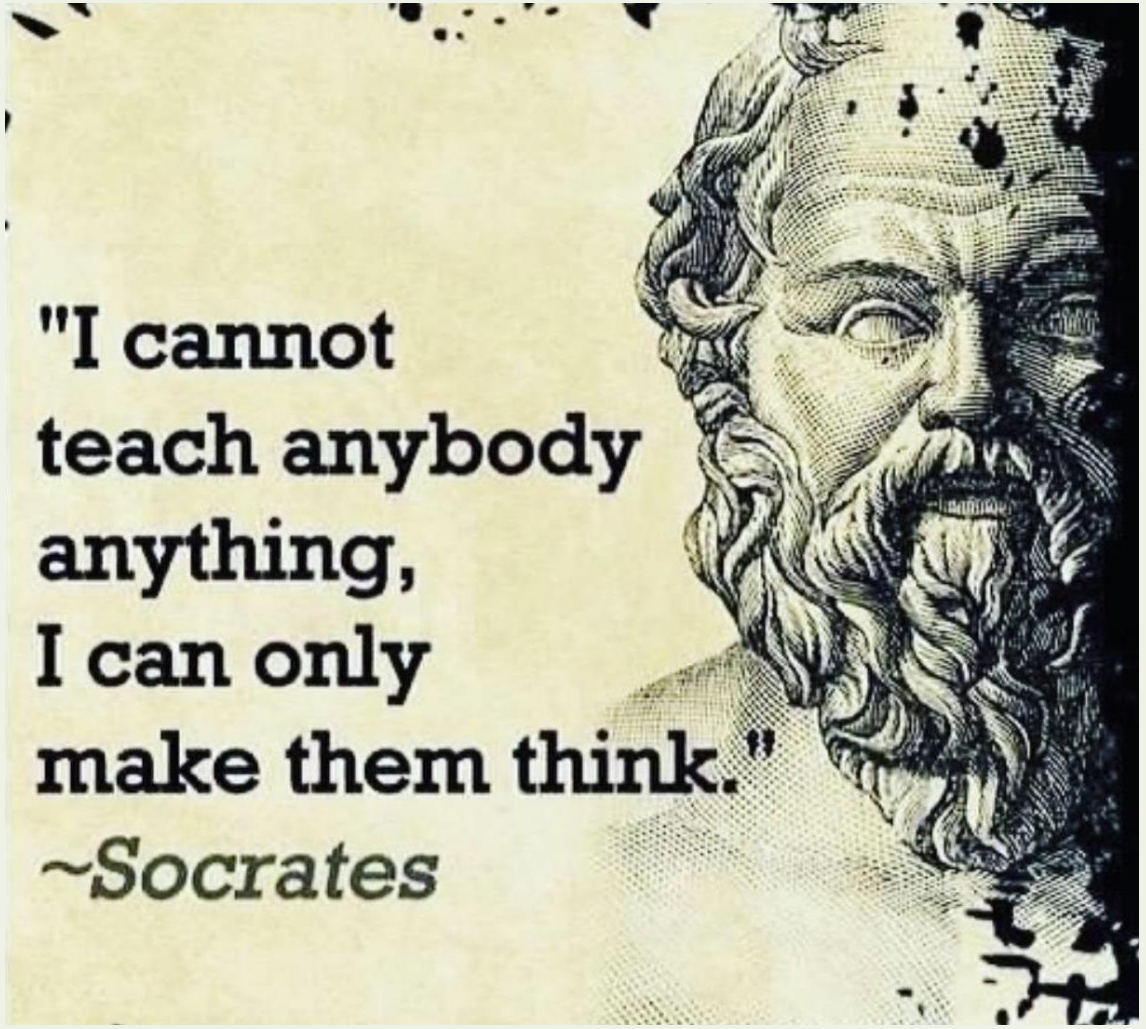

# Disinfection By-Products in Municipal Water Systems.

**Anthony S. Greville.**

# Disinfection By-Products in Municipal Water Systems.



# The Socratic Method of Finding Truth.

The Socratic method is not about winning an argument, but about uncovering the truth through rigorous examination of ideas.

The Socratic Method begins with commonly held beliefs and scrutinizes them by way of question, discussion and argument, to determine their internal consistency and their coherence with other beliefs and so to bring everyone closer to the truth.

This dialectical approach involves examining beliefs and arguments to reveal contradictions and assumptions, aiming to arrive at a more accurate understanding of a topic. It acknowledges that knowledge is often incomplete and encourages individuals to think critically about their own beliefs and the beliefs of others.

# Disinfection By-Products in Municipal Water Systems.

Introduction,

Health Consequences,

Identification of Disinfection By-Products,

Disinfection By-Products Sources,

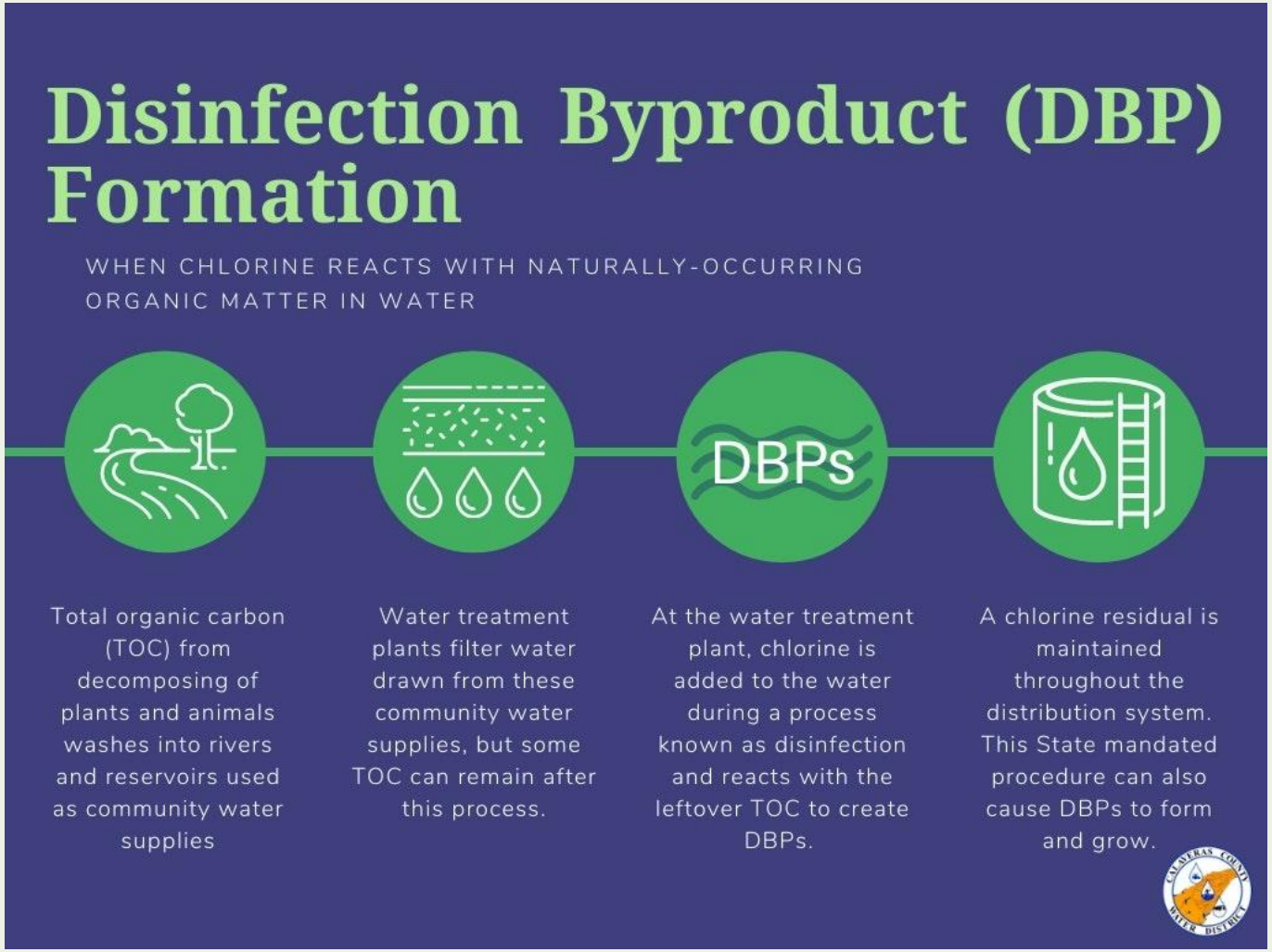
Control Strategies for Disinfection By-Products.

# Disinfection By-Products in Municipal Water Systems.

Free chlorine is the most popular chemical used to maintain a measurable disinfectant residual in Canadian drinking waters. While highly effective against most pathogens, free chlorine will also react with the natural organic matter (NOM), both colloidal and dissolved, present in water to form numerous disinfection by-products (DBPs).

Apart from the limited disinfection efficiency against some chlorine-resistant pathogens, especially Cryptosporidium and Giardia, the main drawback of chlorination is the formation of harmful disinfection by-products resulting from reactions between chlorine and organic matter, both natural and added by humans, present in all source waters, and wastewater treatment plant effluent organic matter, (EfOM), occurring in WTP and associated distribution systems.

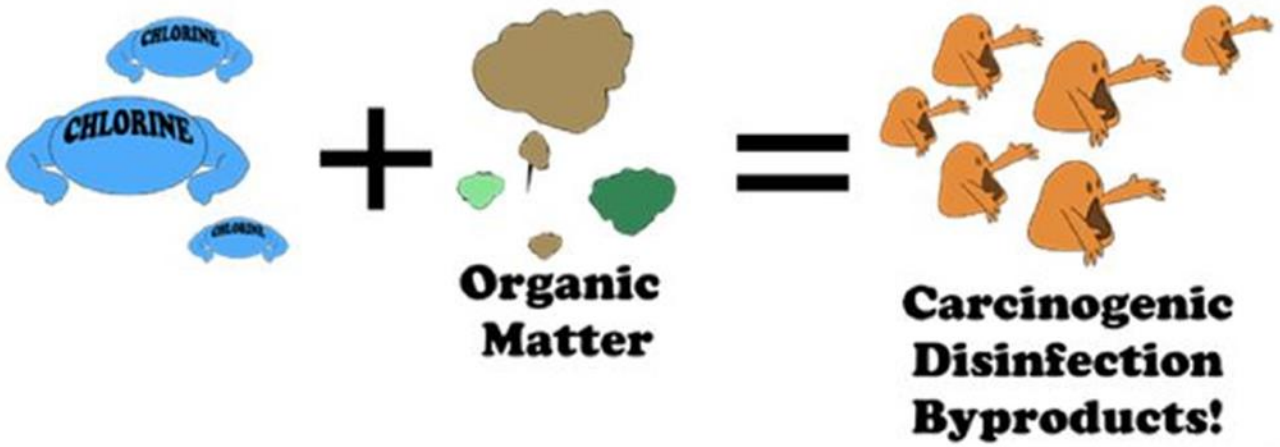
# Disinfection By-Products in Municipal Water Systems.



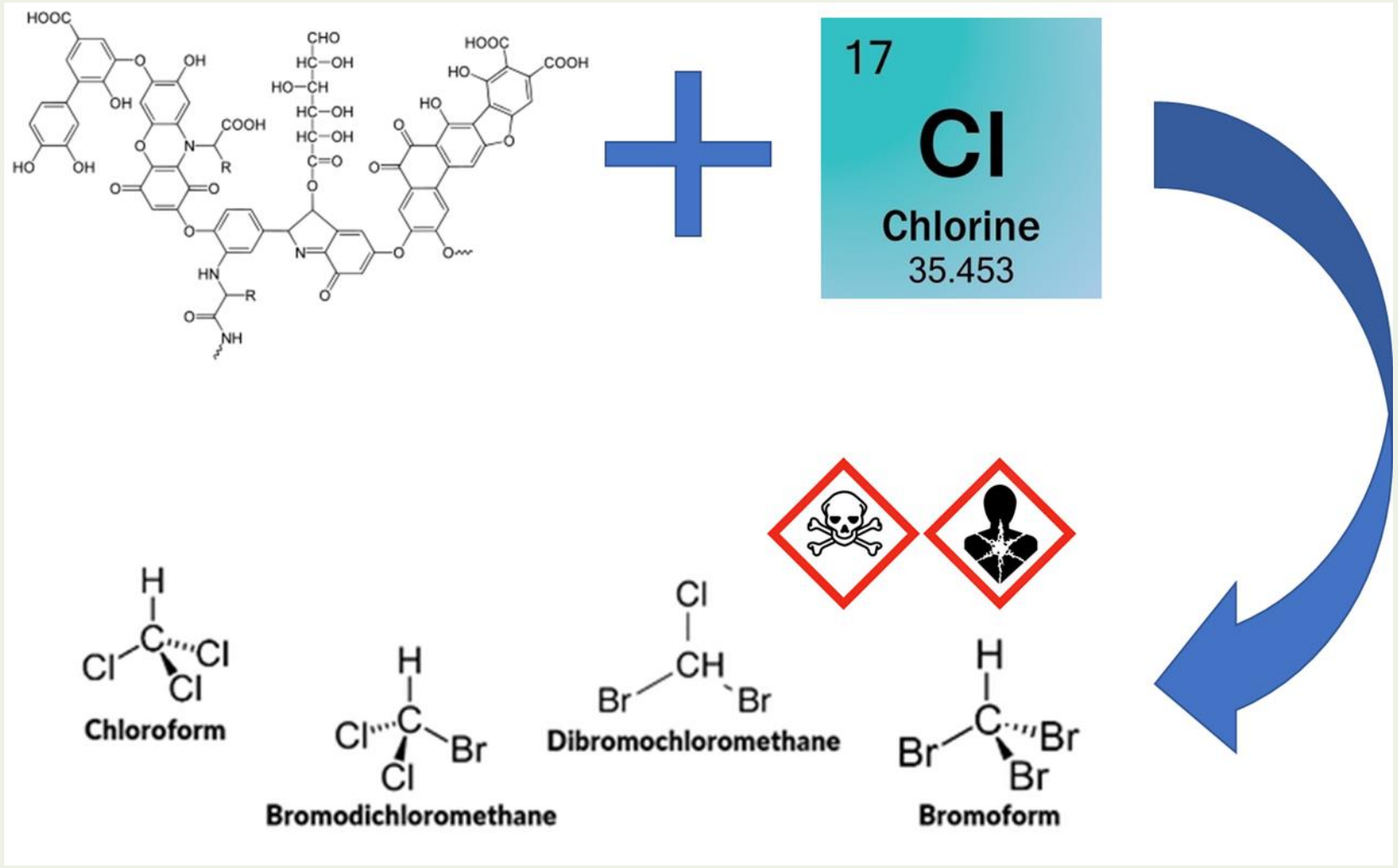
# Disinfection By-Products in Municipal Water Systems.

## Disinfection By-Products

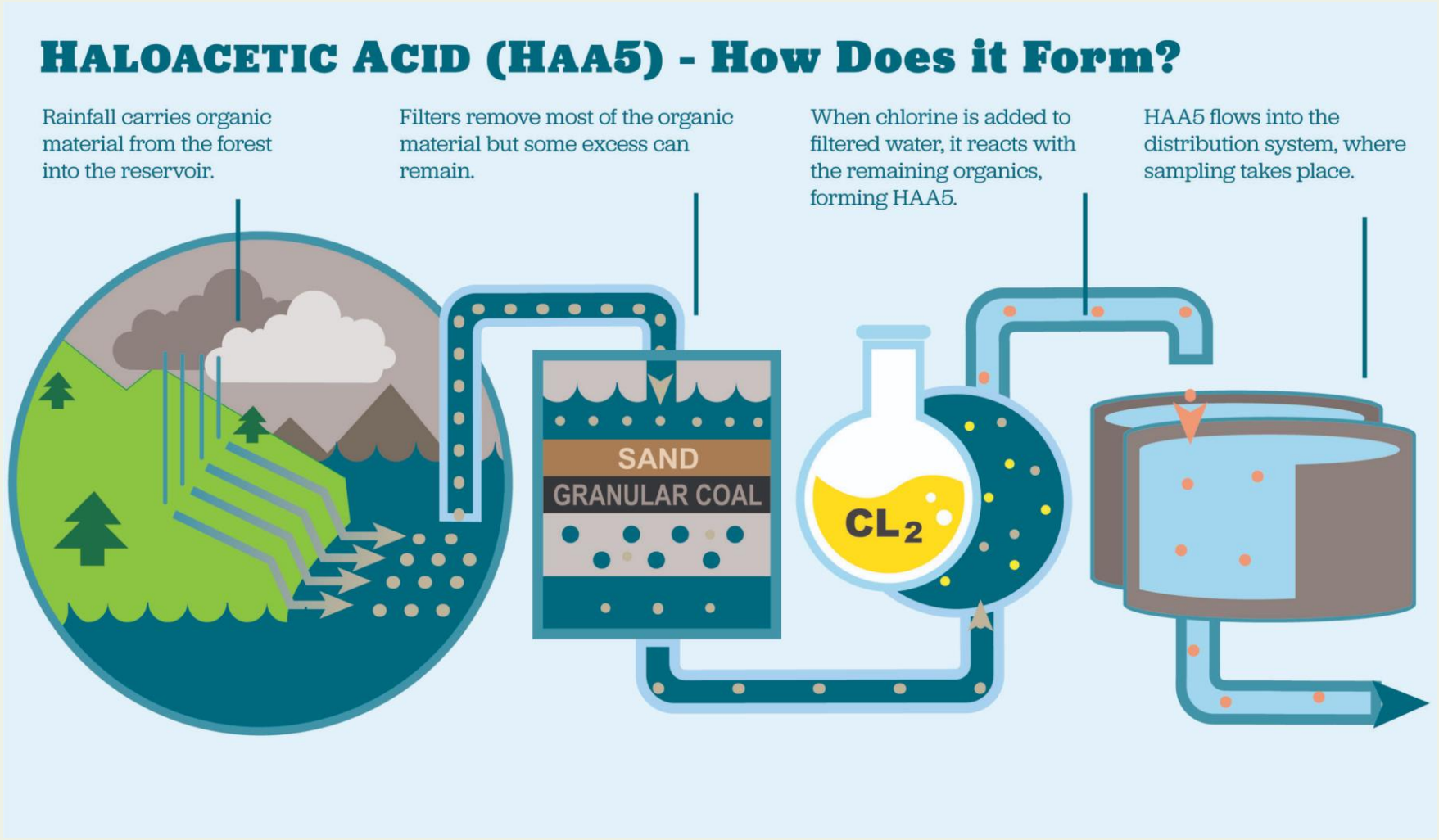
- An unintended consequence: formation of disinfection by-products (DBPs).
- DBPs formed through oxidation and substitution reactions with organic matter



# Disinfection By-Products in Municipal Water Systems.



# Disinfection By-Products in Municipal Water Systems.



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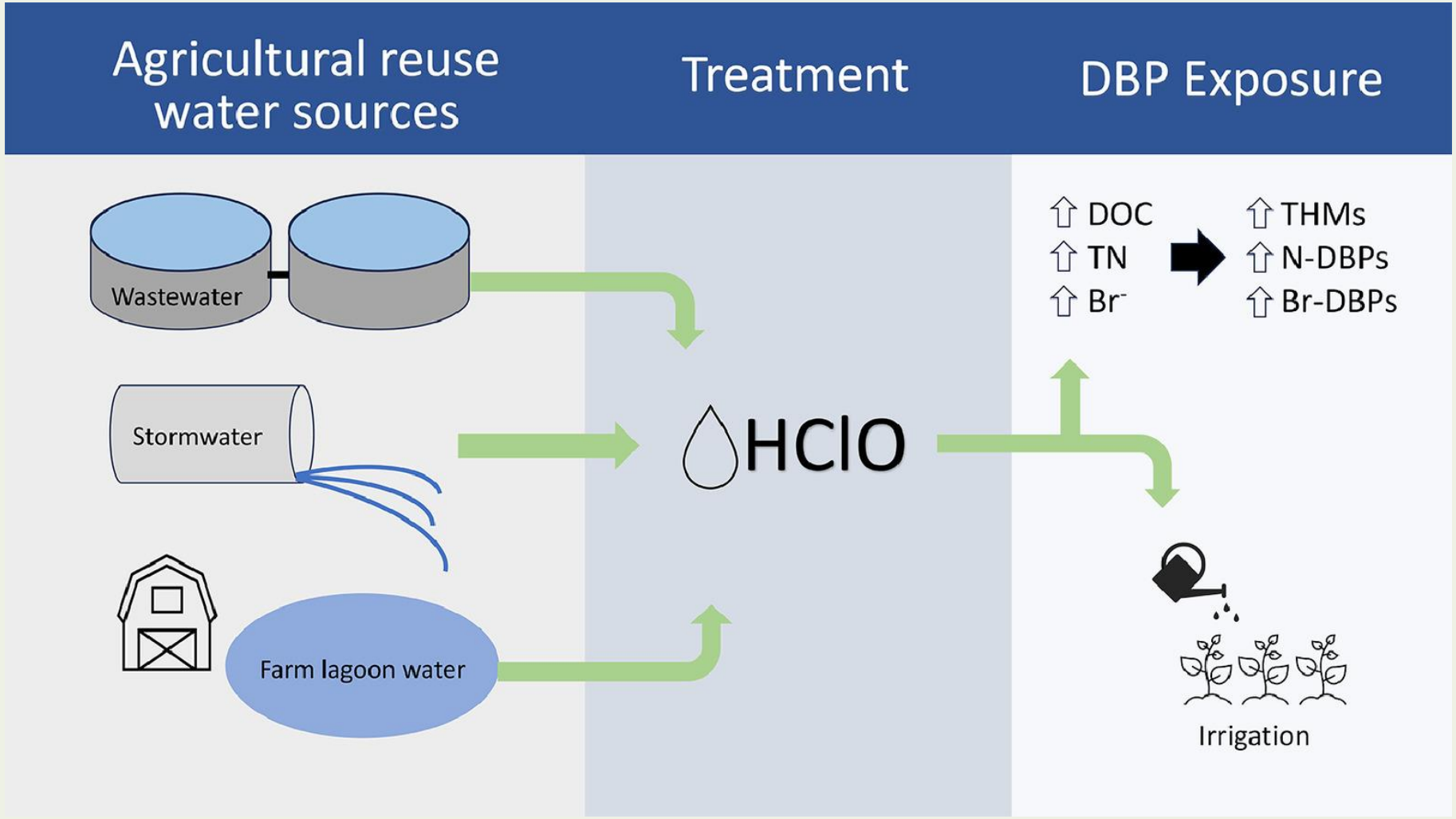

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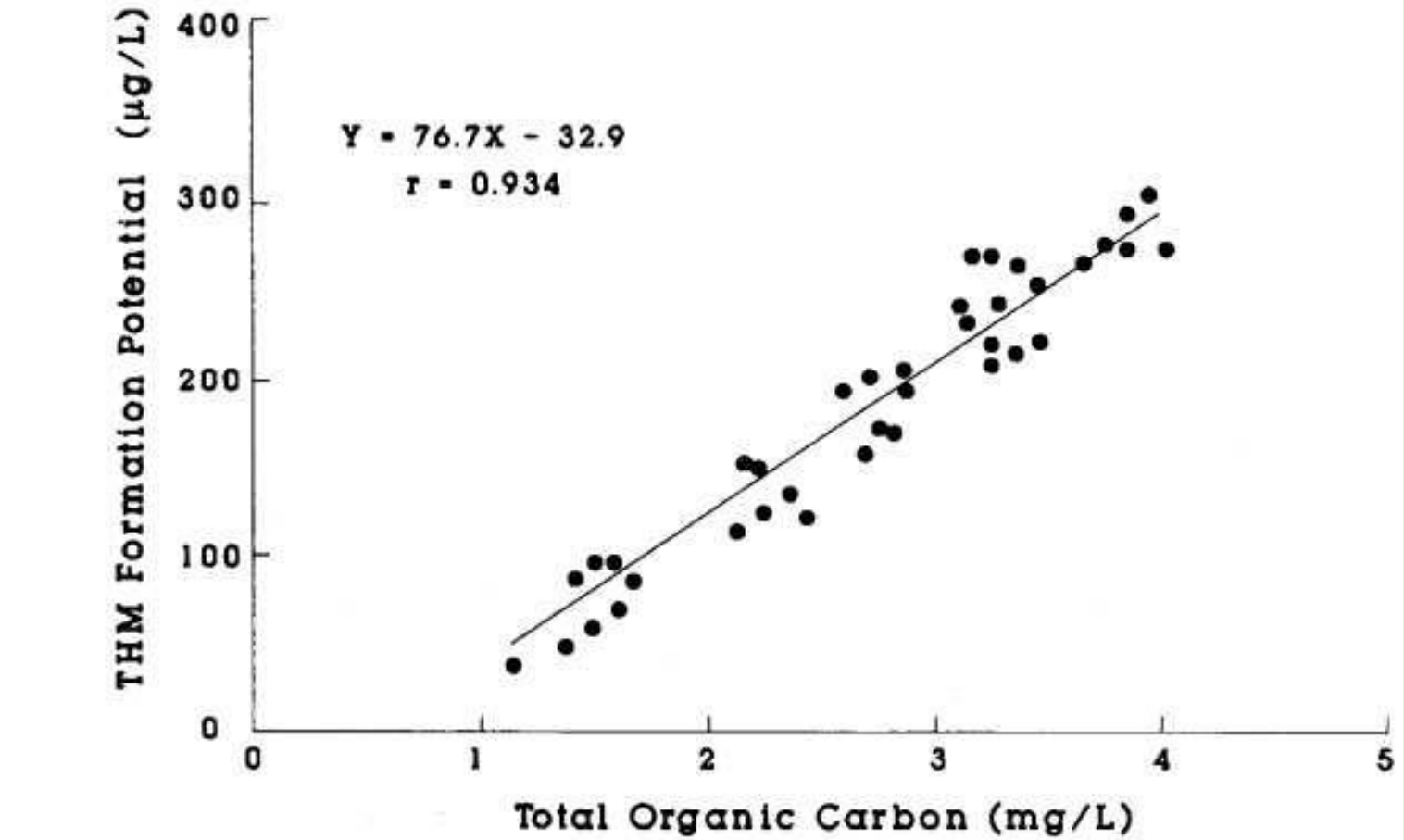
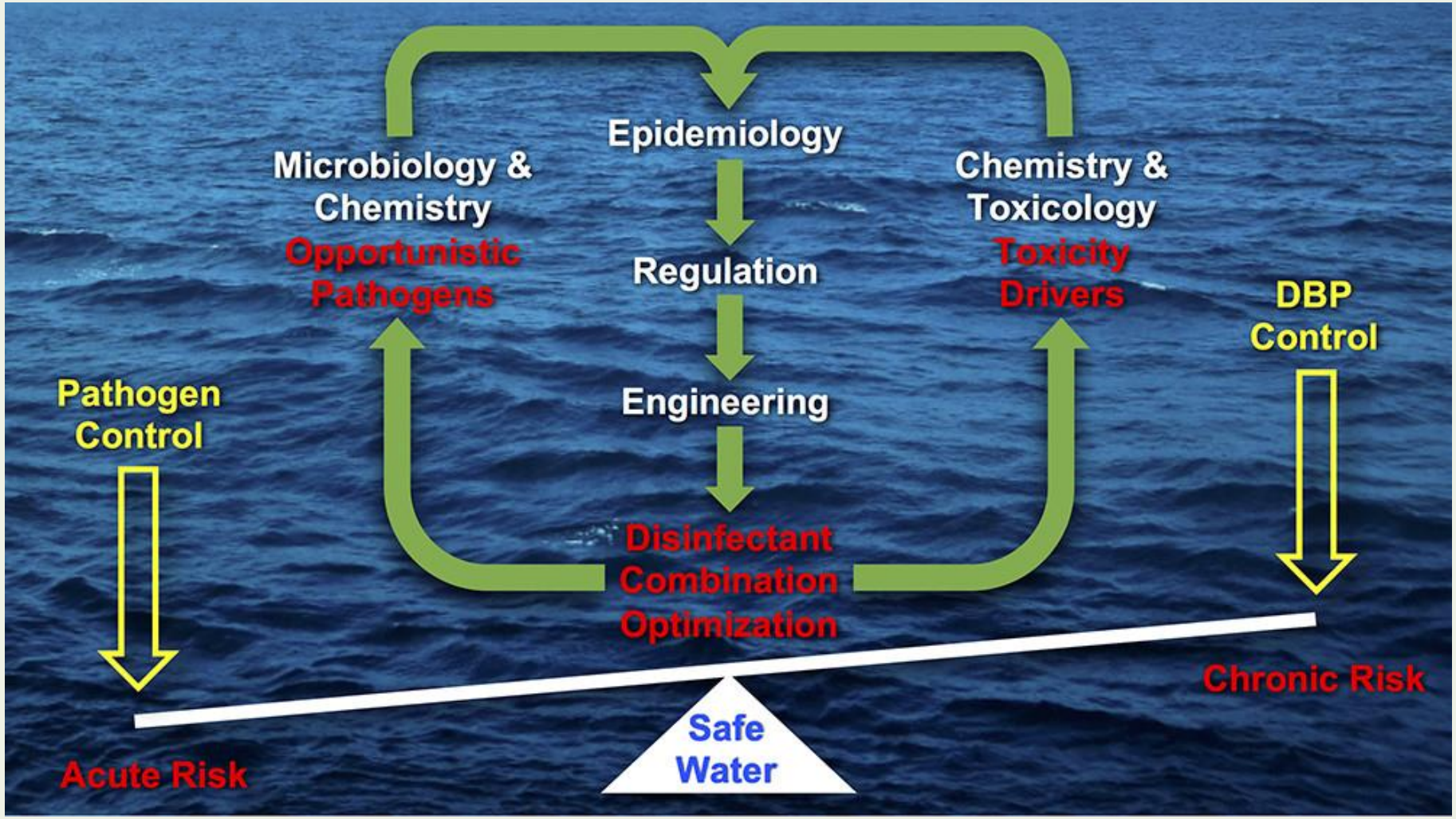



Correlation between THM formation potential (THMFP) opposite total organic carbon (TOC).

# Disinfection By-Products in Municipal Water Systems.



# Health Consequences Associated with DBPs in Municipal Water Systems.

Complex mixtures of disinfection byproducts (DBPs) form when natural source water is disinfected with oxidants, such as chlorine. The use of other oxidants, such as chloramine and ozone also generate harmful DBP.

There has been concern over public health consequences of DBPs since chloroform was first discovered in drinking water by Johannes Rook in the Rhine and Meuse Rivers in 1974, and later identified as a carcinogen in 1976.

Since then, more than 600 DBPs have been identified in drinking water; despite intense identification efforts > 80% of the total organic halogen (TOX) formed during disinfection remain unidentified.

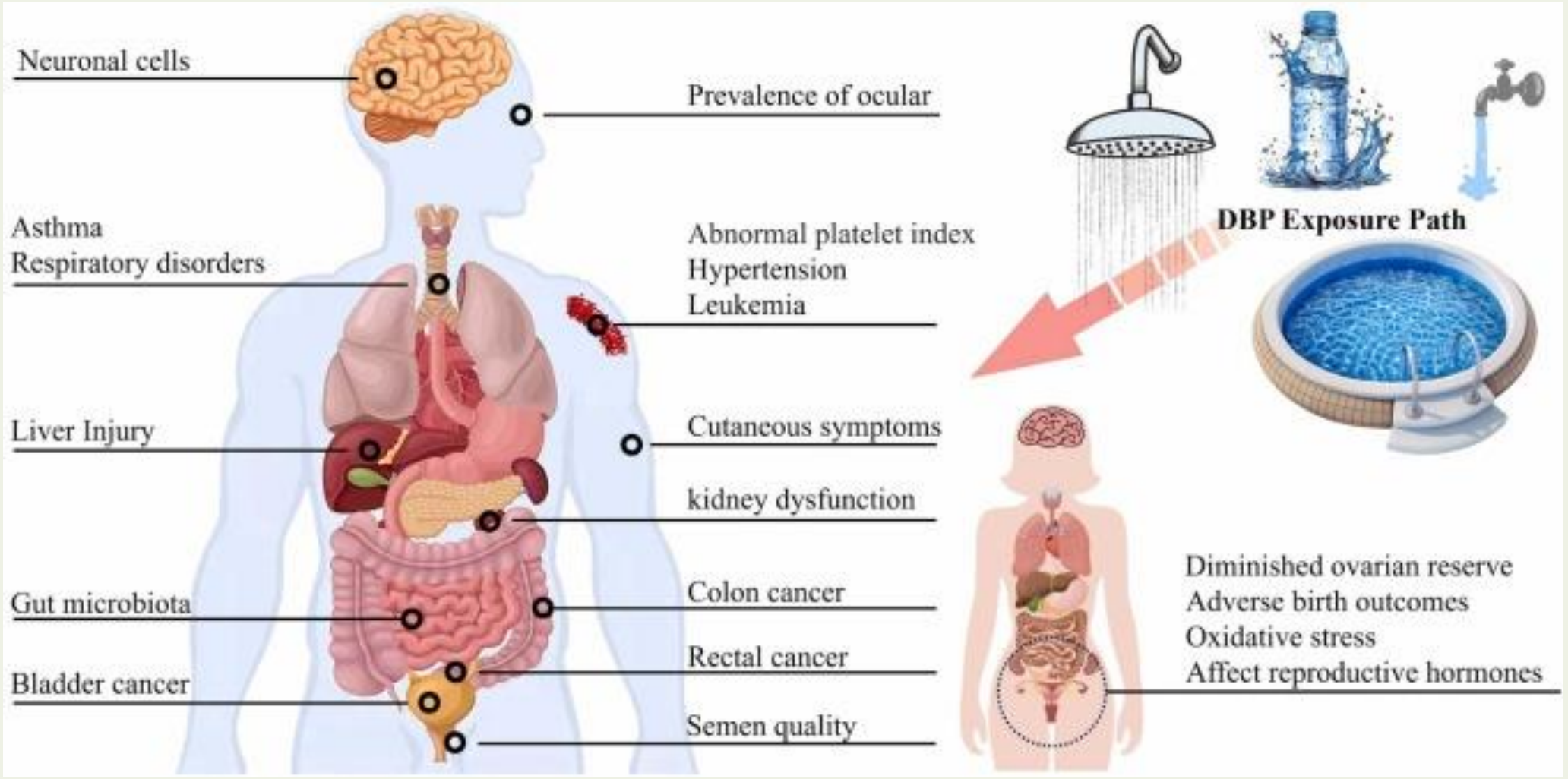
# Health Consequences Associated with DBPs in Municipal Water Systems.

The addition of chlorine to drinking water for effective chlorination results in the formation of various chlorinated disinfection by-products (DBPs). Some, but not all, of these DBPs are carcinogenic and are regulated in most developed countries, including Canada, the US, Europe and by the WHO.

THMs were first regulated by the USEPA in 1979, and HAAs in 1998. Health Canada first regulated THMs in 1978, and HAAs in 2008.

Concerns over DBP exposures have increased through the years due to some epidemiologic studies showing associations between consumption of chlorinated water and bladder cancer, and adverse reproductive outcomes, including spontaneous abortion and low birth weight at term.

# Health Consequences Associated with DBPs in Municipal Water Systems.



# Health Consequences Associated with DBPs in Municipal Water Systems.

Laboratory animals exposed to very high levels of THMs, HAAs and NDMA have been shown to have an increased risk of liver and colorectal cancers.

Several studies on humans also found a link between long-term exposure to high levels of chlorinated disinfection by-products and a higher risk of cancer.

An increased risk of kidney, bladder, and possibly colon cancers, in people who drank chlorinated water for 35 years or more has been proven.

A California study found that pregnant women who drank large amounts of tap water with high THMs had an increased risk of miscarriage.

# Health Consequences Associated with DBPs in Municipal Water Systems.

Haloacetonitriles (HANs) can cause various health issues, including toxicity to gastrointestinal and fetal tissues, and potentially show genotoxicity and carcinogenicity in other mammals.

While human data is limited, studies show that high exposure to HAN can lead to reduced fetal and maternal weight, developmental deformities, oxidative stress, DNA damage, and cellular toxicity.

HANs are also associated with a potential for increased risks to the liver, kidneys, and central nervous system from long-term exposure. In addition to tissue damage, HANs can cause specific cellular damage by reacting with and adducing (binding) to antioxidant proteins.

# Health Consequences Associated with DBPs in Municipal Water Systems.

Exposure to chlorinated surface waters was found to result in a greater risk of cancer compared to chlorinated groundwater. This may be attributed to higher DBP formation potentials, due to the presence of precursors, in surface waters, and in other sources of contamination, when compared to groundwaters.

Surprisingly, ingestion of chlorinated drinking water is no longer considered to be the major route of DBP exposure.

THM levels in blood have been shown to be far higher after exposure to chlorinated drinking water via dermal absorption and inhalation; during showering, bathing or swimming etc., than after direct ingestion.

# Health Consequences Associated with DBPs in Municipal Water Systems.

Ingestion - While DBPs are found in measurable concentrations in all chlorinated water samples, THMs, which are a volatile group of DBPs, have been found in measurably low concentrations in drinks prepared with boiled water and were not detectable at all in most prepared and cooked foods.

Inhalation - Inhalation is an important pathway of exposure to DBPs as these compounds can accumulate in indoor air during showering, bathing, swimming and other activities related to the use of chlorinated water.

THM concentrations in tap water were compared to those in blood, before and after showering, in two different communities. The results showed THM concentrations in blood increased significantly after showering and their distribution shifted towards that found in the tap water.

# Health Consequences Associated with DBPs in Municipal Water Systems.

Dermal - Dermal absorption during showering/bathing is another major route of exposure to DBPs. However, polar molecules of the larger haloacetic acid (HAAs) and haloacetonitrile (HANs), molecules do not readily penetrate the skin.

A major recent finding from pharmacokinetic studies with BDCM (bromodichloromethane) in humans found BDCM concentrations in blood were 25 to 130 times higher due to dermal exposure when compared to the oral ingestion exposure route.

It is now believed the risks associated with chlorinated drinking water are greater due to showering, bathing and swimming, (water flow, type of showerhead, and the air exchange rate etc.) rather than direct ingestion route.

# Identification of Disinfection By-Products in Municipal Water Systems.

Disinfectant effectiveness, especially strong oxidants such as chlorine, chlorine dioxide and ozone, is due to their highly reactive nature.

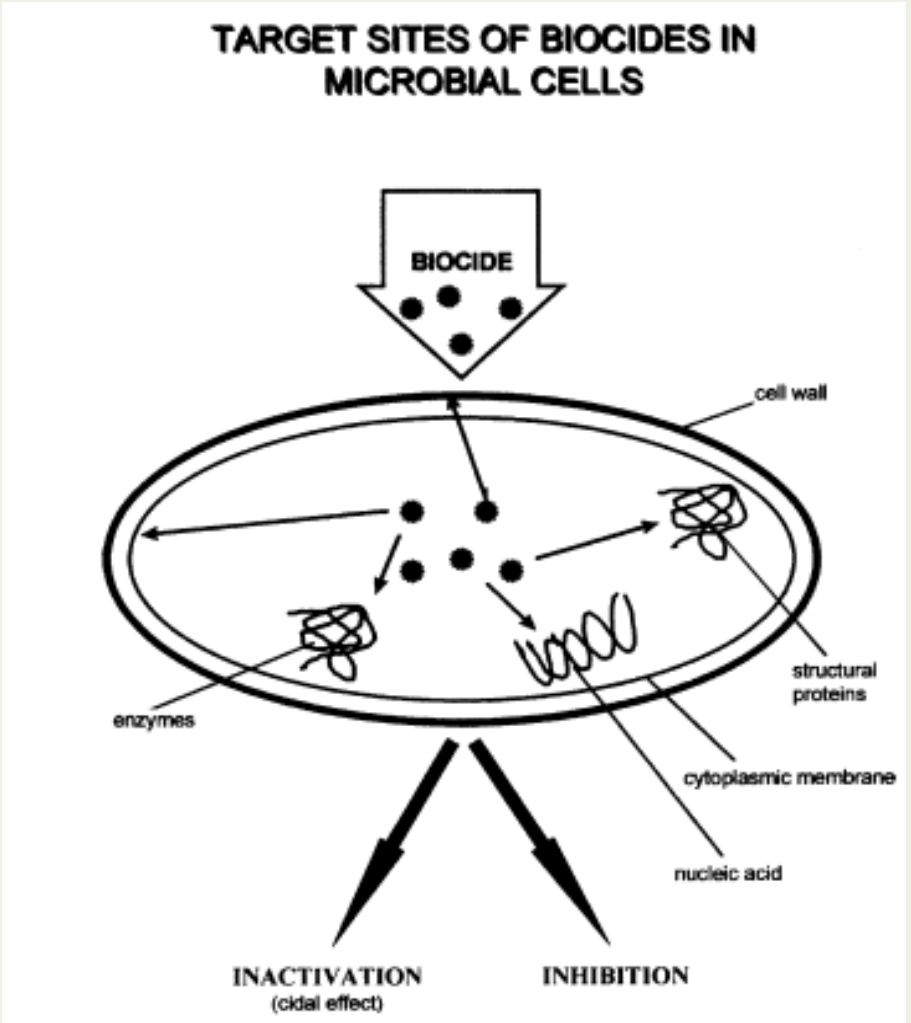
Disinfectants react with, and disrupt, cell membranes, nucleic material and the cellular proteins of the pathogenic microorganisms; unfortunately, they also react with all naturally occurring decaying organic matter (NOM).

Most of the disinfectant demand in water can be attributed to this NOM.

Understanding disinfection by-products (DBPs) potential and the ability to control their formation is critical to meeting regulatory guidelines.

# Identification of Disinfection By-Products in Municipal Water Systems.

Disinfectants effect their killing, or inactivation properties, by reacting with one or more structures in microbial cells. The oxidant can compromise the cell wall peptidoglycan film, the cytoplasmic membranes, outer membrane, structural proteins, thiol groups of enzymes, nucleic acids, viral envelopes, capsids or nucleic acids, and bacterial spore coatings.

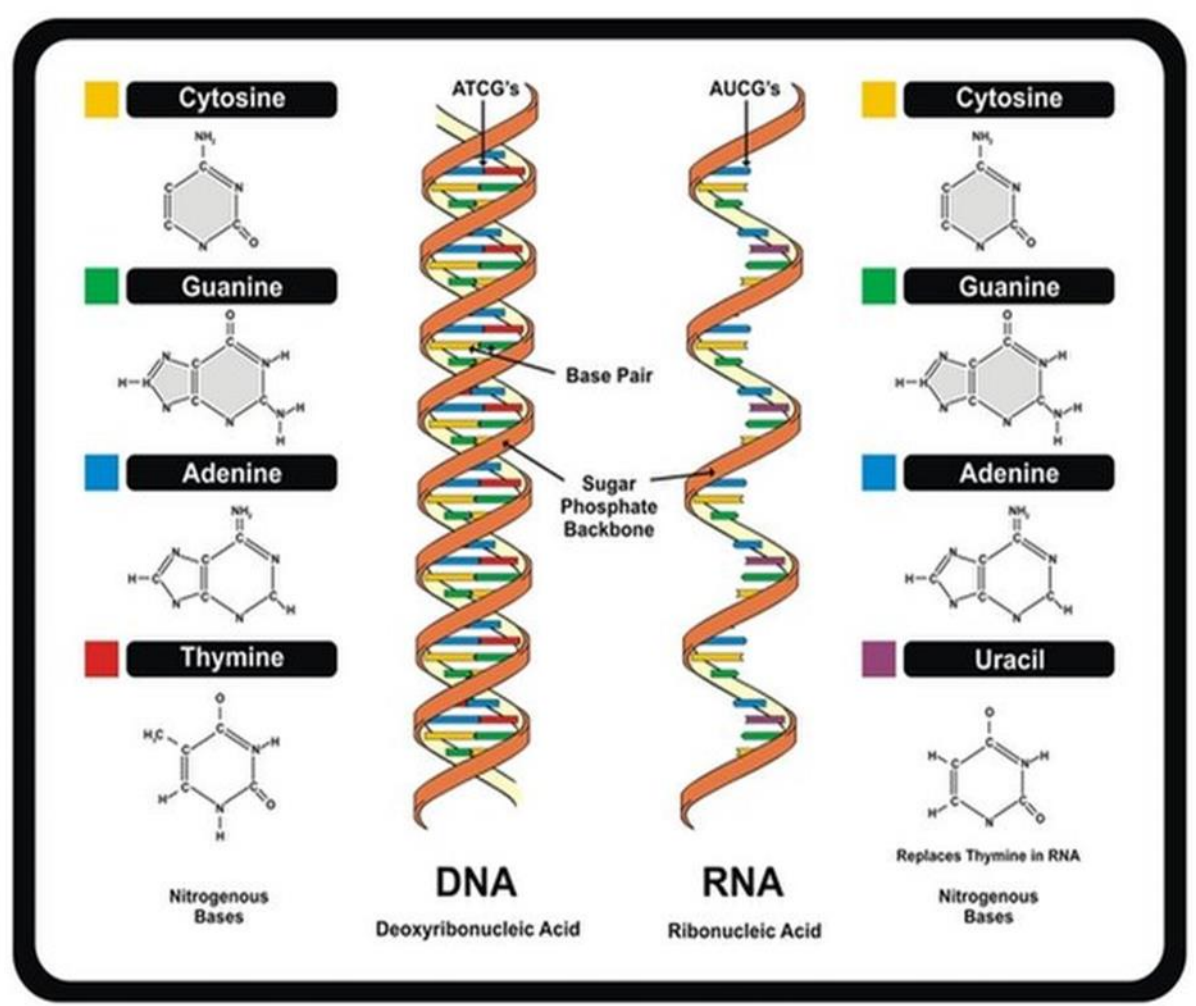


# Identification of Disinfection By-Products in Municipal Water Systems.

DeoxyriboNucleic Acid (DNA)

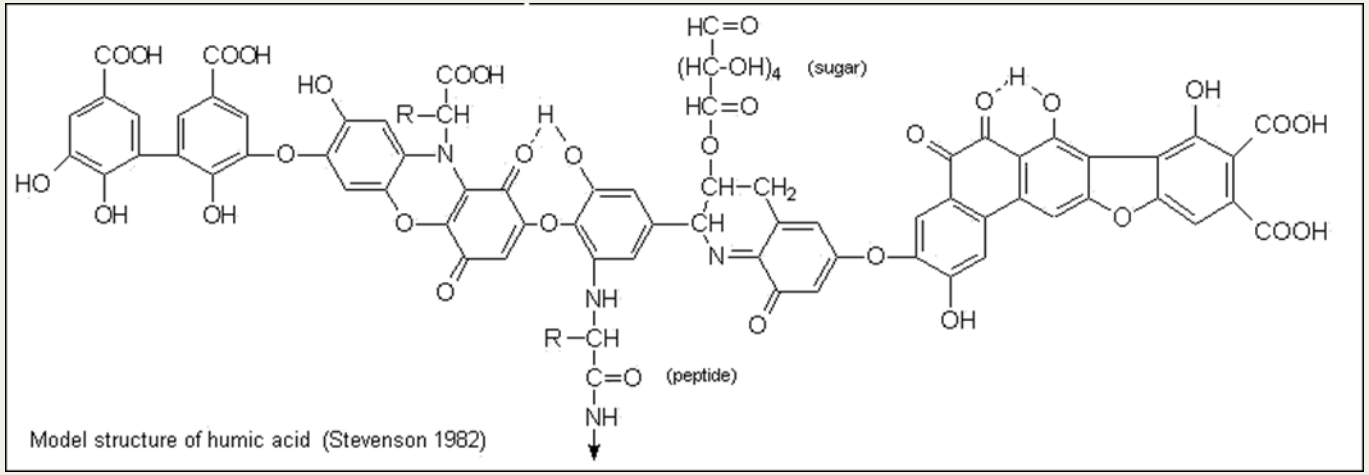
&

RiboNucleic Acid (RNA)

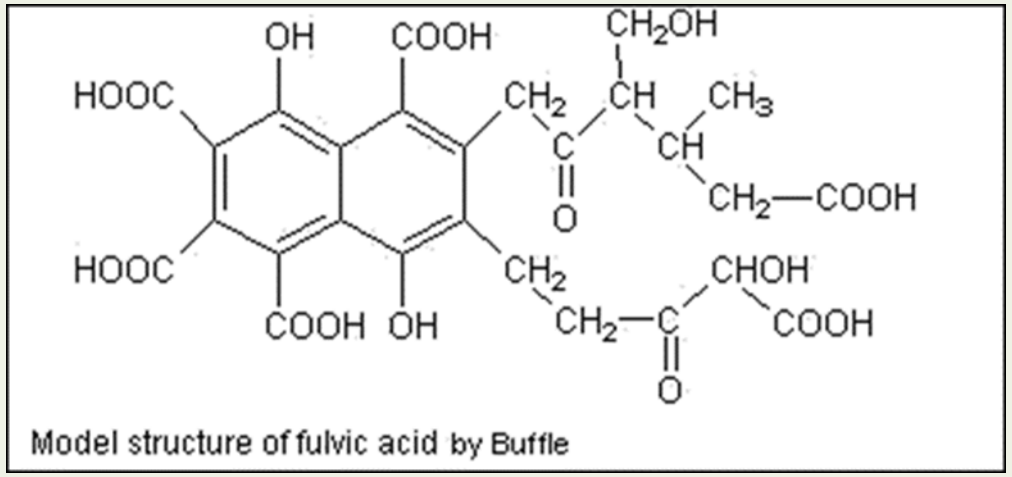


# Identification of Disinfection By-Products in Municipal Water Systems.

Humic Acid.




Fulvic Acid.



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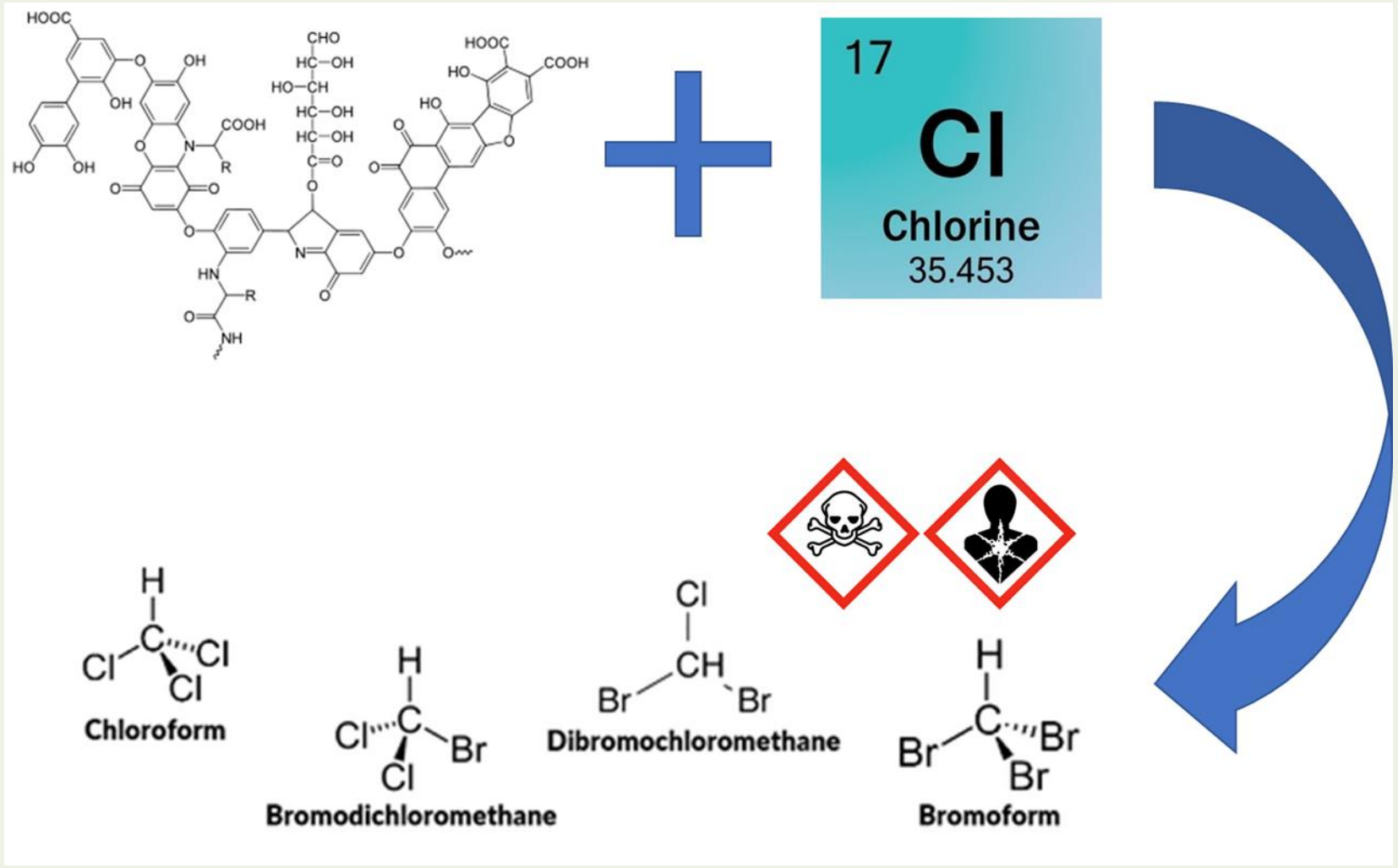


# Identification of Disinfection By-Products in Municipal Water Systems.

DBPs are present in most drinking water supplies that have been subject to chlorination, chloramination, ozonation, or treatment with chlorine dioxide.

Many hundreds of DBPs exist in treated drinking water; at least 600 have been identified, and probably as many as 6,000 molecular structures have yet to be properly identified and catalogued.

The very low concentrations of many of these DBPs, and the analytical costs associated with testing, allow for only a very few of the DBPs to be monitored in any practical manner.

# Identification of Disinfection By-Products in Municipal Water Systems.

## Analytical Results

| Sub-Matrix: Water (Matrix: Water) | | | | Client sample ID | [redacted] | | | ---- |
|---|---|---|---|---|---|---|---|---|
| | | | | Client sampling date / time | 19-Mar-2024 05:35 | 19-Mar-2024 07:00 | 19-Mar-2024 08:45 | 19-Mar-2024 06:25 | ---- |
| Analyte | CAS Number | Method/Lab | LOR | Unit | [redacted] | | | | ------- |
| | | | | | Result | Result | Result | Result | ---- |
| **Volatile Organic Compounds [THMs]** | | | | | | | | | |
| Bromodichloromethane | 75-27-4 | E611B/VA | 1.0 | µg/L | <1.0 | <1.0 | <1.0 | <1.0 | — |
| Bromoform | 75-25-2 | E611B/VA | 1.0 | µg/L | <1.0 | <1.0 | <1.0 | <1.0 | — |
| Chloroform | 67-66-3 | E611B/VA | 1.0 | µg/L | 57.5 | 57.4 | 52.1 | 49.6 | — |
| Dibromochloromethane | 124-48-1 | E611B/VA | 1.0 | µg/L | <1.0 | <1.0 | <1.0 | <1.0 | — |
| Trihalomethanes [THMs], total | ---- | E611B/VA | 2.0 | µg/L | 57.5 | 57.4 | 52.1 | 49.6 | — |
| **Volatile Organic Compounds [THMs] Surrogates** | | | | | | | | | |
| Bromofluorobenzene, 4- | 460-00-4 | E611B/VA | 1.0 | % | 87.5 | 89.2 | 85.2 | 90.8 | — |
| Difluorobenzene, 1,4- | 540-36-3 | E611B/VA | 1.0 | % | 98.8 | 99.2 | 99.9 | 95.2 | — |
| **Haloacetic Acids** | | | | | | | | | |
| Bromochloroacetic acid | 5589-96-8 | E750/WT | 1.00 | µg/L | <1.00 | <1.00 | <1.00 | <1.00 | — |
| Dibromoacetic acid | 631-64-1 | E750/WT | 1.00 | µg/L | <1.00 | <1.00 | <1.00 | <1.00 | — |
| Dichloroacetic acid | 79-43-6 | E750/WT | 1.00 | µg/L | 24.7 | 25.0 | 23.7 | 21.0 | — |
| Monobromoacetic acid | 79-08-3 | E750/WT | 1.00 | µg/L | <1.00 | <1.00 | <1.00 | <1.00 | — |
| Monochloroacetic acid | 79-11-8 | E750/WT | 1.00 | µg/L | 1.12 | <1.00 | <1.00 | 1.02 | — |
| Trichloroacetic acid | 76-03-9 | E750/WT | 1.00 | µg/L | 33.2 | 32.2 | 29.5 | 26.6 | — |
| Haloacetic acids, total [HAA5] | n/a | E750/WT | 5.00 | µg/L | 59.0 | 57.2 | 53.2 | 48.6 | — |

Please refer to the General Comments section for an explanation of any result qualifiers detected.

Please refer to the Accreditation section for an explanation of analyte accreditations.

# Identification of Disinfection By-Products in Municipal Water Systems.

Chlorinated disinfection by-products pose the greatest health concerns; therefore, the focus of most regulators is primarily with the groups of;

Trihalomethanes (THM),

Haloacetic acids (HAA).

These two major groups of DBPs generally account for 30% of the total organic halogen (TOX) [20% THMs and 10% HAAs] with most of the other species remaining unidentified. Haloacetonitriles (HAN) while lower in concentration, also have a high profile as DBPs of concern due to their toxicity.

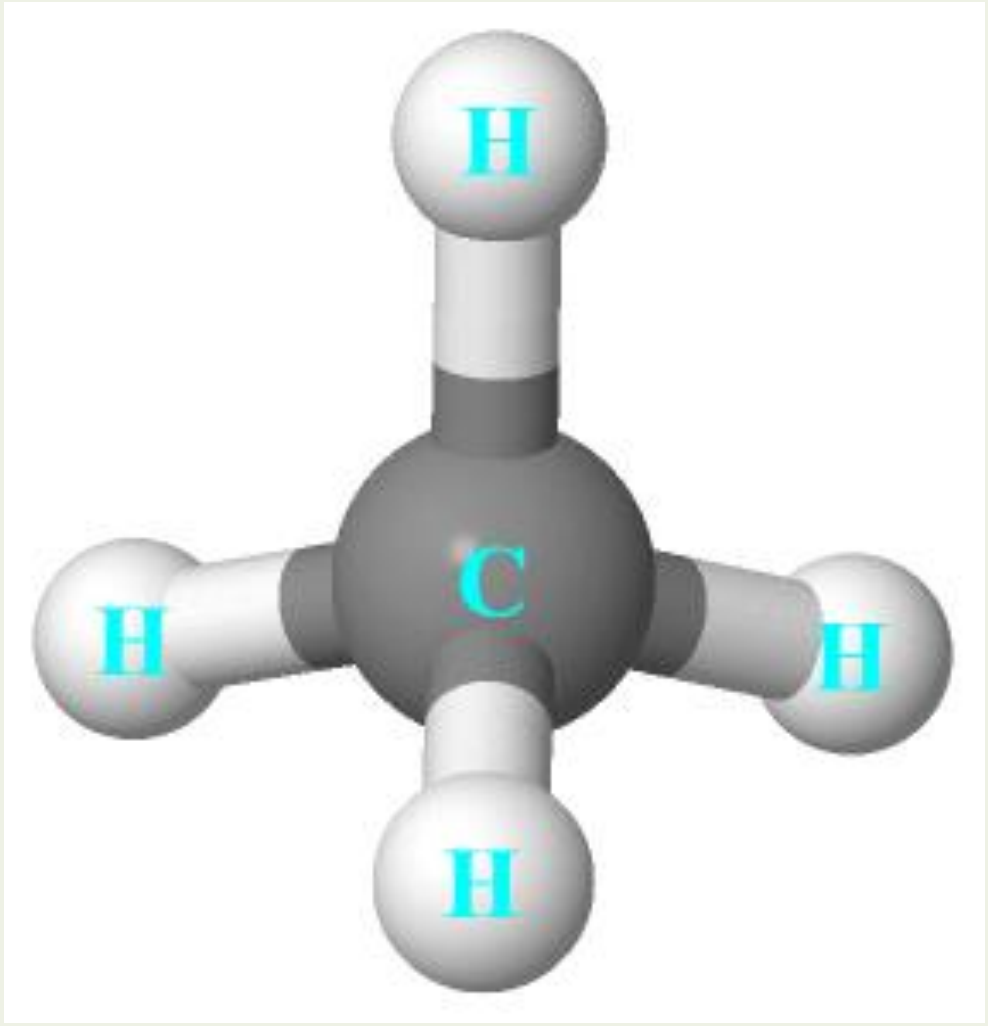
# Identification of Disinfection By-Products in Municipal Water Systems.

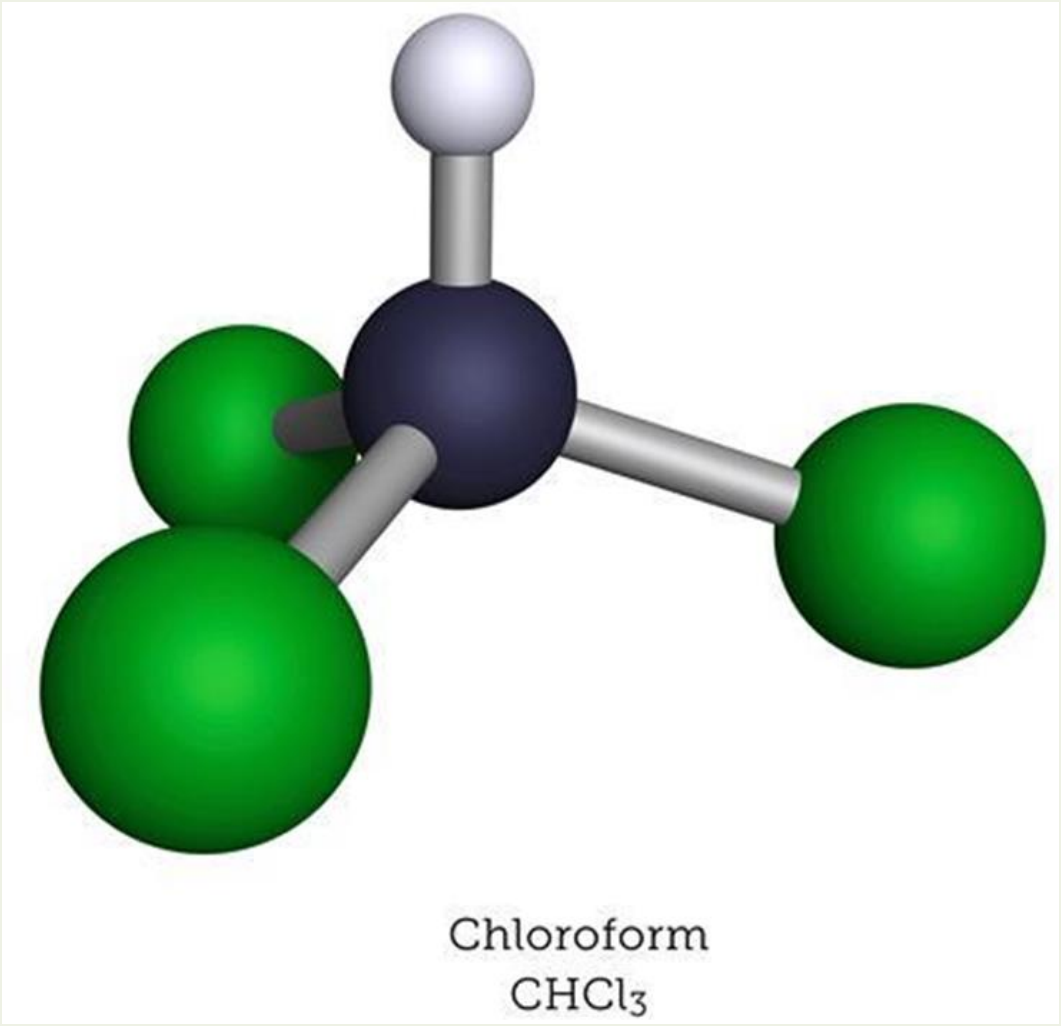
One class of organic chlorine disinfection by-products of concern are the four trihalomethanes (THMs);

Bromoform (tribromomethane),
Dibromochloromethane,
Bromodichloromethane,
Chloroform (trichloromethane).

Together they are regulated as Total THMs, (TTHM) with a combined MAC (maximum acceptable concentration) of 0.1 $mgL^{-1}$, or 100 $\mu gL^{-1}$ (1996, and reaffirmed in 2006).

# Identification of Disinfection By-Products in Municipal Water Systems.



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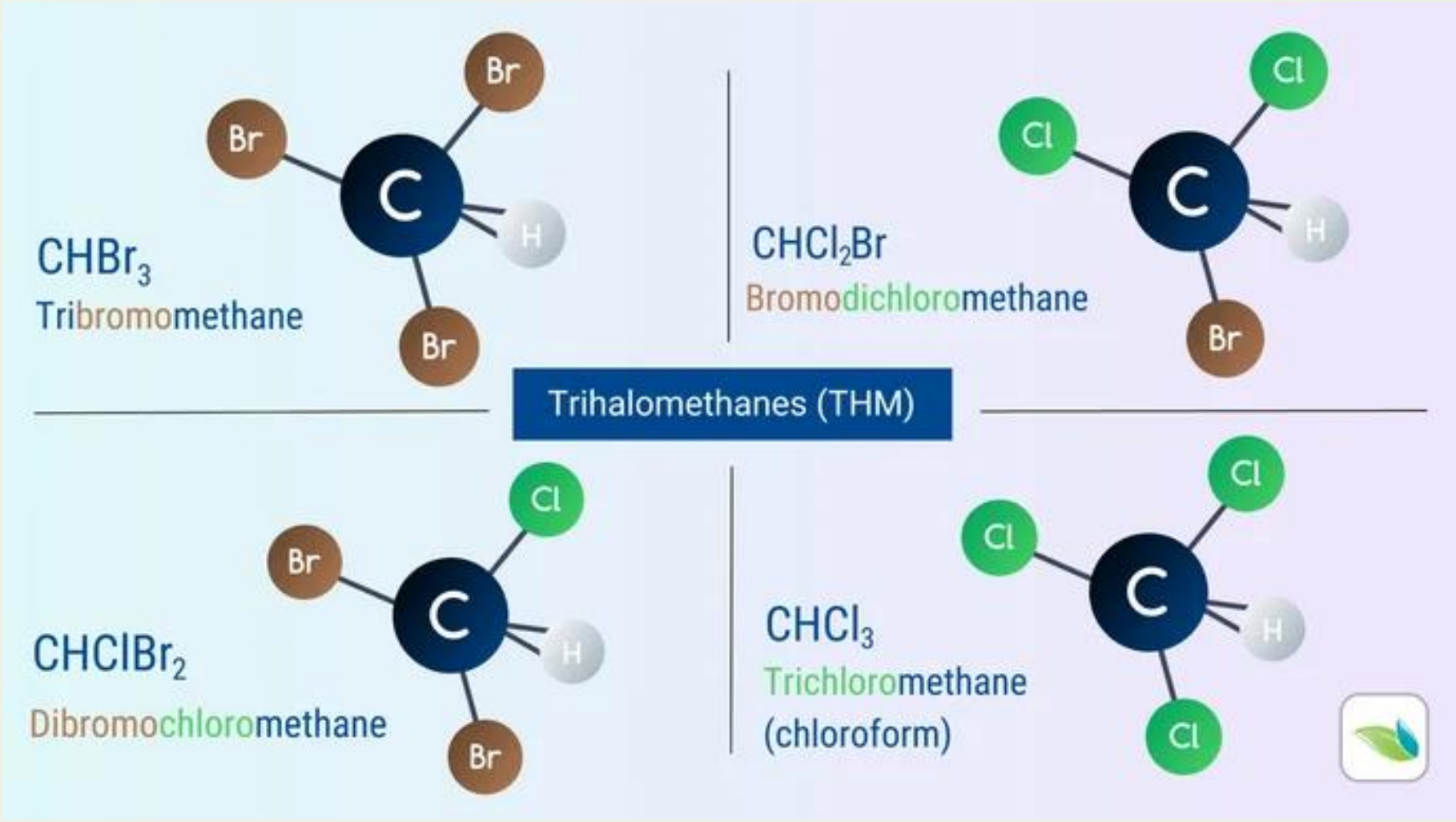

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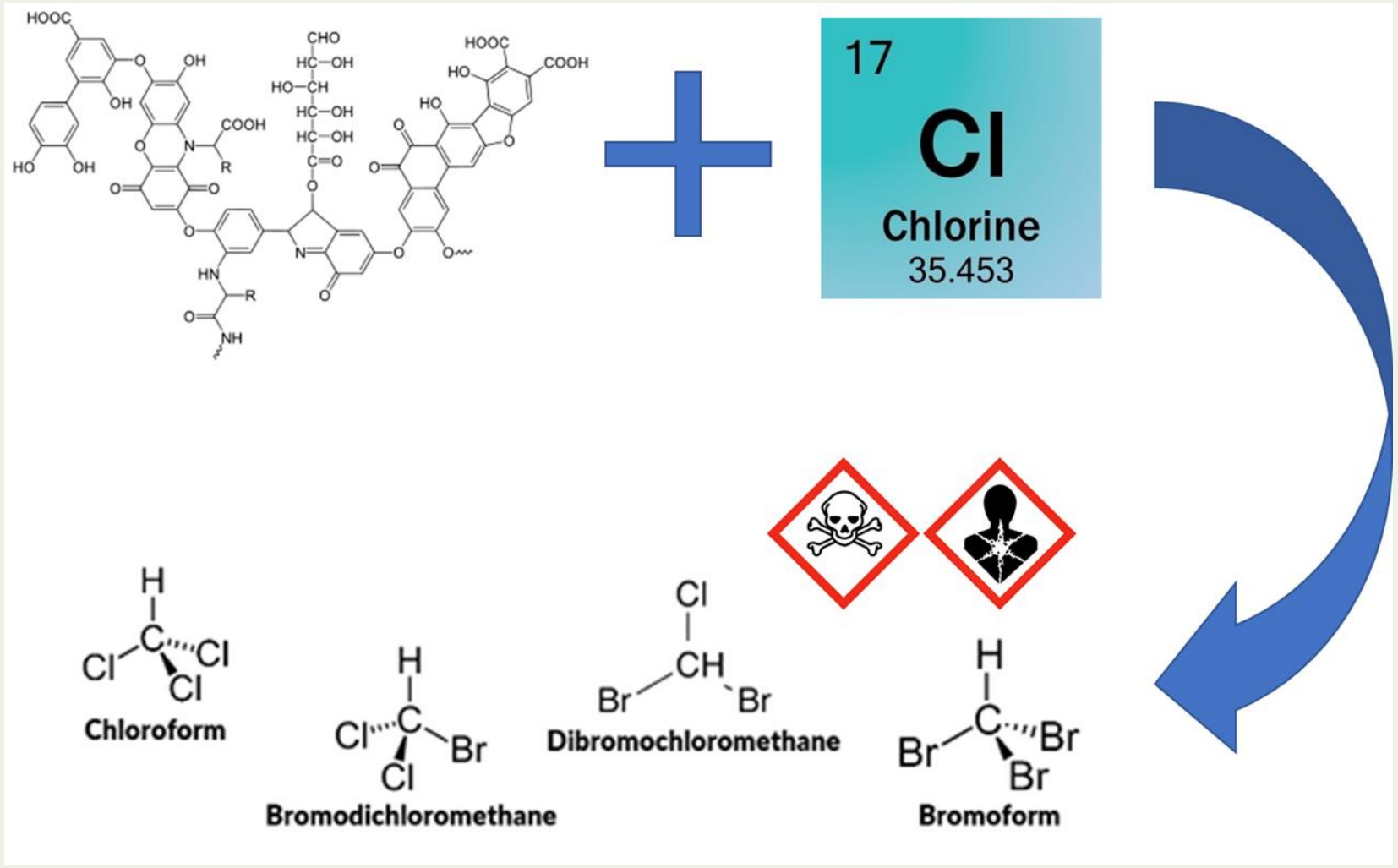

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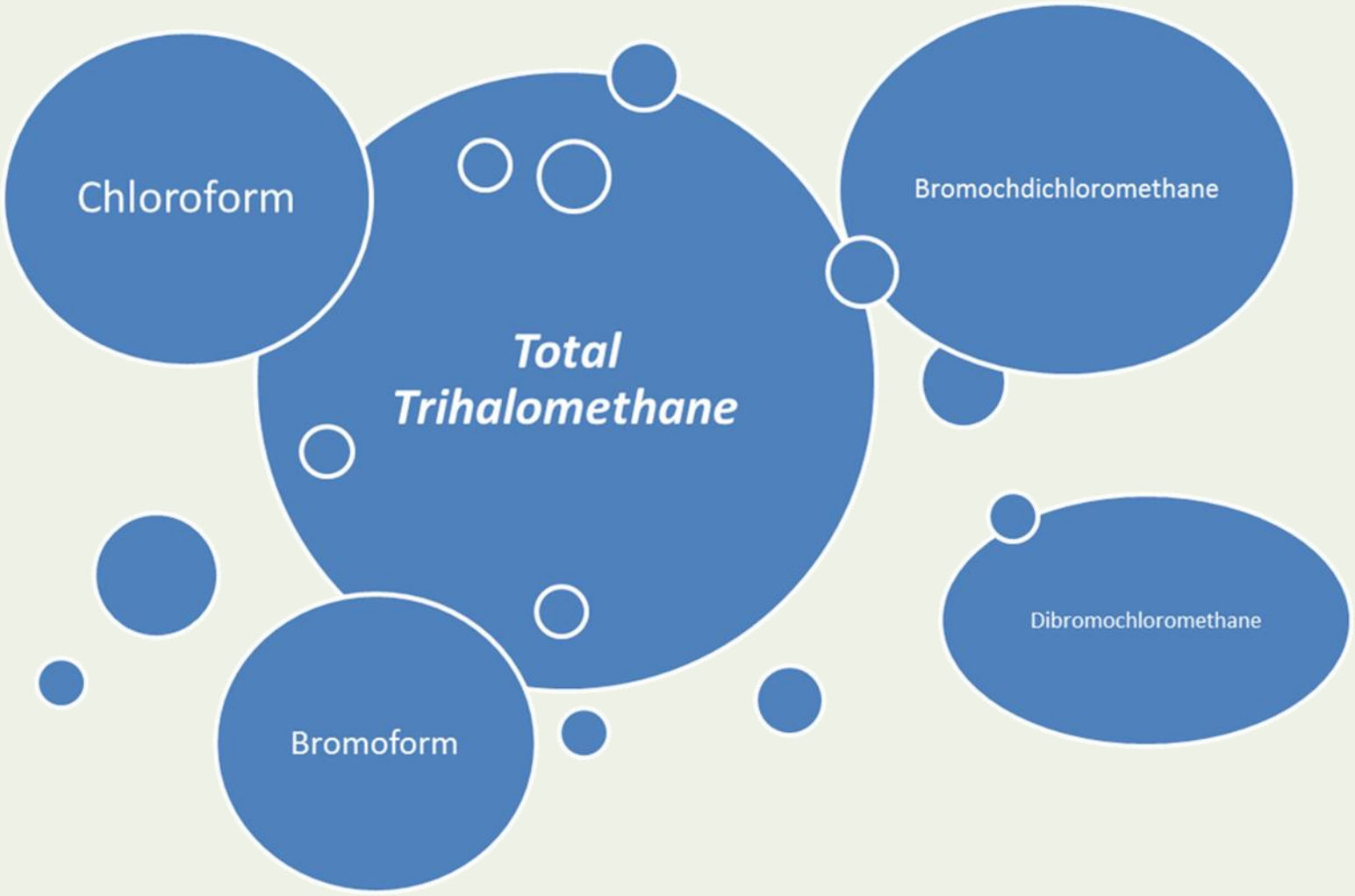
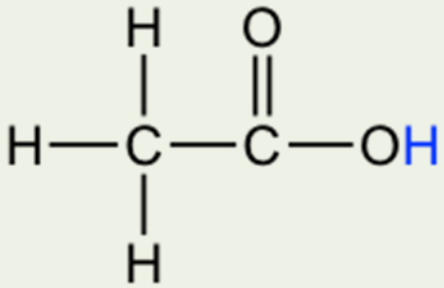


# Identification of Disinfection By-Products in Municipal Water Systems.

The second major classification is the nine possible HAAs, that include chlorine and bromine, sometimes referred to as the “HAA9”;

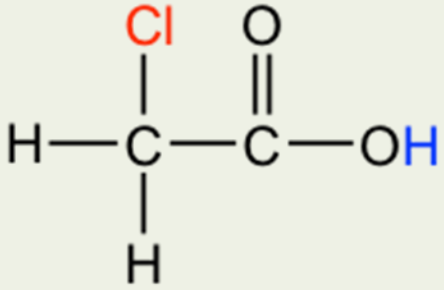
Monochloroacetic acid, MCAA
Dichloroacetic acid, DCAA
Trichloroacetic acid, TCAA
Monobromoacetic acid, MBAA
Dibromoacetic acid, DBAA
Tribromoacetic acid, TBAA
Bromochloroacetic acid BCAA
Dibromochloroacetic acid, DBCAA
Dichlorobromoacetic acid, DCBAA

# Identification of Disinfection By-Products in Municipal Water Systems.



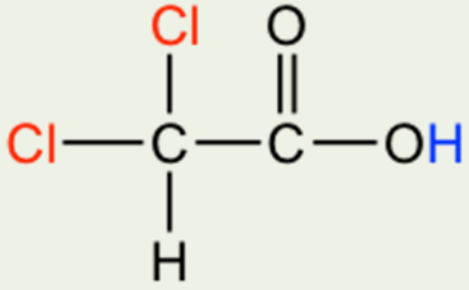

**acetic acid**

$pK_a = 4.8$



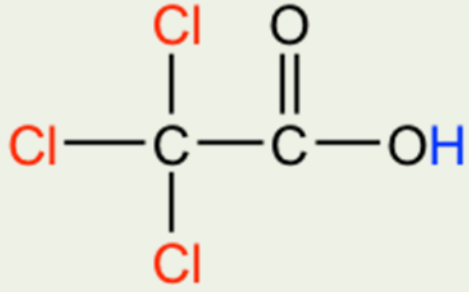

**monochloroacetic acid**

$pK_a = 2.8$




**dichloroacetic acid**

$pK_a = 1.3$

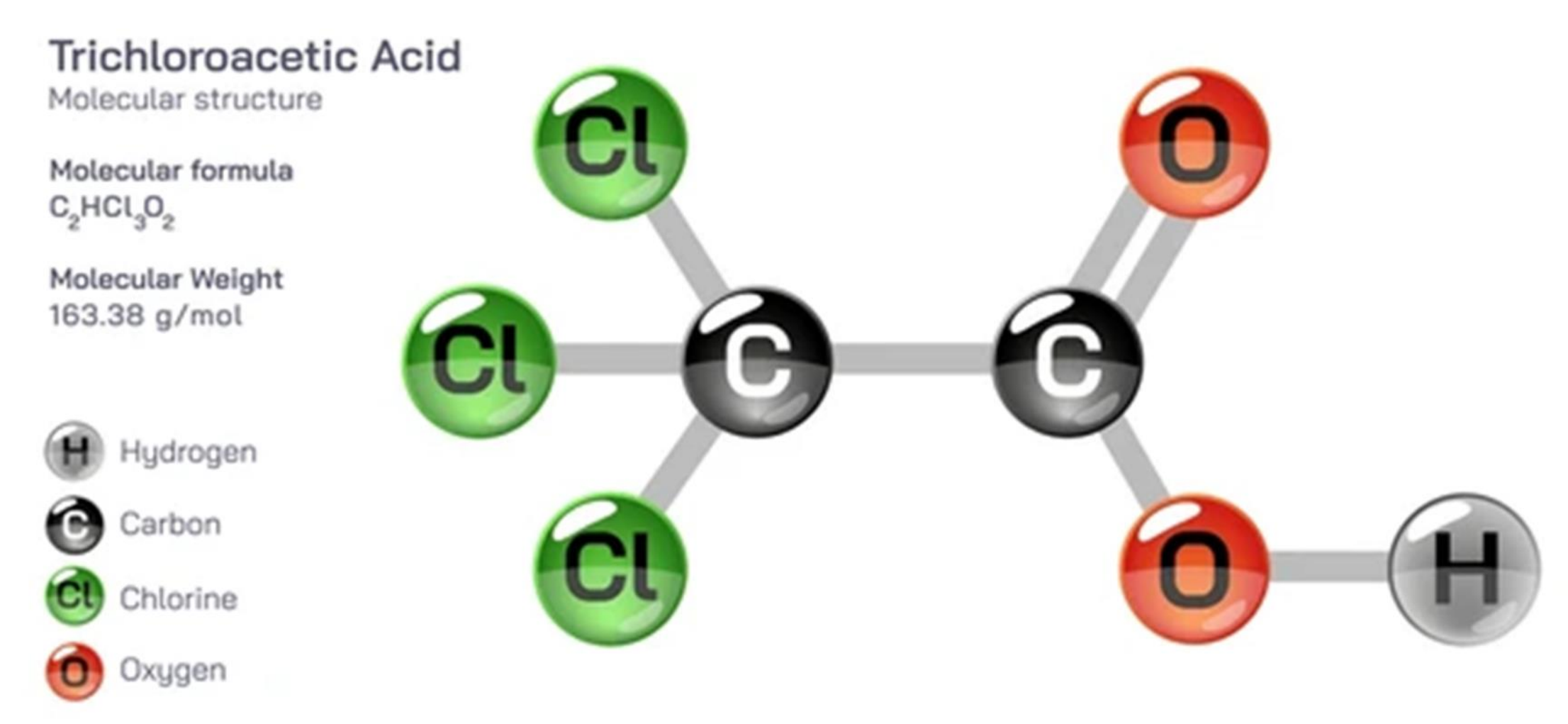



**trichloroacetic acid**

$pK_a = 0.64$

Together they are regulated as Total HAAs, (THAA9) with a combined MAC of 0.08 $mgL^{-1}$, or 80 $\mu gL^{-1}$ - ALARA (2008).

# Identification of Disinfection By-Products in Municipal Water Systems.



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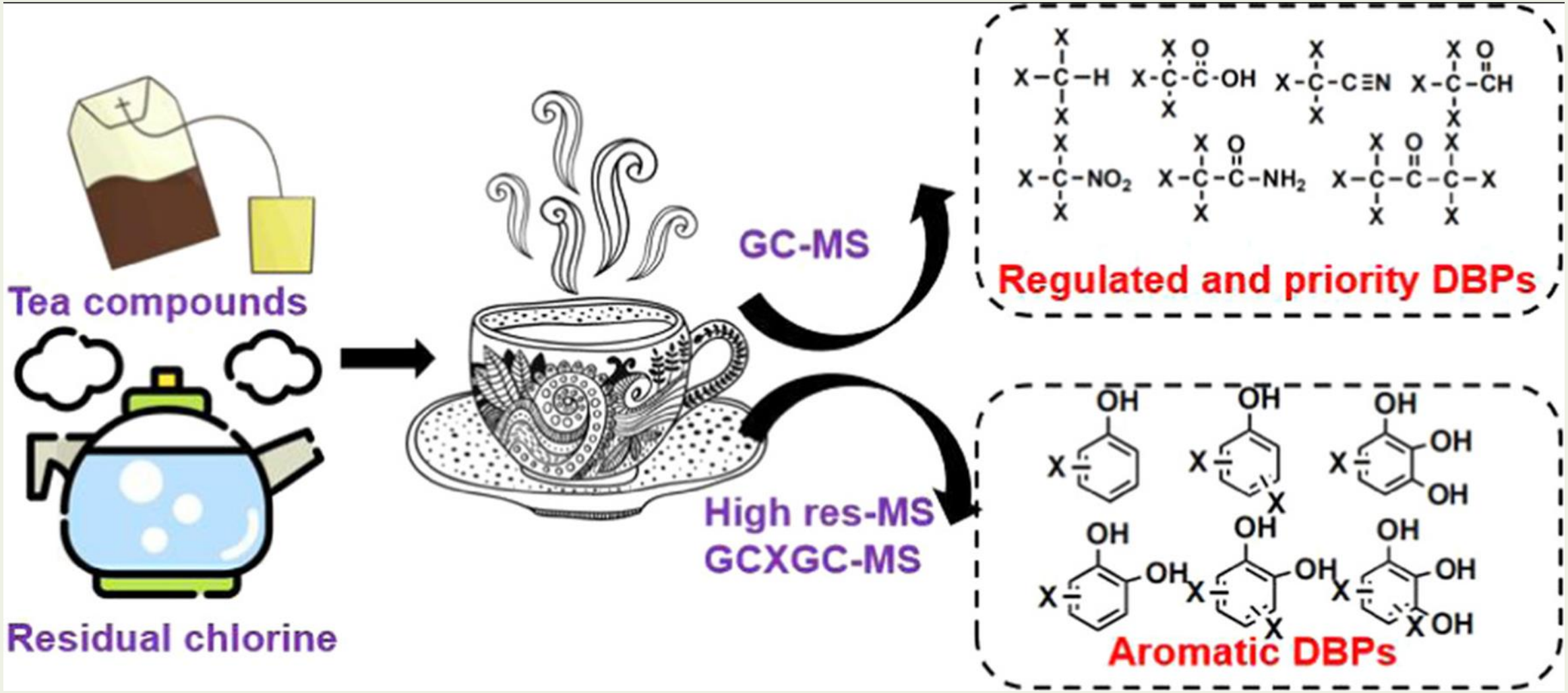


# Identification of Disinfection By-Products in Municipal Water Systems.

The addition of ammonia to water containing a free chlorine residual to form chloramines will hinder, and even stop, the formation of THMs, HAAs, and most other chlorinated products.

Monochloramine, the primary chloramine disinfectant, is a very weak oxidizer compared to free chlorine (and even dichloramine). Monochloramine will not break down the carbon-carbon bonds in the NOM present in water and create chlorinated by-products.

Low concentrations of the THM chloroform and HAA trichloroacetic acid have been found when practicing chloramination - they are probably present due to the low concentrations of free chlorine which may still usually present.

# Identification of Disinfection By-Products in Municipal Water Systems.

Until recently, there were no known DBPs generated as a consequence of chloramine disinfectant additions.

The first evidence of N,N-Dimethylnitrous amide (NDMA) in drinking water was reported in Canada in 1986, where the compound was measured at concentrations between 5 - 115 $ngL^{-1}$ in the Oshweken water supply

Around the year 2000, it was found the reaction of combined chlorine (monochloramine) with organic matter present in some waters may result in the formation of NDMA as a disinfection by-product.

# Identification of Disinfection By-Products in Municipal Water Systems.

The U.S. EPA currently classifies NDMA as a "probable human carcinogen," and has estimated its $10^{-6}$ (one in one million - generally considered negligible or insignificant from a public health perspective) cancer-risk level at 0.7 $ngL^{-1}$.

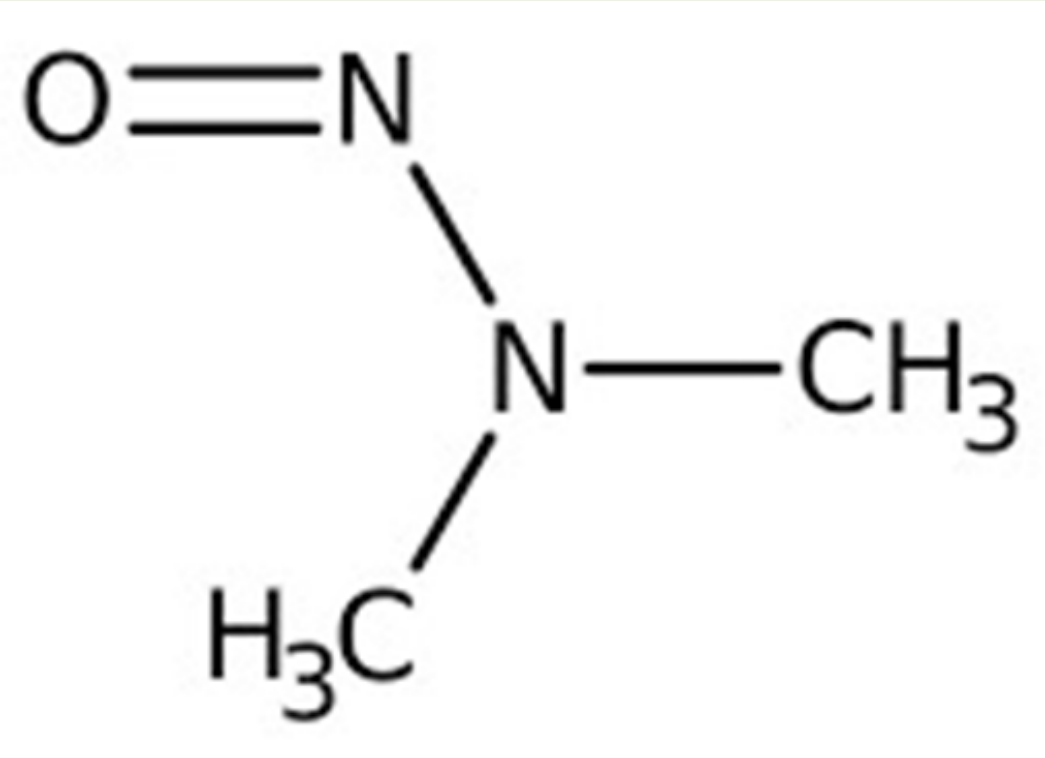
GCDWQ regulate NDMA to a MAC of 0.000 04 $mgL^{-1}$, 0.04 $\mu gL^{-1}$ (2010).

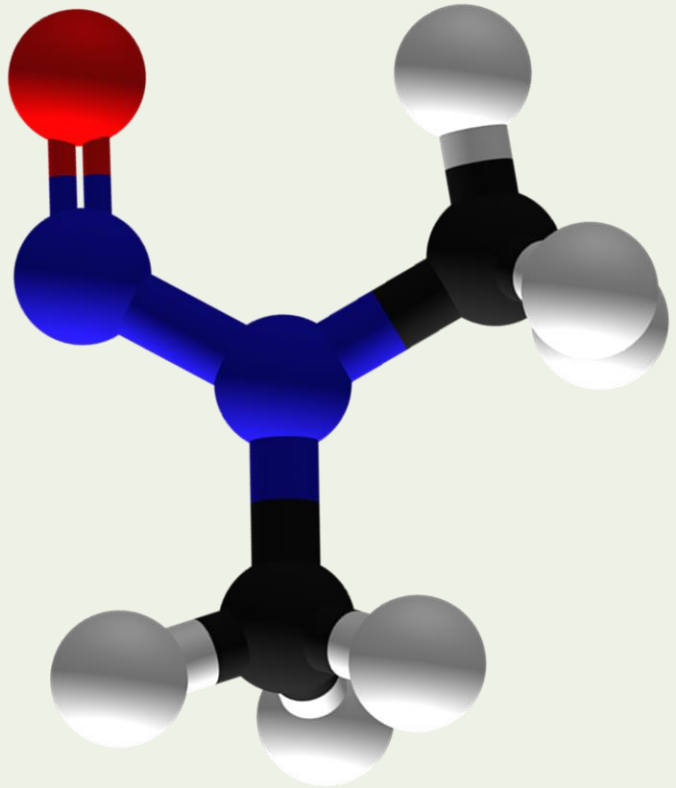
*Health basis of MAC : Liver cancer (classified as probable carcinogen).*

*NDMA formation is a by-product of drinking water disinfection with chlorine or chloramines; industrial and sewage treatment plant effluents.*

# Identification of Disinfection By-Products in Municipal Water Systems.

N,N-Dimethylnitrous amide, $(CH_3)_2NNO$.



# Identification of Disinfection By-Products in Municipal Water Systems.

Haloacetonitriles (HANs) are important drinking water disinfection by-products, formed through the chlorination and chloramination of amino acids, either free acids groups, or  those associated with NOM.

HANs are also a group of unregulated DBPs, first reported to be in drinking water in 1980.  The US EPA, Health Canada, and other world authorities, have defined regulations for certain DBPs, but haloacetonitriles are not a regulated species in drinking water.

Although HAN concentrations in treated water are usually lower than THM, they are still a major concern due to their higher cyto- and genotoxicity.

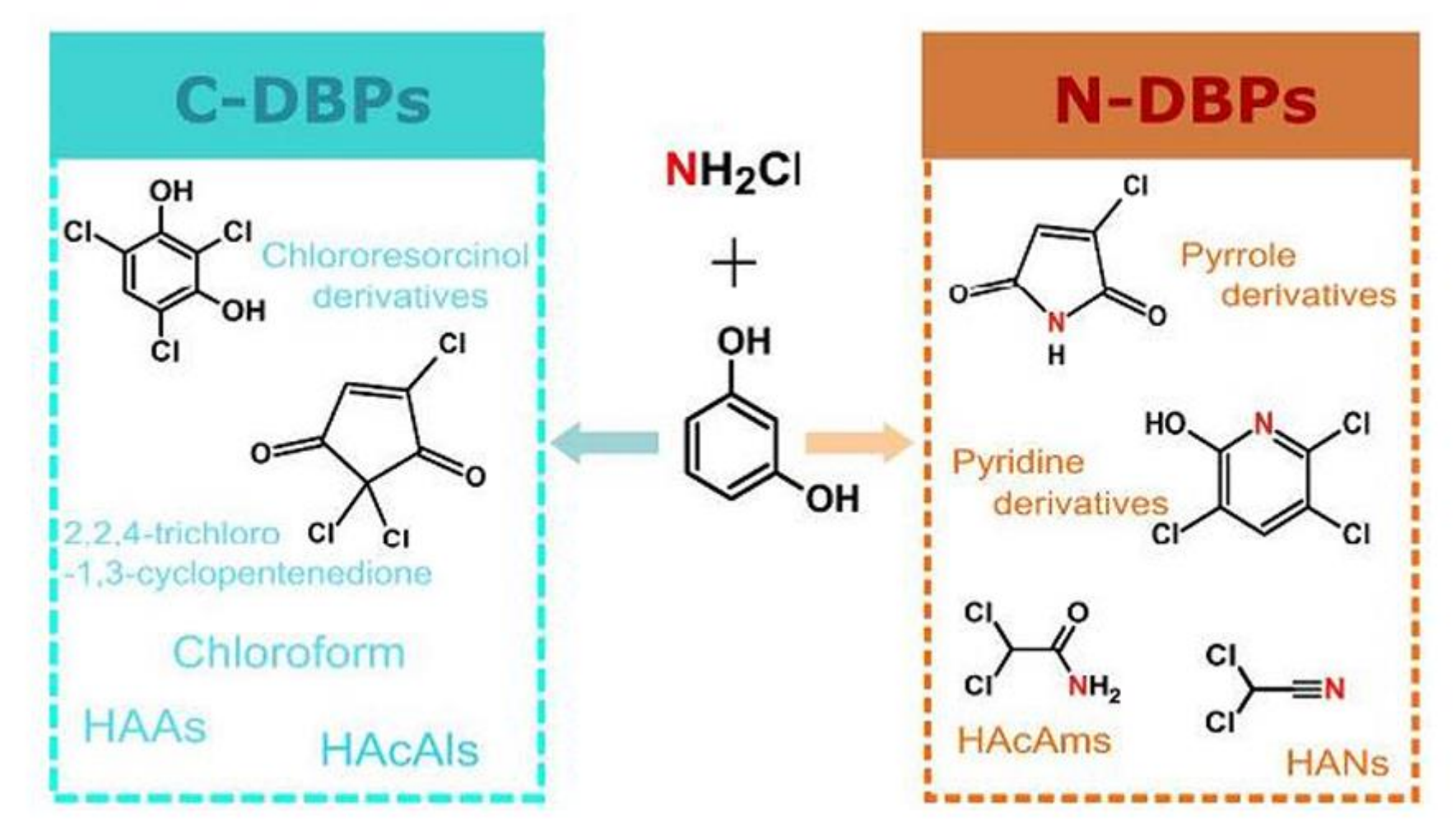
# Identification of Disinfection By-Products in Municipal Water Systems.

Despite research showing that many unregulated DBPs, including HANs, can be more toxic or genotoxic than the THMs and HAAs currently regulated, no new national MAC limit have been recommended or assigned for the HANs.

The EPA and Health Canada are, however, considering regulatory revisions to limit exposure to emerging DBPs of health concern.

Although WWTP effluent HANs are unstable, and, in higher pH waters, undergo chemical transformations by hydrolysis on the hour (trihaloacetonitriles) to week (chloroacetonitrile) time scales; their active removal is most efficiently accomplished using advanced oxidation/reduction processes (AO/RPs).

# Identification of Disinfection By-Products in Municipal Water Systems.



# Identification of Disinfection By-Products in Municipal Water Systems.

Chloral hydrate (CH) is another disinfection by-product formed when the chlorine reacts with naturally occurring organic matter.

Chloral hydrate is also used in human and veterinary medicine as a sedative and in the manufacturing of pharmaceuticals, pesticides, and other chemicals. Chloral hydrate can also be found in drinking water if it is released into the environment from these processes.

However, chloral hydrate is generally found at concentrations significantly lower than those which could pose health risks to humans. CH is not explicitly regulated in drinking water in Canada or the US.

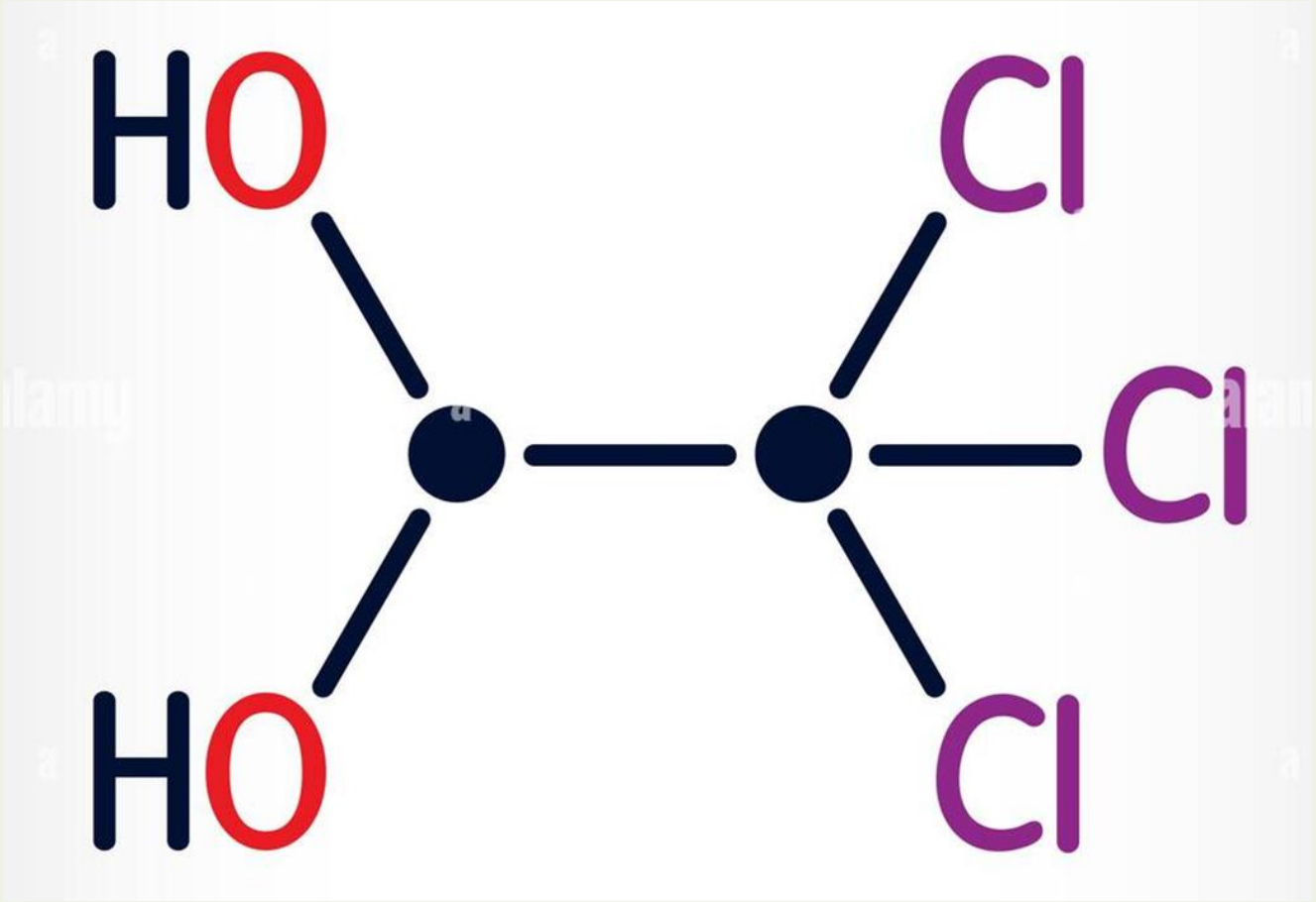
# Identification of Disinfection By-Products in Municipal Water Systems.

Health Canada has issued a Guidance Document (August 2008 - updated in 2014) and has a health-based maximum value of 0.2 $mgL^{-1}$, 200 $\mu gL^{-1}$, derived from risk assessments on a lifetime study in mice, which showed liver cell abnormalities at lower doses and a slight increase in the number of tumours at higher doses; it is not a formal guideline due to current exposure levels.

Concentration levels of chloral hydrate in Canadian drinking water supplies range from 1.2 to 3.8 $\mu gL^{-1}$ in winter and from 3.6 to 8.4 $\mu gL^{-1}$ in summer.

*Health Canada has performed a risk assessment and determined that chloral hydrate is not a concern in drinking water at typical levels, but its potential for harm at higher concentrations warrants monitoring.*

# Identification of Disinfection By-Products in Municipal Water Systems.



# Identification of Disinfection By-Products in Municipal Water Systems.

Other disinfection by-products include inorganic chlorate and chlorite from commercial sodium hypochlorite decay during storage, and from the decay of chlorine dioxide. (MAC for both compounds is 1.0 $mgL^{-1}$).

Bromate (MAC - 0.01 $mgL^{-1}$) may be present from the electrolytic generation of sodium hypochlorite. Bromate ions, $BrO_3^-$, can result from the presence of bromide in commercially produced sodium hypochlorite, as bromide can be present in the salt (NaCl/NaBr) used for the on-site generation of NaOCl.

During ozonation, if bromide is naturally present in the water.

Chlorine gas does not produce inorganic by-products of consequence.

# Identification of Disinfection By-Products in Municipal Water Systems.

Ozone may be responsible for the production of halogenated disinfection by-products if there is natural bromide present in the water being treated.

Ozone will oxidize bromide and form hypobromous acid (HOBr) which in turn will form the same disinfection by-products seen with free chlorine including the well known THMs and HAAs.

The THMs and HAAs generated will be the brominated by-products (bromoform and dibromoacetic acid) identified as serious health concerns.

Decomposition of hypobromous acid and the hypobromite ion can also lead to the bromate ($BrO_3^-$) ion which carries a MAC of 10 $\mu gL^{-1}$.

Bromate is the most significant of the by-products formed by ozone.

# Identification of Disinfection By-Products in Municipal Water Systems.

Bromate ingestion in large amounts can have gastrointestinal symptoms such as nausea, vomiting, diarrhea and abdominal pain. Some individuals also experience kidney effects, nervous system effects and hearing loss.

However, these people were exposed to bromate levels many thousands of times greater than would come from drinking compliant water.

Exposure to high concentrations of bromate, for long periods of time has caused kidney effects in laboratory animals. Long-term exposure to high levels of bromate has also been shown to cause cancer in rats. Whether or not bromate can cause cancer in humans is undetermined.

# Identification of Disinfection By-Products in Municipal Water Systems.

Ozone, the strongest oxidant, is known to react with NOM and may produce a range of low molecular weight (LMW) organic molecules including;

Ketones,

Carboxylic acids,

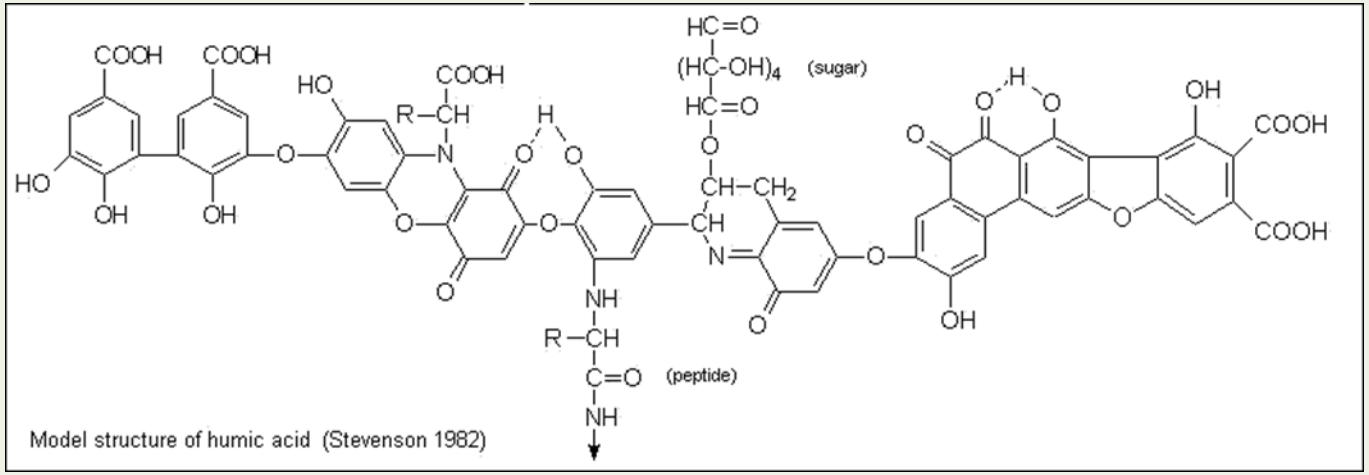
Aldehydes, including formaldehyde.

Ozone has been found to produce significantly greater concentrations of aldehydes and keto-acids than other oxidizing disinfectants.

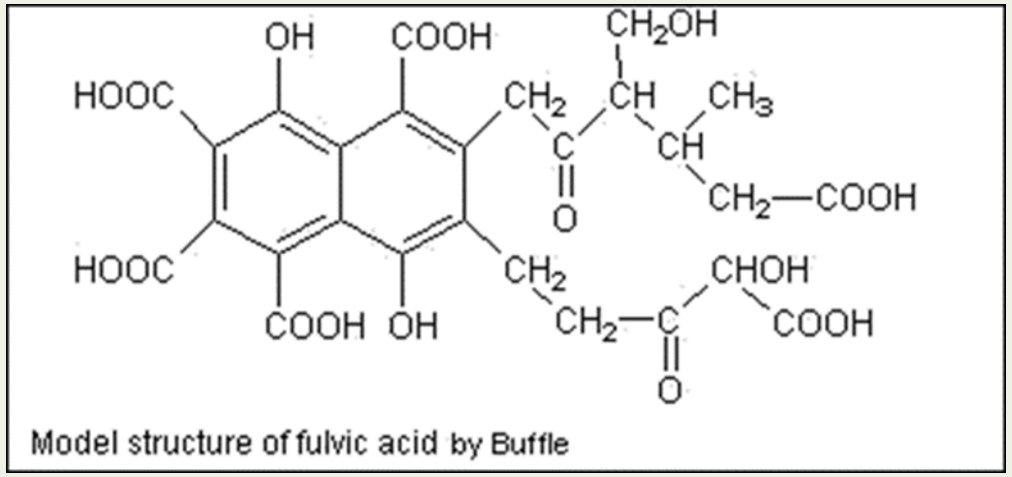
These low MW organic by-products are not regulated by the Health Canada and are not believed to have significant adverse public health effects at the concentrations that occur in drinking water disinfected with ozone.

# Identification of Disinfection By-Products in Municipal Water Systems.

Humic Acid.




Fulvic Acid.



# Disinfection By-Product Sources in Municipal Water Systems - Raw Water NOM.

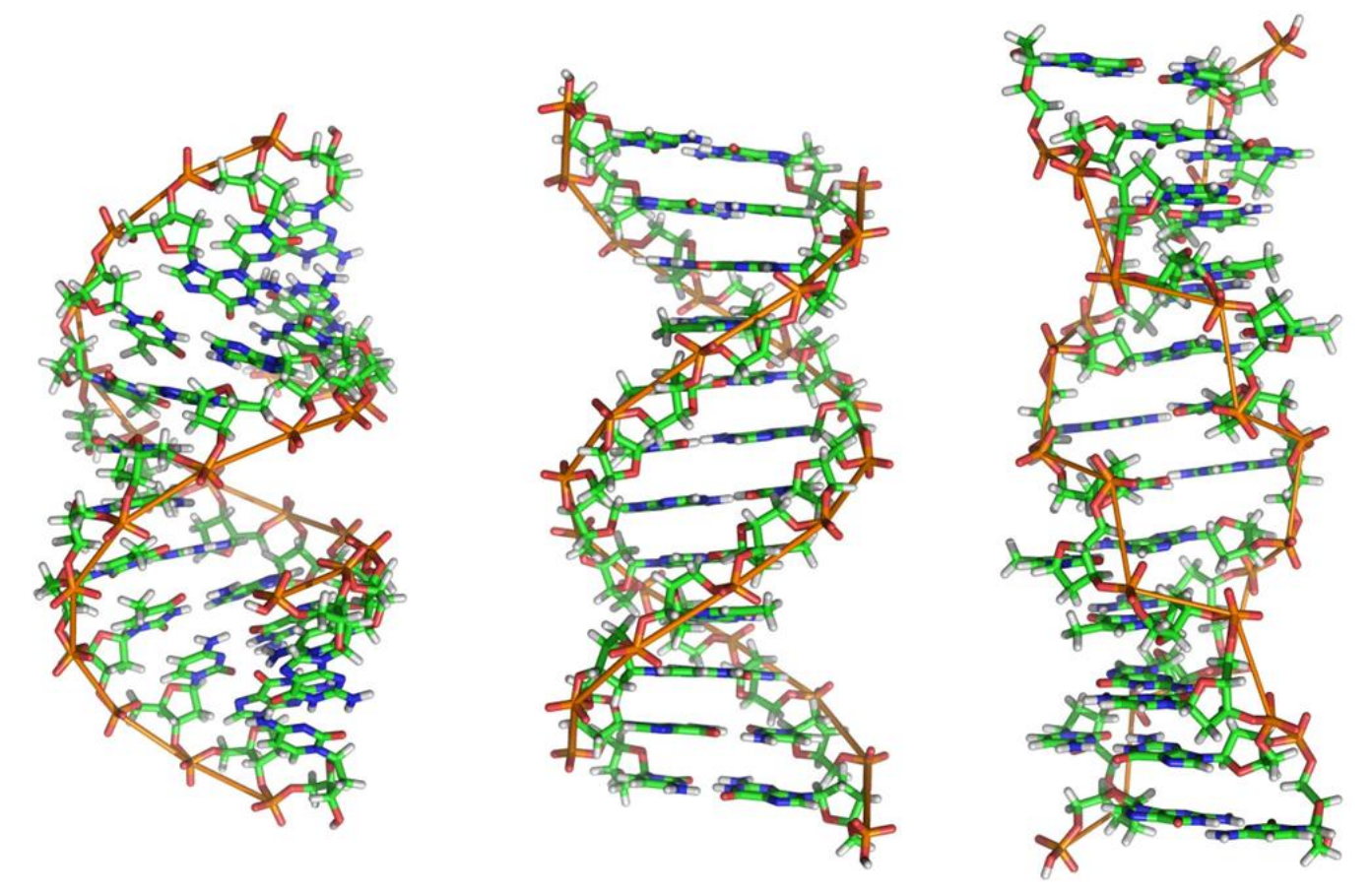
The most significant source of disinfection by-products is the oxidization of raw water, and WWTP effluent, NOM by chlorine during disinfection.

In a typical raw water source, the natural decay of vegetation is accompanied by the conversion of plant DNA into humic and fulvic acids.

Chlorine can break the carbon-carbon bonds in humic and fulvic acids, to generate potentially 6,300 different smaller molecules, although only about 600 of them have been properly identified and classified.

Trihalomethanes and haloacetic acids are two species of DBP deemed harmful to human health, as are nitrogen containing haloacetonitriles.

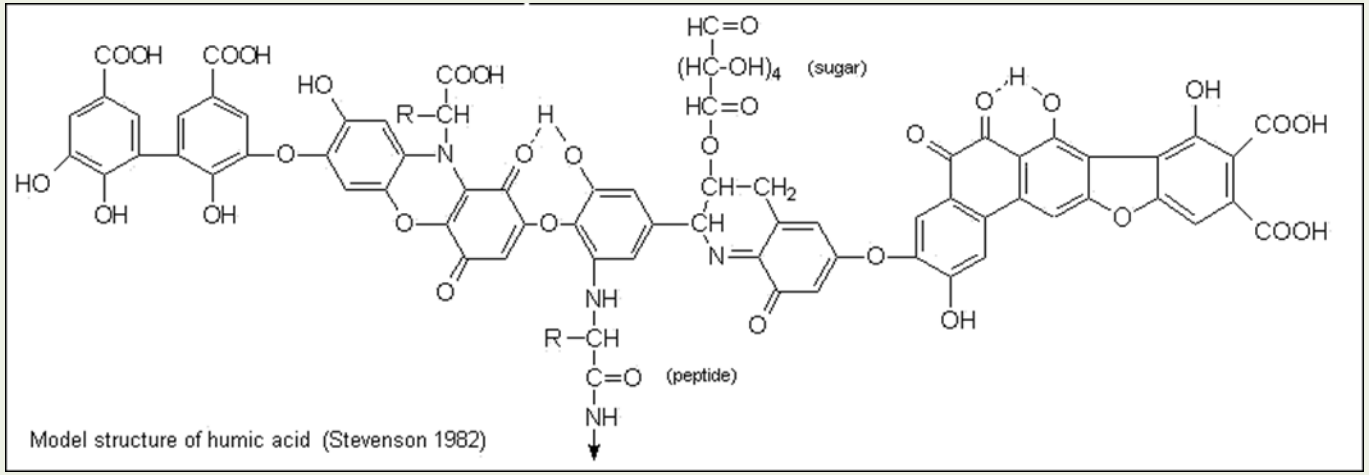
# Disinfection By-Product Sources in Municipal Water Systems - Raw Water NOM.



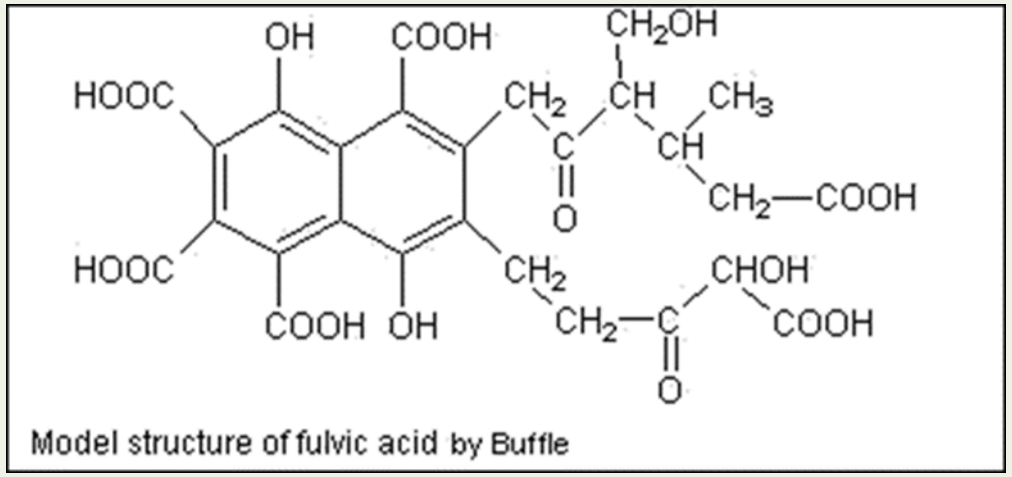
Typical Plant DeoxyriboNucleic Acid (DNA).

# Disinfection By-Product Sources in Municipal Water Systems - Raw Water NOM.

Humic Acid.




Fulvic Acid.



# Disinfection By-Product Sources in Municipal Water Systems - Raw Water NOM.

THM and HAA concentrations are substantially higher than other DBP species. Haloacetaldehydes represent the third largest concentration by class, followed by haloketones, halonitriles, haloamides, and halonitromethanes.

Four nitrosamines, present after chloramination, or the addition of amine-based coagulant aids, have been identified at low concentrations; NDMA, N-nitrosodiethylamine, N-nitrosodibutylamine, and N-nitrosopiperidine.

Recent studies have determined the nitrogenous DBP (N-DBP) are much more toxic than carbonaceous DBP (C-DBP). Haloacetonitriles (HAN) are a class of nitrogen-containing DBP, which are ubiquitous in chlorinated waters, and, due to their high toxicity, require precursor/source control.

# Disinfection By-Product Sources in Municipal Water Systems - Raw Water NOM.

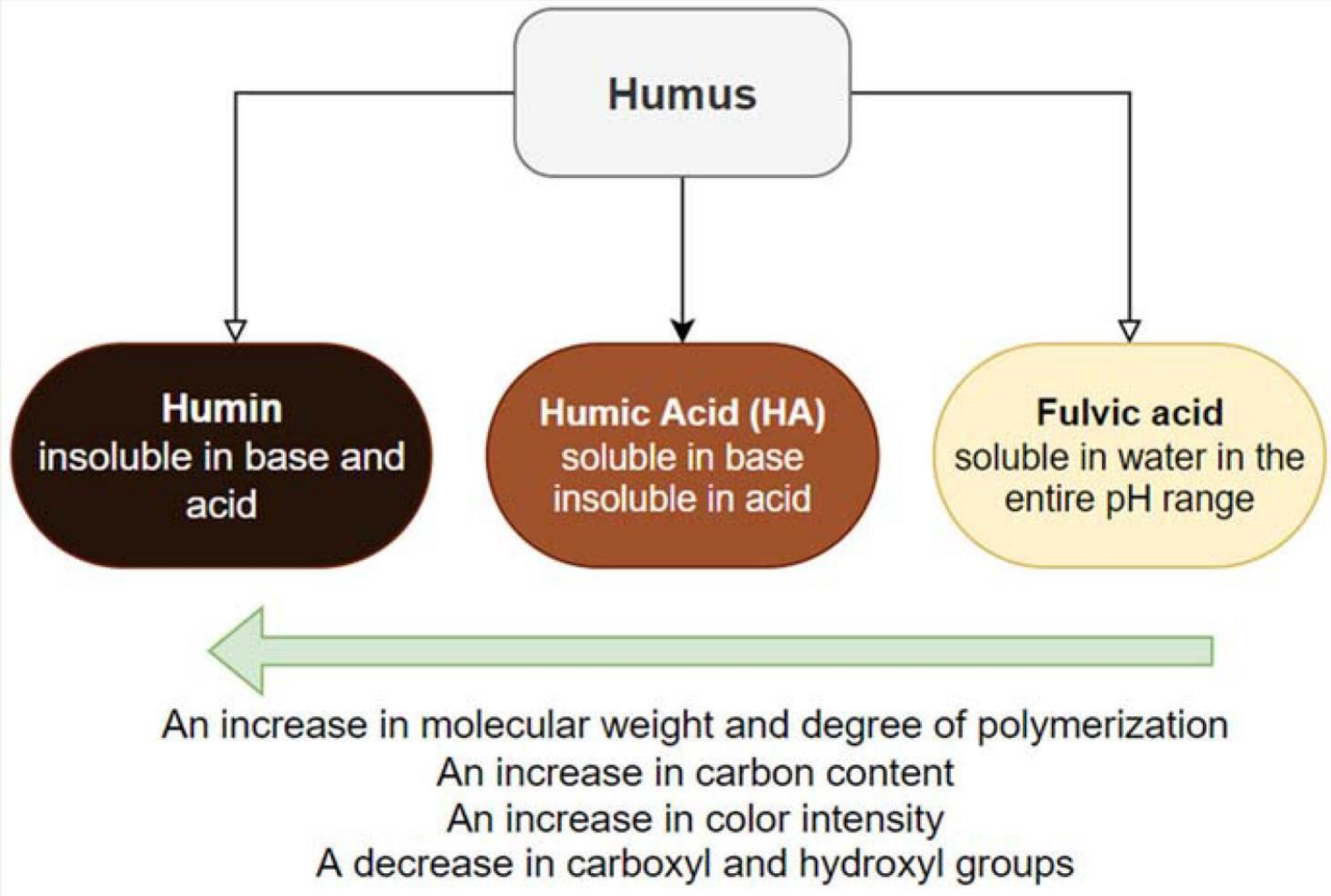
Hundreds of halogenated and non-halogenated DBPs of varying toxicities form during chlorine disinfection, but only eleven are currently regulated (i.e. four THMs, five HAAs, bromate, and chlorite) by Health Canada.

The precursors of HAA and THM are associated primarily with the hydrophobic fraction of their organic precursor molecules, although the hydrophilic fraction can be important.

Coagulation and clarification can offer significant removal rates for the higher molecular weight hydrophobic THM and HAA precursors.

The precursors of HAN are overwhelmingly hydrophilic with only a negligible contribution from the hydrophobic and transphilic fractions.

# Disinfection By-Product Sources in Municipal Water Systems - Raw Water NOM.



# Disinfection By-Product Sources in Municipal Water Systems - Raw Water NOM.

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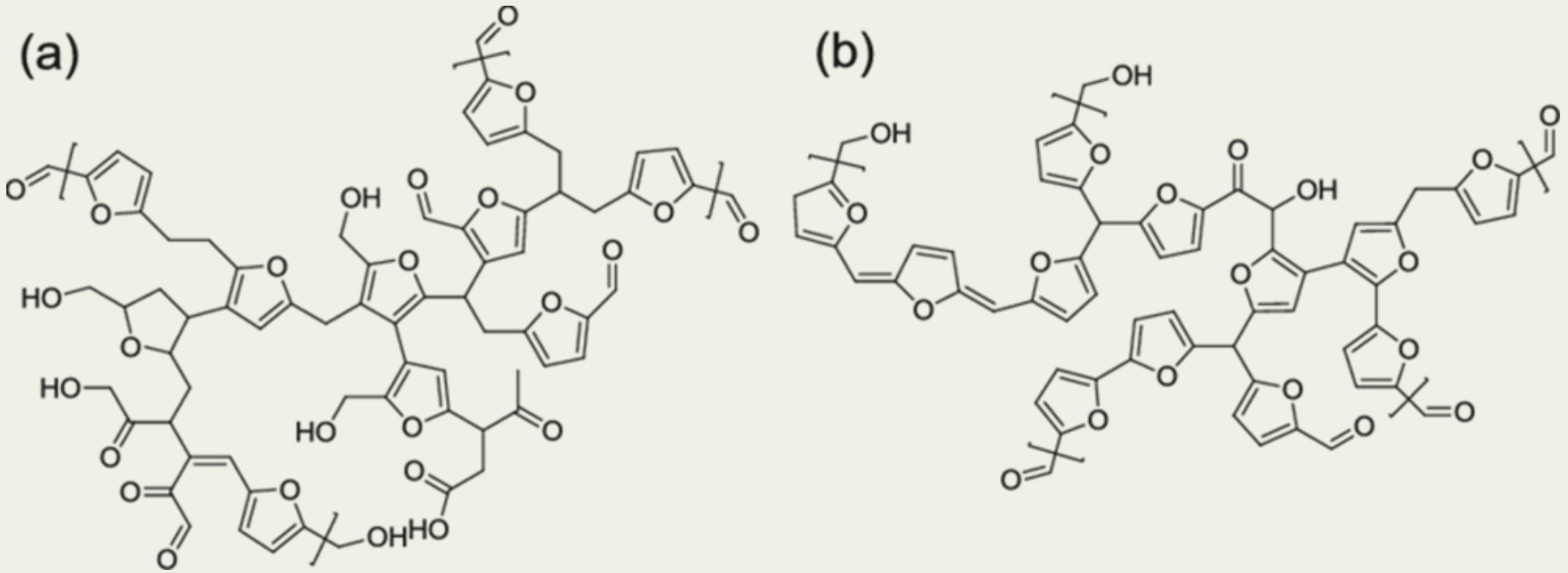
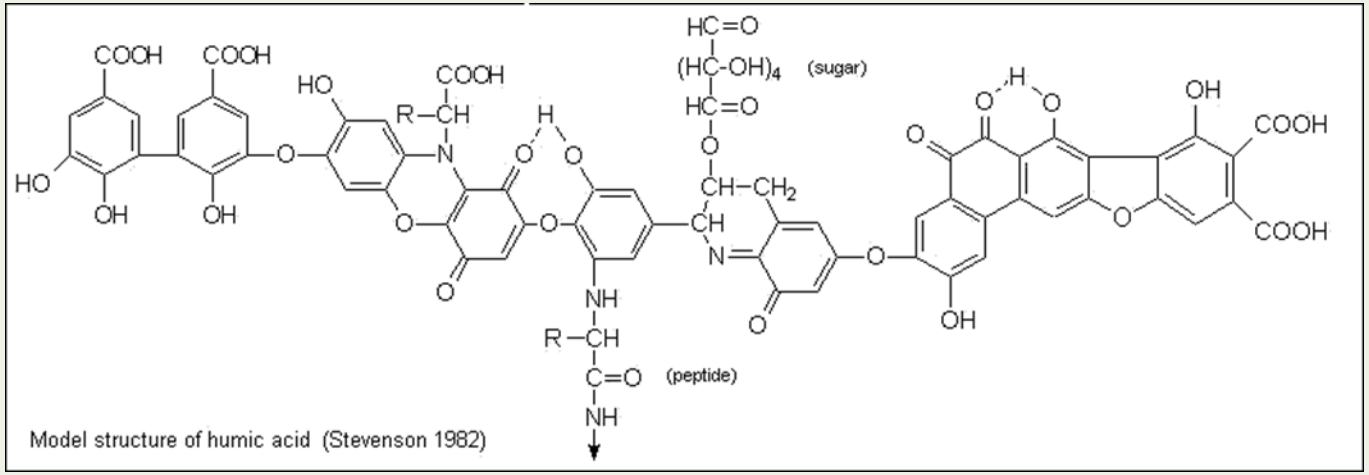


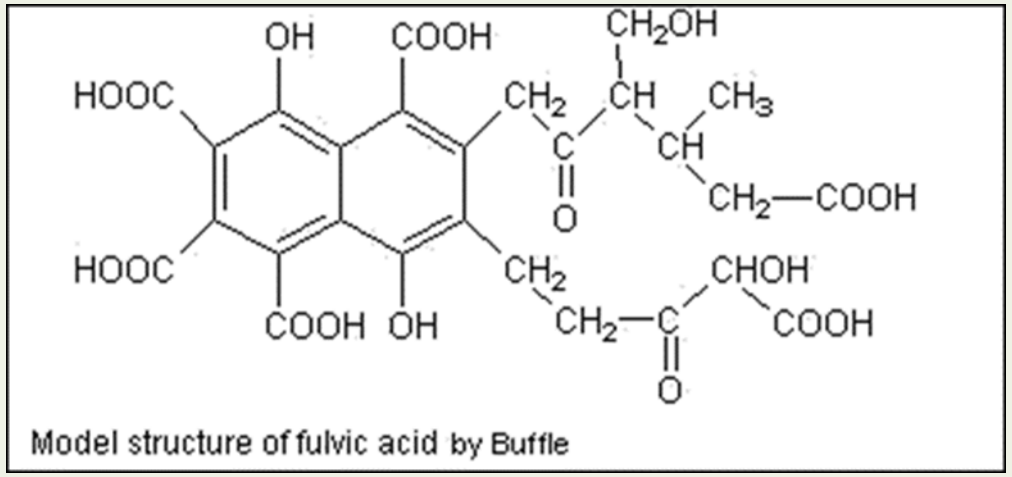

Model representing the medium molecular weight structures for humin fragments linkages for, (a) glucose-derived humins, and, (b) xylose-derived humins. (Adapted from van Zandvoort et al. 2013).

# Disinfection By-Product Sources in Municipal Water Systems - Raw Water NOM.

Humic Acid.




Fulvic Acid.



# Disinfection By-Product Sources in Municipal Water Systems - Raw Water NOM.

The concentrations of THMs and HAAs in treated water are specific to the source water. DBP formation is proportionate to its precursor concentrations.

Surface waters tend to have higher concentrations of NOM than groundwater sources, resulting in much higher concentrations of DBPs in chlorinated surface waters opposite chlorinated groundwaters.

Brominated DBPs form at a much faster rate than do non-brominated DBPs and are generally more toxic than chlorinated DBPs. Coastal areas impacted by saltwater intrusion tend to have high bromine and iodine concentrations in both their surface and groundwaters, and therefore, are likely to have higher brominated and iodinated DBP concentrations.

# Disinfection By-Product Sources in Municipal Water Systems - Raw Water NOM.

Chlorine consumption and THMs formation are initially very rapid, followed by a more gradual chlorine decay and DBP formation rate after 7 hours.

Unsurprisingly, studies have shown the concentration of THMs will also increase as residence time increases - clearwell storage / distribution volumes.

One recent study (2023) considered four sampling points at increasing distances from the treatment plant; the first sample point was the closest to the WTP and the fourth was located at the farthest distance from WTP. At the first, second, third and fourth sample points, total THMs levels were determined to be 24.8 $\mu gL^{-1}$, 37.5$\mu gL^{-1}$, 48.4 $\mu gL^{-1}$, and 61.4 $\mu gL^{-1}$, respectively.

# Disinfection By-Product Sources in Municipal Water Systems - Raw Water NOM.

The fast chromophores (smaller molecular weight colour related NOM - fulvic acids) were consumed at the onset of NOM chlorination, and their molecular cleavage does not seem to be related to a significant release of total THMs and HAAs.

However, the decomposition of slow chromophores (non-colour organic proteins and larger, more polar, amino acids with greater hydrogen bonding potential - humic acids) are more closely related to DBP formation, as demonstrated by strong correlations between the concentrations of these DBPs and the measured differential UV absorbances at 254 and 280 nm.

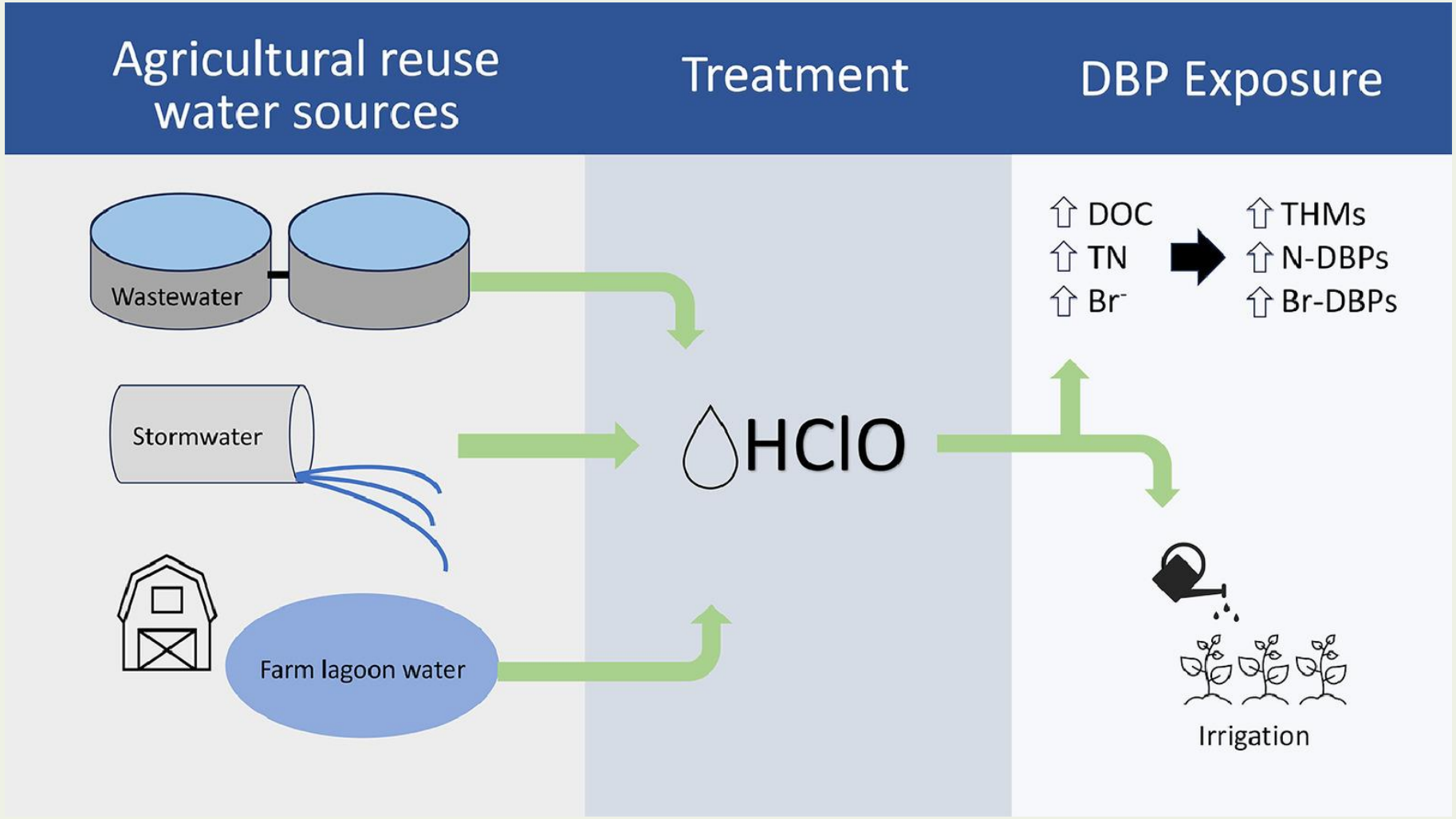
# Disinfection By-Product Sources in Municipal Water Systems - WWTP Effluent.

It has become shown wastewater effluent discharge poses a serious threat to drinking water supplies. Rivers, lakes and groundwater are accepting increased volumes of treated wastewater; drinking water quality has been compromised with a consequent increase in disinfection by-product precursor concentrations.

Wastewater effluent discharges into surface waters can significantly impact the quantity and quality of organic materials at multiple downstream locations.

The presence of various chlorine reacting species, such as ammonium, organic carbon, organic nitrogen, and bromide in wastewater effluents, can lead to the formation of numerous DBPs at high concentration levels upon chlorination.

# Disinfection By-Product Sources in Municipal Water Systems - WWTP Effluent.



# Disinfection By-Product Sources in Municipal Water Systems - WWTP Effluent.

Formation potential tests carried out to determine the DBP precursor loadings in municipal wastewater effluent, showed those WWTPs that achieved superior organic matter removal rates, and practiced full nitrification/denitrification, tended to have lower DBP-FPs in their effluent discharges.

For WWTPs with two treatment processes, THM, HAA and chloral hydrate precursors were the predominant DBP precursors in the primary and secondary treated effluents.

The percent reductions of HAN formation potentials can average as high as 96%, higher in comparison to the reductions of other classes of DBP-FPs.

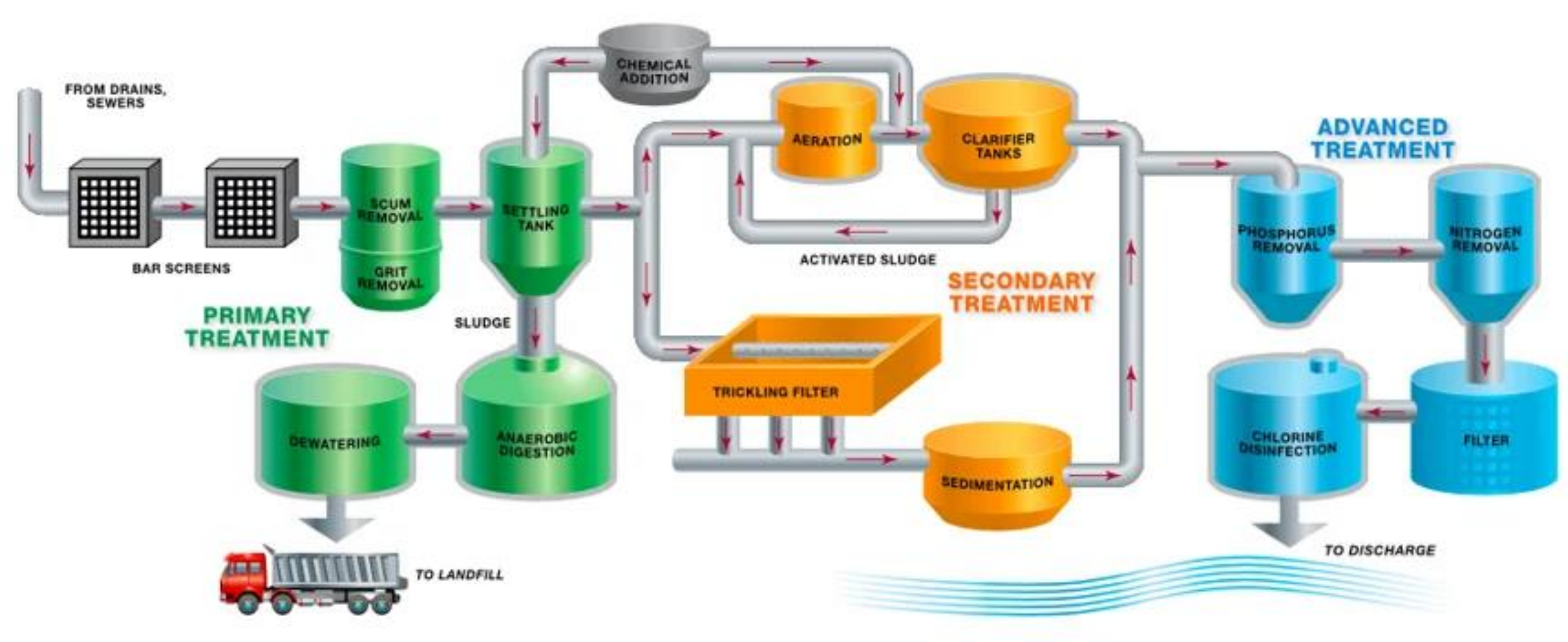
# Disinfection By-Product Sources in Municipal Water Systems - WWTP Effluent.

Further, biological secondary treatment has been shown to change the DBP-FP speciation profile by lowering the HAA-FP/THM-FP ratio.

The DBP yields, and SUVA number, increased after secondary treatment, indicating the residual organic matter in WWTP effluent contained more humic and less fulvic constituents (F/M ratios and food sources in the biological secondary processes).

Oxic and anoxic conditions, including the formation and degradation of soluble microbial products also impacts DBP-FP reductions. The oxic process is more favourable than the anoxic conditions with regard to DBP-FP reductions.

# Disinfection By-Product Sources in Municipal Water Systems - WWTP Effluent.



# Disinfection By-Product Sources in Municipal Water Systems - WWTP Effluent.

# Disinfection By-Product Sources in Municipal Water Systems - SUVA.

Research has shown that organic compounds absorbing UV radiation at 254 nm have a greater tendency to form chlorinated disinfection by-products.

The SUVA value is a measure of the dissolved organic carbon concentration available most likely to form disinfection by-products when chlorinated. This value can also be used in the treatment process to remove/reduce natural organic matter, and, in turn, lower the DBP formation potential.

A higher SUVA number indicates a higher TOC removal percentage potential.

A higher SUVA number also indicates a lower coagulant dosage, based on a “per Kg of DOC removal ” calculation.

# Disinfection By-Product Sources in Municipal Water Systems - SUVA.

Specific ultraviolet absorbance (SUVA) provides a general characterization of the nature of natural organic matter (NOM) in a water sample and is typically performed for the purpose of determining disinfection by-product formation potential.

SUVA is calculated by dividing the UV absorbance at 254 nm ($cm^{-1}$) by the DOC, dissolved organic carbon, ($mgL^{-1}$) of a water sample, expressed in units of L/mg-m.

$$\text{SUVA (L/mg-M)} = \text{UVA 254 } (cm^{-1}) \div \text{DOC (mgL-1) x 100 cm/M}$$

This calculation measurers the potential of the organic content to produce DBPs. A high SUVA number indicates a large portion of humic matter present in the water and that NOM will control coagulant dose. Since aromatic organics have a greater tendency to react with disinfectants to create DBPs, a high SUVA indicates there is a greater potential for the formation of DBP's.

# Disinfection By-Product Sources in Municipal Water Systems - SUVA.

| Parameter | Sample A | Sample B |
|---|---|---|
| UVA ($cm^{-1}$) | 0.175 | 0.135 |
| DOC ($mgL^{-1}$) | 12 | 2.5 |
| SUVA (L/mg-M) | 1.46 | 5.40 |

| SUVA | Inferred From SUVA Calculation DOC | DOC Removal (%) |
|---|---|---|
| < 2 | Mostly Low MW NOM (Fulvic Acids) | < 25% |
| 2 - 4 | Moderate MW NOM (Humic / Fulvic blend) | 25 - 50% |
| > 4 | Mostly High MW NOM (Humic Acids) | > 50% |

# Disinfection By-Product Sources in Municipal Water Systems - SUVA.

The data from many studies show that the aromatic and high molecular weight fraction of NOM, readily removed by coagulation in a lower pH environment, contains the main precursors for HAA, and some of the precursors for THM. However, other research suggests that lower molecular weight, non-humic NOM contributes more prominently in HAA formation.

Chlorine will significantly injure bacterial cells, cause cell permeability dislocation and nucleic acids and enzyme destruction - also precursors for DBP generation.  Chlorine is a good disinfectant, but it does have is limitations.

A well accepted substitute disinfectant is ultraviolet (UV) radiation.

# Disinfection By-Product Sources in Municipal Water Systems - UV Radiation.

Ultraviolet radiation disinfection at dosages between 40 - 150 $mJ/cm^2$, followed by chlorination, does not significantly change regulated DBP formation potentials when compared to the non-UV disinfected water.

However, researchers have found that UV radiation during disinfection will form low molecular weight aldehydes, carboxylic acids and biologically degradable organic carbon (BDOC) or assimilable organic carbon (AOC).

24-hour free chlorine and monochloramine demands will increase when exposed to LP and MP UV radiation. At UV disinfection dosages, the increases are small; 0.1 - 0.6 mg $Cl_2L^{-1}$ for chlorine and 0.1 - 0.3 mg $Cl_2L^{-1}$ for chloramine.

# Disinfection By-Product Sources in Municipal Water Systems - UV Radiation.

The formation of THM-4 (sum of 4 regulated chlorine and bromine containing THMs), while minor, is as a result of chlorine destruction by UV radiation.

Spiking with bromide causes a shift to the bromine-substituted species and increases the molar yield of THM-4 following chlorination. Spiking with nitrate does not impact THM formation or speciation regardless of UV dose. THM-4 formation was significantly lower in chloraminated waters when compared to chlorinated samples.

THM-4 formation increased 15 - 20% with MP UV doses of 1,000 $mJ/cm^2$ followed by chlorination compared to chlorination alone in two utility samples and 30 - 40% in a third test location.

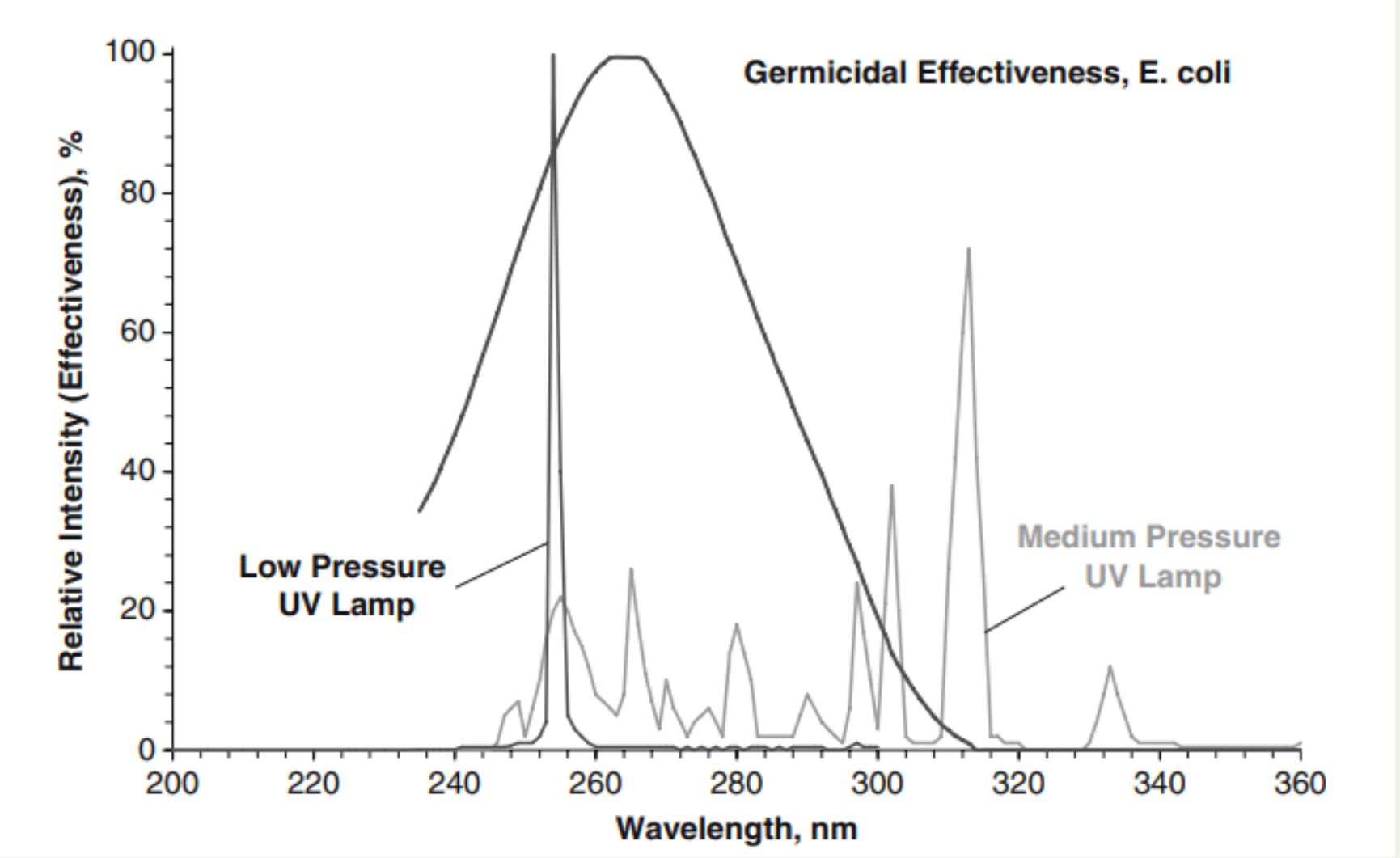
# Disinfection By-Product Sources in Municipal Water Systems - UV Radiation.

The halogenated DBPs (X-DBPs) production clearly is dependent on the halide concentrations in the water phase and on the NOM concentrations, the organic reactivity (humic or fulvic acid), the pH of the treated water, and the temperature and the time of disinfection processing.

The organic absorbance response at 280 nm strongly indicates the formation of X-DBPs such as THM and HAA, and provides an indirect quantification of their formation potentials, all hinting at the aromatic nature of NOMs.

It is well known that humic acid can be fractioned into hydrophobic, transphilic, and hydrophilic mixtures by UV radiation at high dosages.

# Disinfection By-Product Sources in Municipal Water Systems - UV Radiation.



# Disinfection By-Product Sources in Municipal Water Systems – UV/AO Radiation.

Advanced Oxidation, used against PFOA/PFAS, HANs and cyanotoxins, combines high dosages of UV and $H_2O_2$. A recent study investigated changes in DBP formation attributed to UV or UV/$H_2O_2$, followed by free chlorine, required to quench hydrogen peroxide and provide residual disinfection.

At a UV dose of 1,000 mJ/cm$^2$, typical for AO protocols, trihalomethane yield increased by up to 4 mg/mg-TOC and 13 mg/mg-TOC when treated with low and medium pressure UV radiation lamps.

With the addition of hydrogen peroxide, THM yield increased by up to 25 mg/mg-TOC (5 mg-$H_2O_2L^{-1}$) and 37 mg/mg-TOC (10 mg-$H_2O_2L^{-1}$).

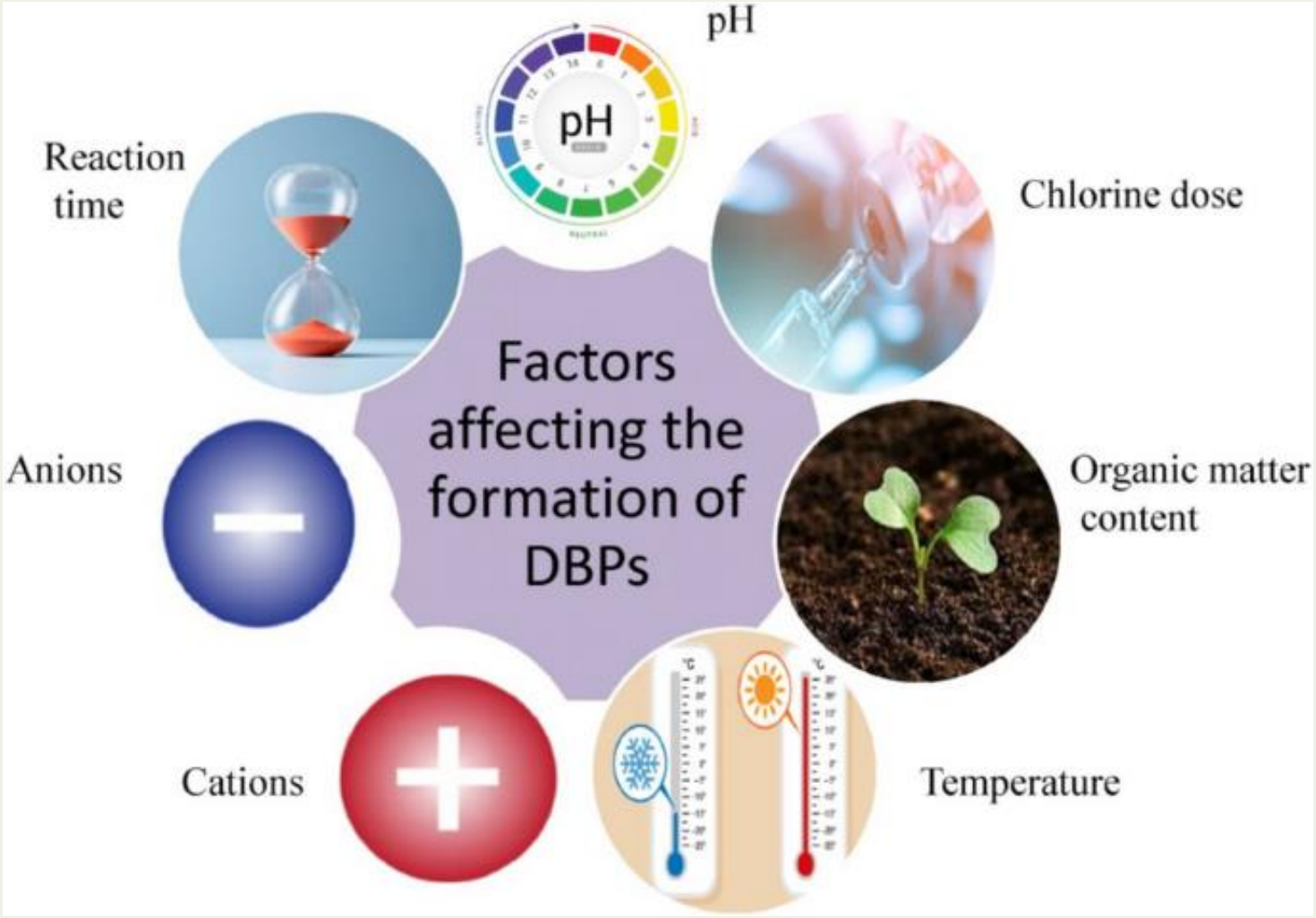
# Disinfection By-Product Sources in Municipal Water Systems – UV/AO Radiation.

HAAs were only measured for Utility A samples and UV had little effect on their formation in these samples, aside from two cases.

UV dosages for disinfection are significantly lower than those required for advanced oxidation, applied for trace organic compound destruction, and generally do not increase DBP concentrations in treated water.

Higher UV radiation dosages, and hydrogen peroxide, utilized in AOP treatment for PFAS and PFOS, HAN, and other environmentally relevant trace organic pollutants (e.g. acetaminophen), are likely to have a greater effect on DOM character and the potential to yield DBPs when post-chlorinated.

# Disinfection By-Product Sources in Municipal Water Systems.



# Control Strategies for DBPs in Municipal Water Systems.

In a nutshell, there are two options to control DBP in drinking water.

Control of disinfection by-products (DBPs) is managed by both precursor removal during treatment, and optimization of the disinfection process itself.

Precursors are removed using methods such as pre-oxidation, enhanced coagulation, activated carbon filtration, NF & RO filtration, and biofiltration.

The disinfection process can be modified by switching to alternative disinfectants such as UV, chloramines or ozone, and reducing contact time, while managing the water in the distribution system to prevent stagnation.

# Control Strategies for DBPs in Municipal Water Systems.

The most effective control strategy for DBP formation is the removal of the organic DBP precursors from the raw water before disinfection.

Pre-oxidation of NOM in the raw water and enhanced coagulation can destroy or remove organic material and significantly lower DBP formation potential.

Granular and powdered activated carbon (GAC & PAC) or NF membrane filtration can physically remove organic precursors from water.

Biofiltration, utilizing processes such as biologically activated carbon, or slow sand filtration, use the DBP precursors as food for microorganisms.

Control of DBP formation potential in municipal WWTPs is an often overlooked option to reduce DBP precursor concentrations in the raw water.

# Control Strategies for DBPs in Municipal Water Systems.

Use of alternative disinfectants, such as chloramines, ozone, or chlorine dioxide is also a recommended and successful strategy.

Ultraviolet (UV) irradiation is an increasingly popular alternative disinfection method that generally does not generate DBPs in measurable concentrations.

Optimizing the applied disinfectant dosage will help minimize DBP formation.

Minimizing the length of time water spends in the pipes, and eliminating dead-end zones or stagnant areas, will ensure adequate water turnover in storage tanks, reducing chlorine contact time and DBP concentrations.

# Control Strategies for DBPs in Municipal Water Systems - Pre-Treatment.

There are many other organic chemical species present in raw source waters beyond decaying NOM, including trace chemicals from foods, drugs, pesticides, plastics and additives, dyes, oils, soaps, detergents, paints, varnishes, solvents, and wastewater treatment plant effluents.

The presence of these organic contaminants, upon disinfection/oxidation by chlorine or ozone, could generate DBP of many and various stripes.

Pretreatment of natural waters with powdered activated carbon (PAC) for adsorption, $KMnO_4$ for oxidation, or biological contact oxidation (BCO) are still found in common practice. The use of PAC and $KMnO_4$, is a frequently used option, especially so in small water systems along coastal B.C..

# Control Strategies for DBPs in Municipal Water Systems - Pre-Treatment.

One recent study showed organic adsorption by PAC was found to successfully capture/eliminate 42.7% of chloroform ($CHCl_3$) precursors.

The removal efficiency of DOC was 76.5% by the BCO process, 69.9% by PAC adsorption, and 61.4% by $KMnO_4$ oxidation.

Elimination of DBP precursor organic matter, utilizing pre-oxidation with $KMnO_4$ or ozone, can result in bacterial cell wall disintegration, commonly known as lysis. Caution must be exercised as water-borne cyanobacteria (or blue-green bacteria/blue-green algae) cell walls could also be breached, releasing cyanotoxin into the raw water source!

# Control Strategies for DBPs in Municipal Water Systems - Enhanced Coagulation.

Enhanced coagulation is a treatment process that optimizes the standard coagulation procedure to remove an increased NOM mass from water.

To lower NOM concentrations in clarified water, enhanced coagulation uses a higher coagulant dosage, and careful control of pH, to maximize the removal of both turbidity and dissolved/colloidal organic material.

Transitioning from conventional coagulation to enhanced coagulation results in improved removal of precursors for TTHM, HAA9, CH, HAN4, and general TOX, plus it will see a reduction in chlorine demand.

Raw waters exhibiting a higher SUVA tend to have higher percent removals of DBP precursors.

# Control Strategies for DBPs in Municipal Water Systems - Enhanced Coagulation.

Unlike conventional coagulation, which focuses on turbidity reductions, enhanced coagulation aims for the highest possible removal of NOM by determining the optimal pH and applying a higher coagulant dose.

The higher coagulant dosage is added to destabilize the smaller, suspended organic particles that are not easily removed by conventional treatment. This optimized coagulant dosage requires the WTP operator to maintain a lower pH and a slight negative bulk water electrical charge, as measured using either a SCM or Zeta Potential reading.

Enhanced coagulation will, therefore, require additional knowledge and attention from the WTP operators.

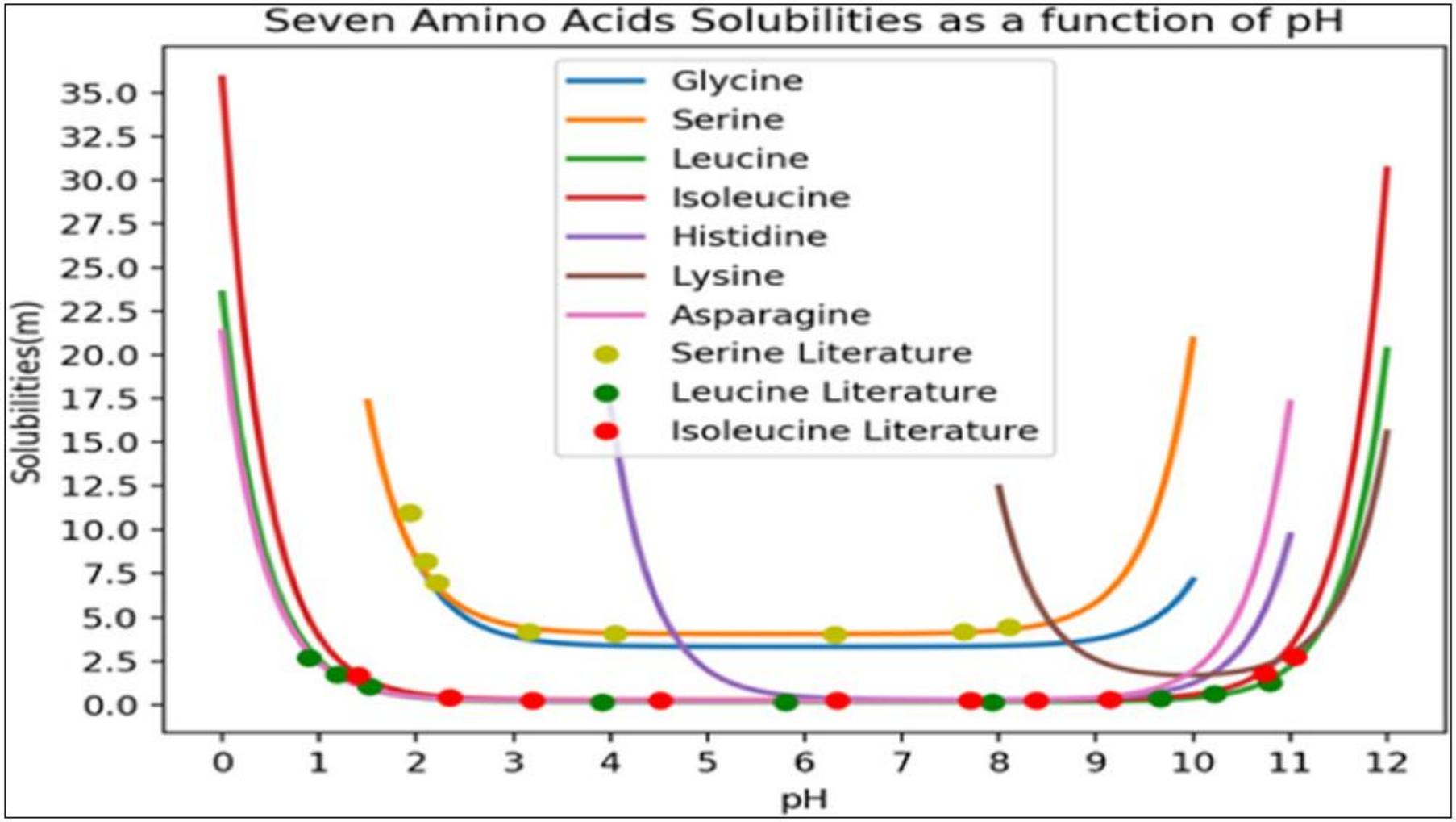
# Control Strategies for DBPs in Municipal Water Systems - Enhanced Coagulation.

Enhanced coagulation is particularly important for treating surface waters that have high levels of organic matter, with high alkalinity, both of which can individually make conventional treatment less effective.

pH, alkalinity, and temperature are critical physical parameters, as they influence the solubility of both the organic material and coagulant speciation. The ideal pH range for the most effective coagulation of NOM is 5.5 - 6.3.

Effluent water at a lower pH does present concerns with distribution system corrosion, so a good alkalinity enhancement protocol will also be required, especially in coastal waters and interior high mountain fed glacial streams.

# Control Strategies for DBPs in Municipal Water Systems - Enhanced Coagulation.



# Control Strategies for DBPs in Municipal Water Systems - Enhanced Coagulation.

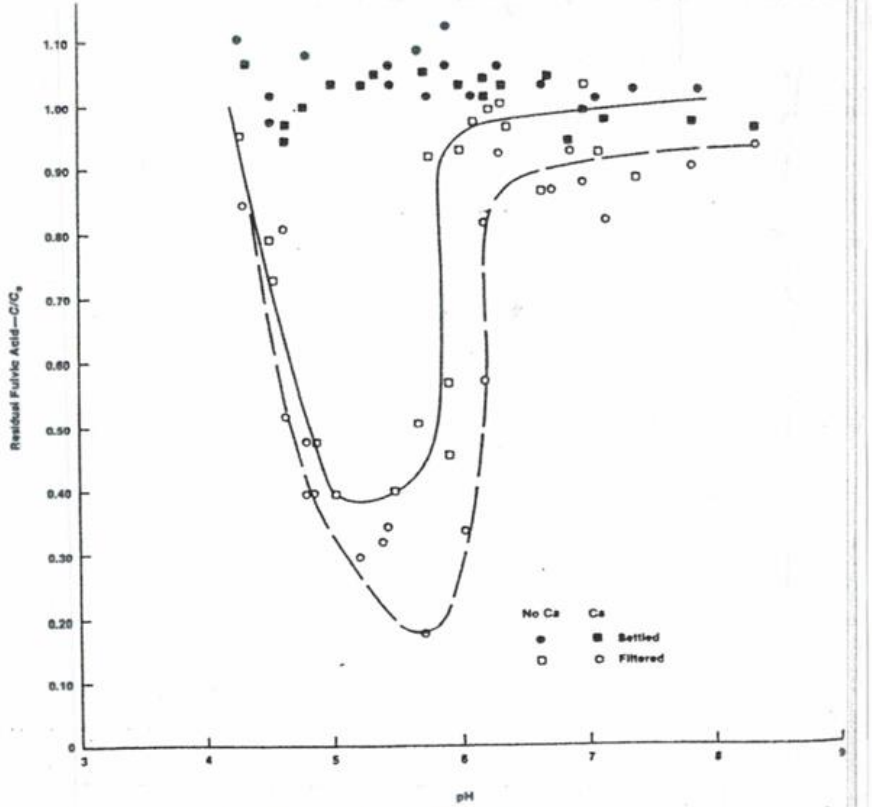



**Figure 7.** Coagulation of DS1 fulvic acid with $1.78 \times 10^{-5} M$ $AlCl_3$ as a function of pH, with and without calcium (*TOC—3.5 mg/L; Ca—$10^{-3}$M*)

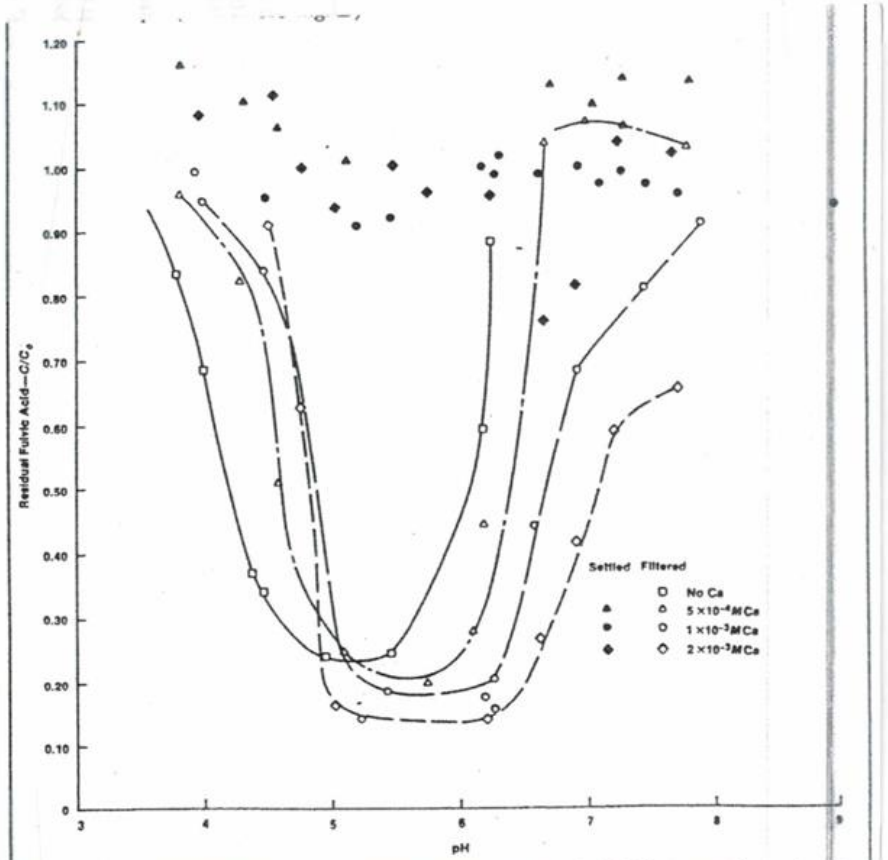
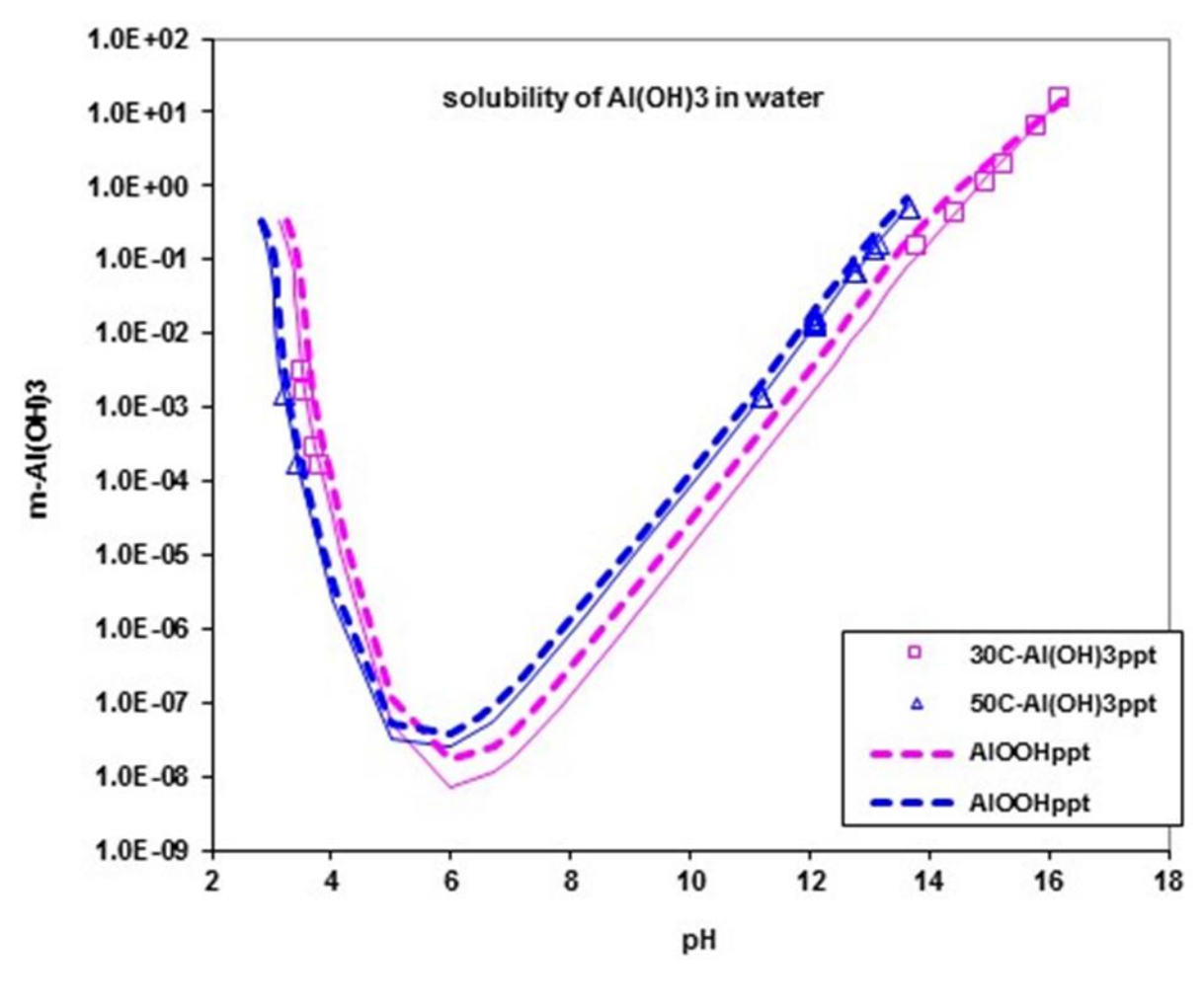



**Figure 11.** Coagulation of DS1 fulvic acid with $1.78 \times 10^{-5} M$ alum as a function of pH and calcium concentration (*TOC—3.5 mg/L*)

# Control Strategies for DBPs in Municipal Water Systems - Enhanced Coagulation.



# Control Strategies for DBPs in Municipal Water Systems - Enhanced Coagulation.

Coagulation and enhanced coagulation, upstream of filtration, are the most frequently employed treatment protocols used to lower DBP precursor concentrations in treated water, prior to disinfection.

As discussed previously, SUVA is an important parameter used to determine the potential for DBP generation. A higher SUVA will result in a greater removal rate for DBP precursors, especially for HAAs.

The USEPA has a table of TOC reduction targets based on raw water TOC and alkalinity concentrations. Note that a TOC removal rate of 50 - 60% would be considered best practice.

# Control Strategies for DBPs in Municipal Water Systems - Enhanced Coagulation.

**TABLE 2-1**

**Required Removal of TOC by Enhanced Coagulation For Plants Using Conventional Treatment: Step 1 Removal Percentages[a, b]**

| SOURCE WATER TOC (mg/L) | SOURCE WATER ALKALINITY (mg/L as $CaCO_3$) | | |
|---|---|---|---|
| | 0 to 60 | >60 to 120 | >120[c] |
| >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% |

Notes:

a. Enhanced coagulation and enhanced softening plants meeting at least one of the six alternative compliance criteria in Section 2.4 are not required to meet the removal percentages in this table.
b. Softening plants meeting one of the two alternative compliance criteria for softening in Section 2.4 are not required to meet the removal percentages in this table.
c. Plants practicing precipitative softening must meet the TOC removal requirements in this column.

# Control Strategies for DBPs in Municipal Water Systems - Enhanced Coagulation.

Enhanced coagulation has two roles in the Disinfectant/Disinfection By-Product (D/DBP) Rule. One is as a treatment technique for the control of precursors for identified and non-identified DBPs. Another is as a best available technology (BAT) for the control of regulated TTHMs and HAA5.

As a treatment technique, water systems are not expected to optimize, or maximize, the removal of DBP precursors. Whether coagulation is enhanced or optimized for the control of DBP precursors is a matter of degree. So as not to be cost prohibitive, systems must meet target percentage removals of TOC where TOC serves as a surrogate for the identified and non-identified DBP precursors.

# Control Strategies for DBPs in Municipal Water Systems - Activated Carbon.

Activated carbon has many applications in water treatment, and is commonly employed as one of two product types;

Granular activated carbon (GAC), usually found as part of the filtration process.

Powdered activated carbon (PAC) finds most of its applications in the pre-treatment process stage.

PAC is also often found in POE/POU applications in households, used to absorb distribution system chlorine and DBP.

# Control Strategies for DBPs in Municipal Water Systems - Activated Carbon.

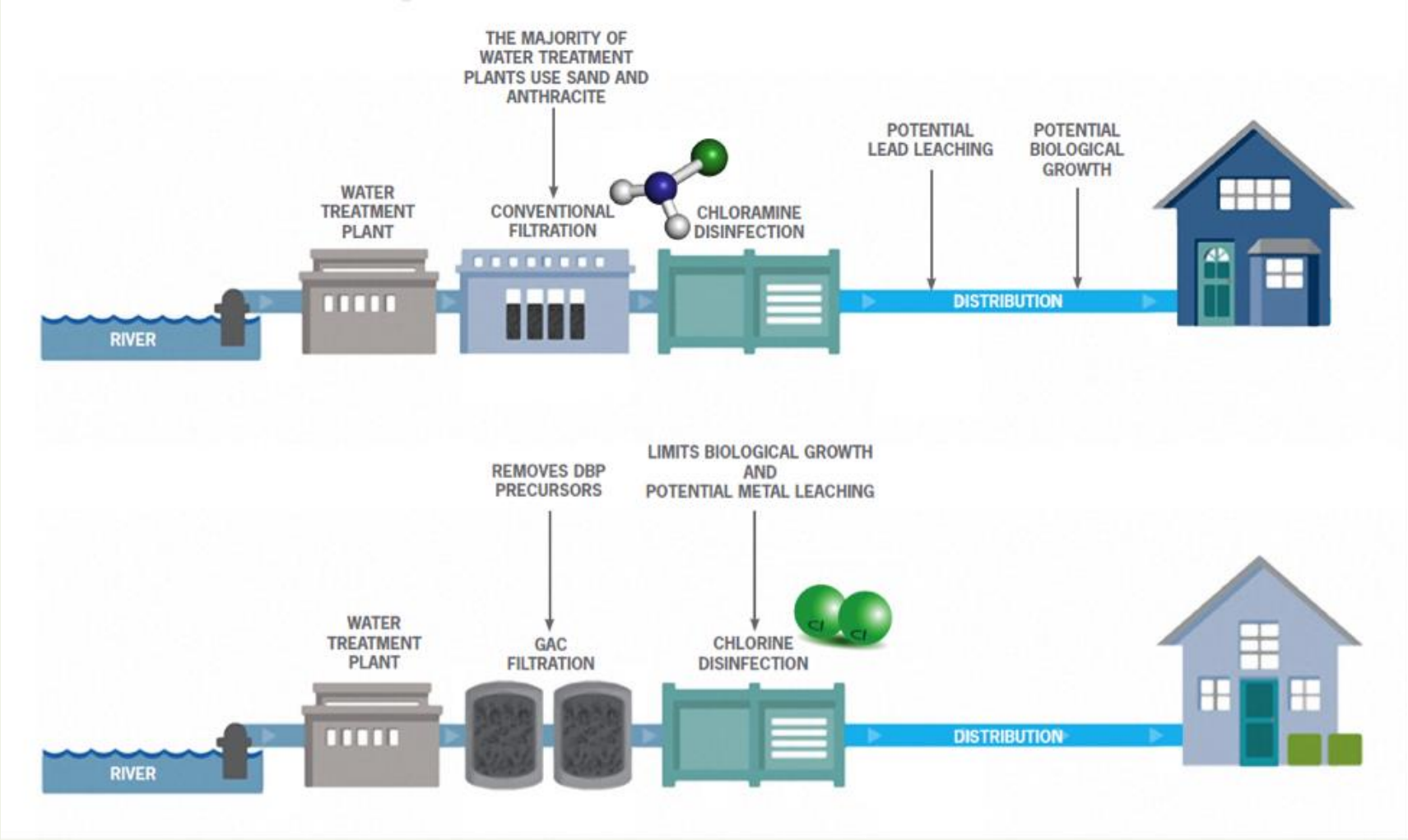
GAC is the activated carbon form commonly used in filtration applications. In a rapid sand filter application, GAC is normally used in combination with other media types, such as sand and garnet, to form dual or multi-media filters.

GAC serves as a general filter, capturing particulate turbidity, and also to remove, by adsorption, residual taste and odour causing organics in water.

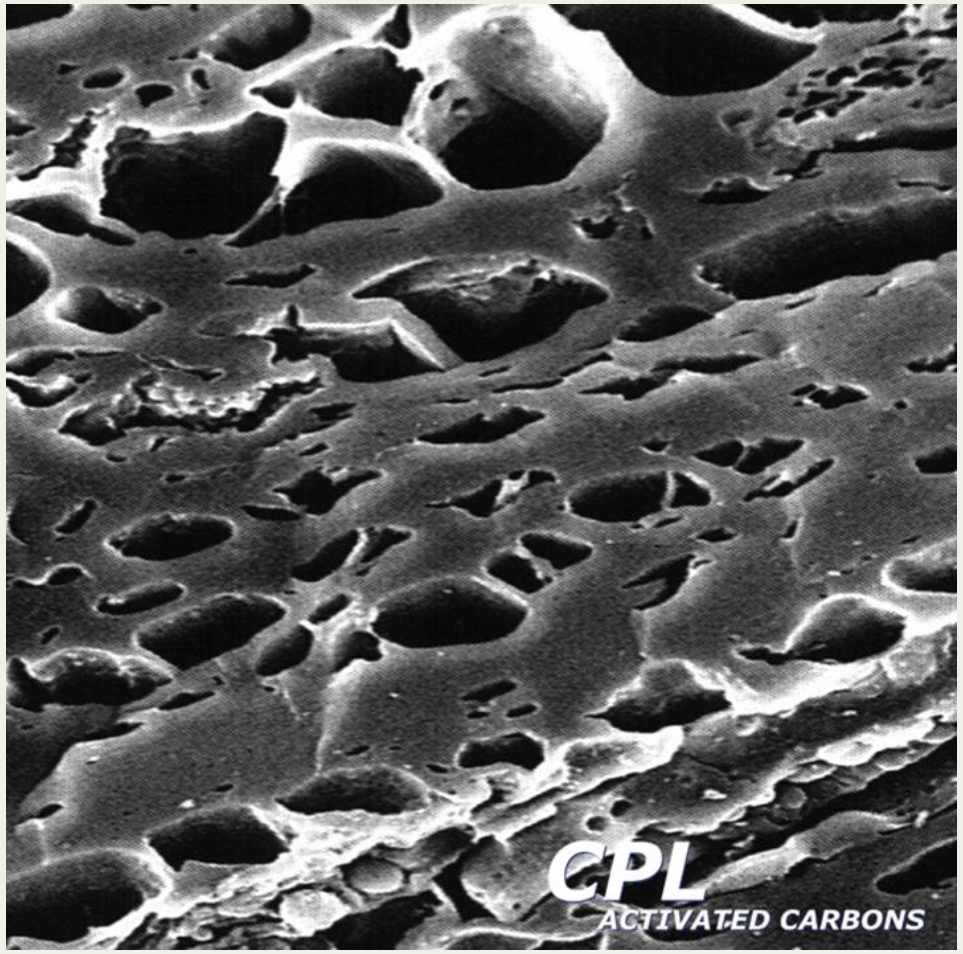
Where there is high TOC, high alkalinity and pH, GAC filters are often found after the clarification stage, as a primary organic adsorption filtration step, prior to granular filtration, and upstream of disinfection.

GAC adsorption can also remove biodegradable organic matter, microbial food, which helps prevent regrowth in the downstream distribution system.

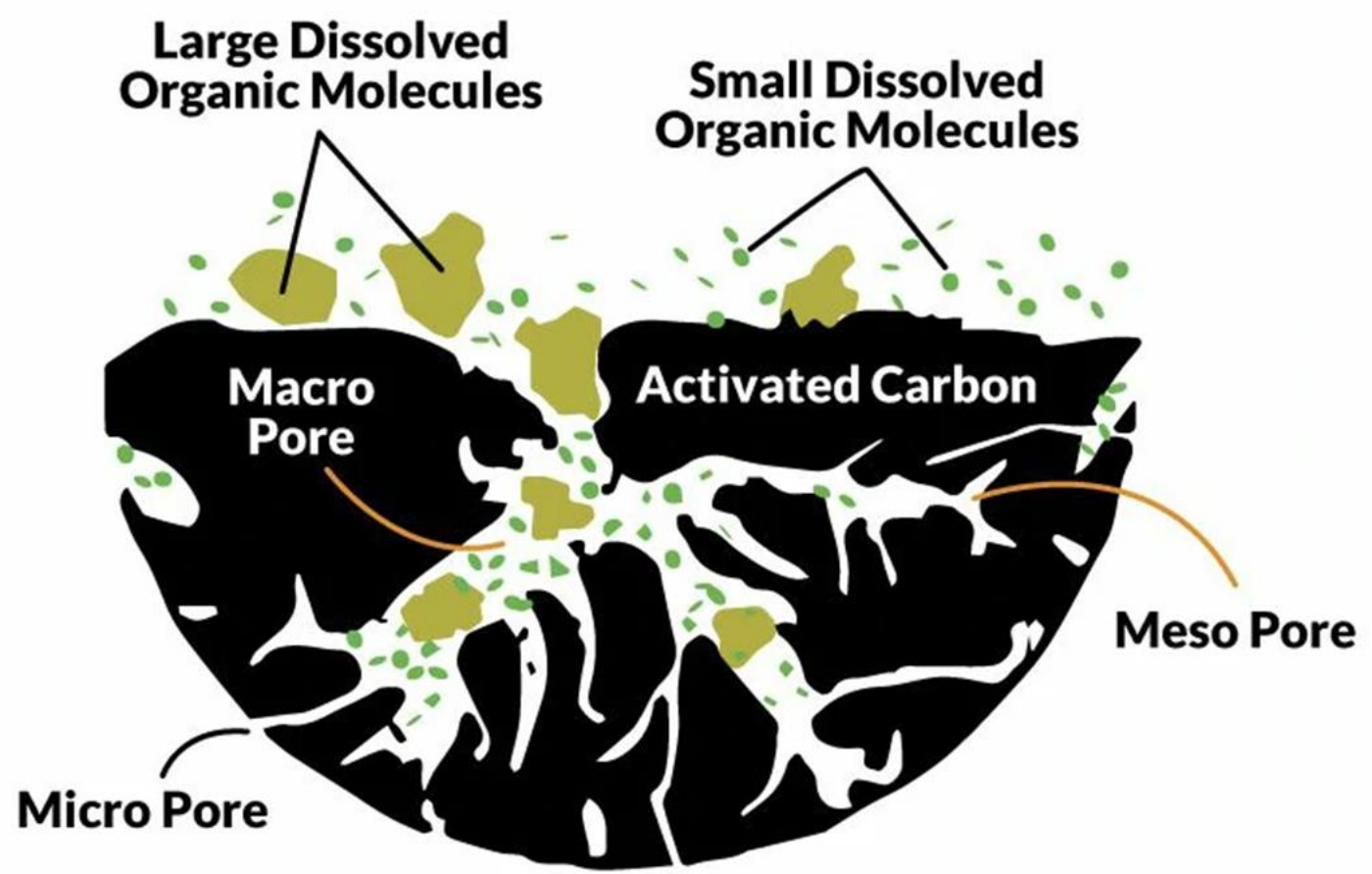
# Control Strategies for DBPs in Municipal Water Systems - Activated Carbon.



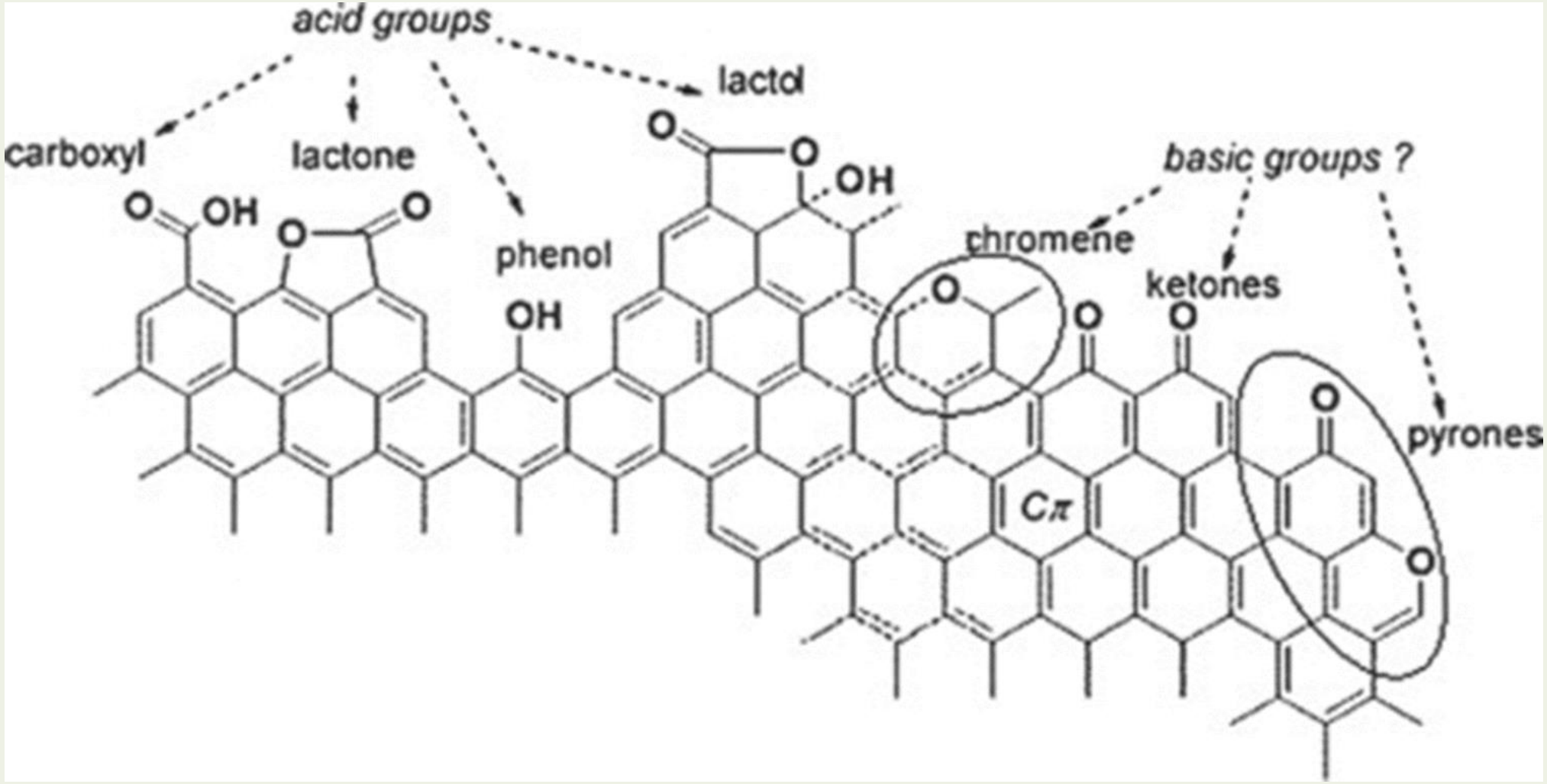
# Control Strategies for DBPs in Municipal Water Systems - Activated Carbon.



# Control Strategies for DBPs in Municipal Water Systems - Activated Carbon.



# Control Strategies for DBPs in Municipal Water Systems - Activated Carbon.



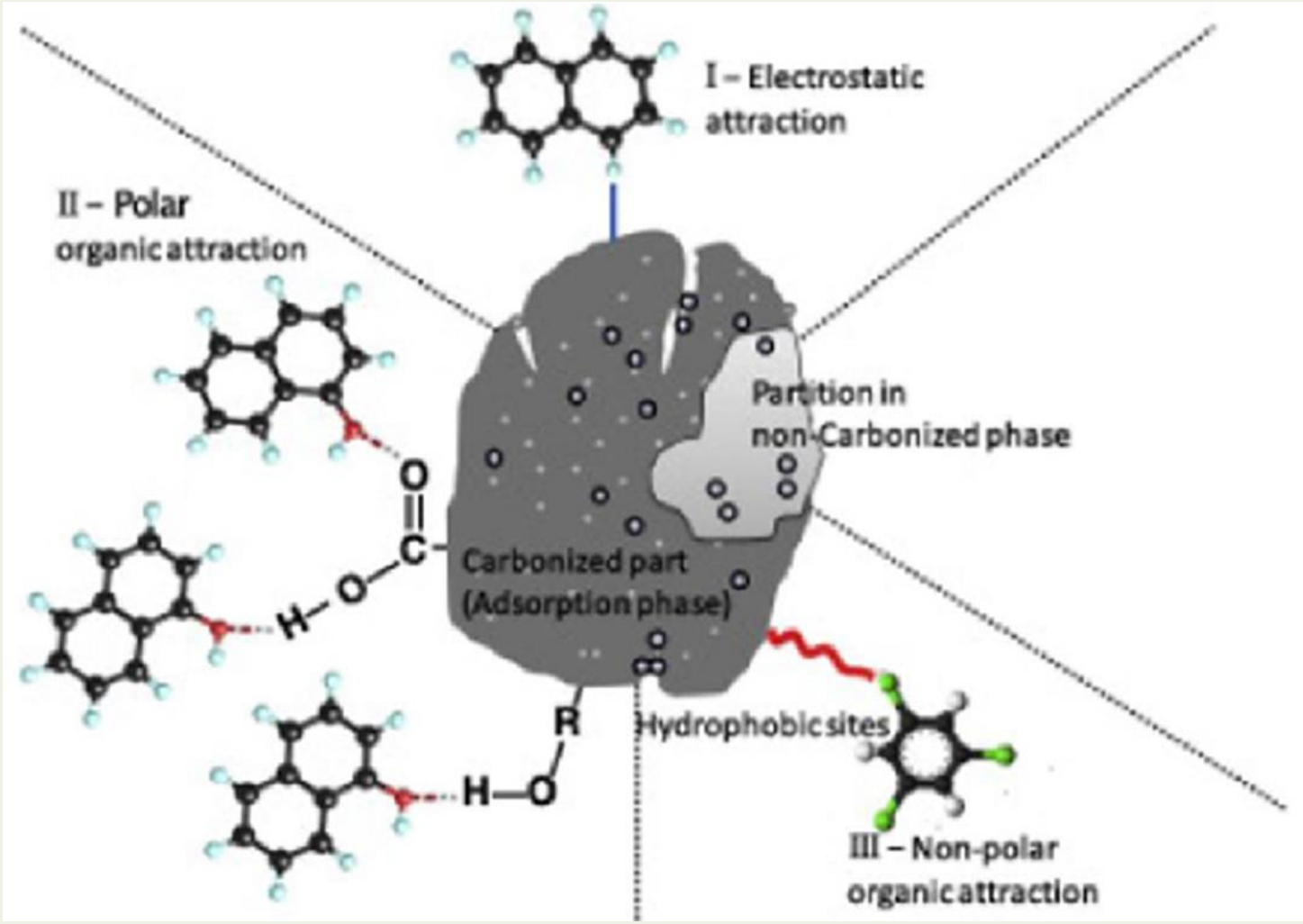
# Control Strategies for DBPs in Municipal Water Systems - Activated Carbon.

Activated carbon is a covalent adsorbent, in that it adsorbs molecules which bond covalently, which is the case for most NOM, especially organic acids.

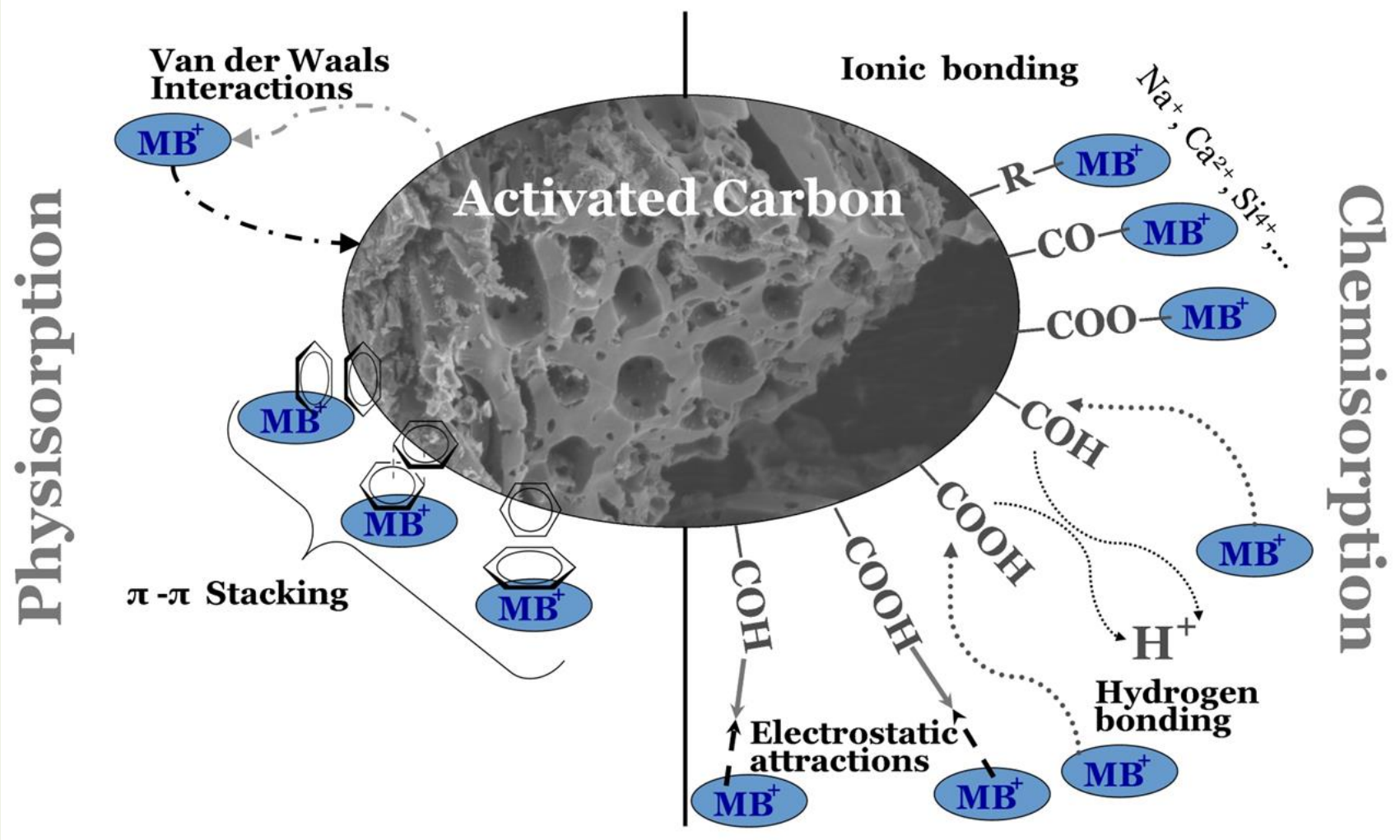
Activated carbon, also called activated coal or charcoal, is a form of carbon processed to have small, low volume pores that substantially increase the surface area available for adsorption or chemical reactions.

Based on Van der Waals Forces, the high surface area pores of activated carbon will adsorb different organic contaminants. The absorbance potential and efficiency is due to the polar nature of the organic molecules.

# Control Strategies for DBPs in Municipal Water Systems - Activated Carbon.



# Control Strategies for DBPs in Municipal Water Systems - Activated Carbon.



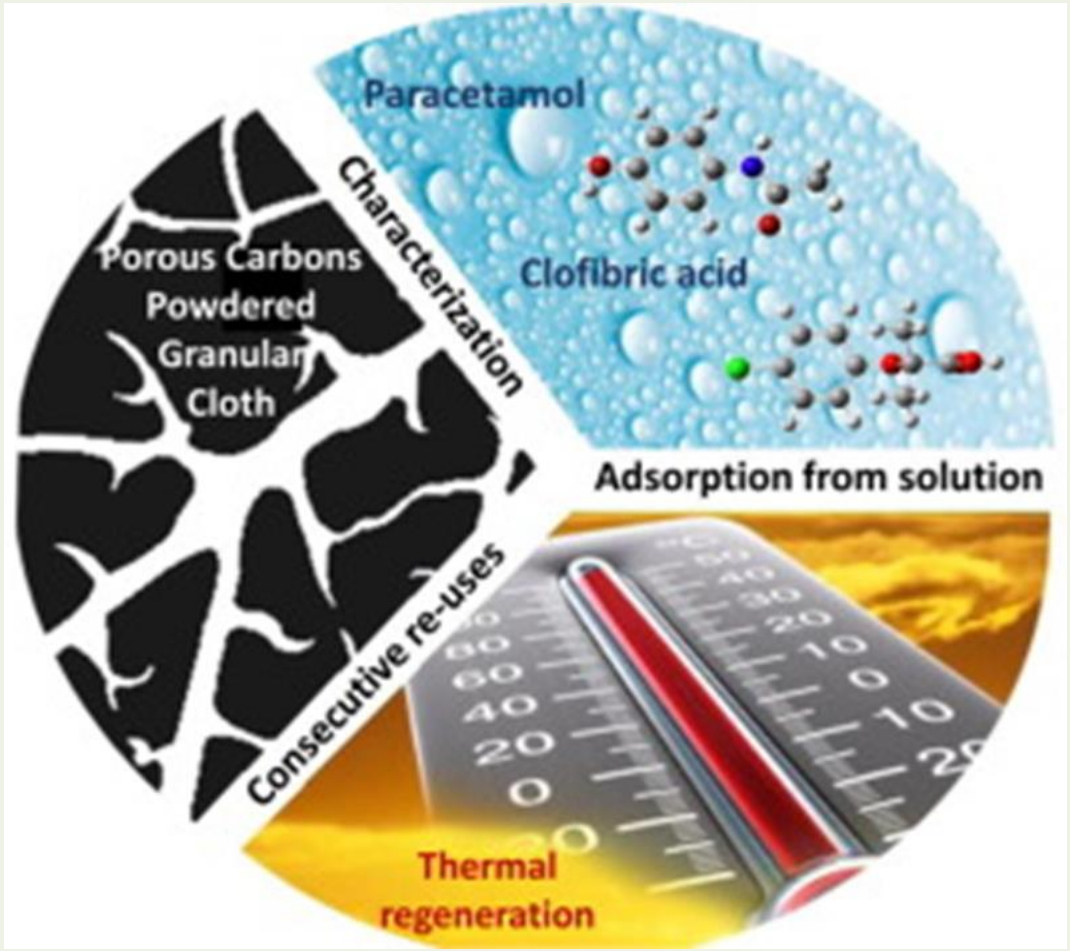
# Control Strategies for DBPs in Municipal Water Systems - Activated Carbon.

Physical adsorption does not cause a change in the chemical structure of the carbon adsorbent or in the organic molecules involved, Therefore, the adsorption process is reversible. Because the organic adsorption is reversible, it is considered to be a surface adsorption process.

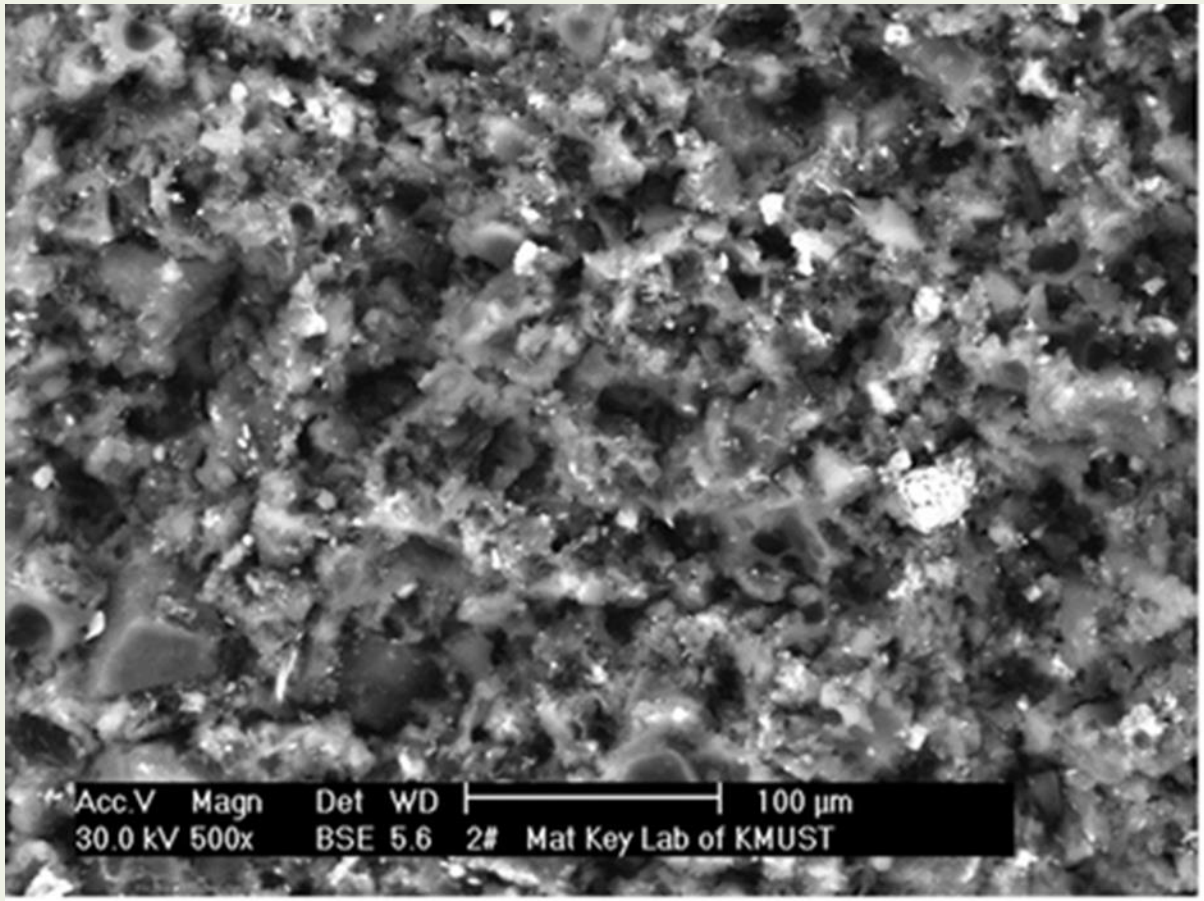
If the organic adsorbate retained is volatile, a sufficient rise in temperature will cause the molecules to be released from the activated carbon.

Regeneration is carried out at temperatures between $500^0$ and $800^0$ C. Non-volatile compounds undergo pyrolysis and gasify at $300^0$ C. The volatile compounds are released from the GAC and gasify at the higher temperatures.

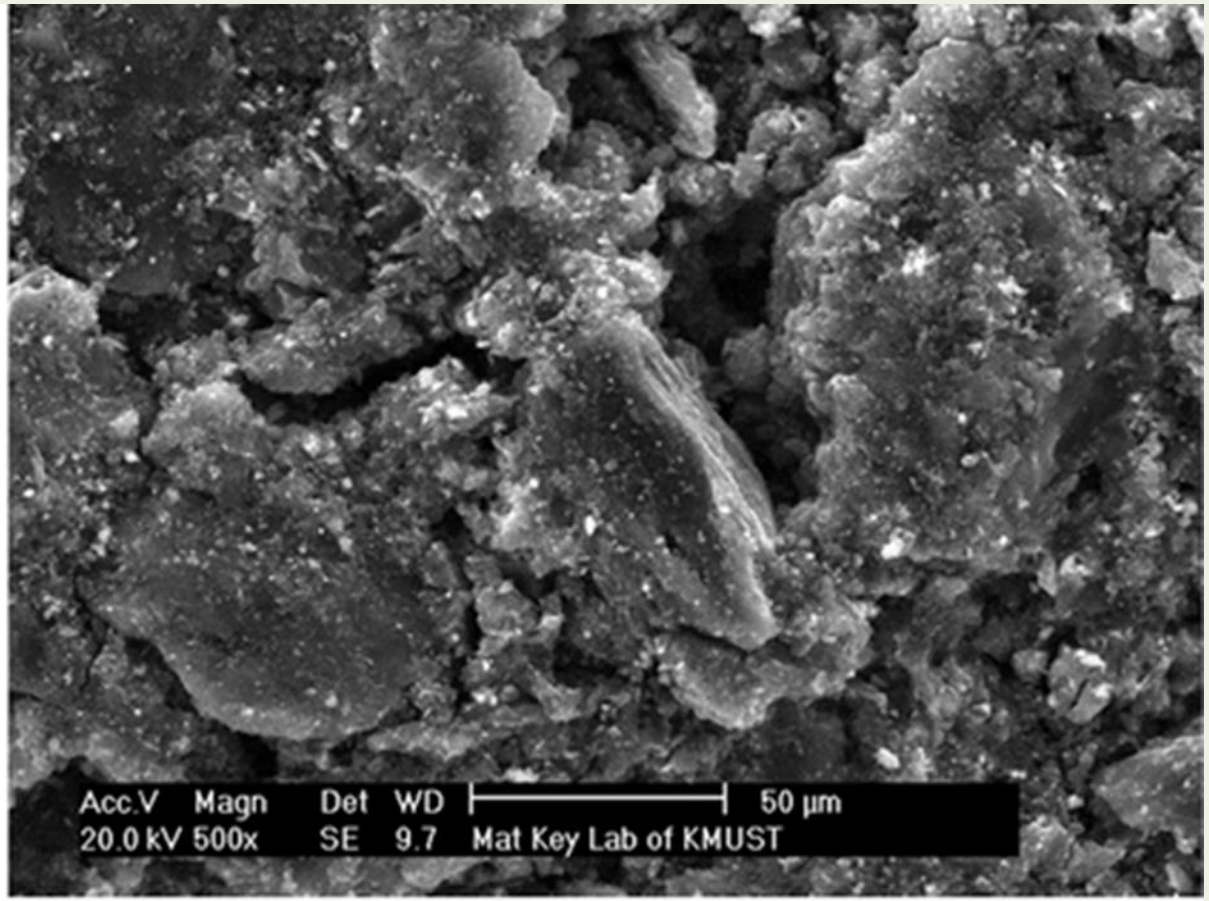
# Control Strategies for DBPs in Municipal Water Systems - Activated Carbon.




# Control Strategies for DBPs in Municipal Water Systems - Activated Carbon.




a. Spent activated carbon




b. Regenerated activated carbon

# Control Strategies for DBPs in Municipal Water Systems - Activated Carbon.

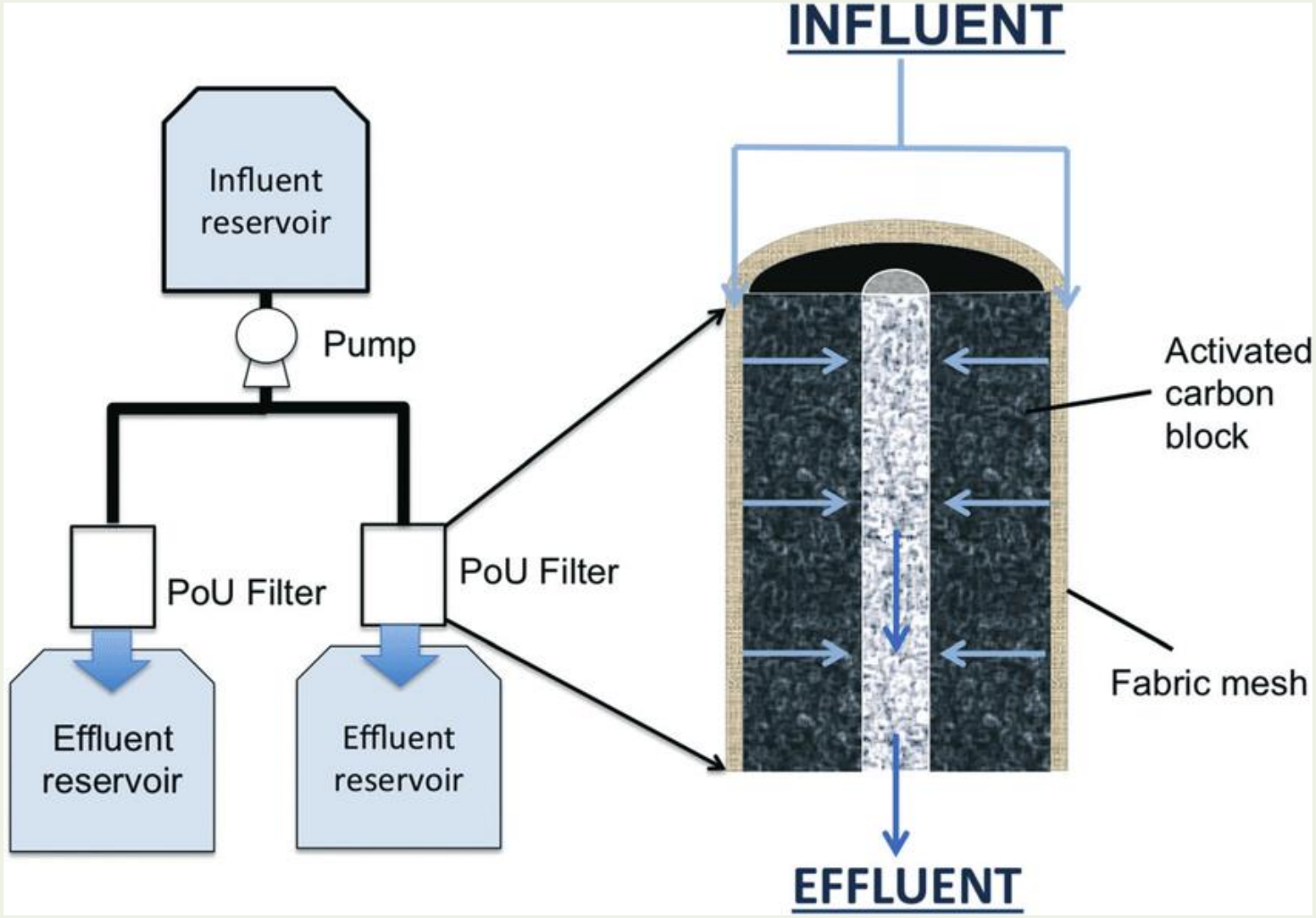
Outside of the WTP, and within the local community, Point-of-Entry (POE) and Point-of-Use (POU) filters utilizing activated carbon are effective at removing taste and odours and many disinfection DBPs, especially THMs and HAAs.

Many POU filters typically show greater then 90% removal efficiency for THM, and slightly lower, at 75% to 90%, for HAA depending on the specific filter and conditions. HAN removal rates can be > 95%.

POE filters distribute water to the entire building, and can be large and cumbersome, requiring significant maintenance. POU carbon filters are widely available in faucet mounted or under-sink models.

# Control Strategies for DBPs in Municipal Water Systems - Activated Carbon.

# Control Strategies for DBPs in Municipal Water Systems - Activated Carbon.



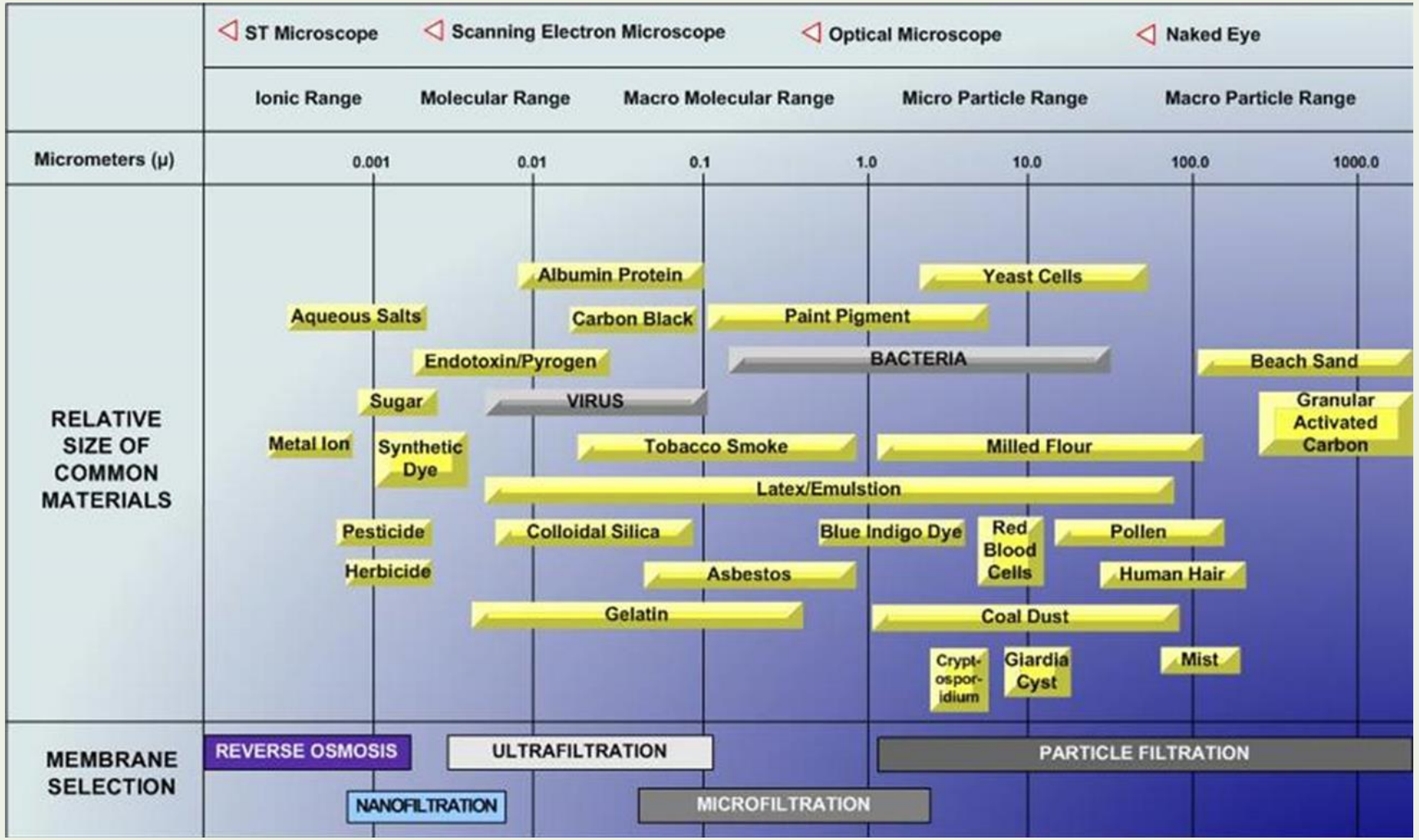
# Control Strategies for DBPs in Municipal Water Systems - Nanofiltration (NF).

Generally speaking, organic matter, especially the smaller dissolved molecules considered precursors to DBP, cannot be filtered from treated water using physical straining.

Some organic material present in water after clarification, is suspended or colloidal, and can be removed from the water using conventional methods; rapid sand and multi-media filters do provide some benefit.

Dissolved organic carbon, DOC, is usually defined as being able to pass through a 0.45 µm filter. A rapid sand filter has an effective pore size of 5 µm, and a MF membrane filter will capture larger dissolved organic molecules, but will allow passage of the smaller DOC molecules.

# Control Strategies for DBPs in Municipal Water Systems - Nanofiltration (NF).



# Control Strategies for DBPs in Municipal Water Systems - Nanofiltration (NF).

Rapid sand and multi-media filters are designed to intercept and capture particulates, and protozoa such as cryptosporidium and giardia.

MF membrane filtration is designed to be able to capture protozoa and bacteria.

UF membrane filtration is designed to capture protozoa, bacteria and viruses.

NF membrane filtration, is designed to remove protozoa, bacteria, viruses and dissolved organic molecules, including NOM/TOC/SOC, the precursors to chlorinated DBPs.

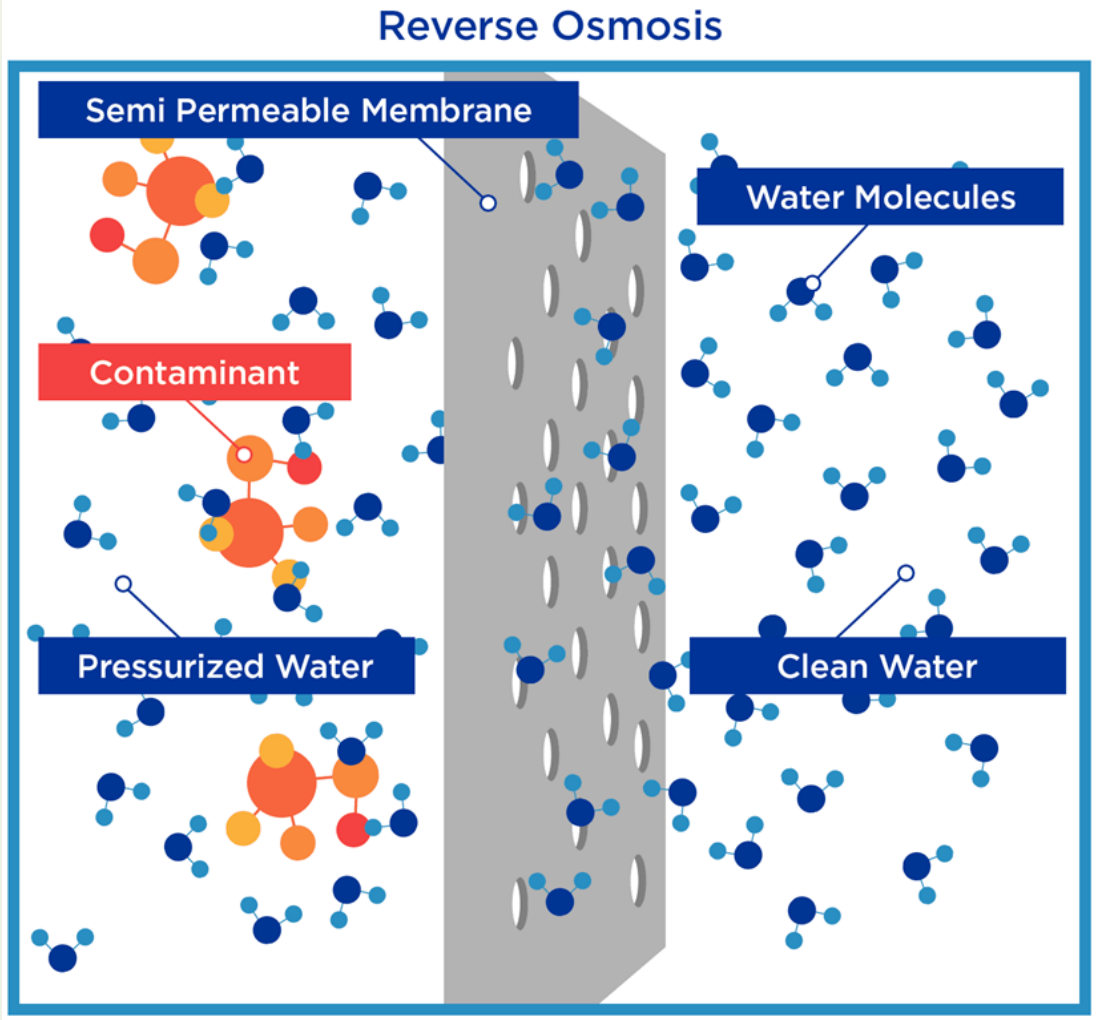
# Control Strategies for DBPs in Municipal Water Systems - Nanofiltration (NF).

Nanofiltration (NF) and reverse osmosis (RO) are a class of semi-permeable membranes used in applications that require the removal of dissolved contaminants; treatment processes include softening, desalination or DBP precursor removal.

The typical range for MWCO levels is less than 100 Daltons for RO membranes, and between 200 and 1,000 Daltons for NF membranes. A Dalton is exactly 1/12 the mass of a carbon-12 atom (a protein might be 50,000 Da).

NF and RO utilize semi-permeable membranes that do not have definable pores. NF and RO processes achieve removal of dissolved contaminants through the process of reverse osmosis (and not by conventional filtration).

# Control Strategies for DBPs in Municipal Water Systems - Nanofiltration (NF).



# Control Strategies for DBPs in Municipal Water Systems - Nanofiltration (NF).

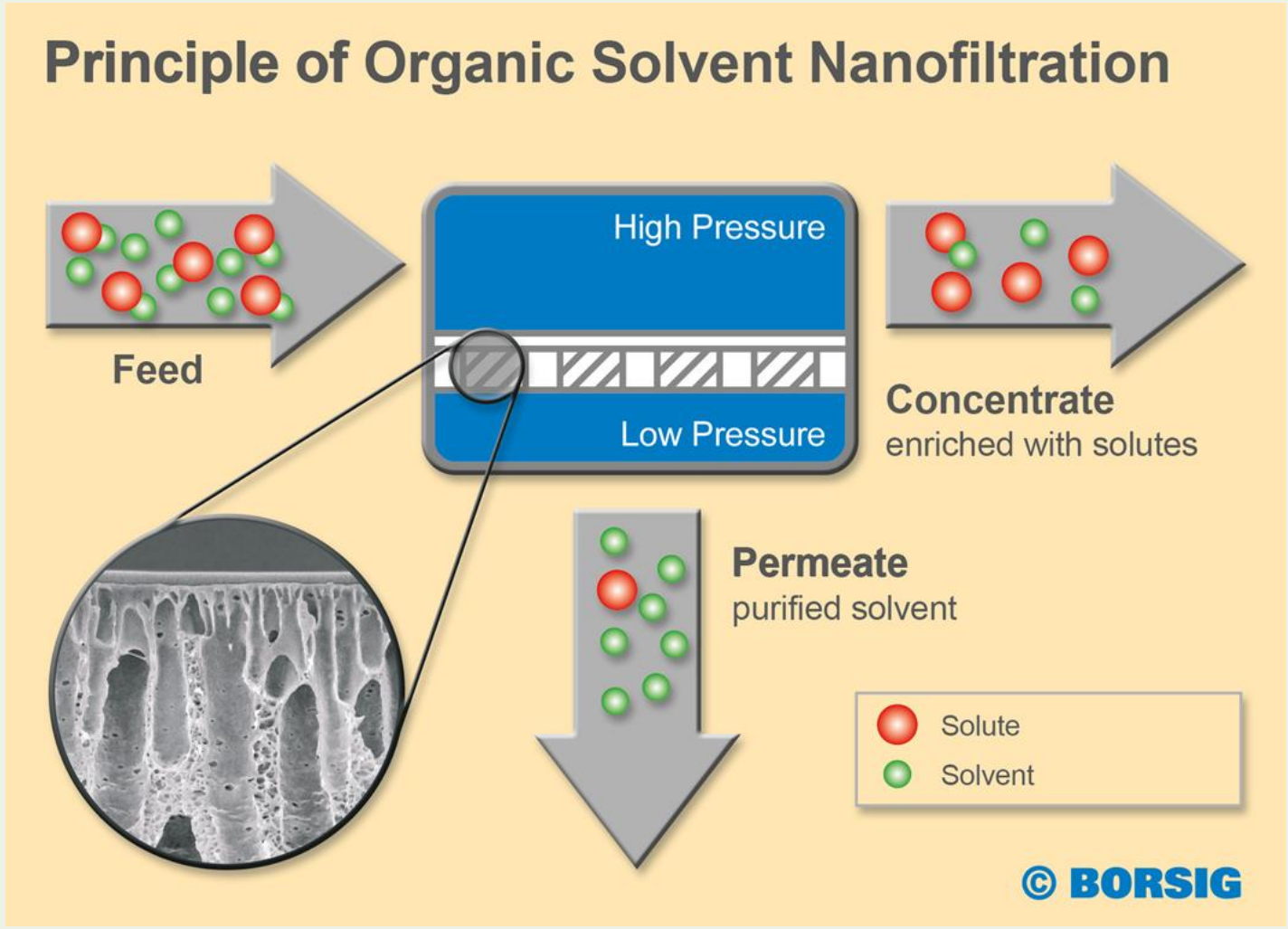
NF and RO target dissolved particles, defined as solids and gases (both organic & inorganic) which will pass through a 0.45 μm filter.

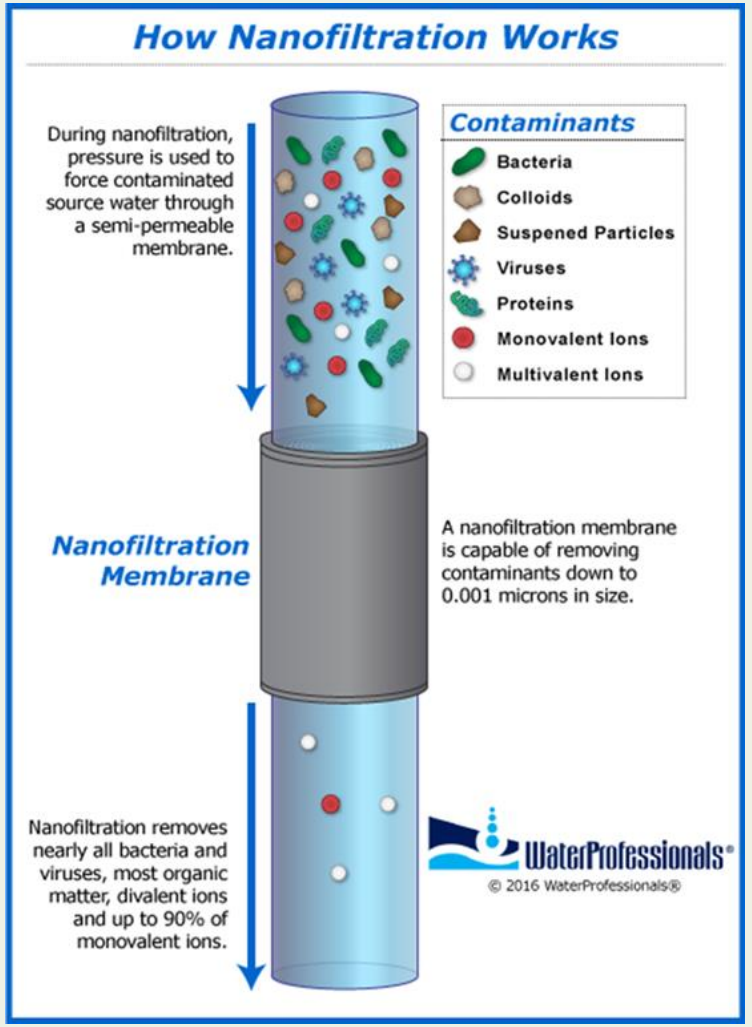
Most often NF and RO are used to remove dissolved metals from groundwater.

The dissolved inorganic molecules commonly found in water at concentrations between 1.0 - 500 $mgL^{-1}$ include calcium, magnesium, sodium, potassium, bicarbonate, chloride, sulphate, and nitrate ions.

The dissolved inorganic species present in water at concentrations between 0.01 to 10 $mgL^{-1}$ include iron, lead, copper, arsenic, and manganese.

# Control Strategies for DBPs in Municipal Water Systems - Nanofiltration (NF).



# Control Strategies for DBPs in Municipal Water Systems - Nanofiltration (NF).

# Control Strategies for DBPs in Municipal Water Systems - Nanofiltration (NF).

Reverse osmosis and nanofiltration are both capable of removing bacteria (0.2 μm) and viruses (0.004 μm) from a water stream.

Nanofiltration membranes, with an “effective pore size” of 0.001 μm, and a corresponding MWCO value between 200 - 500 Daltons, will also remove dissolved organic molecules, including NOM/TOC/SOC, the precursors to chlorinated DBPs trihalomethanes (THMs).

Nanofiltration is also used to remove pesticides and other organic contaminants from surface and ground water sources.

# Control Strategies for DBPs in Municipal Water Systems - Nanofiltration (NF).

Nanofiltration (NF) is an effective technology option for the removal of DBPs and their precursors from water.

NF membranes achieve high rejection rates for the dissolved organic molecules; 90 - 98% for DBP precursors and > 90% for specific DBPs such as trihalomethanes and haloacetic acids.

DBP rejection by nanofiltration is governed primarily by three mechanisms, Size Exclusion, Electrostatic Repulsion and Surface Adsorption.

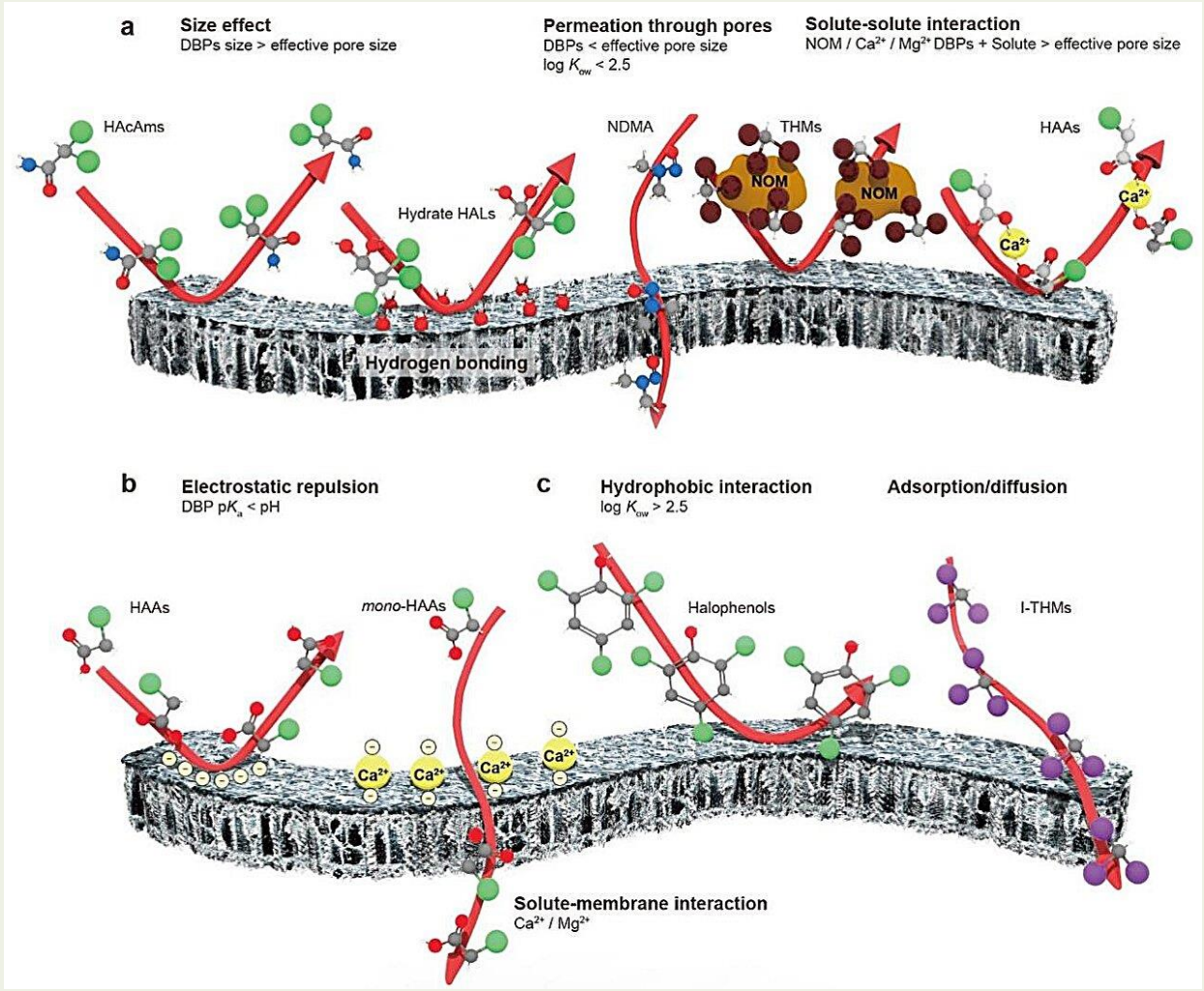
# Control Strategies for DBPs in Municipal Water Systems - Nanofiltration (NF).

Size Exclusion is a non-specific mechanism where the membrane acts as a physical barrier. NF membranes have a MWCO between 200 - 1,000 Daltons and an “effective pore size” of 0.001 - 0.005 µm, efficiently blocking larger DBP molecules and natural organic matter precursors.

Electrostatic Repulsion, commercial NF membranes have a negatively charged surface which repulses similarly charged DBP molecules (such as HAAs) pushing them away from the membrane pores and enhancing rejection.

Adsorption, hydrophobic interactions and hydrogen bonding can cause some DBPs, to adsorb onto the membrane material. This can initially lead to high rejection rates, but may cause long-term fouling and performance decline as the membrane's adsorption capacity is saturated over time.

# Control Strategies for DBPs in Municipal Water Systems - Nanofiltration (NF).



# Control Strategies for DBPs in Municipal Water Systems - Nanofiltration (NF).

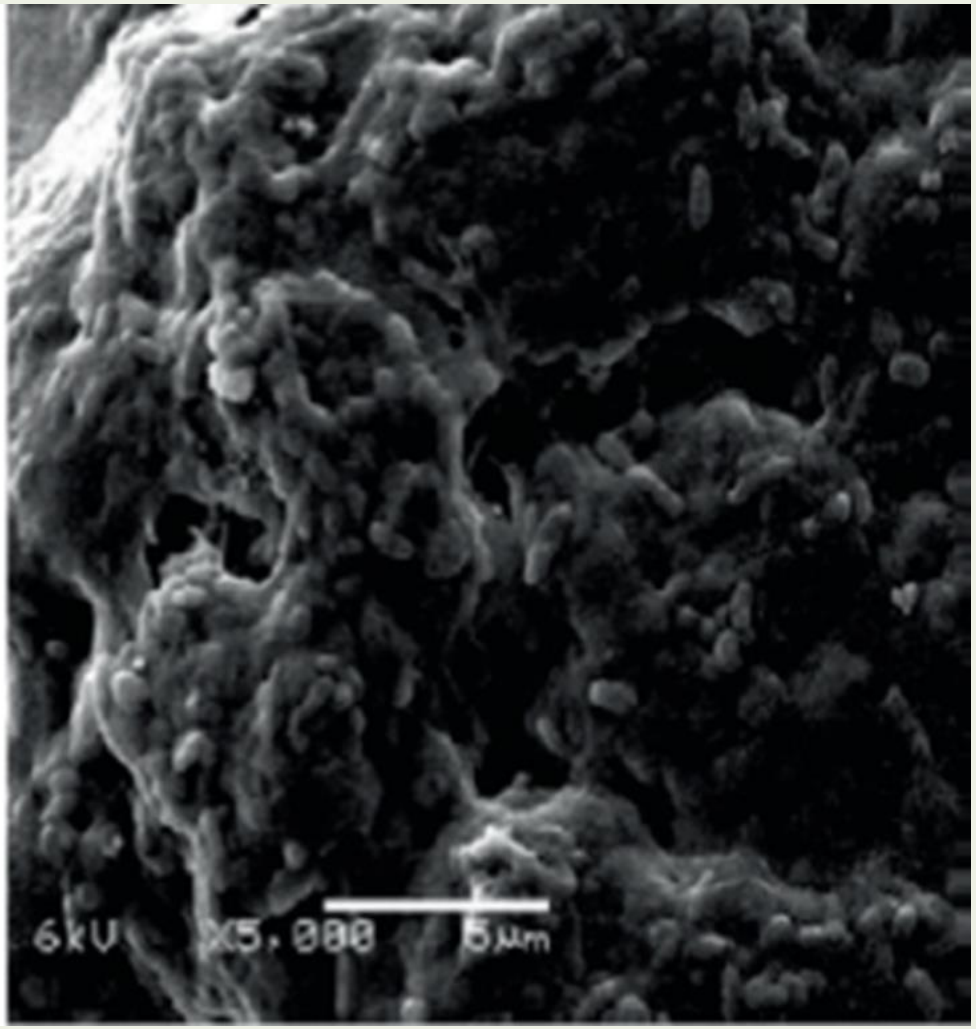
The efficiency of DBP removal by nanofiltration is influenced by several factors;

Membrane Pore Size/MWCO and Surface Charge.

DBP molecular weight & size, electrostatic charge/polarity and hydrophobicity.

Prevailing pH (higher pH values typically increase the negative charge of both the membrane and the DBPs, improving rejection) temperature and the degree of membrane fouling/NOM.

# Control Strategies for DBPs in Municipal Water Systems - Nanofiltration (NF).



# Control Strategies for DBPs in Municipal Water Systems - Biofiltration.

Biofiltration is defined as a filtration process where the filter medium comprised of porous a media material (e.g., sand, garnet, granular activated carbon (GAC), or a synthetic carrier material, plastic beads), which is then colonized by indigenous microbial communities, and where these microorganisms perform at least one of the essential treatment functions of the process.

The primary purpose of biofiltration in drinking water treatment is the removal of biodegradable organic matter (BOM). DBP and DBP precursors are considered as food materials for the microbes, and can also surface adsorb onto the filter substrate. The secondary purpose is the elimination of pathogenic microorganisms, and reductions in other species, such as ammonia, nitrite etc..

# Control Strategies for DBPs in Municipal Water Systems - Biofiltration.

While biofiltration is effective at reducing many DBP precursors, its efficiency varies depending on factors like the type of media used, contact time, and operational parameters such as backwash frequency.

Granular activated carbon is widely used as the supporting media, and once a biofilm forms, it becomes biological activated carbon (BAC). GAC/BAC show the best removal rates for precursors of THMs and HAAs.

Biofiltration is effective after ozonation to degrade the smaller organic molecules that result from ozonation, leading to a lower DBP formation potential. Caution is required as some studies have shown an increase in brominated DBPs due to higher bromide/DOC ratios after biofiltration.

# Control Strategies for DBPs in Municipal Water Systems - Biofiltration.

Biofiltration is highly effective at removing haloacetic acids and precursors for other DBPs such as haloacetonitriles and haloaldehydes, however, it's effectiveness against THMs is more limited as they are less biodegradable.

A 2023 study showed biofilters can consistently remove approximately 52% of the total organic halogens (TOX), 97% of haloacetic acids (HAAs), 14% of trihalomethanes (THMs), and 63% of unknown DBPs (UTOX) from chlorinated drinking water.

Biofilters also effectively remove 46% of TOX, 14% of THMs, 96 % of HAAs, and 48% of UTOX from chloraminated drinking water.

# Control Strategies for DBPs in Municipal Water Systems - Biofiltration.

The biodegradation rate constants for these DBPs increased with increasing temperatures; so, they can be les effective in cold Canadian winters. Extending the Empty Basin Contact Time is also an effective method to improve DBPs removal, particularly in lower temperatures conditions.

The biofiltration before post-chlorine treatment protocol reduced 71% of HAAs, 37% of DHANs, 44% of UTOX and 17% of THMs.

When the biofiltration followed by post chloramine protocol was reviewed, the corresponding formation potential reductions were 90% of HAAs, 83% of DHANs, 43% of UTOX and 10% of THMs at an EBCT of 15 min.

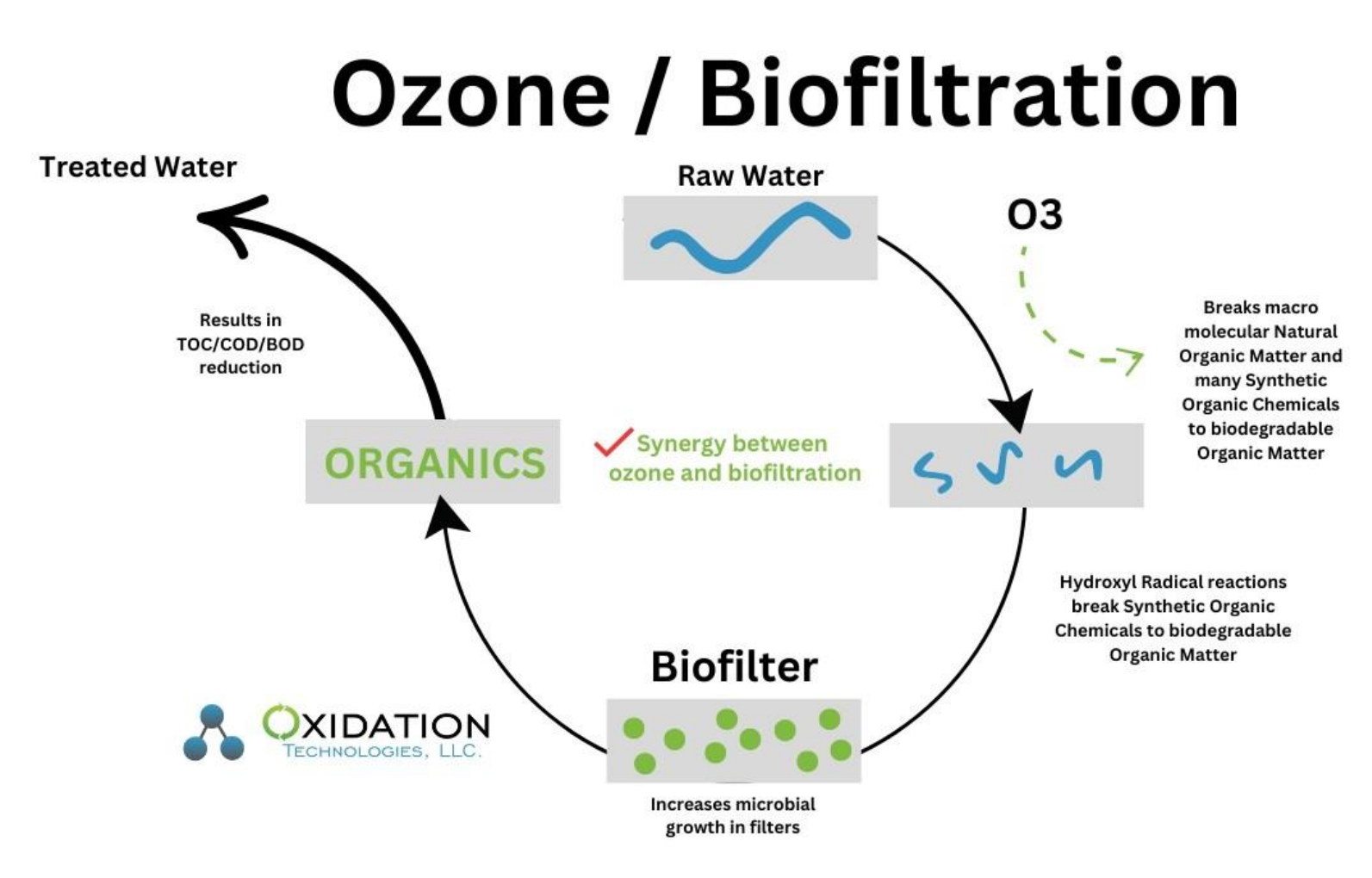
# Control Strategies for DBPs in Municipal Water Systems - Biofiltration.

In a biological filter, living microorganisms attach themselves to, and start growing on, the grains of the granular filter media. Other organisms, and material within the water stream, provide nourishment for this biological growth. In this manner, the living microorganisms act as a biological filter.

As the layer of microorganisms consumes more organic matter, it will grow in size and potentially can cause material to be filtered out by physical straining.

The consumption of material by this biological layer not only captures suspended particulate, but can consume dissolved organics and other nutrients. Biological filtration can be the primary means of filtration for some filters used in the water treatment process.

# Control Strategies for DBPs in Municipal Water Systems - Biofiltration.



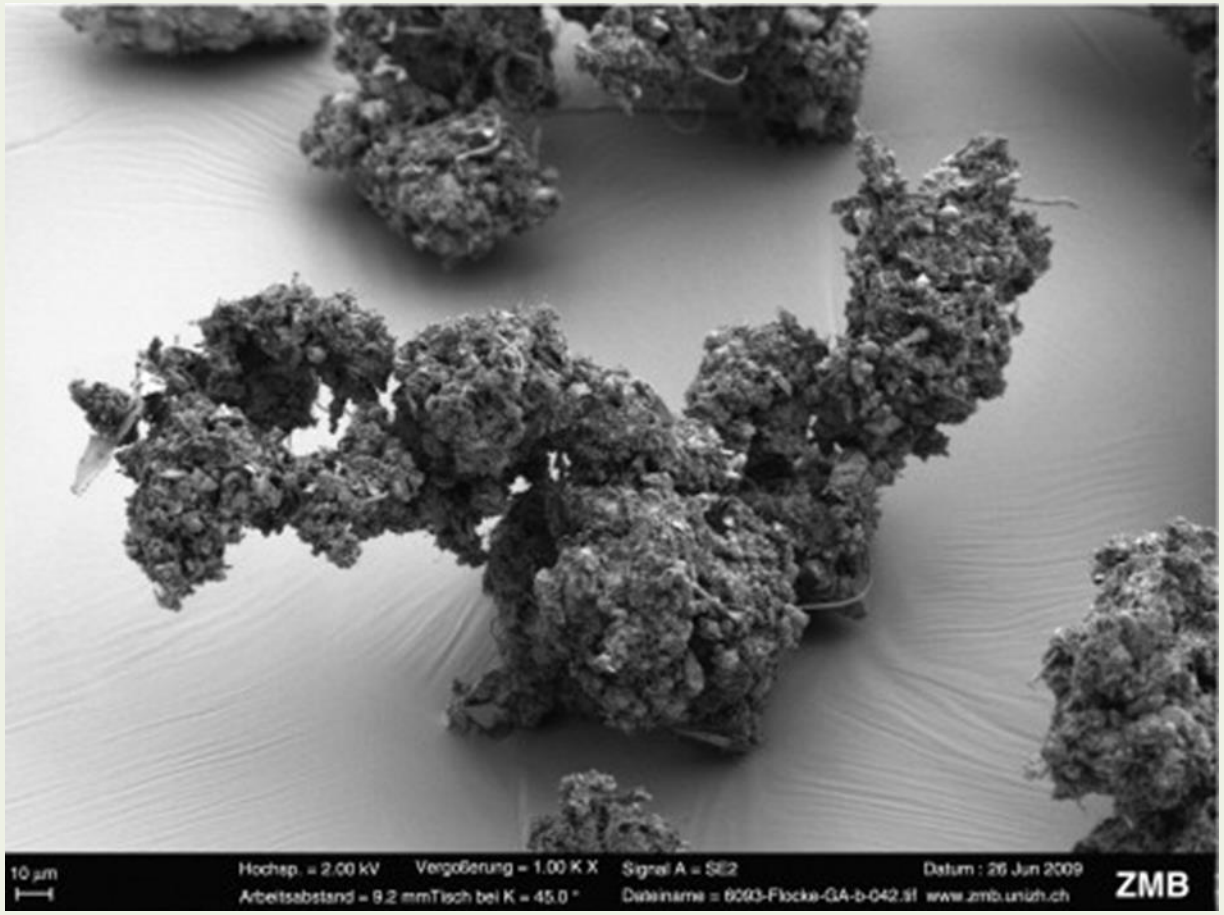
# Control Strategies for DBPs in Municipal Water Systems - Biofiltration.

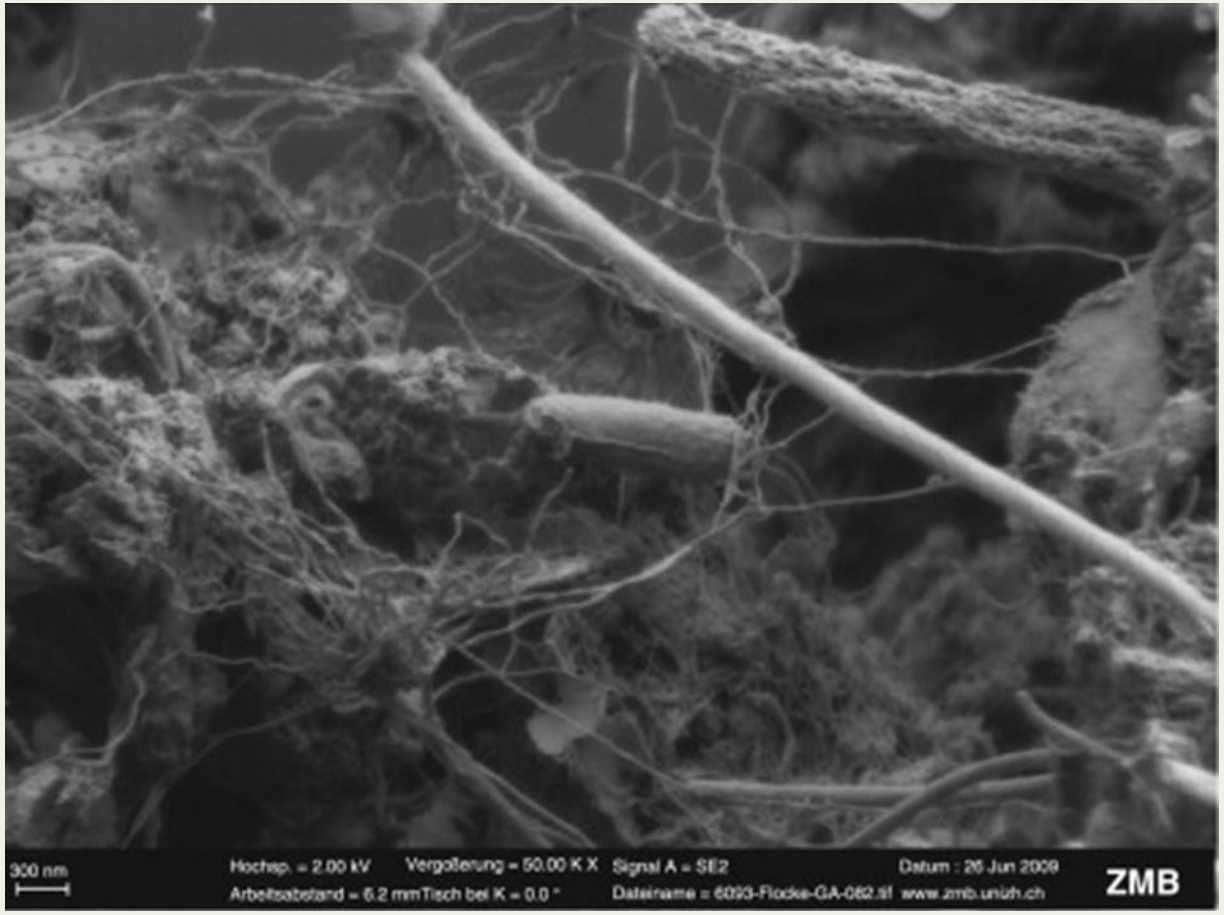
One of the main biological activities in the slow sand filtration process is the use of the biological Schműtzdeckè, a complex biological layer formed on the surface of a SSF, which extends 3 cm above the bed as a slimy matrix.

The Schműtzdeckè consists of the mineral media precipitates and colonized microorganisms comprising a gelatinous biofilm matrix bacteria, fungi, protozoa, rotifer, a range of aquatic insect larvae, and even some larger eukaryotes.

The Schműtzdeckè is the primary contributor to the filtration process while secondary contributors are microbes attached to sand particle in the deeper parts of a SSF. Intermittent scrapping of Schműtzdeckè is essential since its overgrowth can block the percolation process.

# Control Strategies for DBPs in Municipal Water Systems - Biofiltration.



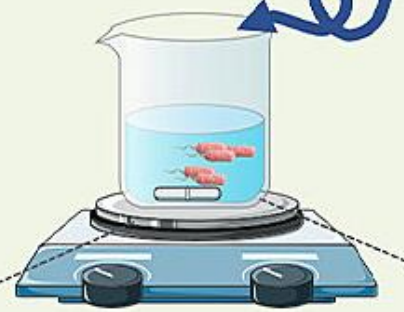



# Control Strategies for DBPs in Municipal Water Systems - Biofiltration.

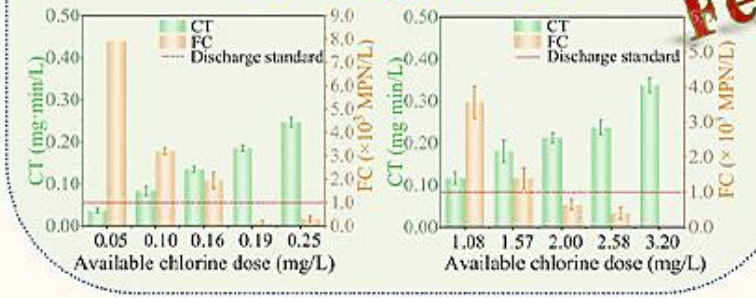
# Control Strategies for DBPs in Municipal Water Systems - WWTP Effluent.

## Intelligent dosing of NaClO in municipal WWTPs

NaClO

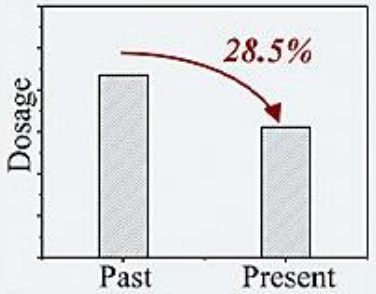


**Optimum CT value:**
**0.20 mg·min/L**



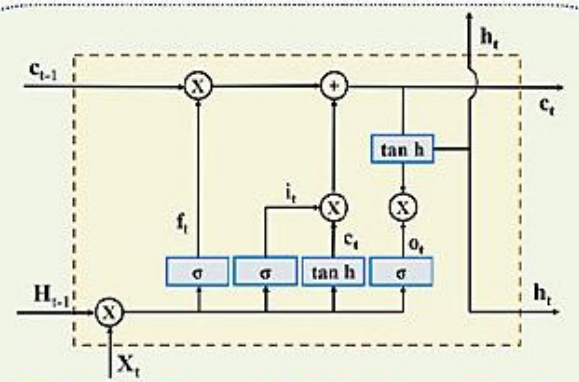

Feedback

$FC_{eff} < 1.0 \times 10^3$ MPN/L

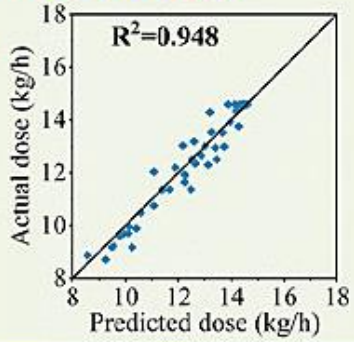



**A significant saving in NaClO consumption**

Feedforward




**LSTM model: Predicting the dosage**



# Control Strategies for DBPs in Municipal Water Systems - WWTP Effluent.

Disinfection is an essential component of the treatment process in municipal wastewater treatment plants, and is required to guarantee public health safety. NaOCl is used extensively for this purpose.

Due to the significant, and uncontrollable, fluctuations in influent wastewater quantity and quality, WWTPs typically maintain a fixed dosage of NaOCl to ensure effluent water continuously satisfies discharge permit compliance.

Consequently, NaOCl is often overdosed, increasing not only chemical costs, but also elevating DBPs loadings in returned waters. A recent study determined fecal coliform counts were less than $1.0 \times 10^3$ MPN/L when the effluent CT value is regulated at 0.20 mg·min/L (calculated as $Cl_2$).

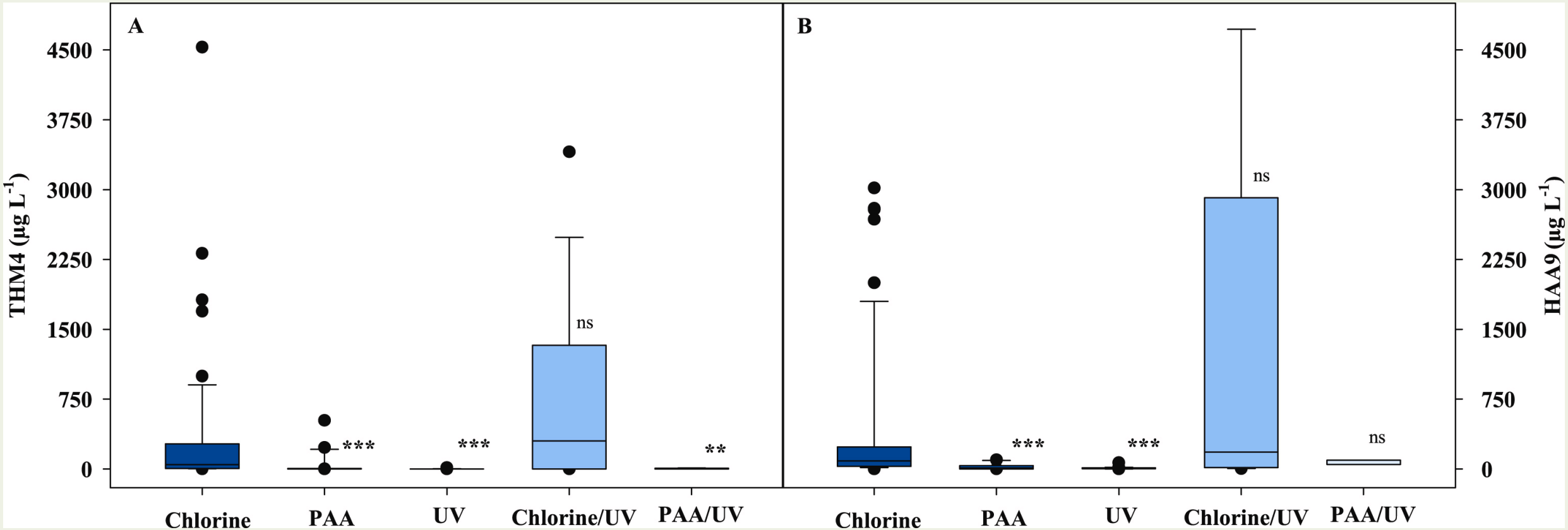
# Control Strategies for DBPs in Municipal Water Systems - WWTP Effluent.

An inactivation step before DBP analyses reduced residual concentrations of THM and HAA.

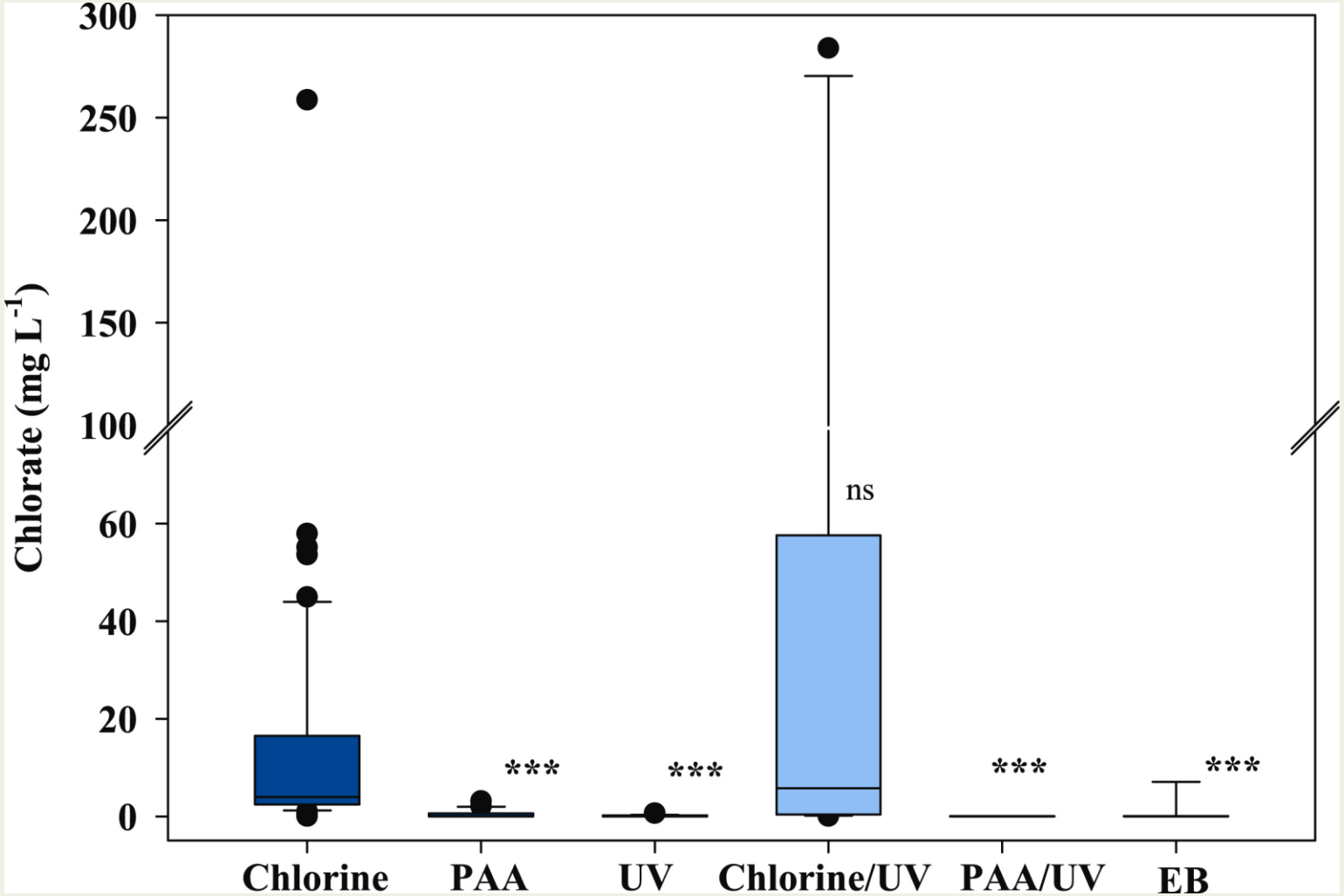
A recent study demonstrated there is a positive correlation between chlorine or chlorine/UV and DBP concentrations. The quality of raw wastewater varies considerably depending on the WWTP, which, in turn, influences DBP formation. In all WWTPs reviewed, chlorine alone or combined with UV significantly increased the presence of THMs, HAAs, and chlorate levels in the treated effluents. When the same WWTPs changed to peracetic acid, or PAA/UV, effluent DBPs concentrations were diminished completely.

Mitigation of DBPs concentrations is similarly possible for reclaimed water intended for irrigation of municipal parks and gold courses etc..

# Control Strategies for DBPs in Municipal Water Systems - WWTP Effluent.



# Control Strategies for DBPs in Municipal Water Systems - WWTP Effluent.



# Disinfection By-Products in Municipal Water Systems - Reference Materials.

## References;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Nanofiltration and Reverse Osmosis offer hope for Removing Disinfection By-Products.

Li Yali -Chinese Academy of Sciences – April 2025.


# Disinfection By-Products in Municipal Water Systems.

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