement, that interference is not present at wavelengths above 230 nm. In addition to chromophores, fluorophores (light emitting groups) are associated with the humic portion of NOM. Distinct classes of fluorophores, such as the humic-, protein- and quinine-like fluorophores, are generally discussed (Leenheer and Crouè, 2003; Cory and McKnight, 2005). Among such surrogate parameters, used to measure and characterize NOM, absorbance of ultraviolet light at 254 nm (A_{254}) and the specific value ($SUVA_{254}$), which is the ratio between A_{254} and DOC are probably the most widely used (Crouè et al., 2000; Kitis et al. 2001; 2002). The choice of such wavelength is because the absorbance at 254 nm is a measure of the overall content of activated aromatic groups in PHA moieties (Traina et al., 1990; Korshin et al., 1996; Crouè et al., 2000). In particular, $SUVA_{254}$ has been widely used because it allows the comparison of different water sources in terms of reactivity for DBPs formation, usually measured as THMs Formation Potential (THMFP) (APHA, 1998) or uniform formation condition protocol (UFC) (Summers et al., 1996). Although $SUVA_{254}$ is the most surrogate parameter used for predicting NOM reactivity, SUVA measurements can be influenced by the pH, nitrate, and iron and more generally questions are raised about the strength of SUVA as indicator of DOC reactivity (Weishaar et al., 2003). Furthermore, the absorbance at 280 nm was also introduced because π-π* electron transition occurs in this UV region (ca. 270– 280 nm) for phenolic substances, aniline derivatives, benzoic acids, polyenes and polycyclic aromatic hydrocarbons with two or more rings (Traina et al., 1990). Strong relationships between the molar absorbance of organic carbon at 280 nm (ε_{280}) and, on the other hand, the aromaticity of NOM and its apparent number- and weight-averaged molecular weight have been found (Chin et al., 1994; Croué et al., 2000; Peuravuori et al., 1997; 2004; 2005). Absorbances UV at both 254 and 272 nm were well correlated with aromaticity, which is the percentage of the total carbon contained in aromatic subgroups (Traina et al., 1990; Chin et al., 1994; Peuravuori and Pihlaja, 1997; Wu et al., 2000). Differential absorbance at wavelengths near 272 nm (ΔA_{272}), corresponding to the peak of differential absorbance, were used because it showed a strong correlation with TOX and concentrations of individual DBPs during chlorination or chloramination (Korshin et al., 1997a; 2002; Roccaro et al., 2008; Yan et al., 2018; Zhang et al., 2021). Relationships between fluorescence and NOM properties were also reported (Crouè et al., 2000; McKnight et al., 2001). Fluorescence excitation-emission matrices (EEM) of isolated fulvic acids revealed two fluorophores, which are related to the allochtonous or autochtonous sources. Based on this evidence a fluorescence index, which is the ratio of the emission intensity at 450 nm to 500 nm (I_{450}/I_{500}), obtained with an excitation of 370 nm, was developed. This index can serve to distinguish the sources of aquatic humic acids (microbially and terrestrially derived) and was well correlated with the aromaticity of fulvic acids. In particular, an inverse relationship between the fluorescence ratio and, on the other hand, aromaticity and molecular weights, was reported (McKnight et al., 2001; Schwede-Thomas et al., 2005). Furthermore, quinones moieties were found to contribute significantly to the fluorescence of humics (Klapper et al., 2002; Cory and McKnight, 2005). It was also observed a pH dependent intensity peak for terrestrially derived DOM samples and humic materials extracted from soils, probably caused by a combination of protonation/deprotonation of active fluorophores, solvent effects, or metal interactions (Cabaniss, 1992; Pullin and Cabaniss, 1995; Mobed et al., 1996). Roccaro et al. (2009) demonstrated that selected fluorescence indices can be

used as surrogates to predict and monitor DBPs formation during chlorination of natural waters. Furthermore, fluorescence indexes have been also used to predict/model/monitor the removal and fate of other trace emerging organic contaminants during different water treatment processes and from laboratory to full scale (Anumol et al.,2015; Sgroi et al., 2017; 2021; Roccaro et al.,2020). Fluorescence signals and related changes can be recorded by using Peak-picking method, Fluorescence regional integration (FRI), or PARAFAC analysis. The latter is a mathematical model for deconvolution of the excitation/emission spectrum signals into 3-7 main components that can give more information on the main fluorophores present but does not necessarily add information useful for the operation of the drinking water treatment plant (DWTP).

Finally, high resolution mass spectrometry (MS), nuclear magnetic resonance mass spectrometry (NMR) (Hertkorn, Harir et al. 2013), Fourier transform infrared spectroscopy (FTIR) (Minor, Swenson et al. 2014) and Fourier transform ion cyclotron resonance (FTICR-MS) (Kellerman, Dittmar et al. 2014, Riedel, Zark et al. 2016) have been employed to investigate dissolved organic matter. While SUVA and EEM are still non-specific bulk methods, advances in MS technology have allowed resolution of individual formulas for dissolved organic matter which is one of the most heterogeneous mixtures in the environment (Woods, Simpson et al. 2010). Orbitrap-MS, which is more accessible as a routine laboratory instrument, has also proven suitable to characterize dissolved organic matter (Hawkes, Dittmar et al. 2016), plus it has the possibility to be coupled to a chromatographic system to enhance performance.

3.2.2 Inorganic precursors

While DBP formation of organic DBPs is related to the presence of dissolved organic matter, the inorganic composition of the disinfected water rules the speciation of DBPs (Krasner 2009). For example, bromide and iodide ions, whose sources could be sea water intrusion in coastal areas or salt deposits from ancient seas in inland areas, affect the speciation of DBPs formed during chlorination processes. Bromide is rapidly oxidized to hypobromous acid (HOBr) by free chlorine, and HOBr reacts with NOM in either substitution or oxidation reactions. The substitution and oxidation reaction of HOBr reacts more rapidly in substitution reaction and more slowly in oxidation reaction, compared with HOCl or OCl^- (Korshin et al., 2004; Westerhoff et al., 2004). Furthermore, previous studies reported the considerably higher (up to 10 times) kinetic activity of bromine than chlorine in reactions with NOM (Cowman and Singer, 1996; Nokes et al., 1999; Westerhoff et al., 2004). Alternatively, HOCl oxidised iodide to iodate which is the desired sink. Nevertheless, chloramines are not as powerful oxidants and convert iodide into HOI which then reacts with organic matter to generate I-DBPs (Bichsel 2000). As a consequence, the presence in water of bromide and iodide, which is expected to be more reactive than bromine, change the speciation of DBPs. Moreover, since the atomic mass of bromine (80) and iodine (127) are higher than chlorine (35.5), the occurrence of bromide and iodide in waters results in much higher total halogenated species, other than in much toxic compounds.

Ozone forms bromate in the presence of bromide in water and generates intermediates for DBP formation upon a final disinfection such as trichloronitromethane.

3.3 Operating parameters

3.3.1 Disinfectant dose

Increase in chlorine dose has been reported to enhance the formation of chlorinated species of organic DBPs (THMs and HAAs). Moreover, higher chlorine dose and residual favour the formation of haloacetic acids (HAAs) over THMs (Krasner, 1999).

It is to highlight the importance of Cl_2 to DOC ratio (Korshin et al., 2004). For instance, at fixed Cl_2 concentration, THMs increase with increasing DOC only if Cl_2 free residual is present. The fact that THMs decrease, with increasing DOC to Cl_2 ratios (Adin et al., 1991), is the evidence of the formation of chlorinated intermediates species which are rapidly produced but have not released THMs. On the other hand, different Cl_2 to DOC ratio results in different HAAs speciation, ranging from the mono-halogenated HAAs to the tri-halogenated ones. Relationship between Cl_2 concentration and DBPs formation is not well reported, probably due to the complexity of the chlorine decay, which is linked to several processes, mainly i) oxidation of NOM sites which are reactive for DBPs formation, ii) incorporation into NOM molecules and iii) oxidation of NOM sites which are not reactive for DBPs formation.

Similar to chlorination, the increasing dose of other disinfectants/oxidants such as chloramine, chlorine dioxide, and ozone results in higher DBPs formation.

3.3.2 Reaction time

Reaction time has a different effect on different categories of DBPs. This is due to the series of reactions which take place during NOM halogenation in chlorinated water. Some DBPs (such as, chloroform and chloral hydrate) are end products of NOM chlorination while other species are intermediates products (Korshin et al., 2000; 2007). As a results THMs and HAAs increase with time, while other intermediates species, such as dichloroacetonitrile and dichloropropanone typically decrease with the extent of reaction. In contrast, the concentrations of some DBPs, such as trichloropropanone, decrease due to hydrolysis reactions, resulting in the formation of other DBPs, such as THMs, while other processes other than hydrolysis (photooxidation, reductive halogenation, strongly reductive conditions, biological degradation and dehalogenation) may lead to a decrease of DBPs concentrations (Xie, 2004). Overall, the higher the reaction time the higher the level of many regulated DBPs.

3.3.3 pH

The effect of pH on DBPs formation is more complex. In general, higher pH results in higher THMs formation and lower HAAs and TOX formation. The effect of pH on DBPs yields and speciation is also related to the increase of hydrolysis reactions with increasing

of pH. As a consequence, some DBPs that undergo hydrolysis reactions, result in lower concentration at higher pH, while some species, which are hydrolysis products, such as THMs, are more abundant at higher pH (Xie et al., 2004). Moreover, low acidic pH should be ensured when applying ClO_2 to minimize its decomposition into chlorate.

Changing pH solution affects the chlorine speciation, because at low pH the dominant specie is HClO, which is a more efficient disinfectant than ClO^-, which is dominant at high pH. Chlorine dioxide has almost the same disinfectant properties as chlorine but the pH-dependency is much less significant (almost none at the pH range 6-10).

Variations on pH might also impact efficiencies of oxidative processes such as ozonation. Increasing pH dramatically increases ozone decay via the conversion of two molecules of ozone and one hydroxide ion into two molecules of oxygen and two free radicals. Hence, oxidation of NOM reactive moieties will be diminished.

3.3.4 Temperature

Generally, DBPs formation tends to increase with increasing temperature due to the faster kinetics, unless a further degradation/transformation takes place (Singer, 1992). For instance, since also hydrolysis reactions are also faster at higher temperature, the result is an overall increase of rates of DBPs formation and decomposition, which leads to higher concentration of end products, such as THMs. In many cases, considerable short- and long-term variations of water temperature exist; they lead to pronounced variability of DBPs concentrations in drinking water (El-Shafy and Grunwald, 2000; Serodes et al., 2003; Toroz and Uyak, 2005).

Variations in THMs and HAAs concentrations are not only important on a seasonal basis but also in the short term (intra-seasonal variations). This is mostly associated with the variations of raw and treated water quality as well as variations in operational parameters concerning chlorination (Rodriguez et al., 2004). Rates of decay of chlorine and chloramine also increase at higher temperatures (Vikesland et al., 2001). As a consequence, more chlorine needs to be added during warmer seasons to ensure the presence of acceptable levels of residual disinfectant in a distribution system. DBPs control becomes challenging in these conditions.

3.3.5 Ammonia

The presence of ammonia affects the formation of DBPs. In aqueous media, hypochlorous acid will react with ammonia and form mono-, di- and tri-chloramines, whose speciation is chlorine vs nitrogen ratio and pH dependent. The main concern associated with chloramination is nitrification in case of an excess of NH_4^+, that will promote the growth of nitrification bacteria and consequently enhancing nitrite and nitrate release (Wilczak et al., 1996).

The presence of ammonia also affects ozonation of water (von Gunten, 2003). Indeed, ammonia and hydrogen peroxide have been widely used to inhibit bromate formation during ozonation (Wu et al., 2020). The best bromate minimization strategies appear to be lowering of the pH or ammonia addition. Once formed, bromate removal is non-economical.

4.0 DBPs REMOVAL

4.1 Bromate

Removal of bromate via conventional treatments is hindered by its higher solubility and stability in water. Thus, preventing its formation is of paramount importance to reduce costs. Bromide is the main precursor of bromate in ozonation processes. Its concentration in waters can be widely variable (ranging from 10 to 1000 μg/L) but become of special concern when reaching > 50 μg/L (Von Gunten, 2003; Jahan et al., 2021).

A physical strategy to successfully decrease bromide and bromate is using membrane filtration technologies, such as reverse osmosis or nanofiltration, which can reach up to 79% to 100% of removal (Jahan et al., 2021). However, it is usually economically unfeasible to implement due to its elevated operating costs (energy, remineralization, managing waste stream, etc.). On the other hand, chemical methods such as coagulation with Al(III) or Fe(III) salts, sulphite, chitosan, or ruthenium oxide lead to ineffective removal percentages (5 to 20%), and require a narrow operational window (low pH and high temperature conditions) which disqualifies them as appropriate procedures. Overall, biological approaches have already been proved as great technologies for removing biodegradable organic contaminants and also lead to successful elimination of bromate (up to undetectable levels) (Jahan et al., 2021; von Gunten, 2003) thanks to its reductive surface activated through microbiological action. Also, they present the advantage of not requiring other chemical reagents neither extra energy supplies, apart from controlling biofilm formation to avoid a loss in efficiency.

Moreover, controlling the ozonation process is important to minimize final concentrations of bromate. Ammonia and peroxide hydroxide had been reported as inhibitors of bromate during ozonation due to their blockage effect on precursor radicals during initial stages (Lim et al., 2022; Wu et al., 2020). Nevertheless, as a counter effect, concentration of other organic DBPs might be enhanced when adding ammonia, such as brominated nitromethanes, acetamides, haloacetamides or nitrosamines, thus contributing to an increase of final cyto- and genotoxicity. In the case of H_2O_2, THMs and HAAs are more prone to be originated, however presenting a lowest impact on overall toxicity (Wu et al., 2020). From the literature bromate formation is influenced by pH, temperature, alkalinity, applied ozone dose, influent bromide concentration, ammonia dose and other ozone scavengers (i.e., DOC). However, while minimizing the bromide concentration and decreasing the dose of applied ozone certainly decreases bromate formation, the impact of pH, alkalinity, ammonia, H_2O_2 and other ozone scavengers (e.g., DOC) needs more research (Jahan et al., 2021). Generally lowering pH is effective for minimizing bromate removal by i) shifting the equilibrium of hypobromous acid and hypobromite, and ii) reducing the degradation of ozone to hydroxyl radical through the hydroxide ion pathway. However, in the presence of hydroxylamine, pH depression was found to enhance bromate formation because pH depression acts as a catalyst to form bromine radical from the reaction of bromide and hydroxyl radical (Yang et al., 2017). Also, pH depression slows down the ozone decomposition, permitting a higher level of ozone exposure which is positively correlated to the formed bromate (Yang et al., 2019).

4.2 Chlorite and chlorate

The reduction of chlorite generated mainly by chlorine dioxide during pre-oxidation or intermediate oxidation, can be accomplished by several alternative processes: i) addition of reducing compounds, such as sulfur dioxide and sodium sulfite; ii) addition of salts, such as ferrous chloride and ferrous sulfate; iii) application of powdered (PAC) or granular (GAC) activated carbon.

One of the most efficient strategies for chlorite removal is by means of GAC filtration, under optimum operating conditions. Indeed, ClO_2^- is reduced to ClO^- by GAC, especially at acidic pH (pH5), while ClO_3^- is not reduced by GAC and is mostly adsorbed on GAC (Gonce and Voudrias, 1994). Furthermore, mineral carbons offer higher removal efficiency for chlorite than vegetal carbons and this is probably because mineral carbon chlorite can be removed by both a surface reduction and an adsorption process (as chlorite can be adsorbed better on mesoporous carbon) while with vegetal carbons chlorite is removed mainly with a reducing process. Finally, an EBCT of 15-20 minutes is required for efficient chlorite removal (Sorlini and Collivignarelli, 2007).

Another process for chlorite removal is the addition of ferrous iron in drinking water. Chlorite cannot be removed by the conventional coagulation process using aluminium sulphate, but dosing micromolar-level ferrous iron (Fe(II)) into aluminium-based coagulants effectively the ClO_2^- can be eliminated (Cassol et al., 2022). This technique offers very good results as a complete chlorite removal can be obtained very fast (3-5 seconds), in pH range of 5 to 7, with a stoichiometric dose of ferrous iron. This technique is very simple to apply for its low investment and operation costs.

Finally, other additional strategies have been studied in the literature by many authors, such as chlorite removal via oxidation by chlorine or ozone, but they are not of practical interest for application on real scale treatment plants and also because such oxidation processes produce chlorate (Sorlini and Collivignarelli, 2007).

4.3 THMs, HAAs and other halogenated organic DBPs

GAC columns can remove many volatile and non-volatile organics from water, with a better removal of HAAs than THMs. However, desorption phenomena, especially of weakly adsorbing THMs, often occur after saturation and must be considered in the design and use of GAC systems (Babi and Makry, 2007). GAC filters can also remove MX-analogues via adsorption and/or biodegradation (Weinberg et al., 2002).

PAC adsorption is less efficient than GAC adsorption for the removal of THMs, HAAs and other DBPS. The main advantage of PAC use is the low capital cost and the flexibility of application that is the ability to change its dose as the water quality changes.

Biodegradation in GAC beds colonized by bacteria, so called biological activated carbon (BAC), with or without the use of pre-ozonation of the influent water, is also effective for the removal of HAAs and other biodegradable organics, but not for the removal of the non-biodegradable THMs (Babi and Makri, 2007).

The most effective and economical process for the removal of HAAs is biological filtration (Liu et al., 2017). Table 2 reports a summary of the results on the removal of HAAs by

biological processes obtained in different pilot or full-scale studies. However, the use of adsorbent materials such as GAC in biological filters also allows for the removal of HAAs by adsorption. Generally, after the adsorption capacity is exhausted, biodegradation becomes dominant (BAC process is operated). BAC has the advantage that does not require replacement of GAC and of effectively removing various biodegradable compounds, including taste and odor, and various organic compounds including HAAs and their precursors.

Membranes do not efficiently remove HAAs, even reverse osmosis is not always effective (Wang et al., 2018).

Table 2. Removal of HAA by biofiltration

SCALE	EXPERIMENTASL CONDITIONS	REMOVAL	REFERENCES
LAB.	BAC	~100%	Xie and Zhou, 2002
LAB.	Two stages biofiltration	~28%	Fu et al., 2017
PILOT	Biofiltration/adsorption on GAC	>80%	Wobma et al., 2000
PILOT	GAC (EBCT = 20 min.)	>80%	Xie and Zhou, 2002
PILOT	GAC (EBCT from 5 to 20 min. and T from 4 to 30 °C)	Increasing with EBCT o T (>50% for T=4°C and EBCT>10 min. or T>10°C and EBCT>5 min.)	Wu and Xie, 2005
PILOT	Rapid GAC filter.	>90%	Kim and Kang, 2008
PILOT	BAC (EBCT from 10 - to 60 min.)	88%	Lou et al., 2014
FULL	DBPs monitoring at 5 WTPs with advanced treatment process (ozone)	~50% (ozone effect negligible)	Zeng et al., 2016
FULL	5 WTPs in USA	~70%	Arora et al, 1997

Several innovative processes have been reported in the literature for the removal of HAAs and their precursors. Among these are adsorption on adsorbent nanomaterials, advanced oxidation processes (AOPs), non-thermal plasma processes (Srivastav et al., 2020), photolysis and photocatalysis (Wang et al., 2020), electrochemical reductive processes (Korshin and Jensen, 2001; Zhao et al., 2014) and combined processes such as ion exchange followed by electrodialysis (Yin et al., 2020). However, some of the above processes have been studied primarily for tertiary wastewater treatment because they also allow for the removal of other trace organic compounds. Furthermore, the results obtained are often conflicting and the technical-economic feasibility has not been evaluated. Since these are processes that have high costs or technological application

limitations, further studies are needed in order to evaluate their effectiveness, efficiency and cost-effectiveness.

Air stripping is an effective treatment method for the removal of volatile DBPs, such as THMs, especially chloroform. However, it can require from 30 minutes to several hours of air stripping (Babi and Makri, 2007; Belgiorno et al., 2007). Therefore, it could be too much expensive. Furthermore, air stripping cannot be employed to remove other non-volatile DBPs, such as HAAs.

4.4 NDMA

NDMA removal is very challenging. For instance, in full-scale RO plants NDMA rejections lower than 60% have been observed, while much higher NDMA precursors removal (ca 90%) was reported. The most effective technology to remove NDMA is photolysis but high doses of UV irradiation (up to 1000 mJ/cm^2) are required (Sgroi et al., 2015; Plumlee et al., 2008). UV/H_2O_2 Advanced Oxidation Process (AOP) is also effective because OH radical can degrade NDMA (Ho et al., 1996) but direct photolysis of NDMA is more efficient (Stefan and Bolton, 2002). Furthermore, in some case UV/H_2O_2 may form NDMA if some precursor such as DMF is present (Sgroi et al., 2015). Although UV treatment can effectively remove NDMA, there is considerable interest in the development of less expensive alternative treatment technologies. These alternative technologies include in situ bioremediation (activated sludgy, biological treatment-fluid bed reactor, biofiltration or biological activated carbon) (Sgroi et al., 2018).

5.0 PRECURSORS REMOVAL

5.1 Biodegradation

Biological filtration is a process in which an otherwise conventional granular filter is designed to remove not only fine particulates but also dissolved organic matters (e.g., DBP precursors) through microbially mediated degradation. DOM is utilized by the filter bacteria as a substrate for cell maintenance, growth, and replication. The biological filtration process is cost effective, since the bacteria are naturally present in the water supply, can colonize existing filter media, do not produce a residual that needs disposal, and require almost no modification of ambient conditions. The only prerequisite for maximizing bacterial substrate utilization in filters is the absence of disinfectant in the filter influent or backwash water. The filter media colonized by bacteria can be sand, anthracite, or GAC (referred as biological activated carbon, BAC). Since the relatively lower proportion of biodegradable fractions in NOM (biodegradable DOC/DOC = 0.1–0.3) (Escobar & Randall, 2001), the single biological filtration process may not well play the biodegradation function. Fu and co-authors (2022) reviewed the removal of DBP precursors by biological activated carbon process, generally employed after ozonation. This is a mature technology widely used to control the DBP levels in many DWTPs and some sewage treatment plants for potable reuse. In particular, biological activated carbon process can effectively decrease the formation potential of nitrogen containing DBPs, which are considered to be more toxic than the carbonaceous DBPs (Bond et al., 2011). Liu and co-authors (2017) also reviewed more than 100 papers on this topic and found that biofiltration can remove a fraction of the precursors of halogenated DBPs (THMs, HAAs, HKs, HAs, HANs, HAMs, and HNMs), while also demonstrating capability in removing bromate and halogenated DBPs, except for THMs. However, the effectiveness of biofiltration mediated removal of nitrosamine and its precursors appears to be variable.

5.2 Adsorption

Adsorption is the most basic and commonly used method employed in water purification (Gusain & Kumar, 2021). Activated carbon (AC) is a highly porous, effective adsorbent widely used for drinking water treatment for colour, odour, taste and organic contaminants including NOM removal. The AC serving as adsorbent can be categorized into cylindrical AC, granular AC (GAC), powder AC (PAC) and AC fibre in terms of their shape and appearance. AC very actively removes aromatic NOM molecules, which are precursors for THMs and HAAs (Ding et al., 2019).

The effectiveness for precursor removal is dependent on a number of design issues such as carbon type, filter location, filter depth, filter flow rate, and blending choices. It is also dependent on a number of water quality parameters such as initial precursor concentration, precursor adsorbability, precursor adsorption kinetics, temperature, dissolved oxygen levels, pH, and bromide concentration. GAC is used in columns or beds that permit higher adsorptive capacities to be achieved and easier process control than is possible with powdered activated carbon (PAC) that can be use seasonally or intermittently. The higher cost for GAC often can be offset by better efficiency, especially when organics must be removed on a continuous basis (Rizzo et al., 2007). Overall, the

reactivity of carbon surfaces to DOM and NOM uptake depended on the raw material type, activation conditions and surface treatment (Karanfil et al., 1999). A comparison of molecular weight distributions of organic polyelectrolytes demonstrated that small molecular size components are adsorbed preferentially, suggesting that it may be a rather general feature of the adsorption of polyelectrolyte mixtures from solution by activated carbon (Kilduff et al., 1996). On a mass basis, iron-impregnated (HDFe) and ammonia-treated (HDN) activated carbons showed significantly higher DOM uptakes than the virgin GAC, suggesting that GACs with higher mesoporosity and iron contents are expected to exhibit higher DOM uptakes from raw and treated waters (Cheng et al., 2005). However, it is critical to have both a proper carbon surface chemistry and pore size distribution for the enhanced adsorption of DOM by activated carbons (Dastgheib et al., 2004). Furthermore, iron oxide coated pumice may also be effective in controlling the formation of disinfection by-products in drinking water treatment, due to preferential removal of high UV-absorbing NOM fractions (Kitis et al., 2007).

However, AC moderately and even poorly removes DON and TDN in water, thereby leading to a high ratio of DON to DOC in the AC-treated water, which may increase the ratios of N-DBPs to C-DBPs during the subsequent chlorination and chloramination (Chiu et al., 2012). Also, another issue both in adsorption and biodegradation in adsorption with activated carbon is the increase on Br/TOC ratio increase which is responsible for a relative increase bromine containing DBPs after treatment. Similarly, iodide is not well removed by activated carbon, so I-DBP formation can also increase upon final disinfection. To solve this issue impregnated activated carbon can be used. Studies on bromide and/or iodide removal using adsorption techniques (Layered double hydroxides, silver impregnated activated carbons, carbon aerogels, ion-exchange resins, aluminium coagulation, and soils) showed varied results, with the primary limitation being interference from competing anions and NOM causing lowering of halide adsorption. Despite this limitation, adsorptive techniques continue to be a promising area of research due to the relatively low cost and ease of application of these technologies (Watson et al., 2012).

DOM is partially ionized at neutral pH conditions due to the presence of acidic (e.g. carboxyl) functional groups. Therefore, its removal by anion exchange resins through ionic group attachment is feasible. Moreover, the ion exchange resins can be regenerated efficiently on-site making ion exchange a cost-effective alternative or addition to conventional treatment facilities. Compared to conventional treatment processes that remove DOM based on its hydrophobicity (e.g. coagulation, carbon adsorption), ion exchange removes DOM through a different mechanism (Tan et al., 2005). For example, enhanced coagulation with MIEX was found to be more effective for removing trihalomethane (THM) and haloacetic acid (HAA) precursors from nine waters compared to alum coagulation alone (Singer and Bilyk, 2002). Therefore, it has the potential to remove NOM components resistant to removal by conventional treatment processes, such as more charged and hydrophilic components, which can make significant contributions to DBP formation during chlorination. The removal efficiency of ion exchange is determined by several resin characteristics. For instance, Boyer and Singer (2008) have reported that polyacrylic resins remove fulvic acids better than

polystyrene resins, hypothesizing that the mechanism of removal is based on size exclusion.

5.3 Separation

5.3.1 Filtration and coagulation

Sand filtration (rapid and slow) as well as microfiltration are unable to decrease the DOM to those levels that will prevent DBP formation below the set standard limit (Tak & Vellanki, 2018). Enhanced coagulation for surface water systems using conventional treatment, GAC adsorption and membrane filtration were suggested by U.S. EPA (1999a) to remove the precursors for DBPs.

The most common technique employed for the removal of DOM from water treatment systems is coagulation-flocculation followed by clarification (sedimentation or flotation), filtration and disinfection. Enhanced coagulation typically refers to the process of improving the removal of disinfection byproduct (DBP) precursors in a conventional water treatment plant. U.S. EPA (1999c) has developed a TOC-based performance standard for enhanced coagulation and enhanced precipitative softening, described in the section dealing with the regulatory context. It has long been recognized that NOM can be partially removed from solution by coagulation with alum or ferric based coagulants. $FeCl_3$ is usually better in removing NOM than alum. The dominating mechanism in water treatment conditions is usually the sorption of NOM onto the precipitated metal hydroxides. However, these conventional treatment processes preferably remove high molecular weight hydrophobic fractions of NOM, and therefore, considerable concentration of DBP precursors still exists in the effluent. Moreover, with the improvement of water quality standards and the increased fluctuation in source water quality, conventional coagulation becomes challenging. In this sense, enhanced coagulation involving three types of coagulants (metal-based coagulants, organic polymers, and organic-inorganic hybrid coagulants) has become more relevant to reduce DBP precursors. Wang et al., (2021) reviewed the literature and found that metal-based coagulants could achieve a reduction in DBP formation potential of approximately 20%–60% in natural water under enhanced coagulation conditions. Both the organic polymers (used as coagulant aids) and novel hybrid coagulants increase the removal of DOM and exhibit high potential for mitigating DBP formation. One specific aspect that needs to be mentioned is the increase of NAs, specifically NDMA, when using quaternary ammonium polymer coagulants such as polydadmac (Padhye et al., 2011).

5.3.2 Membrane processes

Other techniques used to separate DOM are reverse osmosis, nanofiltration and electrodialysis membranes. Although energetically demanding, these techniques offer the advantage to not only remove DOM but also inorganic ions such as bromide and iodide from water at different degrees (Watson et al., 2012). However, nanofiltration could influence the speciation of DBPs in the downstream disinfection. Similar to AC treatment, which can increase the molar ratio of Br-DBPs to Cl-DBPs in its permeate, even if chlorination of nanofiltered waters produced lower DBPs (Ding et al., 2019). Indeed, many NF membranes exhibit high rejection for NOM, in part due to size exclusion, and

in part because many NF membranes carry a negative charge, which repels the negative charge on NOM functional groups. NOM removal using NF and related membrane processes is an effective strategy to reduce the formation of disinfection by-products, including trihalomethanes and haloacetic acids. However, bromide is rejected much less efficiently than NOM, increasing the Br/DOC ratio in NF permeate, which can shift disinfection by-product speciation to more brominated species. Flux decline caused by natural water foulants may result from concentration polarization, from pore blockage by solute adsorbed on the membrane surface or within pores, and from the formation of a cake layer on the membrane surface, which presents a resistance to flow in addition to the membrane itself. Flux decline can be mitigated by controlling recovery, through careful choice of membrane material, through improved pre-treatment, and by optimizing hydrodynamics to improve mass transfer properties (Kilduff, 2007). The major drawback of NOM removal by membrane process is the fouling due to NOM itself. Although such fouling is well documented, the fouling mechanism is incompletely understood. Methods that have been used to reduce NOM fouling include frequent backwashing and application of advanced pre-treatment processes. Fouling can also be reduced by adding adsorbent particles that remove the foulants upstream of or directly in the membrane system. Therefore, integrated adsorption/membrane processes, using different adsorbents, are under investigation as a promising technology for drinking water treatment (Zhang et al., 2003; Li et al., 2004). Some studies indicate that resins are most efficient in removing more aromatic DOM with high molecular weight, while some researchers report the opposite. The lack of consensus in the literature suggests that more research is needed into the role of secondary removal mechanisms such as entropy-assisted adsorption, and the role of competition for ion exchange sites from inorganic ions such as sulphate (Tan et al., 2007).

Electrodialysis Reversal (EDR) uses direct current (DC) power as a driving force to transfer ionic species from source water through cathode (positively charged ions) and anode (negatively charged ions) to a concentrate stream, creating a more dilute stream. EDR is a variation of the electrodialysis process, that uses electrode polarity reversal to automatically clean membrane surfaces. EDR works the same way as electrodialysis, except that the polarity of the DC power is reversed two to four times per hour. When the polarity is reversed, the source water dilute and concentrate compartments are also reversed and so are the chemical reactions at the electrodes. At the negative electrode, reactions produce hydrogen gas and hydroxide ions.

Hydroxide raises the pH of the water, causing calcium carbonate ($CaCO_3$) precipitation. At the positive electrode, reactions produce acid, oxygen, and some chlorine. The acid tends to dissolve any calcium carbonate present to inhibit scaling. Cell pairs form the basic building blocks of an EDR membrane stack. A cell pair consists of the following:

- Anion permeable membrane
- Concentrate spacer
- Cation permeable membrane
- Dilute stream spacer

The number of cell pairs necessary to achieve a given product water quality is primarily determined by the source water quality. The alternating exposure of membrane surfaces

to the product dilute and brine concentrate streams provides a self-cleaning capability that enables purification and recovery of up to 94% of source water, reducing the burden on water sources, and minimizing the volume of waste that requires disposal.

Over the past forty years EDR has earned a reputation as a membrane desalination process that works economically and reliably on surface water supplies when designed and operated properly.

Typically, maximum salt removal for any hydraulic stage is 55–60%with normal design values at 40–50%. To increase the amount of salt removal in a EDR system, additional hydraulic stages must be incorporated. In systems where high capacities are required, additional hydraulic stages are made by simply adding more stacks in series to achieve the desired water purity.

To increase water recovery some functions can be incorporated into the EDR system to take advantage of a substantial increase in recovery and production rates at minimal costs. In this sense, three main flows are recycled: concentrate stream, off-specification product and electrode stream. With those products water can be recycled back to the system feed, eliminating the need to send it to waste. To achieve this water recovery, it could be necessary to dose some chemical into the system. In this sense, an antiscalant (1–5 mg/L) can be added into the concentrate stream to control calcium scaling, and acid (HCl) is continuously feed into the electrode flow and into the concentrate stream to maintain the Langelier Saturation Index (LSI) at +1.8 for calcium carbonate control.

In addition, EDR membranes can operate on waters with up to 0.5 mg/L chlorine to control the biological nature of feed water, and can also be shock-chlorinated up to 30 mg/L for maximum cleaning efficiency if required.

5.4 *Pre-Oxidation*

Li and co-authors (2023) investigated different oxidative treatments of NOM and its impact on DBP formation in post-chlorination. In particular they reviewed the effect of O_3, Fe(VI), Mn(VII), and ClO_2 as pre-oxidants during drinking water treatment and investigated the change on bulk properties (e.g., total organic carbon, ultraviolet absorbance), fractional constituent (e.g., molecular size, hydrophilicity/hydrophobicity), and elemental composition (e.g., functional group). The selected oxidants are selectively reactive toward electron-rich moieties in NOM (e.g., phenols, amines, and olefins) and can for example decreased hydrophobicity but increased hydrophilicity (Yang et al., 2013, Swietlik et al., 2004, Yang et al., 2015). In general, the formation of DBPs in post-chlorination is reduced after the pre-oxidation of NOM by selective oxidants, although several of them (e.g., HNMs, CH, and HKs) often increased via direct generation from the oxidation of reactive NOM precursors. There is a growing interest in advanced oxidation processes as pre-oxidant, however, they are not yet fully mineralizing the NOM (Matilainen & Sillanpää, 2010). Hence, combination of pre-oxidation with coagulation has shown to remarkably enhance the removal efficiency of NOM precursors and DBP formation potentials (Gerrity et al., 2009; Liu et al., 2012a; Cui et al., 2020).

6.0 ALTERNATIVE DISINFECTION

The goal of water facilities during disinfection is to enhance inactivation of waterborne pathogens in order to ensure water safety without the expenses of increasing toxicity through DBPs generation. Switching in alternative disinfectants as well as optimising the position of disinfection points along the treatment train can turn onto a successful praxis to accomplish this main objective. As far as DBP generation would be influenced by both organic and inorganic precursors, pre-oxidation processes capable of reducing those agents could result in a final decrease of the undesired compounds. However, finding a suitable methodology would depend on balancing several factors such as raw water characteristics and operational conditions (Li et al., 2023; Gilca et al., 2020).

Replacing initial chlorination with a pre-oxidation with some alternative disinfectants like chlorine dioxide (ClO_2), ferrate (Fe (VI)), ozonation (O_3) or permanganate (Mn (VII)) could help reduce DBP precursors and subsequent DBP generation in a final disinfection step. Thus, chlorination can be delayed after operations prone to remove hydrophobic high molecular weight NOM fractions (main precursors) including coagulation, filtration and / or sedimentation. Implementing such measures could lead to a substantial reduction of DBPs, specially THMs and HAAs, upcoming to more than 50% (Rougé et al., 2020). This way, a secondary disinfection can be added at the final points to ensure a stable residual dosage able to maintain controlled levels of pathogenic microbes in the distribution system without exceeding permitted levels of DBPs.

6.1 Pre-oxidation

The key of pre-oxidative treatments is promoting a reduction of test and odour, contaminants of concern, DBP precursors, changing NOM reactivity and as a knock-on effect it can enhance subsequent coagulation efficiency and mitigate DBP formation. In fact, selection of an appropriate pre-oxidant for drinking water facilities should be assessed carefully considering raw characteristics. Upon the most common oxidants O_3, ClO_2, Mn(VII), and Fe(VI) can selectively react towards electron rich moieties in NOM (phenols, amines and olefins) minimizing their forthcoming reactivity to form DBPs (Li et al., 2023; Glica et al., 2020). A brief summary of main advantages and disadvantages of most popular pre-oxidation methods is presented in

Table *3*. Derivative changes on NOM properties can be reflected on DOC concentrations, spectroscopical intensities (UV absorbance, fluorescence), electron donating capacity (EDC), an effect of structural and elemental alterations (Li et al., 2023; Wenk et al., 2013).

HMW hydrophobic fractions of NOM are constituents acting as main DBPs precursors. Typically, they are conformed by large conjugated and aromatic structures. When reacting with an oxidant, those electron-rich structures can be attacked via electrophilic reactions resulting on a loss of hydrophobicity and formation of oxygenated moieties (hydroxyl, alcohol, carbonyl and carboxyl) with reduced reactivity against chlorine and at the latest, resulting in a lower formation of THMs and HAAs. Coagulation-sedimentation is highly efficient in removing high molecular weight organic matter but less efficient in eliminating free amino acids (Wang et al., 2021).

Table 3. Summary of pre-oxidation methodologies main advantages and disadvantages

METHOD	PROS	CONS
OZONE	- Highly oxidant towards DBP precursors (saturated moieties)	- Promotes formation of bromate when significant concentrations Br^- are present in the media - Unstable residual
CHLORINE DIOXIDE (ClO_2)	- Minimization of THMs - Effectively removes HANs and HAcAms precursors	- Prone to inorganic DBP (chlorite and chlorate) formation - Unstable residual
FERRATE (Fe(VI))	- Effectively removes THMs and HAAs, NDMA and HANs precursors	- High reactive dosing
PERMANGANATE (Mn(VII))	- Great oxidant towards N-containing moieties DBP precursors	- High reactive dosing
AOPs	- Non-selective highly oxidative pathways	- High capital and energy costs

Ozonation and biological activated carbon filtration can remove protein-bound compounds more effectively than humic-like substances, which makes it desirable to integrate multiple methods to meet high water quality standards (Lin et al., 2020; Wang et al., 2017). Through the generation of OH· radicals, ozone turns out the most reactive oxidant towards saturated moieties (fragmenting aromatic rings and lowering MW), thus comporting great reductions of UV_{254} and fluorescence as well as DOC. However, before selecting O_3 as a pre-oxidant, considerations about present levels of bromide should be considered as in significant amounts it can enhance production of bromate and Br-DBPs (Ramírez et al., 2023; Chaukura et al., 2020).

Chlorine dioxide can also selectively react against amino acids and amines and effectively reducing precursors of HANs and HAcAms. Though it presents the advantage of barely generating THMs (Chaukura et al., 2020) it can increase concentrations of inorganic DBPs (chlorite and chlorate) (Snyder et al., 2009; Gan et al., 2019). NOM oxidation via ClO_2 can generate intermediate aldehydes and ketones precursors of CH and HKs.

Ferrate can act directly on aromatic phenols and amines through electron-transfer pathways reducing overall aromaticity thus lowering UV_{254}, but effects on TOC/DOC are arisen by the coagulation of ferric species. By all this, reductions of 6% – 32 % of aromatic carbon relative abundance had been reported after NMR analysis (Lin et al., 2022; Yang et al., 2015). Through those reaction pathways, ferrate can oxidate precursors of THMs and HAAs (attacking aliphatic/aromatic moieties containing hydroxy groups), and reduce NDMA and HANs (via oxidation of amino acids/amines) up to a 84 % (Li et al., 2023; Lin et al., 2022; Gilca et al., 2020).

A particular feature of permanganate relies on its ability to capture electrons, thus being a great candidate towards oxidation of N-containing moieties, such as amines (further converted into nitroso-/nitro- compounds), as well as a remarkable effect on bond cleavage, strengthening reduction of certain DBPs (TCM and DCAN) up to a 45% on optimal doses (Lin et al., 2022). Thus, it is the best selective oxidant to diminish electron donating capacities of NOM (Rougé et al., 2020).

In all cases, dosages and reaction conditions might play a significant role in final efficiency of pre-oxidation processes. Usually, increasing the exposure to the oxidants, via rising dosages or contact times, should result on a lower DBP formation. However, under some specific conditions oxidation onto smaller MW compounds can overcome onto increasing intermediate DBP precursors such as ketones or aldehydes promoting the formation of other minor DBPs like chloral hydrate or haloketones. Also, pH represents a key parameter, especially with ferrate, in regulating performance of oxidants.

While O_3 and Fe(VI) can achieve TOC/DOC reductions around 5% to 28% depending on the doses, little NOM mineralization effect can be achieved with Mn(VII) or ClO_2 (Lin et al., 2022). Such differences are driven by the several oxidative pathways each reagent promotes. Generally, absorbance is reduced through oxidation due to their effect on electron-rich aromatic moieties. Though higher concentrations of oxidant usually lead to greater diminutions on optic parameters, occasionally the breakdown of larger aromatic structures into smaller fractions could entail higher spectroscopical properties.

An alternative approach to selective pre-oxidation is the implementation of advanced oxidation processes (AOPs). Through the generation of strong non-selective oxidizing agents, mainly reactive oxygen species (ROS) such as hydroxyl radicals, sulphate radicals, and reactive chlorine species (RCS), those processes are reported to be highly efficient in degradation of organic and inorganic pollutants (pharmaceuticals, personal care products, NOM, herbicides, etc.) even for the most recalcitrant ones (Khajouei et al., 2022; Li et al., 2023). UV-AOPs are the most common and studied processes in which oxidants (ozone, peroxide, chlorine, etc.) are activated through external energy (UV radiation), affecting to NOM properties and impacting subsequent DBP formation.

Upon the most common AOPs, UV/H_2O_2 had been reported to partially mineralize NOM reducing below 30 % on overall DOC concentrations by generating LMW fragments. Under same conditions, UV/O_3 presented slightly better results, upgoing 31% of reduction. Generally, OH· radical breaks up aliphatic fractions of NOM by H-abstraction leading to LMW carboxylic acids at the time that hydroxylates benzene rings and double bonds. However, pre-treatments using that kind of OH-based AOPs could promote the formation of C-DBPs (THMs, HAAs) in subsequent chlorination, as they generate intermediate precursors. To a late extend, those can be reduced by increasing H_2O_2 doses or irradiation times. Li et al., (2023) summarized several efficiencies in DBPs removal from previously reported studies. Yet large differences in experimental conditions hiders the possibility to stablish a systematic comparison and draw conclusions about the clear effects on DBP-FPs.

An alternative AOP lately gaining interest are the UV/chlorine combination in which not only ROS but RCS. As a benefit, RCS attack selectively in oxidation processes towards

electron-rich moieties through one-electron oxidations, H-abstractions and addition to unsaturated C-C bonds, plus they enable a final residual for the distribution system (Khajouei et al., 2022). Apparently, these processes can lead to a reduction of organic DBPs, specially THMs in comparison to HAAs or HANs (Li et al. 2023) but in under some conditions can increase formation of inorganic DBPs such as chlorate (Khajouei et al., 2022). Again, discrepancy in experimental conditions lead to inconclusive results.

Overall, although pre-oxidation of NOM via AOPs can mitigate formation of some DBP precursors, depending on the conditions (doses, irradiation time, UV source, pH, matrix, etc.) eventually they can increase reactivity of NOM moieties towards subsequent chlorine/ chloramine disinfection processes thus increase DBP formation.

6.2 *Final disinfection*

After a primary disinfection (mainly a pre-oxidation) where microbiological activity can be blocked and DBP precursors might be reduced, apart from helping remove odour/taste compounds, turbidity, etc. a secondary/final disinfection is mandatory to reach and maintain microbiological quality through the distribution system and ensure safety water in household taps. When the distribution system is long the further addition of disinfectant is required and boost chlorination station are usually employed. In some WTPs an intermediate disinfection is employed usually dosing chlorine before filtration to avoid microbial growth in the filter.

Performance of the alternative disinfectants abovementioned as secondary disinfectants might not be suitable as their lack of residual stability. While ClO_2 is as a strong disinfectant with microorganisms, it is not stable, decomposes with UV radiation and its prone to evaporation through aeration because of its volatility. Ozone might enhance NOM removal and DBP precursors, as well as removing microbiological activity thanks to its strong oxidizing capacity, however it is unstable and cannot ensure an after effect through the distribution network. Also, UV radiation (including some AOPs) miss a persistent effect as their oxidizing capacity dissipates easily in water matrices over time.

With this, from the available methodologies to this day, the most appropriate secondary disinfectants relay on chlorine and chloramine. Chlorine is widely used because of his cost-benefit balance. It has a strong and stable residual dosage though it can enhance formation of C-DBPs (THMs, HAAs, etc.). As an alternative to those cases where maintain appropriate levels of regulated DBPs can be a challenge, chloramine could turn a suitable option, even though N-DBPs can be formed and nitrification may take place in waters.

Thus, to select the optimum disinfectant it is crucial to characterize and perform an in deep analysis of the water matrix to discern the main DBP precursors and accordingly choose the most suitable reagent and operational conditions to minimize formation of DBPs while ensuring water quality.

7.0 APPROACHES FOR CONTROLLING DBPS AT DRINKING WATER TREATMENT PLANTS

7.1 New DBPs regulations driving water treatment plants upgrade

Member States from the European Union must implement specific national laws to meet the new European Directive (EU) 2020/2184 on drinking water. The Drinking Water Directive sets the legal framework to secure human health from the adverse effects of any contamination of water intended for human consumption. This must safeguard essential measures to ensure water for human consumption is free from micro-organisms and parasites, and from any substances, which can constitute a potential threat to human health.

The Commission launched a Union-wide public consultation driven by the conclusions of the European citizens' initiative "the Right2Water", which underlined certain provisions needed to be updated, and performed a Regulatory Fitness and Performance (REFIT) Evaluation of the preceding Directive 98/83/EC. The list of quality-based parametric values, the limited reliance on a risk-based approach, the imprecise provisions on consumer information, and the discrepancies between approval systems for materials that encounter water intended for human consumption and the implications such discrepancies have for human health were all identified as four areas that offered room for improvement.

In detail the European Directive (EU) 2020/2184 includes the following new standards for DBPs:

- chlorate (0.25 mg/L; up to 0.70 mg/L in case of disinfection with ClO_2);
- chlorite (0.25 mg/L; up to 0.70 mg/L in case of disinfection with ClO_2);
- haloacetic acids (60 μg/L) as the sum of the following five representative substances: monochloro-, dichloro-, and trichloro-acetic acid, and mono- and dibromo-acetic acid.

Such new standards at to the limits already set by the Directive 98/83/EC on:

- trihalomethanes (100 μg/L) as the sum of chloroform, dichlorobromomethane, dibromochloromethane and bromoform;
- bromate (10 μg/L).

The accomplishment of the new DBPs standards will impact the treatment trains of WTPs that may need to be upgraded to remove specific DBPs/precursors or to switch to alternative disinfection methodologies such as chloramines, a less common practice in Europe compared to USA. For instance, an increasing concern is moving in Europe to control levels of HAAs. Therefore, operational parameters such as chlorine doses, contact time, temperature, pH, and NOM quantity and relative quality will play a key role in their formation. To minimize DBPs, best recommended strategy by US EPA such as enhanced coagulation are needed to maximize NOM removal. This can be accomplished by achieving TOC removal between 15 and 50%. Moreover, if the goal is also the removal

of formed HAAs, one of the most efficient reported treatments can be biofiltration (bioactivated GAC), that can lead to removals up to 80%.

7.2 Case studies

7.2.1 Chlorine vs. alternative disinfectants (AWWA Survey, USA)

In 2017, a massive survey carried out for the American Water Works Association (AWWA) in the United States reported some of the main concerns related to industrial disinfection in water facilities. From over 375 responses, approximately 70% relied on free chlorine as disinfectant, up to 20% switched to chloramines and less than 7% applied alternative methodologies such as ClO_2, O_3 or UV irradiation (Figure 2). From the vast majority using chlorine, the main restrain towards moving to unconventional advanced methodologies such as ozonation or UV disinfection was a matter of costs, particularly related to implementation, maintenance, and training of operators. Also, concern about DBPs generation, specially chlorite and chlorate, awakened when considering implementing ClO_2, although it can contribute to reduce other DBP precursors when used as a primary disinfectant in pre-oxidation treatments; in fact, this was the main incentive of those facilities employing this methodology (36%), applying principally maximum doses between 0.2 to 2 mg/L on raw water.

The reported number of users of O_3 was similar to the ones of ClO_2, with bases that comprised principally removal of tase/odour compounds, oxidation of micropollutants and DBP precursor reduction. Majority of facilities implemented this methodology after post-clarification, and only bit more than half replied dosing directly on raw water. Combination of ozonation with filters was also reported as a growing practice (37%), where 44% out of them had optimized for biological treatment (BAC) according to their performance on reducing biodegradable DBPs such as HAAs. However, bromate generation, as well as operational, power, and maintenance costs, plus the training of operators are some of the challenges users manifested against shifting to this advanced methodology.

Another alternative approach currently gaining popularity is employing UV irradiation though investment costs was reported to be one of the main factors affecting decision making into the transition of the methodology. Perceived benefits related to its application involve additional protection against microorganisms such as Cryptosporidium, and the lack of DBP formation, yet it is a novel implemented methodology (46% of the current users switched in between the las 1 to 5 years). Amongst the responses, main UV disinfection points were located in combination with filters, using medium pressure lamps (63%) at doses between 10-20 mJ/cm^2.

Although there is a growing concern about novel non-conventional methodologies, the main reducing strategies related to DBP minimization, installation of advanced treatments was straight behind the consideration of reducing chlorine doses or moving addition points. Chlorine is still the most widespread method of disinfection, either as a primary disinfectant (>80%), as secondary disinfectant, or used to prevent bio-growth in filters. Thus, dosing points can differ from pre-clearwell (60%), raw water (38%), pre-filter (35%) or others such as pre-clarification, post-clearwell or at some point of the distribution system. To ensure safe disinfection performance, typical maximum residuals ranged 2–3 ppm of Cl_2 (21%) followed by 1.5–2 ppm (17%). More than half of the

respondents agreed that securing residual levels in distribution networks after only a primary disinfection was much challenging so that justifies a need for boosting final step.

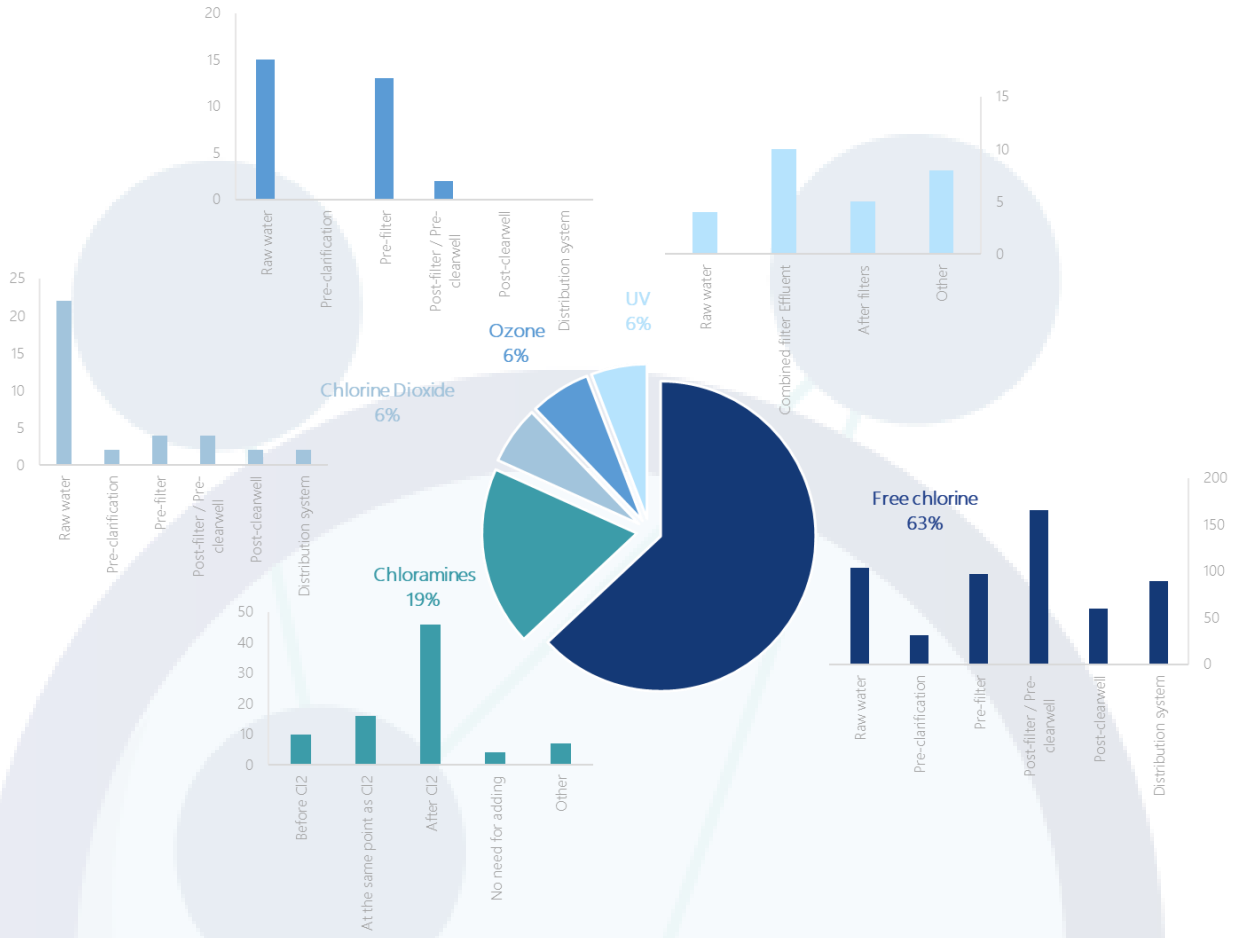


Figure 2. Disinfection practices in USA based on US AWWA Survey from 2017 (AWWA, 2017).

When meeting legislation requirements of THMs and HAAs becomes a major dispute, chloramine becomes a suitable candidate. Utilities reporting the use of chloramines for more than 20 years represented the majority (52%), while only 3% had been using chloramines in the last 5 to 10 years, and less than 1% switched in the last year. Preferred source of ammonia for chloramination is aqueous ammonia, followed by ammonia gas and liquid ammonium sulphate, and most employed analytical methodologies to verify successful formation of chloramine comprise grab analysis of total chlorine, free ammonia, monochloramine, and free chlorine. From the responding utilities, 51% used chloramine as secondary disinfectant and only 23% in primary disinfection. To assess performance of chloramines when used as a secondary disinfectant, total chlorine and pH are the most important parameters to monitor in distribution systems, with minimum required residuals below 0.5 mg/L.

Periodically, 31 out of 70 respondents declared converting to free chlorine in the distribution system during certain periods of time (mainly warmer seasons of spring and summer), to control nitrification, as well as achieve better disinfections and meet local/statal regulatory requirements. Nitrification is one of the major concerns associated to the use of chloramines. In fact, it is one of the main drivers of deny. However, 34% of the users reported no incidents related to chlorine depletion in the distribution system associated with nitrification, and 41% just occasionally (1 to 3 times per year). To avoid this issue, the most common actions include conducting routine monitoring for relevant water quality parameters in low flow rate areas of the distribution system and periodic flushing within the distribution system. Overall, one of the most challenges of using chloramine, also associated to the use of alternative disinfectants, was related to uncertainty over further regulations and the generation of DBPs.

7.2.2 Effects of BAC implementation in HAAs removal (USA)

Tung and Xie (2011) reported the effect of the presence of activated carbon biological filters in the treatment trains at WTPs on the concentrations of HAA5. The study was conducted using the U.S. Information Collection Rule (ICR) database. The selected ICR database is based on the data of 368 plants of which 34 with biological filtration treatment on GAC or on GAC and sand (double layer filters). Plants that treat groundwater or plants with other advanced treatments (e.g. ozone) have been excluded. The data analysis is also organized according to the seasons, i.e. in six different periods of the year. The results show that the mean concentrations of HAA5 in all ICR plants with GAC and in all seasons of the year were much lower than those in plants without GAC. Furthermore, in plants without GAC the highest levels of HAA5 were observed in the quarters April to June and July to September, while in plants with GAC the highest levels of HAA5 were observed in the quarters April to June and from January to March. This profile of higher HAA5 levels was inversely correlated with water temperature and biological activity, highlighting that the primary process of HAAs removal in GAC filters is biological degradation. However, it should be noted that the presence of GAC filters was not effective for controlling the level of THMs. Ultimately, the study indicated that the GAC biofiltration process plays an important role in reducing the concentration levels of HAAs in drinking water.

7.2.3 Control of chlorate at SMAT WTP (Turin, Italy)

The new DWD 2020/2184 regulates chlorite and chlorate under 250 μg/L (700 μg/L where a disinfection method that generates chlorite/chlorate, in particular chlorine dioxide, is used for disinfection of water intended for human consumption). As such DBPs are mainly formed because of degradation of chlorine based disinfectants (hypochlorite ion and chlorine dioxide), conventional methodologies to minimize their concentration involve i) reduction of chlorine dioxide dosages, ii) employing alternative pre-oxidants (e.g., $KMnO_4$), iii) removal of chlorite and/or chlorate by adsorption using GAC filters. The combination of both processes has been reported to reduce the final ClO_2 demand up to a 50%, thus mitigating chlorite/chlorate formation, as demonstrated at both laboratory and pilot scale (Sorlini et al., 2014). As a case study, the drinking water treatment plant of SMAT water utility in Turin (Italy) compared the effects of applying different pre-oxidants, including ClO_2, ozone and chlorine before coagulation/clarification and GAC

filtration (conventional treatment). Results showed a distinct effect of hypochlorite aging on chlorate formation that added to the chlorate formation via reaction of chlorite or chlorine dioxide with chlorine. Following such study, SMAT has employed the use of refrigerated tanks for hypochlorite storage that have been confirmed as an important measure to reduce the formation of chlorate (Fiore et al., 2012).

7.2.4 DBPs precursors removal via enhanced coagulation and EDR at ATL - Llobregat DWTP (Barcelona, Spain)

The Llobregat and the Ter rivers, typical Mediterranean catchments in Northeast Spain, supply drinking water to more than 4.5 million inhabitants residing in the metropolitan area of Barcelona. Ens d'Abastament d'Aigua Ter – Llobregat (ATL), a public company of the Autonomous Government of Catalonia has been appointed to manage the system, processing and distributing more than 11m^3/s, through 117 municipalities and 1340 km of pipelines, from the Drinking Water Treatment Plants (DWTP & SWRO) to the municipal tanks. Subsequently, local suppliers manage the distribution to the tap consumer. The Llobregat DWTP takes the raw water directly from the river, located at 35 km from the coastal sea. The Llobregat river has a low and irregular flow. It presents quality problems such as high salinity, stemming from the brines associated with the important mining activities on the salt deposits located in the upper part of the basin, with a significant presence of sulphates, Ba^{2+}, Sr^{2+}, Na^{+}, Ca^{2+}, K^{+}, Cl^{-} and Br^{-}. The potash mine industry has been exploiting potassium chlorides since 1920s generating important volumes of tales. The drainage of these areas contributes to increasing the saline content of the pristine headwaters. As a result, the raw water in the inlet of the Llobregat DWTP shows large concentrations of those parameters. Furthermore, many problems are associated with the increase in micropollutant and microbiological levels due to both urban and industrial sewage. These problems produce many interruptions of the process, some of them lasting many hours. As a consequence, the high levels of bromide (ranging between 0.5 and 1.2 mg/L), NOM and T, produce high concentrations of THMs after chlorination, showing a high brominated profile.

Removal of THMs precursor material before chlorination is carried out in many utilities using enhanced coagulation or adsorption processes. Although not all of the NOM is removed, this procedure does reduce the levels of THMs. Because neither enhanced coagulation nor granular activated carbon (GAC) adsorption effectively remove bromide, the ratio of bromide to natural organic matter is higher in the treated water and can result in a shift to the formation of more brominated disinfection by-products. In this sense, the concern about THMs at the Llobregat DWTP has to do with changes in the treatment process, starting with enhanced coagulation in 1994, followed by the inclusion of a new step of GAC. In 2009 a new step of desalination using Electrodialysys Reversal (EDR) was introduced. Then the DWTP can process up to 3,2 m^3/s with the conventional treatment, including: pre-oxidation with potassium permanganate, coagulation, flocculation, oxidation with chlorine dioxide, sand filtration, granular activated carbon filtration (GAC), EDR and final chlorination using NaClO. After GAC, the EDR step takes feedwater by means of a derivation of filtered water pipeline. Plant configuration has a cartridge filter and two hydraulic EDR stages, including 576 EDR stacks, all of which

makes it the world's largest plant using this technology. When necessary, remineralization dosing lime and CO_2 was applied. Whenever quality of raw water permits, product water from conventional treatment will be blended to produce up to 3,2 m^3/s.

From 2009 to 2022, the EDR plant has produced more than 275 hm^3 and the technology has showed to be very robust, in spite of the instability of the raw water quality and working in parallel with the changes related with the state of the art of the technology.

EC Values for Llobregat river water range between 400 and 1800 µS/cm, with high concentrations of bromide (0.1–1.2 mg/L), chloride (40–3800 mg/L), and significant levels of Ba^{2+} (37–92 µg/L), Sr^{2+} (634–2720 µg/L), sulphates (60–175 mg/L), ammonia-NH^{4+}(0.5–2.5 mg/L) and TOC (1–9,7mg/L) (data 2018-2022, n=63).

The EDR step reduces the contents of significant parameters from GAC filtered water. Analytical data shows the reduction of main parameters values during the period of January 2018 to March 2023 (n=113). Results expressed as average±std removal were the following: Br^-: 76±6%, Cl^-: 75±7%, NO_3^-: 75±6%, SO_4^{-2}: 76±7%, Ca^{+2}: 82±7%, K^+: 68±10%, Mg^{+2}: 78±7%, Na^+: 51±11%, conductivity: 68±8% and TOC: 40±10%. During this period the range of temperature and conductivity were 671-1.730 µS/cm and 3-29 ºC respectively. In addition, this salt reduction modifies the taste of the water and improves the aesthetic assessment by the consumer.

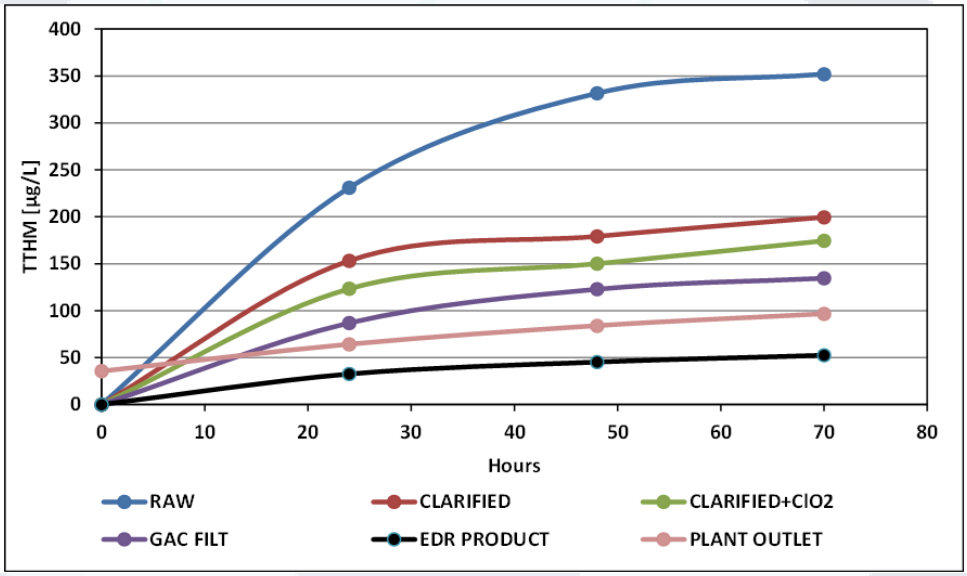


Figure 3. THMs-FP (25°C, 72h) in different steps of the Llobregat DWTP

Regarding the THM-FP (25ºC) results, Figure 3 shows the levels obtained at different contact time for the plant samples after forced chlorination. GAC filtered water represents the end of the process without EDR showing a level higher than EDR product obtained in the next step. Plant outlet is the product, blended between the two waters: GAC (30%) and EDR (70%) in a proportion calculated to have the lower level of THMs in the distribution system.

The analysis of THMs carried out in the laboratory are reinforced with 5 specific on-line analyzers installed in plants and in the network supply.

7.2.5 Full-scale minimization and control of DBPs at Valmayor DWTP – CANAL (Madrid, Spain)

The Valmayor DWTP is located in the NE of the Community of Madrid (central Spain). It is managed by Canal de Isabel II (CANAL) and supplies to Madrid province through Canal de Valmayor encompassing 17300 km of pipelines. With a maximum treatment capacity of 1.036.000 m^3/day (second biggest DWTP in Spain). Water is collected from Valmayor reservoir gathering rivers Guadarrama, Aulencia, and Alberche. The whole treatment train includes a first pre-oxidation (O_3) followed by a second pre-oxidation with chlorine dioxide and/or permanganate), followed by a coagulation (aluminium) flocculation, micro–sand addition (ballasted settling), sand filtration, advanced oxidation process (O_3/H_2O_2), filtration on GAC, and final disinfection (chloramine). From 1968 to 1975, Canal de Isabel II built several water treatment plants adding monochloramine as a secondary disinfectant. All DWTPs use monochloramine as a secondary disinfectant. Because of the long piping to reach the distribution systems, monochloramination is preferred to chlorine disinfection to ensure higher residual stability along the network and control biofilm growth in the pipes. One of the main concerns associated to this practice is nitrification as it could compromise disinfection efficiency, promote biofilms, and form nitrites and nitrates in the produced water. However, after several decades of experience, non-significant episodes had been reported and compliance with DBPs standards has been guaranteed. It is noteworthy to mention that this is a unique experience of chloramination in Europe that adds to the switching from chlorine to chloramine already experienced in USA. In light of the novel standards set in Europe for HAAs such experience could be of interest for many European utilities that deal with the control of HAAs.

The combination of different NOM characterization techniques for Valmayor DWTP promoted an optimization of several operations constituting the treatment train (oxidation, solid-liquid separation, adsorption, and disinfection). This encompassed advanced techniques such size exclusion chromatography (LC-OCD-OND) and fluorescence, paired to most conventional ones like total organic carbon and UV-absorbance. A deeper knowledge about NOM behaviour allowed to stablish removal indicators that assisted the targeting removal of halogenated and nitrogenous by-product precursors in solid-liquid separation processes (coagulation/flocculation – sedimentation – filtration) and oxidation processes. As a surface water with moderate concentration of DOC, water from the Valmayor reservoir presented high concentration of biopolymers with lower amino acid content (15-25%), and a mixture of humic compounds with the common composition from large rivers with anthropogenic impact. Humic substances presented an average molecular wight of 604 ± 14 g/mol and aromaticity of 2.75 ± 0.42 $L/mg^{-1}\cdot m^{-1}$. In terms of fluorophores, zones C1 and C2 revealed influences from humic and fulvic compounds associated to biological activity; and zone T2 related to amino acids (tryptophan-like) with an anthropogenic origin. After the overall solid-liquid separation, reductions higher than 48% and 50% of TOC and SUVA respectively were achieved. The advanced

characterization of the NOM revealed that those reductions could be assignable to a reduction of 48 – 66 % of humic substances and in between 52 – 83% of biopolymers. Thus, removal rates of 50% were assumed as the threshold indicator of process efficiency.

The four regulated THMs (chloroform, bromoform, diclorobromomethane, and bromodicloromethane) and HAA5 (monocloroacetic acid, monobromoacetic acid, dichloroacetic acid, trichloroacetic acid, and dibromoacetic acid) were analysed and the concentrations of 25 μg/L and 10 μg/L, respectively, were not exceeded. Table 4 and Figure 4 show the final DBP levels, which in both cases were below the limits.

Table 4. HAA5 concentration in Valmayor DWTP

	MCAA	DCAA	TCAA	MBAA	DBAA	∑HAA5
Concentration (μg/L)	0.6	2.3	2.1	<LOQ	0.2	5.3

Apart from the usage of an alternative disinfectant, special interest is set on the ozone-BAC to reduce DBP formation at full scale. Molecular ozonation (without generation of hydroxyl radicals) is a selective process that attacks compounds with a kinetic constant kO_3>100 $M^{-1}\cdot s^{-1}$, especially C=C double bonds, non-protonated amines and aromatic systems active (von Gunten, 2003a; 2003b). This industry partners follows the effectivity by measuring the fluorescence spectrum represented as an excitation/emission matrix in the region corresponding to humic compounds (Li et al., 2016), which serves as a surrogate parameter for the elimination of compounds susceptible to being oxidized by ozone. A reduction greater than 50% of this measurement has been correlated with a complete elimination of these ozone-sensitive compounds. Additionally, the same author (Li et al., 2017) has correlated reductions in this measure with increases in biodegradable organic carbon and with the formation of bromate from bromide (respectively 80% and 90%). For this reason, this parameter has been studied as a surrogate for the oxidizing efficiency of ozone by molecular means, limiting it to 50%-80%. Since, this specific WTP has the peculiarity to disinfect waters with chloramines and hence there is the risk of NDMA formation, CANAL proved this method to be efficient also to remove NDMA precursors in agreement with previous research (De Vera et al., 2014, Russell et al., 2017). Finally, since CANAL is also using chlorine dioxide during pro-oxidation, they are studying novel adsorbent materials based on Metal-Organic Frameworks (MOFs) to remove chlorite and chlorate.

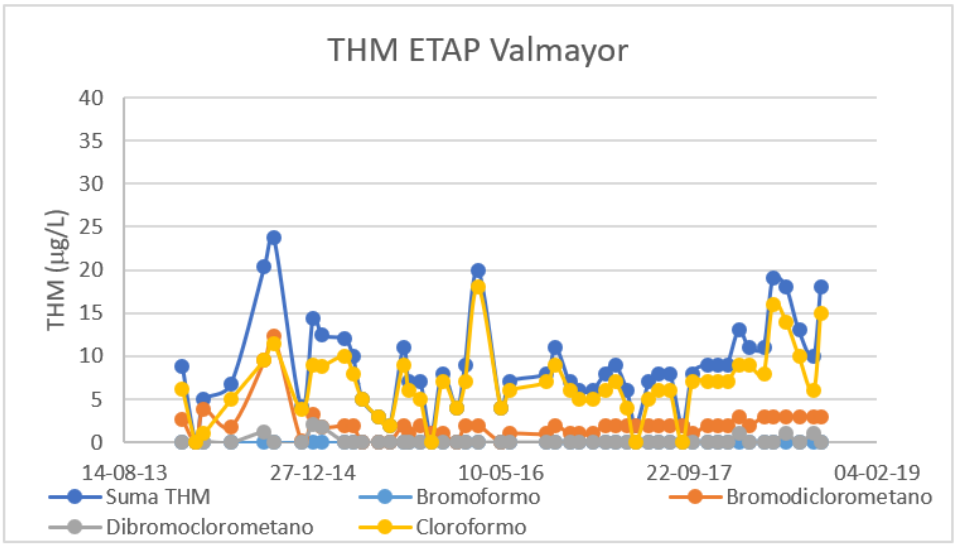


Figure 4. Concentration of regulated THM and sum of total THMs in Valmayor DWTP

7.2.6 A multifunctional system for simultaneous injection of solid, liquid, and gaseous reagents - MITO3X® (Aquasoil, Italy)

The most common industrial techniques used to remove DBP precursors are coagulation-flocculation followed by clarification (sedimentation or flotation), filtration, and disinfection. Very often pre-oxidation is also used at the inlet of the plant. Nevertheless, non-conventional or advanced methods have shown to be very effective for DBP control. Some of them include adsorption, membrane filtration, ion exchange, biofiltration, AOPs, ozone or integrated methods such as AOP/ozone followed by BAC. In order to achieve system economic feasibility, the integration of AOPs and biological systems such as BAC is one of the best possible alternatives (Tak & Vellanki, 2018), although BAC filter age can shorten the total elimination rate (Yu et al, 2021; Wang et al 2022). Also, carcinogenic bromate might potentially be produced due to O_3 step, so it needs to be well controlled. Chen and co-authors (2007) studied for 2 years various water treatment processes at pilot scale to enhance organic matter removal. The tested process combinations included the conventional process, conventional plus advanced treatment (GAC and O_3+BAC), pre-oxidation (Pre O_3 and Pre-$KMnO_4$) plus conventional process and pre-oxidation plus conventional plus advanced treatment. The efficiency of each kind of process was assayed with the comprehensive indices of COD_{Mn}, TOC, UV_{254}, AOC, BDOC, THMs, and HAAs and their formation potential. The best combination for integrated removal of organic matter to meets the required standards was the conventional process and O_3-BAC. Nevertheless, the relatively stringent and quite universal drinking water standard for bromate (10 µg/L) often limits ozone applications for disinfection purposes.

A novel technology capable of integrating multiple water treatment processes to guarantee DBP precursors removal is MITO3X®. MITO3X® is a multifunctional system that allows simultaneous injection of solid, liquid, and gaseous reagents in liquid flows

that are immediately and intensively mixed and exposed to high-pressure conditions (Santoro et al., 2013). This leads to high mass-transfer and nearly immediate dispersion of injected reagents into the fluid. By doing so, parallel, and synergistic treatment processes are enabled, making it possible to perform various water treatment processes in a single stage and with short residence time. Some proven injected reagents have been coagulants like aluminium polychloride with sodium hypochlorite for co-precipitation of arsenic (Pio et al., 2015), ozone and hydrogen peroxide for micropollutant oxidation (Piras et al., 2020), and aluminium polychloride, zeolite, powdered activated carbon and sodium hypochlorite for integrated coagulation/flocculation/disinfection/ion-exchange processes for advanced wastewater treatment (Santoro et al., 2013).

When applied for ozonation and pre-oxidation, vigorous mixing and high-pressure conditions could be highly beneficial. Firstly, those conditions ensure a homogeneous distribution and higher dissolved ozone concentration in water. Secondly, it promotes the formation of finer bubbles with a high inner pressure and gas volume fraction, which increases the contact surface area and consequently improves the mass transfer between ozone and DBPs precursors molecules. Thirdly, it increases the contact time between molecules, facilitating the oxidation of pollutants by ozone. By optimizing these two factors, less ozone gas is wasted, and more ozone is available to react with pollutants in water, which allow higher disinfection efficiency and a lower DBP formation potential (Li & Tsuge, 2006; Moslemi et al., 2010; Chu et al., 2012). In the same way, high pressure and strong mixing conditions can also boost coagulation and flocculation processes. High pressure can increase the collision frequency and intensity between the DBPs precursor particles and the coagulants, resulting in faster and more efficient floc formation. Strong mixing can also improve the distribution and contact of the coagulants with the precursors, ensuring more uniform and optimal coagulation (Lin et al., 2020).

7.3 *Alternative strategies and treatment trains for controlling DBPs in drinking water*

In order to control DBPs formation in drinking water without reducing microbial protection, the following strategies can be employed (adapted from U.S.EPA, 1999a):

- source water quality control;
- disinfection strategy selection;
- removal of already formed DBPs;
- removal of DBPs precursor.

Source water control strategies involve managing the source water to lower the concentration and reactivity of NOM and bromide ion in the source water. For instance, nutrient and algal management could be one method of controlling DBPs formation potential of source waters, while preventing brine or salt water intrusion into the water source could avoid the presence of bromide. Overall, the protection of source water is always a priority and a winning approach and can avoid multiple upgrading WTPs over time.

Disinfection strategy selection include:

- if possible, move the point of disinfection downstream to avoid DBPs formation at locations where precursors are still present at high concentration;

- avoid or minimize intermediate disinfection (chlorine usually added before filtration);
- use two or more different disinfectants or oxidants at various points in the treatment plant to produce less DBPs formed from a single disinfectant:
  - substitute chlorine as a pre-oxidant with alternative oxidants such as ozone, chlorine dioxide, potassium permanganate, ferrate, chloramines, AOPs;
  - use an alternative or supplemental disinfectant such as chloramines or chlorine dioxide as secondary/final disinfection.

More information on the disinfection strategy selection is reported in §6.0.

Detailed information on the removal of DBPs and DBP precursors are reported in §4.0 and §5.0, respectively.

The implementation of such strategies requires the upgrade of many WTPs that are built with a convention coagulation system (coagulation, flocculation, sedimentation, sand filtration, disinfection). It is noteworthy to mention that such conventional WTP scheme may be simplified by skipping sedimentation (direct filtration) or skipping both flocculation and sedimentation (inline filtration) when the raw water is less turbid. On the other hand, the addition of other reagent (pre-oxidation), in addition to the coagulants (iron or aluminium salts) is often required for test and odour control or for iron and manganese removal.

Regardless of the type of conventional WTP, several upgrading options are available to better control DBPs in drinking water. Therefore, alternative treatment train configurations are proposed (Figure 5) that include the knowledge discussed above and in prior sections.

As discussed in §6.0, adding a pre-oxidation (using either permanganate, ferrate, ozone or chlorine dioxide) prior to coagulation can help to reduce not only taste and odour, iron and manganese, turbidity, but also many DBPs precursors. AOPs may be also used for pre-oxidation, even though the UV based AOPs are not very effective because of the high turbidity, while ozone based AOPs seem good options. Furthermore, the use of an alternative oxidant to chlorine in the pre-oxidation will lead to lower THMs and HAAs even though other DBPs can form. The use of a multifunctional system for simultaneous injection of solid, liquid, and gaseous reagents such as MITO3X, is very useful for the upgrade of conventional WTPs for DBPs control (§7.2.6). Overall, the balanced use of different oxidants can help to fulfil the standards set by the European Directive (EU) 2020/2184 for different classes of DBPs. Finally, the secondary disinfection usually performed by chlorination that guarantee a stable residual in the distribution system can be substituted by monochloramine that offers a good stability and biofilm control in the network and can lower the THMs and HAAs (§7.2.5). Chlorine dioxide can be also used as final disinfection only for small distribution systems due to its low stability.

As discussed in §4.0 some processes such as GAC adsorption, reduction, biofiltration, etc. can be used to remove the already formed DBPs, while the removal of precursors (§5.0) by enhanced coagulation, GAC adsorption and ozone/BAC can be employed to minimize the concentration of DBPs precursors (Figure 5).

Finally, in specific cases the use of high pressure membranes (NF, RO, EDR) is needed to remove DBPs and their precursor that are recalcitrant to the above-mentioned

processes. It is the case of bromide removal, as reported in the case study of ATL (§7.2.4).

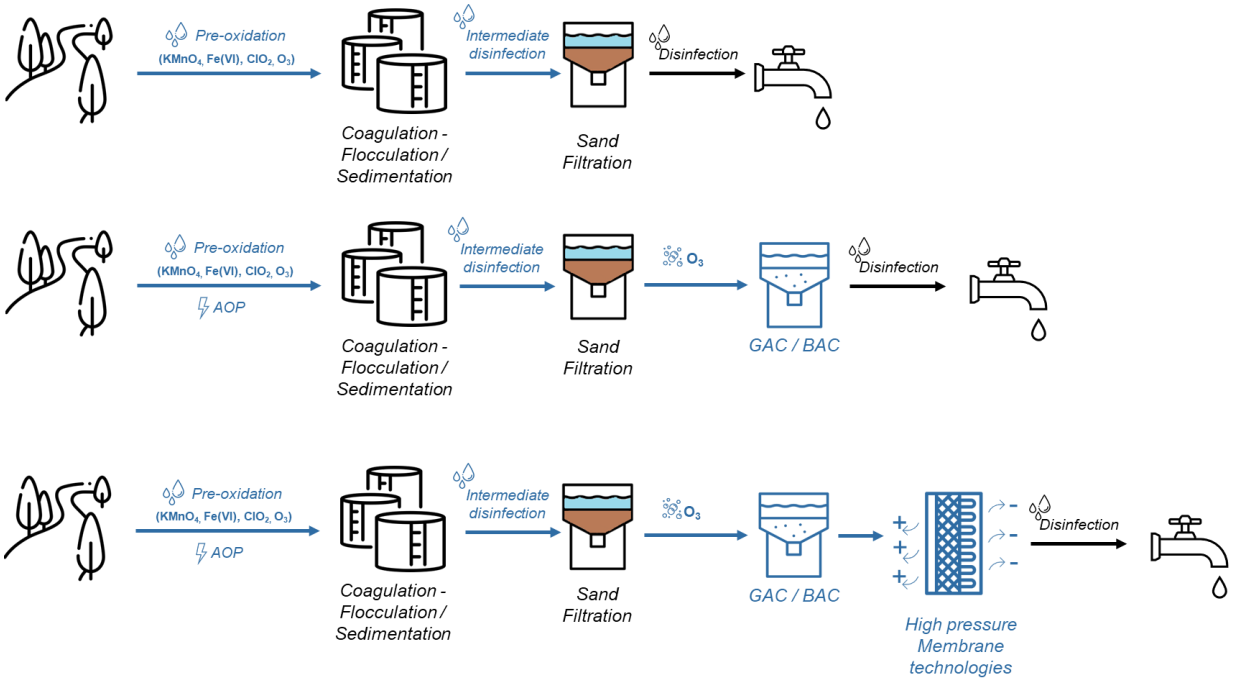


Figure 5. Alternative treatment trains (advanced units (blue) are embedded into a conventional configuration).

Although the selected treatment trains may enhance the control of many DBPs, it is virtually impossible to establish a single optimal configuration. The success of DBPs minimization depends on the selection of most appropriate processes, operational conditions, as well as economic and energetic factors that are site-specific. Therefore, Table 5 is designed as a guideline for decision-makers that need to select the most appropriate treatment configuration (Figure 5) considering the characteristics of each water and site specific issues.

Table 5. Guidelines to select mitigation solutions for controlling regulated DBPs at WTPs.

DBPs	CAUSES OF GENERATION	MITIGATION SOLUTIONS
ALL REGULATED	Disinfectant dose, type and point of addition	- Move the point of disinfection downstream; - Lower disinfectants dose; - Avoid/minimize intermediate disinfection; - Use two or more different disinfectants/oxidants (e.g., substitute chlorine as a pre-oxidant with alternative oxidants; use an alternative disinfectant for final disinfection).
	High levels of precursors in water	- Advanced removal of organic precursors by selected pre-oxidation, enhanced coagulation, adsorption on PAC/GAC, O_3/BAC;

		- Enhance removal of inorganic precursors (e.g. bromide) by high pressure membrane (EDR, RO, NF, etc.) or ion exchange if economically feasible; - Use two or more different disinfectants/oxidants (e.g., substitute chlorine as a pre-oxidant with alternative oxidants; use an alternative disinfectant for final disinfection).
THMs	Chlorination and related operating conditions	- Move the point of disinfection downstream; - Lower chlorine dose; - Avoid/minimize intermediate chlorination; Use two or more different disinfectants/oxidants (e.g., substitute chlorine as a pre-oxidant with alternative oxidants; use an alternative disinfectant for final disinfection).
	High levels of precursors in water	- Add pre-oxidation process with ClO_2, O_3, Fe(VI) or Mn(VII); - Promote organic precursors removal via enhanced coagulation/flocculation processes, PAC/GAC adsorption, O_3/BAC; - Enhance removal of inorganic precursors (e.g. bromide) by high pressure membrane (EDR, RO, NF, etc.) or ion exchange if economically feasible.
	Others/general	- Lower pH to slow the THMs formation; - Remove THMs by adsorption, even though low effective.
HAAs	High dose of disinfectant	- Move the point of disinfection downstream; - Lower chlorine dose; - Avoid/minimize intermediate chlorination; - Use two or more different disinfectants/oxidants (e.g., substitute chlorine as a pre-oxidant with alternative oxidants; use an alternative disinfectant for final disinfection).
	High levels of precursors in water	- Add pre-oxidation process with ClO_2, O_3, Fe(VI) or Mn(VII); - Promote organic precursors removal via enhanced coagulation/flocculation processes, PAC/GAC adsorption, O_3/BAC, biological filtration; - Enhance removal of inorganic precursors (e.g. bromide) by high pressure membrane (EDR, RO, NF, etc.) or ion exchange if economically feasible.
	Others/general	- Remove HAAs by biological filtration.
BROMATE	O_3 doses	- Lowering O_3 dose by improvement of water quality (e.g., removal of NOM before adding O_3, even though O_3 is often used as pre-oxidant); - Optimize O_3 dosing; - Add ammonia or H_2O_2 as inhibitors but pre-test are strongly advised; - Lower pH may decrease bromate formation but pre-test are strongly advised.
	High levels of precursor (Br^-) in water	- Implementing membrane technologies (NF, RO, EDR, etc.) to remove Br^-, if economically feasible.
	Others/general	- Remove BrO_3^- by biofiltration (e.g., BAC);

		- Implementing membrane technologies (NF, RO, EDR, etc.) to remove BrO_3^-, if economically feasible.
CHLORITE	ClO_2 dose	- Lowering ClO_2 dose by improvement of water quality (e.g., removal of NOM before adding ClO_2, even though ClO_2 is often used as pre-oxidant); - Optimize ClO_2 dosing.
	Others/general	- Removal of ClO_2^- via reduction by: i) addition of reducing compounds, such as sulfur dioxide and sodium sulfite, ferrous chloride and ferrous sulfate; ii) addition of powdered (PAC); - Combine the use of ClO_2 with O_3 or free Cl_2 but ClO_3^- will be formed; - Removal of ClO_2^- via reduction by GAC filtration at low pH, high EBCT (>15 min.), and mesoporous mineral-based GAC.
CHLORATE	ClO_2 dose	- Lowering ClO_2 dose by improvement of water quality (e.g., removal of NOM before adding ClO_2, even though ClO_2 is often used as pre-oxidant); - Optimize ClO_2 dosing.
	Instability hypochlorite stock solution	- Use hypochlorite solutions that contain less than 1500 mg chlorate/L, have a pH greater than 12, and contain less than 0.08 mg/L of transition metals; - Use hypochlorite solutions within 3 months from delivery; - Store hypochlorite solutions in a cool dry location where the temperature does not exceed 30°C and away from sunlight.
	Others/general	- Removal of ClO_3^- by GAC adsorption under optima conditions to be determined; - Avoid the combination of ClO_2 with O_3 or free Cl_2.

8.0 CONCLUSIONS AND RESEARCH NEEDS

From the literature review and from selected cases studies, the following conclusion can be drawn on DBPs formation and control:

- DBPs include several organic and inorganic species. Among the organic DBPs, THMs and HAAs are generally present at the highest levels (ppb) in chlorinated water. Chlorite and bromate are the major inorganic DBPs, but interest on chlorate has been recently risen due to the new drinking water Directive (EU) 2020/2184;
- European Directive (EU) 2020/2184 includes the following new standards for DBPs: i) chlorate (0.25 mg/L; up to 0.70 mg/L in case of disinfection with ClO_2), ii) chlorite (0.25 mg/L; up to 0.70 mg/L in case of disinfection with ClO_2), iii) haloacetic acids (60 μg/L) as the sum of the five representative substances (monochloro-, dichloro-, and trichloro-acetic acid, and mono- and dibromo-acetic acid). Such new standards at to the limits already set by the Directive 98/83/EC on: i) trihalomethanes (100 μg/L) as the sum of chloroform, dichlorobromomethane, dibromochloromethane and bromoform; and ii) bromate (10 μg/L).
- Although more than 500 DBPs have been reported in the literature, more than 50% of the total organic halide (TOX) formed during the chlorination of drinking water and approximately 60% of the assimilable organic carbon (AOC) measured in ozonated drinking water is unaccounted for. Some of the identified DBPs have been shown to be carcinogenic, mutagenic and/or teratogenic in animal studies. Brominated and iodinated DBPs are more toxic than chlorinated analogues, while nitrogenous DBPs are much more toxic than the carbon-based DBPs. Recently, more attention has been risen on a big fraction of higher-molecular-weight, non-volatile DBPs (HMW-DBPs) that are analyzed by liquid chromatography mass spectrometry.
- DBP concentration is dramatically affected by the type and dose of disinfectant, the content and reactivity of organic precursor (NOM and/or EfOM), concentrations of inorganic precursors (bromide and iodide), chlorine dose, pH, temperature and reaction time. The mechanism and pathway of DBPs formation in disinfected water is not fully understood, yet. For instance, the formation of THMs and HAAs depends on the complexity of both NOM and the halogenation process, while the impact of pH, alkalinity, ammonia, H_2O_2 and other ozone scavengers on the formation of bromate during ozonation needs more research. Finally, the formation of chlorite and chlorate are mostly related to the use of chlorine dioxide but other causes are significant, such as the formation of chlorate from hypochlorite aging at high temperatures.
- The accomplishment of the new DBPs standards, set by the Directive (EU) 2020/2184, will impact the treatment trains of WTPs that may need to be upgraded to remove specific DBPs/precursors or to switch to alternative disinfection processes such as chloramines, a less common practice in Europe compared to USA. The main strategies to minimize DBPs in drinking water are listed in the following:
  - source water quality control: managing the source water to lower the concentration and reactivity of NOM and bromide ion in the source water;

  - disinfection strategy selection:
    - move the point of disinfection downstream;
    - lower disinfectants dose;
    - avoid/minimize intermediate disinfection;
    - use two or more different disinfectants/oxidants (e.g., substitute chlorine as a pre-oxidant with alternative oxidants; use an alternative disinfectant such as monochloramine for final disinfection).
  - removal of already formed DBPs: THMs and bromate are difficult to remove once formed, while HAAs may be removed by biofiltration; chlorite and chlorate may be removed by adsorption, even though chlorite reduction is the most efficient removal process that may be achieved by using PAC/GAC or adding some reagents such as such as sulfur dioxide and sodium sulfite, ferrous chloride and ferrous sulfate;
  - removal of DBPs precursor is the most efficient approach that can be achieved by selected pre-oxidation, enhanced coagulation, adsorption on PAC/GAC, O_3/BAC;
  - enhance removal of inorganic precursors (e.g. bromide) can be achieved by high pressure membrane (EDR, RO, NF, etc.) or ion exchange, even though they are not always feasible;
- The case studies discussed in this report confirm that such strategies are crucial to minimize DBPs in drinking water. For instance, the use of chloramine experienced in USA and in Madrid represents a very effective solution to reduce THMs and HAAs in the distribution network, while controlling both microbial and biofilm growth. Biofiltration have been proven useful to remove HAAs once formed, even though more demonstration at full scale are needed. Chlorite and chlorate control also requires more full scale applications. The case study in Barcelona demonstrated that in some case the use of high pressure membrane is necessary to remove inorganic precursors, such as bromide. Finally, the need for alternative pre-oxidation processes and technologies are paramount to control the DBPs formation.
- The above-mentioned strategies have been listed in Table 5 that can be used as guideline for the selection of alternative water treatment trains that have been also proposed to minimize DBPs in drinking water.
- From the literature review, the main research gaps are:
  - better understanding the mechanisms of DBPs formation, with particular reference to chlorate that is less investigated than other regulated DBPs;
  - explore the formation, toxicity, and removal of HMW-DBPs in drinking water;
  - more studies are needed on the removal of both DBPs and precursors by biofiltration, including O_3/BAC;
- From the industrial point of view, it seems that a relevant research gap is related to the use and optimization of novel processes/technologies for pre-oxidation of water and/or for final disinfection that may minimize the level of DBPs.

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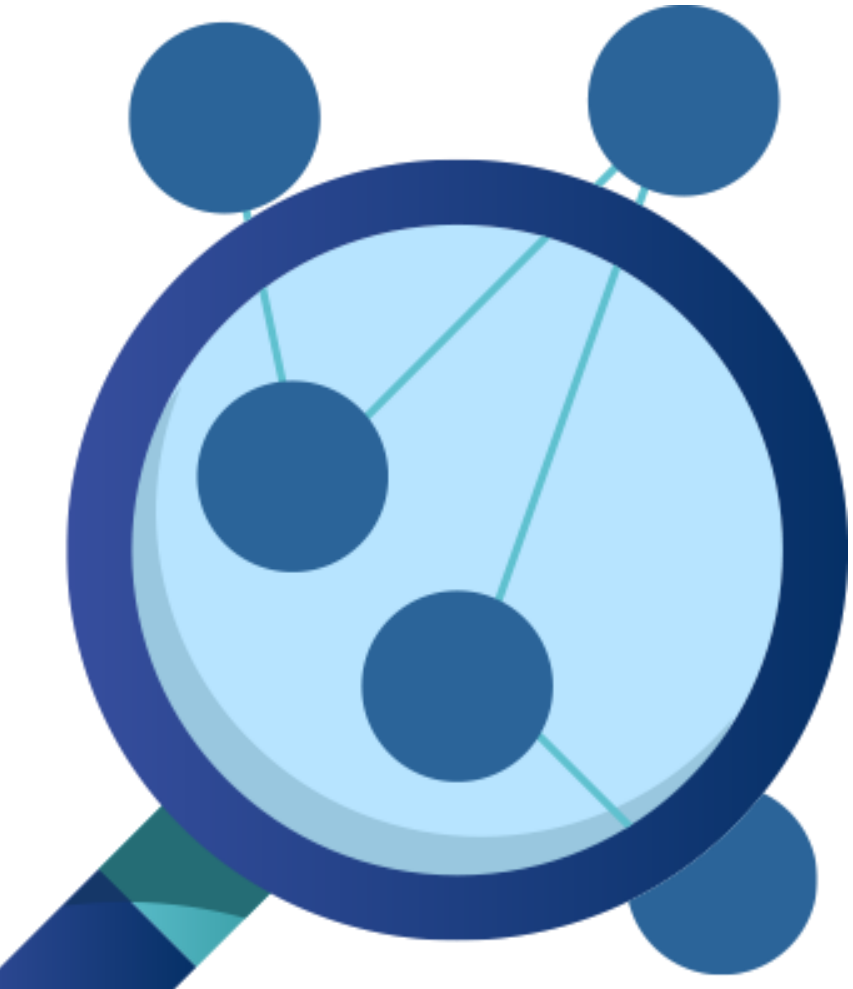
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