# DISINFECTANT AND DISINFECTANT BY-PRODUCTS

**Takako Aizawa**
*Chief of Water Supply Engineering, National Institute of Public Health, Tokyo, Japan*

**Mari Asami**
*Senior Researcher of Water Supply Engineering, National Institute of Public Health, Tokyo, Japan*

**Yasumoto Magara**
*Professor of Engineering, Hokkaido University, Sapporo, Japan*

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## Summary

Terminal disinfection of drinking-water supplies is of paramount importance and is almost universal, as it is the final barrier to the transmission of waterborne bacterial and viral diseases. Although chlorine and hypochloride are most often used, water may also be disinfected with chloramines, chlorine dioxide, ozone, and ultraviolet irradiation. Those disinfectants have their own property and administrators should provide an appropriate disinfectant for preserving pathogenic safety while minimizing the level of disinfection by-products, DBPs.

Chlorination is known to generate chlorination by-products in reaction with natural organic matter (NOM) and with bromide, both present in water. Chloroform was considered the by-product generated in the course of reaction between humic substances and chlorine. These chlorination by-products have induced general concerns about health risk. Hundreds of chlorinated organic compounds have been reported in chlorinated water. The most prominent group is the trihalomethanes (THM) which includes chloroform, bromodichloromethane (BDCM), dibromochloromethane and bromoform, which are halogen-substituted single-carbon compounds. Cancer risks have been estimated on the basis of the fact that bromodichloromethane induces kidney tumors in male mice, for example. Bromate, an ozonation by-product, is also considered highly carcinogenic.

It should be noted that the use of chemical disinfectants in water treatment usually results in formation of chemical by-products, some of which are potentially hazardous. However, the risks to health from these by-products at the levels that they occur in drinking water are extremely small in comparison with the risks associated with inadequate disinfection. Thus, it is important that disinfection should not be compromised in attempting to control such by-products. Control strategies and the best available technology approach for control of disinfectants and DBPs in drinking water are introduced.



## 1. Introduction

Terminal disinfection of drinking-water supplies is of paramount importance and is almost universal, as it is the final barrier to the transmission of waterborne bacterial and viral diseases. Although chlorine and hypochloride are most often used, water may also be disinfected with chloramines, chlorine dioxide, ozone, and ultraviolet irradiation.

## 2. Disinfection and Disinfectants

### 2.1. Chlorine

Chlorine, $Cl_2$, is used in the form of gaseous chlorine or hypochloride ($OCl^-$). In water, it is very reactive with other elements and exists in another form shown below.

$$Cl_2 + H_2O \rightarrow HOCl + HCl \qquad (1)$$

$$HOCl \Leftrightarrow OCl^- + H^+ \qquad (2)$$

Hypochlorous acid, HOCl, is a weak acid with a pKa of approximately 7.5 at 25 $^oC$. Hypochlorous acid, the prime-disinfecting agent, is therefore dominant at pH below 7.5 and a more effective disinfectant than hypochloride ion, which dominates above pH 7.5. When chlorine is isolated as a free element, chlorine is a greenish yellow gas, which is 2.5 times heavier than air.

Because it is highly reactive, chlorine is usually found in nature bound with other elements like sodium, potassium, and magnesium and it also reacts with a variety of compounds, in particular those that are considered reducing agents (e.g. hydrogen sulfide, manganese (II), iron (II), sulfite, bromide, iodide and nitrite).

Liquid chlorine is manufactured by electrolysis and refining. Sodium hypochloride is generated with chlorine absorption into caustic soda or on-site electrolysis. Calcium hypochloride is also utilized. Chlorine inactivates bacteria through direct reaction with the cell membrane, by cell component leakage and by damaging enzymes.

Chlorination is simple, easy and cost-effective as a means of disinfection. Chlorine is used not only for disinfection but also for pre-oxidation of ammonia, iron (II), manganese and algal contaminants which multiply in water treatment process. Chlorination is better conducted at low pH, below 7, for sufficient disinfection. Chlorinated water demonstrates odor caused by chlorinated ammonia, chlorinated phenols and other compounds.

After the formation of trihalomethanes and other chlorination by-products was revealed, use of chlorination was reviewed and sequential injection of ammonia and chlorine and appropriate control of their concentration were recommended to reduce formation of chlorination by-products.

Another reaction that occurs in waters containing bromide ion and hypochloride is the production of hypobromous acid, HOBr, which yields brominated organic by-products.

Chlorine is widely used as a disinfectant because of its workability and sustainability in distribution networks and no specific adverse treatment-related effects in humans and animals have been reported. The taste and odor thresholds for chlorine in distilled water are 5 and 2 mg $L^{-1}$, respectively. Most individuals are able to taste chlorine or its by-products (e.g. chloramines) at concentrations below 5 mg $L^{-1}$, and some at levels as low as 0.3 mg $L^{-1}$. A residual chlorine concentration of between 0.6 and 1.0 mg $L^{-1}$ will generally begin to cause problems with acceptability. The taste threshold of 5 mg $L^{-1}$ is a health-based guideline concentration.

## 2.2. Chloramines

Monochloramine ($NH_2Cl$), dichloramine ($NHCl_2$) and trichloramines ($NCl_3$) are formed when ammonia-containing water is chlorinated. Monochloramine is most abundant and causes odor. To utilize chloramine for disinfection, it is necessary to first dissolve free chlorine in water then add ammonia or ammonium sulfate. Chloramine is more persistent in water than chlorine and it is effective for inactivation. Another advantage of chloramination is restriction of disinfection by-products, although the toxic cyanogen chloride may be formed as a by-product of the chloramination of water.

## 2.3. Ozone

Ozone, $O_3$, is a highly oxidative agent, having standard electrode potentials in acidic solution of +2.07V. Ozone is very selective in its chemical reactions, especially with aromatic compounds and reduced organic species such as nitrite and sulfite and low oxidation state metals such as manganese (II), copper (I) and iron (II). In the chain decomposition of ozone in water, the OH radical is yielded as a most significant radical intermediate. In natural water, the OH radical is formed by a complex set of chemical reactions initiated by substances in the water. The OH radical is a very powerful oxidant, as indicated by its standard electrode potential (+2.80V), and it is highly reactive with and oxidizes organic and inorganic compounds. In ozonation of natural water, formation of bromate and aldehydes, which are subsequently oxidized to carboxylic acids, are of concern. Bromate is formed by ozonation of bromide in natural water, and is highly carcinogenic.

Ozone is generated by an *in situ* gas generator with a high voltage electric discharge tube. It is very effective for eliminating odor and color in water. It is also effective for inactivation of spores of *Cryptosporidium* and other pathogenic protozoa. Ozonation has been installed in advanced water treatment processes prior to final disinfection. For elimination of oxidized organic compounds in ozonation, an activated carbon process is often installed following ozonation.

## 2.4. Chlorine Dioxide

Chlorine dioxide, $ClO_2$, is used for drinking water disinfection as well as for its ability to oxidize ions such as manganese (II). The effectiveness of chlorine dioxide as a disinfectant is nearly the same as chlorine and the amount of by-product formed by chlorine dioxide treatment is much less than that formed by chlorination. It has a volatizing nature when temperature is high, but it is persistent in the distribution network especially when temperature is low. Chlorine dioxide is a powerful oxidizing agent that can decompose to chlorite; in the absence of oxidizing substances and in the presence of alkali. It dissolves in water, decomposing with the slow formation of chlorite and chlorate:

$$2ClO_2 + H_2O \rightarrow ClO_2^- + ClO_3^- + 2H^+ \quad (3)$$

Chlorine dioxide is produced with an on-site generator by mixing NaClO, HCl and $NaClO_2$. The most crucial by-product of chlorine dioxide is chlorite ion ($ClO_2^-$), which has been shown to cause methaemoglobinaemia in experimental animals.

## 2.5. UV

Ultraviolet disinfection is effective against active bacteria; irradiation by UV provides extremely quick disinfection (within seconds). UV treatment does not affect the odor, taste, pH and chemical composition of water, and hardly produces harmful by-products. UV disinfection efficiency is not dependent on pH levels in water supplies. Maintenance costs with UV disinfection are very low; for example there is no need to monitor pH and chemical concentration levels. The only maintenance required is the replacement of UV lamps.

Disinfection by UV is applicable only to clear water, since considerable turbidity or dissolved organic carbon will lessen the radiation. Since there is no residual effect of disinfection by UV, it is necessary to remove biodegradable organic carbon and maintain the distribution network.

## 2.6. Advanced Oxidation Process

Combination of these oxidants yields hydroxyl radicals, which have high standard electric potential. Combinations of 'ozone and UV', '$H_2O_2$ and UV', and 'ozone and $H_2O_2$' have been proved to have a sound practical use. The hydroxyl radical is produced by self-decomposition of oxidative disinfectants in chain reaction and is highly reactive with most of the chemicals that exist in water.

## 2.7. Efficiency

The efficacy of any disinfection process depends upon the water being treated beforehand to a high degree of purity, as disinfectants will be neutralized to a greater or lesser extent by organic matter and readily oxidizable compounds in water. Microorganisms that are aggregated or are adsorbed to particulate matter will also be partly protected from disinfection, and there are many instances of disinfection failing to destroy waterborne pathogens and fecal bacteria when the turbidity was greater than 5 nephelometric turbidity units (NTU). It is therefore essential that the treatment processes preceding terminal disinfection are always operated to produce water with a median turbidity not exceeding 1 NTU and not exceeding 5 NTU in any single sample. Values well below these levels can regularly be attained with a properly managed plant.

Normal conditions of chlorination (i.e. a free residual chlorine of $\geq$0.5 mg per liter, at least 30 minutes contact, pH less than 8.0, and water turbidity of less than 1 NTU) can produce more than 99% reductions of *E. coli* and certain viruses, but not of the cysts or oocysts of parasitic protozoa.

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**Biographical Sketches**

**Takako Aizawa** is Chief of Water Quality Management Division at National Institute of Public Health in Japan, where she has been in office since 1971. She has served as Chief of Division since 1988. She received her degree of Bachelor of Education at Yokohama National University in 1968. Since 1971, her research and professional activities have been on micro-pollutant in the water environment, and have included analysis and safety evaluation of micro-pollutants, evaluation of disinfectants and disinfection by-products for water supply, and development of new water treatment technology for micro-pollutant removal. In the meantime, she also obtained a PhD in Engineering from Hokkaido University. At present, she teaches irregular course of post-graduate level on risk management of pesticides in the water environment.

She has authored or co-authored more than 50 research articles and has written books on the water environment.

**Mari Asami** is Senior Researcher of the Water Quality Management Division in the Department of Water Supply Engineering at National Institute of Public Health, where she has been in office since 1993. She obtained a Bachelor Degree of Engineering from Department of Urban Engineering, University of Tokyo, in 1991 and a Master Degree in 1993 from the Graduate School of the same department. At National Institute of Public Health, she mainly works on Risk Assessment and Management of Drinking Water and Analysis of Trace Chemicals in Drinking Water, using GC/MS, IC and LC/MS.

She also works with Peking University, China on cooperative research entitled Risk Minimization of Hazardous Chemicals in Water.

**Yasumoto Magara** is Professor of Engineering at Hokkaido University, where he has been on faculty since 1997. He was admitted to Hokkaido University in 1960 and received the degree of Bachelor of Engineering in Sanitary Engineering in 1964 and Master of Engineering in 1966. After working for the same university for 4 years, he moved to National Institute of Public Health in 1970. He served as the Director of the Institute since 1984 for Department of Sanitary Engineering, then Department of Water Supply Engineering. He also obtained a Ph.D. in Engineering from Hokkaido University in 1979 and was conferred an Honorary Doctoral Degree in Engineering from Chiangmai University in 1994. Since 1964, his research subjects have been in environmental engineering and have included advanced water purification for drinking water, control of hazardous chemicals in drinking water, planning and treatment of domestic waste including human excreta, management of ambient water quality, and mechanisms of biological wastewater treatment system performance. He has also been a member of governmental deliberation councils of several ministries and agencies including Ministry of Health and Welfare, Ministry of Education, Environmental Agency, and National Land Agency. He performs international activities with JICA (Japan International Cooperation Agency) and World Health Organization. As for academic fields, he plays a pivotal role in many associations and societies, and has been Chairman of Japan Society on Water Environment.

Professor Magara has written and edited books on analysis and assessment of drinking water. He has been the author or co-author of more than 100 research articles.