

Disinfection By Products

Disinfection By-Products (DBPs) are defined as "Chemical compounds formed by the reaction of a water disinfectant with a precursor in a water supply". This is a fairly generic and non-specific definition. The concern with DBPs is that certain of the compounds affect aquatic toxicity and some can pose a risk to human health. Those of greatest concern are the DBPs formed when halogens, typically chlorine and/or bromine, used as biocides or disinfectants react with organic matter in the water being disinfected. Related to human health risks, if the halogen reacts with natural organic matter, such as humic and/or fulvic acids, in drinking water being produced from water sources such as rivers, lakes or reservoirs Halogenated Organic Compounds (HOCs) formed can be hazardous and some are carcinogenic. Another source of DBPs is from industrial waters, such as cooling water, that have been halogenated and then discharged directly to natural water courses. Humic and Fulvic acids can be part of the organic matter found in natural water courses and, as they typically have higher aromatic carbon content than other natural organic matter in surface waters, they produce greater amounts and concentration of DBPs.

The DBPs of concern can be sub-divided into groups related to the type of compound produced, namely **Trihalomethane** (THM) and **Haloacetic Acid** (HAA).

Trihalomethanes that may be formed are

Chloroform



Bromoform



Bromodichloromethane (BDCM)

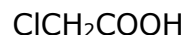


Dibromochloromethane (DBCM)



Haloacetic Acids that may be formed are

Monochloroacetic Acid (MCA)



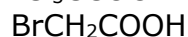
Dichloroacetic Acid (DCA)



Trichloroacetic Acid (TCA)



Monobromoacetic Acid (MBA)

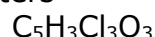


Dibromoacetic Acid (DBA)

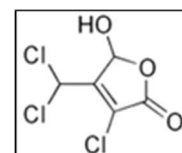


In addition, a Mutagen can be formed in chlorinated waters

Mutagen X (MX)



3-chloro-4-(dichloromethyl)-5-hydroxy-5H-furan-2-one



Although not commonly used, iodine is another halogen that can be used as a biocide or disinfectant, in which case the THMs and HAAs formed as by-products would be organic iodine compounds

Iodoform		CI_3
Monoiodoacetic Acid	(MIA)	ICH_2COOH
Diiodoacetic Acid	(DIA)	I_2CHCOOH
Triiodoacetic Acid	(TIA)	I_3CCOOH

THM, HAA and MX have been linked to cancer, miscarriages, stillbirths and birth defects. The cancer potency of Mutagen X is 170 times greater than that of chloroform¹.

Chloramine may be used as a biocide or disinfectant in which case a possible DPB is

N-nitrosodimethylamine	(NDMA)	$(\text{CH}_3)_2\text{N}_2\text{O}$
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There are also some "emerging" DPDs of concern which include

Halonitromethanes

Haloamides

Halofuranones

Halobenzoquinones

Nitrosamines

Haloacetamides

Haloacetonitriles

Swimming pools have been found to contain Trihalomethanes, mainly chloroform, both in the water and air above swimming pools. Trichloramine (NCl_3) can be formed by the reaction of chlorine with Urea and Uric Acid from urine and perspiration, which gives indoor swimming pools their distinctive odor. Salt water swimming pools tend to generate higher levels of Trihalomethanes, mainly Bromoform, than fresh water pools.

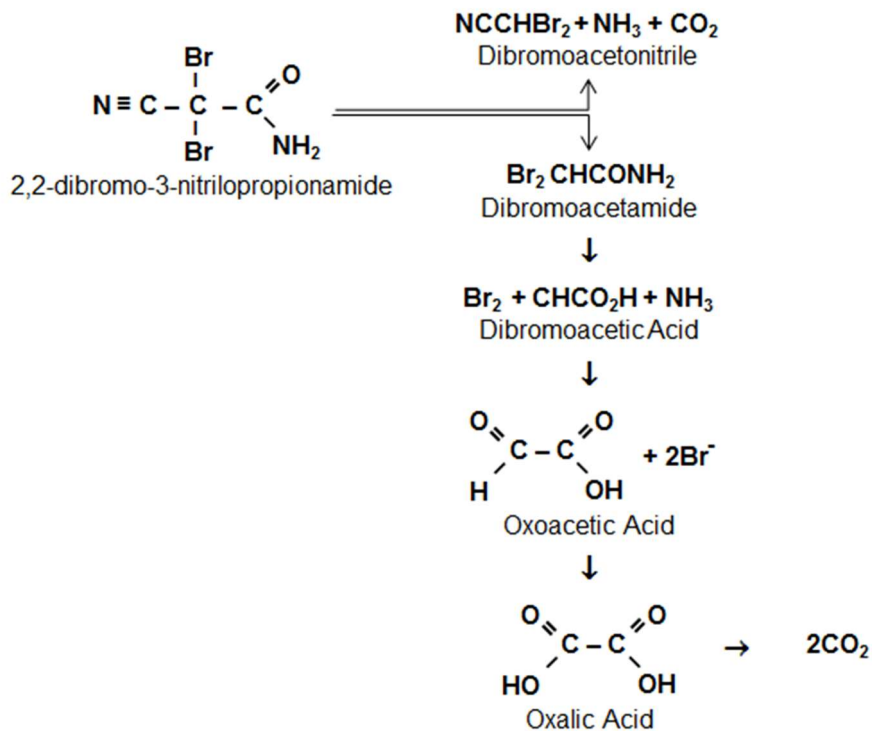
Ozone, used as a biocide or disinfectant, can also form DPBs such as Ketones, Carboxylic Acids, and Aldehydes, including Formaldehyde (HCOOH). Bromide (Br^-) in source waters can be converted into the carcinogen Bromate (BrO_3^-) through reaction with ozone.

¹ Harvard Medical Dental & Public Health School, 25 January 2002

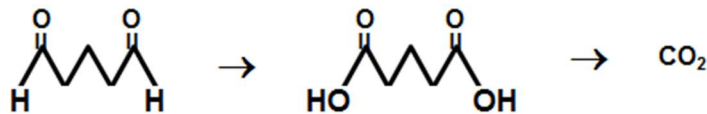
Based on the above concerns, a more precise definition of Disinfection By-Products would be "Chemical compounds formed by the reaction of an oxidizing water disinfectant with an organic precursor in a water supply".

However, other biocides or disinfectants produce by-products, not only caused by chemical reaction but by decomposition or degradation, or, simply by the presence of dissolved biocide or disinfectant in treated water or in effluent from a plant. A few examples are given below.

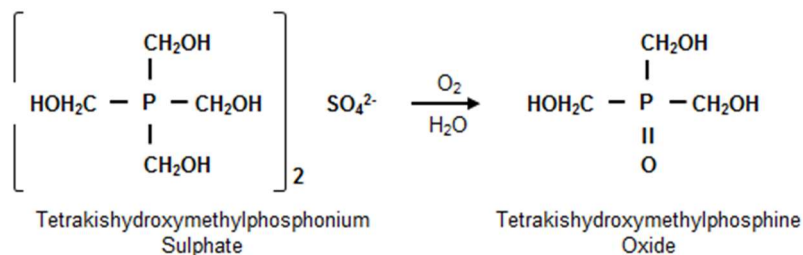
Dibromonitrilopropionamide (DBNPA) eventually hydrolyses to Carbon Dioxide (CO₂).



Glutaraldehyde decomposes to Glutaric Acid and eventually Carbon Dioxide.



Tetrakis(hydroxymethyl)phosphonium Sulphate (THPS) oxidizes to the oxide (THPO).



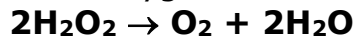
Chlorine Dioxide end products of disinfection and/or degradation are Chlorate and Chlorite compounds.



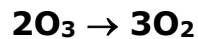
The ratio of Chlorate and Chlorite produced depends upon their concentration in the applied Chlorine Dioxide solution, the concentration of Chlorine Dioxide solution applied, and photolysis or exposure of water containing Chlorine Dioxide to sunlight.

Unlike halogens such as Chlorine and Bromine, Chlorine Dioxide functions as a highly selective oxidant due to its unique one electron transfer mechanism. Chlorine Dioxide attacks the electron rich centers of organic molecules, where it is reduced to chlorite ions². This reaction with organic matter does not result in the formation of THMs or HAAs, and as such Chlorine Dioxide has many Environmental and Health benefits compared to Halogens.

Hydrogen Peroxide degrades to Oxygen and Water.



Ozone degrades to Oxygen.



In some cases, degradation products fall within the same category as by-products formed through reaction of halogen with organic matter, yet no external free halogen has been involved in a reaction, the halogen being inherent in the original organic compound. On the other hand, Ozone degrades to innocuous Oxygen, but in the presence of Bromide can form a carcinogenic Bromate compound.

Regarding Environmental Impact and Risk to Human Health, halogenated organic compounds are a major concern. Not all halogenated compound fall within the category of THM or HAA. Halogenated organic compounds may be formed through reaction between a halogen and an organic compound, or through degradation or inherent composition of an organic compound containing halogen. For instance, Carbon Tetrachloride or Tetrachloromethane, CCl_4 , is a Tetrahalomethane and therefore does not fall under either of the categories Trihalomethane (THM) and Haloacetic Acid (HAA). Yet Carbon Tetrachloride poses a significant health risk.

Collectively, there are series of Halogenated Organic Compounds (HOCs) that can be determined and quantified analytically. The organically bound halogen can be Chlorine, Bromine or Iodine, but not Fluorine, and are reported as a Chloride concentration, such as $\mu\text{g/l Cl}^-$ or mg/l Cl^- for water or liquids, or, as $\mu\text{g/g Cl}^-$ or mg/g Cl^- for solids or sludge.

² Hoehn et al., 1996

Adsorbable Organic Halogen (AOX) is HOC which can be absorbed on activated carbon.

Extractable Organic Halogen (EOX) is HOC which can be extracted in a non-polar solvent.

Purgeable Organic Halogen (POX) is HOC contained in a sample that can be purged in the gas phase under defined conditions with an auxiliary gas.

Of these, AOX is the class of compounds most commonly monitored and analysed.

In water, AOX is a sum parameter describing or quantifying the total organic halogen load. The parameter covers a large group of substances ranging from simple volatile Trihalomethanes to complex organic molecules such as Dioxins and Furans, which have a variety of toxic properties.

Almost all of the persistent organic pollutants, such as Polychlorinated Biphenyls (PCBs), the insecticide Dichlorodiphenyltrichloroethane (DDT), and Dioxins are HOCs. AOX compounds are of concern because they have a long half-life and are resistant to breaking down, and therefore they are very persistent in the Environment.

AOX does not categorize HOCs by structure or composition but by one of their chemical properties, namely they absorb on Activated Carbon under specific conditions and can be detected by Coulometric Titration which subsequently measures all organic halides.

One of the major sources of AOX discharge to the Environment is from the Pulp and Paper Industry, where chlorine is widely used to bleach pulp. Lesser amounts of AOX are formed by routine chlorination of Drinking Water, Swimming Pools, Industrial and Commercial Cooling Water, Industrial Process Waters and Laundries. Another source of AOX is effluent of industries that use Halogen containing organic substances. This sector includes the Chemical Industry, Metal Surface Treatment, Textiles, Waste Treatment, Printing and Dry Cleaning. AOX can be reduced or eliminated by using an alternative oxidizing agent such as Chlorine Dioxide, Ozone, Hydrogen Peroxide or Peracetic Acid.