

# Treatment of Organic-Laden Surface Water for Total Organic Carbon

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## What is Total Organic Carbon?

The amount of carbon bound in an organic compound is known as TOC and is often used as a nonspecific indicator of water quality. With passage of EPA's Safe Drinking Water Act, TOC analysis emerges as a quick and accurate alternative to the classical biochemical oxygen demand (BOD) and chemical oxygen demand (COD) tests traditionally reserved for assessing the pollution potential of wastewaters. The TOC is determined by removing inorganic carbon, oxidizing the remaining carbon to carbon dioxide using combustion or chemical oxidation with persulfate, and measuring the carbon dioxide produced using a conductivity detector or nondispersive infrared detector. Dissolved organic carbon (DOC) is determined similarly to TOC, but the sample is filtered through a 0.45  $\mu\text{m}$  filter prior to oxidation. The ultraviolet absorbance (UVA) is measured by filtering a sample with a 0.45  $\mu\text{m}$  filter and measuring absorbance at 254 nm. The specific ultraviolet absorbance (SUVA) is calculated by dividing UVA by DOC and multiplying by an appropriate unit correction factor.

Surface waters are found to contain appreciable amounts of TOC, and the removal

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of color and DBPs can be related to TOC removal. The natural organic content of Florida surface water is typically high, with TOC values often greater than 15 mg/L and true color values as high as 700 platinum-cobalt units (PCU). Historically, surface water treatment facility costs and performance decision making procedures were primarily based on turbidity and pH. With the implementation of EPA's Stage 2 DBP Rule, TOC must now be integrated into the decision making process when it comes to treatment selection processes.

Figure 1 illustrates a representation of humic acid, a DBP precursor, and one component of natural organic matter. Instead of volumetric size, NOM is commonly characterized by molecular weight (MW), molecular weight fractionation, and resin isolation into hydrophobic, intermediate, and hydrophilic fractions (Fabris et al, 2008; Kim et al, 2010). Polysaccharides and peptidoglycans are considered high MW compounds, whereas aromatics (i.e., lignin and tannin derivatives) are abundant in the intermediate-high MW fractions of NOM. Nonhumic, aromatic and aliphatic amines, amino acids, polysaccharides, and proteins are considered hydrophobic low molecular weight compounds.

## Regulatory Considerations

Regulations drive the need to treat organic-laden surface waters. In December 1998, EPA published the Stage 1 Disinfectant/Disinfection Byproducts Rule (D/DBPR) that established treatment techniques for the control of precursors to disinfectant byproducts. This section requires enhanced coagulation or enhanced softening to remove a certain percentage of organic carbon based on the source water's TOC and alkalinity for all public water systems using surface water or groundwater

Many drinking water plants use water from rivers, reservoirs, or lakes as their raw water sources. These surface waters invariably contain some levels of pathogens that must be inactivated prior to distribution, as well as organic material (such as decaying plant matter). To ensure that water is safe to drink, the U.S. Environmental Protection Agency (EPA) mandates that a sufficient quantity of disinfectant be added to generate a residual concentration at the customer's tap. Disinfectants can react with the organic material in drinking water to form disinfectant byproducts (DBPs), and epidemiological studies have identified that certain classes of DBPs are human carcinogens. The DBPs form when water that contains total organic carbon (TOC), also referred to as natural organic matter (NOM), is mixed with certain forms of chlorine. The DBP precursor compounds are a subset of NOM and are found in natural waters. The NOM is most commonly found in surface water where organic matter frequently enters the water body from runoff, and also from aquatic organisms. Public water systems using surface water must disinfect the water prior to delivery to the first customer.

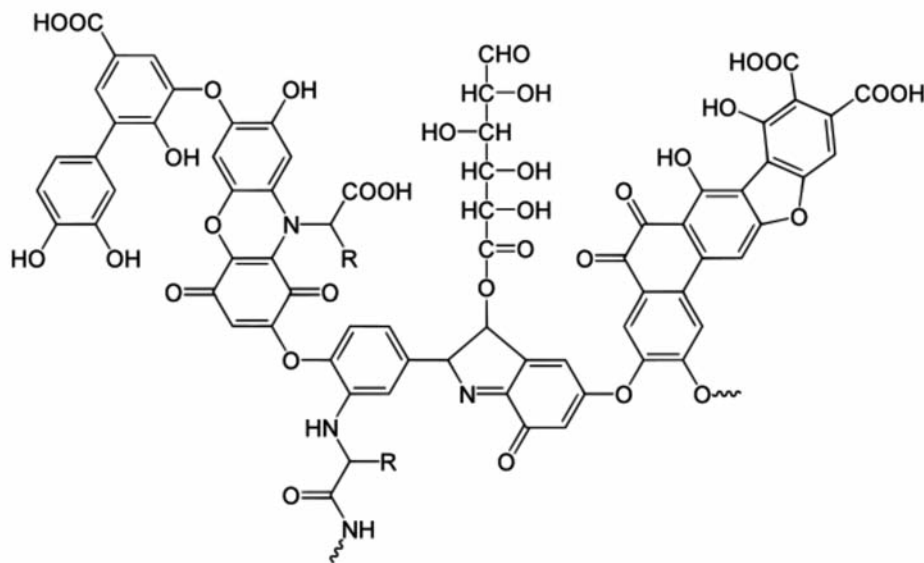


Figure 1. Representative Structure of Humic Acid, a Component of Total Organic Carbon

Source: Stevenson (1994)

under the direct influence of surface. In January 2006, EPA published the Stage 2 D/DBPR that required water utilities to comply with a reduced maximum contaminant level (MCL) of 80 µg/L for total trihalomethanes (TTHMs: chloroform, bromoform, and dibromochloro- and dichlorobromo-methane) and a new MCL of 60 µg/L for the sum of five haloacetic acids (HAA5: monochloro-, dichloro-, trichloro-, monobromo, and dibromo-acetic acid) at *each individual monitoring location* in a distribution system (i.e., locational running annual averages).

The rule sets up several alternatives to removal, one of which is SUVA of source or finished water. The SUVA is an analysis of water that uses UV absorbance and DOC levels. Previous studies established a relationship between SUVA and the levels of humic substances that are removed during enhanced coagulation and/or enhanced softening. If SUVA levels meet certain requirements, it is logical for the enhanced coagulation or softening to be unnecessary. Stage 1 D/DBPR allows an exemption from costly TOC removal requirements if SUVA levels for source or finished water are below 2.0 L/mg-m. It also provides for SUVA-level substitutions when calculating TOC removal compliance.

The EPA has set required TOC removal levels for water systems that use conventional treatment, as shown in Table 1. Water systems that use surface water and conventional filtration treatment are required to remove specified percentages of organic materials, measured as TOC, that may react with disinfectants to form DBPs. Removal is to be achieved through a treatment technique (enhanced coagulation or enhanced softening). Enhanced coagulation has been identified as one of the most effective treatment methods for lowering TOC concentrations, and subsequently, DBP formation potential.

As a result of the D/DBP Rule, there has been increasing emphasis by the water community on the removal of NOM from water supplies; important NOM removal options are coagulation, granular activated carbon (GAC) adsorption, membrane filtration, and anion exchange. Of these processes, coagulation is the most widely used in the water industry. But, when coagulation cannot remove adequate concentrations of NOM so that DBPs can be controlled, other treatment technologies, such as GAC, nanofiltration, and anion exchange may need to be used. Chemical softening has been used with variable success. Also, ozone and advanced oxidation may also be utilized, but typically must be combined with another unit operation.

Table 1. Required Total Organic Carbon Removal Requirements for Conventional Treatment Plants<sup>1, 2</sup>

Source: EPA, June 2001. Stage 1 Disinfectants and Disinfection Byproducts Rule Fact Sheet. EPA 816-F-01-014

**Required Removal of Total Organic Carbon by Enhanced Coagulation and Enhanced Softening for Subpart H Systems Using Conventional Treatment<sup>1</sup>**

Source Water TOC (mg/L)	Source Water Alkalinity (mg/L as CaCO <sub>3</sub> )		
	0-60	>60-120	>120 <sup>2</sup>
>2.0-4.0	35.0%	25.0%	15.0%
>4.0-8.0	45.0%	35.0%	25.0%
>8.0	50.0%	40.0%	30.0%

1-Systems meeting at least one of the alternative compliance criteria in the rule are not required to meet the removals in this table.

2-Systems practicing softening must meet the TOC removal requirements in the last column to the right.

### Total Organic Carbon Removal by Softening

Removal of NOM is significant to the drinking water community in that color, TOC, and DBPs are NOM subsets and controlled by water treatment due to regulatory and/or aesthetic constraints. Not all NOM or TOC produces color or regulated DBPs; hence, TOC is a more universal measure of organic material in drinking water. Most if not all of the TOC removed during lime softening is in the form of nonpurgeable dissolved organic carbon (NPDOC). The TOC can be in a suspended or gaseous form in some drinking water sources; however, these TOC forms are either easily removed during drinking water treatment or are not DBP precursors, which prior to disinfection are in the form of NPDOC.

Bench-scale tests demonstrate the importance of magnesium hydroxide precipitation and NOM characteristics on precursor removal by softening. The maximum percentage TOC removal achieved for lime and soda ash dosages evaluated for nine waters examined ranged from 23 to 50 percent (Thompson, 1997).

Investigators have found that softening removed TOC, but was less effective for TOC removal than coagulation; addition of coagulants during softening enhanced TOC removal and the chemical structure affected TOC removal. A survey of water treatment plants participating in the information collection rule (ICR) found that 30 to 40 percent of TOC was removed during lime softening in the 2=4 mg/L and 4-8 mg/L TOC groups, respectively. They suggested additional TOC removal should not be required by regulation after 0.2 meq/L Mg removal, 0.8-1.2 meq/L alkalinity removal, or if major changes of existing facilities were required to accommodate the more slowly settling magnesium hydroxide, or

Mg(OH)<sub>2</sub>, floc, or the additional sludge (Clark and Lawler, 1996). Increasing doses of ferric sulfate to 9.5 mg/L Fe<sup>+3</sup> were observed to increase TOC removal to 75 percent, as softening pH increased to 10.3 (Quinn et al, 1992).

Bench-scale jar testing using waters from nine utilities found that TOC removal was correlated with increasing TOC concentration, hydrophobic TOC fraction, and the magnesium removed during softening. A significant relationship between the TOC removed and magnesium removed was observed (Thompson et al, 1997). Softening of Mississippi River water was found to remove less TOC than coagulation, although higher molecular weight hydrophobic organic solutes were removed by both processes (Semmens and Staples, 1986). Liao and Randtke (1986) suggested coprecipitation was the primary mechanism for removal of organic solutes during softening, and organic removal was limited to anionic compounds, which could adsorb onto calcium carbonate (CaCO<sub>3</sub>) solids.

### Calcium and Magnesium Precipitation

During lime softening, calcium removal due to CaCO<sub>3</sub> precipitation increases with pH to pH 10.3. At pH 10.3, nearly all of the calcium or carbonate alkalinity has been precipitated as CaCO<sub>3</sub> because of equilibrium (K<sub>2</sub>, K<sub>sp</sub>). Removal of calcium hardness is typically optimized at pH 10.3 in lime softening. Past pH 10.3, there is not enough carbonate alkalinity to precipitate the calcium solubilized from lime. Some slight additional calcium removal will be realized in a caustic softening process, but typically the vast majority of CaCO<sub>3</sub> precipitation is complete at pH 10.3. Because of Mg(OH)<sub>2</sub> equilibrium, adequate magnesium removal is typically not achieved

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until pH  $\geq$  10.8. The exact pH for optimized  $\text{CaCO}_3$  and desired  $\text{Mg}(\text{OH})_2$  precipitation may differ slightly from 10.3 and 10.8 due to calcium and magnesium interactions with other solutes. However,  $\text{CaCO}_3$  and  $\text{Mg}(\text{OH})_2$  precipitation occurs in different pH ranges and can be related to TOC removal.

The EPA and Water Research Foundation have investigated the removal of color, TOC, and DBP precursors (Taylor, 1984; Taylor, 1986; Randtke, 1999). The studied waters vary from a soft water with low magnesium content and low TOC concentration (Lawrence, Kan.) to a hard water with high magnesium content and high TOC concentration (Grand Forks, N.D.). The TOC varied directly with both calcium and magnesium hardness for these three waters and the TOC removal increased with pH for each. Prior to pH 10.3, the TOC removal varies from approximately 20 to 30 percent. The initial total hardness reduction of approximately 50 percent at pH 10.3 is due to  $\text{CaCO}_3$  precipitation and occurs simultaneously with 20 to 30 percent TOC reductions. Past pH 10.3 TOC reduction is increased by approximately 25 percent and is associated with approximately 30 percent reduction of initial total hardness, which is due to  $\text{Mg}(\text{OH})_2$  precipitation. The TOC removal due to  $\text{CaCO}_3$  precipitation was limited to 30 percent and the TOC removal was increased to 55 percent when  $\text{Mg}(\text{OH})_2$  was precipitated, which indicates that removal of magnesium hardness in a softening process will increase TOC removal.

## Coagulation

Coagulation is a treatment process that includes chemical addition, rapid mixing, and flocculation. The TOC removal can be influenced by the type of coagulant dosage, pH, mixing, water quality change, and the order of chemical addition. Maximum TOC removal tends to occur at pH values between 5 and 6 and low alkalinity water may require the addition of lime to maintain the pH in this range. Full-scale treatment plants have demonstrated that moving the location of the disinfection process to a point following coagulation and sedimentation, or modifying the coagulation process for increased removal of organic materials (or both), can result in substantial reductions in DBP formation. Coagulation can be an effective pretreatment technique subsequent to GAC or membrane filtration in that it removes particles that might clog GAC beds, which reduces the frequency of carbon regeneration and replacement, and it removes TOC, notorious for shortening membrane lives.

Typically, magnesium coagulation at pH 11.3 to 12.0 accompanied 80 to 98 percent color removal, 20 to 40 percent TOC removal, and 40 to 65 percent trihalomethane formation potential (THMFP) removal. Optimum THMFP reduction was always accompanied by optimum TOC and color reduction (Taylor, 1984). Alum used as a coagulant aid at pH 11.5 increases THMFP, TOC, and color removal by about 10 percent.

Enhanced coagulation and enhanced softening were developed specifically for conventional filtration treatment systems where rapid mix and flocculation were followed by gravity sedimentation; this is the normal treatment scheme for most surface water plants. However, some plants that do not use this conventional scheme can be adversely affected by practicing enhanced coagulation or enhanced softening, as these treatment techniques were not intended to be utilized in nonconventional filtration treatment systems. For example, some systems do not use gravity sedimentation for particulate removal; instead, liquid alum and a polymer chemical are dosed at optimum conditions to create pin floc, which is removed through a pressurized clarifying filter. Enhanced coagulation in this treatment scheme could easily lead to floc particle formation larger than what the system is designed to filter. Prematurely clogged filters and shorter filter runs are likely to result under enhanced coagulation conditions. Similar operating problems are anticipated for other forms of alternate treatment technologies or filtration systems.

## Granular Activated Carbon

The EPA has identified the best available technology (BAT) for achieving compliance with the maximum contaminant levels for both TTHMs and HAA5 as treatment with GAC having a 10-minute empty bed contact time (EBCT) and a 180-day replacement frequency with chlorine as the primary and secondary residual disinfectant. The GAC adsorption is an effective technology employed for the removal of NOM, and is typically used as a medium as a filter-adsorber in many water treatment plants (Babi et al, 2007). Normally, 80 to 90 percent of the NOM measured in raw water sources can be removed by GAC adsorption (Roberts and Summers, 1982; Karanfil et al, 2007). Research by Owen and colleagues (1998) has shown that rapid small-scale column tests (RSSCTs) can be successfully used to predict NOM breakthrough-behavior GAC columns in terms of TOC and UV 254; additionally, it has been determined that several RSSCTs should

be performed with differing batches of influent waters that represent the seasons of interest. The GACs with large surface areas and pore volumes in pores  $>1$  nm and basic pHPZC values should be selected for DBP precursor control. Removal of high molecular weight NOM during conventional treatment processes prior to filtration significantly increases the operational time of GAC for DBP formation control. Therefore, the impact of conventional treatment processes on GAC adsorption and DBP formation control should be evaluated in designing and operating GAC adsorption systems.

## Membranes

Membrane processes have been demonstrated to effectively and economically remove DBP precursors in water containing high concentrations of organic matter. There are four kinds of membranes: reverse osmosis (RO), nanofiltration (NF), ultrafiltration (UF) and microfiltration (MF). Table 2 presents an overview of TOC and DBP precursor removal using membranes. In general, membranes with a molecular weight cutoff (MWCO) of less than 1,000 daltons are necessary to remove substantial levels of NOM (Taylor, Thompson, and Carwell, 1987); a MWCO of less than 500 is usually necessary to reject greater than 90 percent of DBP precursors (Duranceau and Taylor, 2010; Metsamuuronen et al, 2014).

Low pH and high ionic strength can decrease the apparent molecular size of organic matter and its electrostatic repulsion from the membrane surface and then decrease its removal. Bromide has been shown to have a significant effect on the formation of DBPs after chlorination of membrane permeates; in general, its removal by membranes is 20 to 70 percent. As the membrane MWCO decreases, the TOC removal increases. The resulting increase in the bromide-to-TOC ratio favors the formation of brominated DBPs after chlorination. However, if enough of the TOC is removed by the membrane, the absolute concentrations of the DBPs will be limited, regardless of relatively high bromide levels.

Yoon and researchers (2005) have reported significant NOM removal of 70 to 86 percent with hydrophobic polyethersulfone (PES) and sulfonated PES membranes, although less than 10 percent rejection would have been expected when the average MW of NOM and membrane pore sizes is considered. This is attributed to hydrophobic interaction and electrostatic exclusion between the hydrophobic and charged membrane surface and the NOM molecules.

The NF membranes are able to remove

compounds from macromolecular size to multivalent ions, but at higher transmembrane pressure as compared to UF. Almost complete NOM rejections were achieved with NF membranes having cut-off values in the range of 100–400 daltons (Duranceau and Taylor, 2010). However, NF is more susceptible to fouling when treating surface water supplies, as was noted by Reiss and colleagues (1999).

Because of the larger pore sizes (0.005 to 5µm), the removal of NOM with MF and UF is substantially less than that observed with either NF or RO. By polypropylene 0.2µm MF membrane, it demonstrated a 15 percent removal of TOC and total THMFP from a flowing stream. By 0.05µm ceramic tubular membrane on blended river waters with an average TOC concentration of 8.2mg/L, it was reported reduced to approximately 30 percent removal of TOC and the THMFP was reduced by 10 to 20 percent by both the 0.05µm and 0.2µm ceramic tubular membrane. The removal of DBP precursors can be improved by the feedwater pretreatment of UF and MF. The two most common types of pretreatment are coagulant and polyaluminum chloride (PAC) addition. Using MF, with the addition of 10 to 15 mg/L of ferric chloride, the removal of THMFP from surface water could be increased from 15 to 60 percent. Using 0.05µm ceramic tubular membranes, the removal of TOC was from 30 to 60 percent and the removal of THMFP improved approximately 30 percent. Table 3 lists TOC removals for treatment using adsorbents such as PAC or iron oxide particles in combination with MF and UF.

## Anion Exchange

The NOM in water contains significant amounts of high-molecular-weight soluble and colloidal humic and fulvic acid anions, which are often associated with the soluble and colloidal iron, manganese, and silica in the water. In the 1960s, macroporous weak-base anion (WBA) resins were used to remove color from river water, and in the 1970s, macroporous strong-base anion (SBA) resins were used to successfully treat highly colored groundwater. Also in the 1970s, polyacrylic strong-base resins were developed, which were less prone to irreversible fouling compared with the standard polystyrene resins in universal use. Following the discovery of the formation of THMs and other DBPs in water in the mid-1970s, various strong- and weak-base anion exchange resins were found to be capable of removing DBP precursors from water. Experimental use of resins for TOC removal

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Table 2. Summary of Trihalomethane Formation Potential Removal by Membrane Technology, Water Source, and Pretreatment

Citation	Water Source	Pretreatment	Membrane Technology	Feed Water THMFP (µg/L)	Treated THMFP (µg/L)	Percent THMFP Removal (percent)
Taylor, Thompson and Carswell, 1987	Ground	Anti scalant,	NF	961	28-32	97
		Prefiltration	NF	961	31-39	96-97
		Screening	UF	961	326-947	2-66
Amy Alleman and Cluff, 1990	Surface	Prefiltration	NF	157-182	55-84	49-70
	Ground	Prefiltration	NF	176-472	6-95	78-98
Parker, 1991	Surface	None	MF	60-630	40-420	20
		Coagulation	MF	70-80	30-40	40-60
Tan and Amy, 1991	Ground	Prefiltration	NF	259	39	85
Duranceau, Taylor and Mulford, 1992	Ground	pH adjustment, prefiltration	NF	120	6	95
Laine, Clarke, and Mallevalle, 1993	Surface	Prefiltration	UF	40-460	NR	<10
		Prefiltration	NF	40-460	NR	30-90
		UF	NF	40-460	NR	90
Kouadio and Madeleine, 2005	Surface	Media filtration	NF	155	20	87
	Surface	Media filtration	NF	117	19	84
	Surface	Media filtration	NF	170	24	86

Table 3. Removal of Total Organic Carbon by Ultrafiltration and Microfiltration with Adsorbent Pretreatment

Reference	Process	Influent TOC (mg/L)	Percent TOC Removal (UF or MF Only)	Adsorbent Dose (mg/L)	Percent TOC Removal (UF or MF with adsorbent)
Lainé, 1990	UF+PAC	3.0	40	250	85
Adham et al, 1991	UF+PAC	2.8-3.1	5-10	25	32-47
Jacangelo et al, 1995	UF+PAC	1.1-11	12-14	10-200	17-82
Chang and Benjamin, 1996	UF+IOP	4.5	10-23	170	47-85
Scanlan et al, 1997	MF+PAC	4.5	6.5	20	11
Kang and Choo, 2010	UF+PAC	4.8	30	367	70

**Table 3 Notes:**

MF=microfiltration  
PAC=powered activated carbon

UF=ultrafiltration  
IOP=iron oxide particles

continued through the mechanism of NOM removal by strong-base resins. Magnetic ion-exchange resins have emerged as an effective method for treating surface water for organic matter (Comstock and Boyer 2014; Drikas et al, 2011; Mergen et al, 2008).

In slightly acidic, neutral, and alkaline water, the acidic functional groups on NOM are negatively charged. Thus, TOC molecules are naturally attracted to anion exchange resins, which contain positively charged amine functional groups attached to a polystyrene or polyacrylic polymer matrix. Karpinska and colleagues (2013) have shown that a proprietary resin (MIEX) can remove over 89 percent of the DOC from the surface water. Anion exchange has been used to remove DOC and hardness simultaneously (Phetrak et al, 2014; Apell and Boyer, 2014).

Weak-base anion resins contain weakly basic-primary, secondary, or tertiary amine-functional (exchange) groups, which are positively charged (protonated) only in acidic solution. These resins function as anion exchangers only when the solution is  $\text{pH} \leq 6$ . When  $\text{pH}$  is above 6, the amine functional groups are neutral and do not exchange ions. But, some WBA resins can function as adsorbents for TOC at  $\text{pH} \geq 6$ .

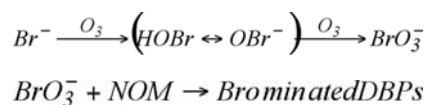
Strong-base anion resins contain quaternary amine functional groups typically attached to a polystyrene or polyacrylic matrix. The more common macroporous polyacrylic resin types, unlike the microporous polystyrene resin types, are often used because of their lower organic fouling potential. Both resins have quaternary amine functional groups that are ionized (positively charged) and function as anion exchangers throughout the 3 to 13  $\text{pH}$  range. Regarding porosity, macroporous resins have measurable Brunauer-Emmett-Teller (BET) surface area (measured by  $\text{N}_2$  adsorption), whereas microporous (or gel) resins have no measurable BET surface area. In aqueous solution, both types of resins have apparent porosity because they are swollen with water and readily allow hydrated ions to enter the hydrated polymer (Singer, 1999).

Compared with GAC, WBA, or SBA, resins have greater sorption capacity for NOM, remove NOM faster, and are easier to regenerate (Boening, Beckman, and Snoeyink, 1980). When operated at  $\text{pH}$  6.5 to 8.5, the WBA resins adsorb the NOM, whereas SBA resins operate by the mechanism of ion exchange. Various studies reported by Singer (1999) have demonstrated that it is not possible to reliably predict THMFP removal based on the surrogates of color or TOC removal.

## Ozone Oxidation

Ozone has been used in the treatment of drinking water since the end of the 19th century (Langlas, Reckow, and Brink, 1991). Although the original applications of ozone were disinfection, as experience increased, and since the mid-1970s, ozone has also been recognized as an important tool in controlling halogenated DBPs. Ozone is powerful and can react with many organic and inorganic solutes in water. By preozonation, followed by chlorination at low  $\text{pH}$ , it can reach the greatest net decrease in THM formation (Singer, 1999). High bicarbonate concentration can also help to improve THM control by ozone. Because ozone itself can decompose to form secondary oxidant species, one of which is hydroxyl radical ( $\cdot\text{OH}$ ), bicarbonate can act as a free radical scavenger that consumes hydroxyl radicals; then, the decomposition of ozone is slowed down, and the chance of solutes reacting with ozone is increased. On the other hand, with the reaction of hydroxyl radicals, bicarbonate can form bicarbonate radicals, which are more moderate radicals and may help to destroy DBP precursor sites (Malley, Edzwald, and Ram, 1986; Legube et al, 1985). Weiner (1995) had shown that ozone destroys the fast-reacting THM precursors, which are mainly activated aromatic structures and can react with ozone easily; then, the THM formation is slowed. Among the HAAs, trichloroacetic acid (TCAA) can be destructed by ozone easily, while dichloroacetic acid (DCAA) is unaffected. Some compounds, such as halogenated ketones and aldehydes, will form at greater concentrations as a result of prior ozonation. In general, ozone can reduce HAAs, total organic halides (TOX), and THMs to a great extent until the time that the water is consumed.

There are many advantages to applying ozone as an alternative to chlorine at the head of the treatment plant. It can delay or even avoid the formation of DBPs from free chlorination. It can also increase the biodegradation, as well as better control tastes and odors, and remove turbidity or filtration effect. Ozone may react with bromide to form hypobromous acid; then, hypobromous can continue to react with NOM to form brominated DBPs:



Lowering the  $\text{O}_3$  dosage may minimize the formation of  $\text{BrO}_3^-$  but increase the formation of other DBPs. On the other hand, higher  $\text{O}_3$  dosages can lead to significant  $\text{BrO}_3^-$  formation, particularly at high  $\text{Br}^-$  levels and at ambient  $\text{pH}$ .

Ozonation converts humic and hydrophobic organic compounds into smaller fragments, but as it does not lead to full mineralization of most compounds, the initial DOC concentration decreases only slightly. Oxidation may produce harmful byproducts and increases assimilable organic carbon (AOC) content, and thus, the potential for bacterial regrowth in the distribution systems. However, these problems can be avoided by combining oxidation with a downstream biological activated carbon (BAC) process prior to the membranes. The granular media filters are widely used prefilters for membrane processes. The media filters capture particles of large-size distribution and, may reduce fouling of the downstream membrane, if employed.

## Advanced Oxidation

Advanced oxidation processes (AOPs) have been studied intensively for decades. Various combinations of oxidants, radiation, and catalyst have been developed for the removal of TOC, NOM, and organic pollutants; for example,  $\text{O}_3/\text{H}_2\text{O}_2$ ,  $\text{UV}/\text{H}_2\text{O}_2$ ,  $\text{UV}/\text{O}_3$ ,  $\text{UV}/\text{TiO}_2$ ,  $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ ,  $\text{Fe}^{2+}/\text{H}_2\text{O}_2 + \text{hv}$ , vacuum ultraviolet radiation, or ionizing radiation (Fujishima, 1971; Glaze et al, 1987; Legrini et al, 1993; Frimmel, 1994; Nagata et al, 1996; Fukushima et al, 2001; Thomson et al, 2002). These processes involve the generation of highly reactive radical intermediates, especially the  $\text{OH}$  radical (Glaze et al, 1987). The appeal of AOPs is the possibility to gain complete oxidation or mineralization of organic contaminants through a process that operates near ambient temperature and pressure. Sitnichenko and researchers (2011) reported that greater than 90 percent of fulvic acids could be destroyed using a photocatalytic oxidation by oxygen using UV light and titanium dioxide in surface water over a wide range of  $\text{pH}$  (3-8).

## Summary and Suggested Disinfection Byproduct Water Quality Goals

Removal of organic solutes using a variety of unit operation processes is unique to a given water source. However, some generalizations can be made regarding softening:

- ◆ **Calcium Carbonate Precipitation** - Generally removes from 10 to 30 percent of the color, TOC, and DBP precursors. Has the least capacity for organic removal of solids generally precipitated in precipitative softening.
- ◆ **Magnesium Hydroxide Precipitation** - Generally removes from 30 to 60 percent of the TOC and DBP precursors, and 50 to 80 percent of the color. Requires primary recar-

bonation to remove excess calcium if lime is used, produces excess magnesium and calcium sludge, and requires either additional sedimentation basins or solids loading on filters if excess calcium is removed.

- ◆ *Iron and Aluminum Augmentation* - Generally removes an additional 5 to 15 percent of the color, TOC, and DBP precursors in either calcium or magnesium precipitation. Will cause excess sludge formation. Aluminum may be passed through the process and postprecipitate in distribution system.
- ◆ *Sequential Treatment* - Coagulation following softening will remove additional color, TOC, and DBP precursors; however no additional color, TOC, and DBP precursors will be removed if softening precedes coagulation.
- ◆ *GAC* - Normally, 80 to 90 percent of the NOM measured in raw water sources can be removed by GAC adsorption.
- ◆ *Oxidation* - Various combinations of oxidants, radiation, and catalyst have been developed for the removal of TOC, NOM, and organic pollutants.

The TOC removal must now be taken into account when evaluating treatment technologies for treatment of surface water supplies. Table 4 provides a recommended listing of sug-

gested water quality goals for DBPs for communities seeking to establish treatment targets.

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Table 4. Suggested Water Quality Goals for Disinfection Byproducts

Water Quality Goals for DBPs (µg/L)			
DBP	LRAA MCL	Example Targets	
		Annual Average	Peak
TTHM	80	40	64
HAA <sub>5</sub>	60	30	48

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