Chapter 2
Disinfection By-Products

2.1 *Disinfection*

Disinfection of drinking water is defined as a treatment process for the purpose of the destruction or inactivation of human pathogens, up to a given level of safety that should be maintained throughout water storage and distribution. The process depends on the type and concentration (or intensity) of the disinfectant, type and concentration of the microorganisms, and the physical and chemical properties of the source water. The disinfection process should balance the ability to kill or inactivate a wide variety of microbial pathogens, maintain a residual and minimize the formation of harmful by-products. Recently, combinations of primary and secondary disinfectants are being used in an attempt to minimize the formation of harmful by-products.

In the 1800's, waterborne diseases such as typhoid, cholera and dysentery occurred regularly in the water systems of Canada, the United States and other developed nations (Wigle, 1998). The introduction of disinfectants into the water systems in the early 1900's led to a dramatic decrease in the number of illnesses and fatalities caused by waterborne diseases. Presently, disinfection mainly with chlorine continues to be the best option to control the outbreak of waterborne diseases and thus is a mandatory water treatment practice in many parts of the world.

There are a variety of disinfection methods utilized worldwide for the treatment of water. Some of the main disinfection techniques are listed in Table 2.1 (Connell,1996).

Table 2.1: Disinfection Techniques

Disinfection Method	**Example**
Physical	Heat; storage
Light	Ultraviolet radiation
Metals	Silver
pH	Acids; alkalis
Oxidants	Chlorine; chlorine dioxide; ozone; iodine; chloramine
Others	Surface active agents

The most commonly used disinfectants are:

- **chlorine**
- **chloramination**
- **chlorine dioxide**
- **ozone**
- **ultraviolet radiation**
- **mixed oxidants**
- **iodine**

The main features of these commonly used disinfectants are listed in Table 2.2.

Throughout North America, **chlorination** is the most widely used method of disinfection. Chlorine is used mainly because:

- it is effective against a broad range of pathogens including bacteria, viruses and protozoa;
- it provides residual protection by preventing microbial growth after the treated water enters the distribution system; and
- the technology associated with chlorine disinfection is simpler than other disinfection technologies and can be utilized in treatment plants of all sizes.

Chlorine can be administered to a water system in both gaseous and liquid forms as listed in Table 2.3.

Table 2.3: Forms of Chlorine Utilized in the Chlorination Process

Chlorine	State
Chlorine Gas	Gas
Sodium hypochlorite	Liquid
Calcium hypochlorite	Solid + Water = Liquid

All forms of chlorine invariably react with the water to form hypochlorous acid which acts as the effective disinfectant. The hypochlorous acid, in turn, dissociates into the hypochlorite ion depending on pH and temperature.

Table 2.2: Comparison of Disinfectants and Applications

Characteristics	Chlorine	Chloramines	Ozone	Mixed Oxidants	UV Light	Iodine
Classification	Primary & Secondary	Secondary	Primary	Primary & Secondary	Primary	Primary & Secondary
Effectiveness						
Bacteria	Very Good (HOCl)	Poor	Excellent	Very Good	Very Good	Very Good
Viruses	Very Good (HOCl)	Poor	Excellent	Very Good	Very Good	Good
Protozoa	Fair	Very Poor	Very Good	Good	Fair	Good
Helminths	Good	No Information	Excellent	Good	No Information	No Information
Water Quality						
pH	Strong Effect	Strong Effect	Little Effect	Moderate Effect	No Effect	Strong Effect
Turbidity	Strong Effect	Strong Effect	Strong Effect	Strong Effect	Strong Effect	Strong Effect
Temperature	Strong Effect	Strong Effect	Strong Effect	Strong Effect	Strong Effect	Strong Effect
Organic Matter	Strong Effect on Chlorine Demand	Little Effect	Ozone Demand	Less affected than chlorine	No Effect	Little Effect
THMs	Can develop with precursors	Not Formed	Little Formation	Less than chlorine	None	Not Formed
Experience	Wide experience	Little	Limited	Limited	Limited	Limited
Cost of Other Disinfectants Relative to Chlorine Gas	1.00	3.4	3.5	0.8-1.5	3.5	6.10

Chlorine + Water → Hypochlorous acid

Hypochlorous acid ⇌ Hydrogen ion + Hypochlorite ion

The **chlorine dosage** is the amount of chlorine added to the water. As was shown above, hypochlorous acid (HOCl) and hypochlorite ion (OCl^-) develop in water treated with chemicals for chlorination. The amount of hypochlorous acid and hypochlorite ion in water is defined as the **free available chlorine**. The **chlorine residual** is the amount of chlorine measured in the water when it is analyzed. When chlorine is added to impure water, chemicals present in the raw water begin to react with or use up the chlorine, exerting a demand for the chlorine. The difference between the chlorine dosage and the chlorine residual that would be expected by analysis is called the **chlorine demand**. Chlorine existing in combined chemical forms with ammonia or organic nitrogen compounds is referred to as **combined available chlorine** or **combined residual chlorine**. When all of the ammonia has been consumed and all of the combined chlorine has been oxidized, the chlorine added becomes equal to the chlorine residual. This chlorine dosage is called the **breakpoint**. Beyond the breakpoint, the chlorine added is in the form of free available chlorine.

The order in which the chlorine will be used up is as follows:

Stage I

The hypochlorous acid will first react with dissolved iron, hydrogen sulphide and other inorganic material. The products that are formed as a part of this reaction have no disinfecting capacity.

Stage II

After reactions with the impurities in Stage I, the next set of reactions will be with reducing compounds and organic material. The products that are formed with these reactions have only a slight capacity to disinfect.

Stage III

After the stage II reactions, the next set of reactions will be with background ammonia levels in the water. The exact reactions depend on the pH of the water. For water supplies with natural ammonia levels, **chloramines** will be formed. The first compound that is formed is called **monochloramine**. As more chlorine (in the form of hypochlorous acid) is added, it combines with some of the monochloramines to form **dichloramines**. The chloramines are called the combined chlorine residual and can provide good disinfection protection.

Stage IV

As more chlorine is added, the chloramines that were formed in stage III are destroyed. After the chloramines are destroyed, any more chlorine added to the water will remain as hypochlorous acid or the hypochlorite ion (*free chlorine residual*).

The chemical products of stage III and IV, will result in a working disinfectant, while products from stages I and II, have no real disinfecting power.

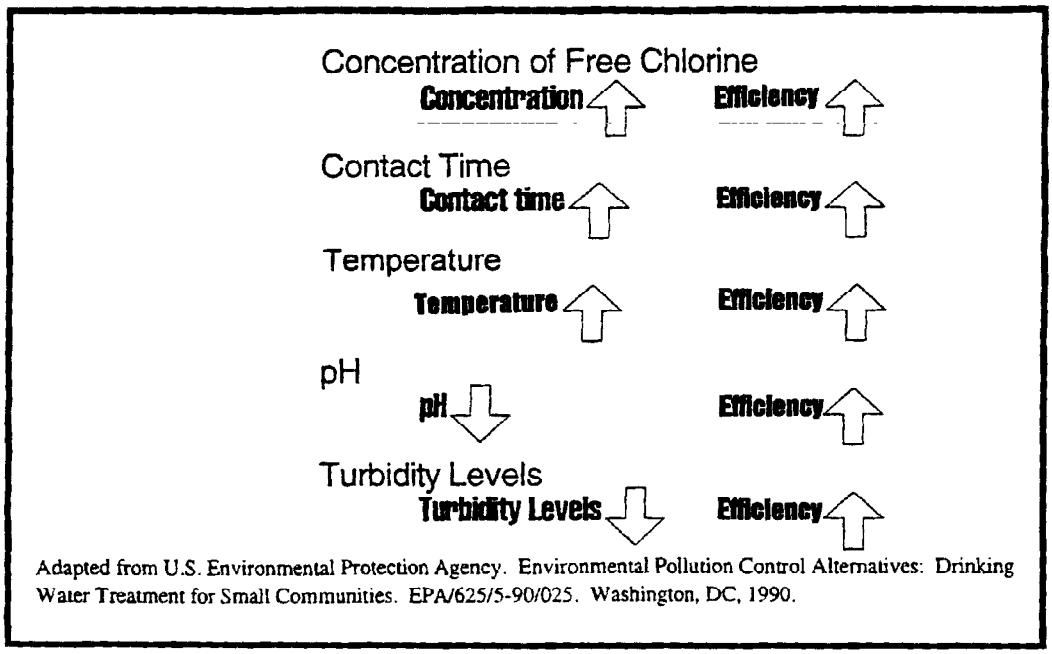
Chlorine does not kill microorganisms on contact; it takes time. In addition to the concentration of free chlorine, the ability to destroy disease-causing microorganisms is determined by the time that the organisms are in contact with the disinfectant. This is called the **CT concept** - ***C*** for the concentration of the disinfectant in mg/L and ***T*** for the contact time expressed in minutes. The concentration and time are multiplied together to get the CT value. A high number for CT (that is a high level of disinfection) can be achieved in two ways: 1) a low dose of disinfectant in contact with water for a long period of time **or** 2) a heavy dose of disinfectant in contact with water for a short period of time.

In addition to contact time and chlorine dose, other factors such as pH and turbidity also play an important role in determining disinfection efficiency. Disinfection is more effective at lower pH. However, pH also influences the corrosive nature of the disinfectant and the potential for formation of disinfection by-products. Turbidity, or the presence of suspended matter in the water being treated, reduces the level of disinfection achieved because it prevents contact of the disinfectant with the microorganism. The influence of these factors on chlorine efficiency is shown in Figure 2.1.

Overall, numerous factors affect the disinfecting power of chlorine. They are summarized as follows:

- **contact time**
- **chlorine or disinfectant dose**
- **chlorine demand**
- **turbidity**
- **water temperature**
- **sunlight**
- **pH**

Many of these factors may be working at the same time, and may be working against each other. It is essential to take each factor into consideration when using chlorination as a method for disinfecting drinking water.



Adapted from U.S. Environmental Protection Agency. Environmental Pollution Control Alternatives: Drinking Water Treatment for Small Communities. EPA/625/5-90/025. Washington, DC, 1990.

Figure 2.1: Factors Affecting Chlorine Efficiency

2.2 *Formation of Disinfection By-Products (DBPs)*

All of the techniques discussed in the previous section, including chlorination, accomplish the essential task of disinfection to varying degrees. However, all chemical disinfectants form various types of **disinfection by-products** (DBPs). The formation of DBPs has been an area of concern to water consumers, water purveyors and regulators because of possible health effects.

The formation of disinfection by-products is a complex process controlled by numerous parameters. In simple terms, disinfection by-products are the result of the chemical reaction between disinfectants used for water treatment and **natural organic matter (NOM)** present in raw drinking water.

Disinfectant + NOM = DBPs

NOM is the complex matrix of organic material present in all natural surface waters (CWRS Workshop Notes, 1995). NOM results from the decomposition of matter from the environment surrounding the watershed such as leaves and aquatic plants. Water quality parameters such as **water colour** and **total organic carbon (TOC)** are considered as a good indicator of the presence of NOM in natural water. TOC is comprised of **dissolved organic carbon (DOC)** and **particulate organic carbon (POC)**, of which DOC makes up approximately 99% of the TOC (CWRS Workshop Notes, 1995). It has been determined that increased levels of water colour and TOC (or DOC) indicate that there is a significant amount of NOM present. The DBPs formation potential is directly related to the levels of NOM in natural water and the quantity of disinfectant used to disinfect the water. However, in addition to the disinfectant and NOM, other parameters such as pH, water temperature, water turbidity, disinfectant dose and contact time also affect the formation of DBPs. Stevens *et al.* (1989) reported that pH, in particular, was an extremely important chemical variable in DBP formation. Overall, there are numerous factors that must be taken into consideration in dealing with the issue of DBP formation and control.

There are a variety of DBPs (e.g., trihalomethanes, haloacetic acids, halocetonitriles, etc.) formed from all methods of disinfection by both halogen substitution and/or oxidation reactions (Singer, 1999). The DBPs result from the most common methods of disinfection including chlorination, chloramination, ozonation and disinfection with chlorine gas (Singer, 1999). Among all of these DBPs, trihalomethanes have been the most controversial issue of research and debate. THMs are the one set of DBPs with a significant amount of available information.

In the early 1970's, Rook (1974) and Bellar *et al.* (1974) discovered that the reaction of chlorine with dissolved organic materials in water formed a class of chlorination disinfection by-products (CDBPs) called **trihalomethanes (THMs)** (Connell, 1996). THMs are defined as halogen-substituted single carbon compounds with the general chemical formula CHX_3, where X is normally

chlorine or bromine or some combination of the two (CWRS Workshop Notes, 1995). THMs appear in the following four forms:

- **chloroform**
- **dibromochloromethane**
- **bromodichloromethane**
- **bromoform**

The chemical structure of each of these four forms of THMs is shown in Figure 2.2. Among the four THMs, chloroform is the most common and detected in the greatest concentrations.

Trihalomethanes are the most common CDBPs in chlorinated drinking water (Singer, 1999). THMs are considered to be an indicator of the possible presence of other CDBPs. They are known to be carcinogenic in laboratory animals and are probably carcinogenic to humans (Health Canada, 1996). Thus, public concern about THMs in drinking water has increased dramatically throughout the past decade. This report will deal with the issue of THMs in drinking water due to widespread use of chlorine as a disinfectant throughout Newfoundland and Labrador, and presence of high levels of NOM in our natural waters.

2.3 *Chlorinated By-products and Health Effects*

Toxicology (the study of the harmful effects of chemicals on living organisms) and epidemiology (a branch of medical science that deals with the incidence, distribution, and control of disease in a population) are the two key factors to assess the health risks associated with the consumption of disinfected drinking water.

2.3.1 *Toxicology Studies*

A number of animal studies have been performed to determine the carcinogenicity of a variety of chlorinated by-products. For example, it was found that chloroform induced significant increases in kidney tumours in male rats when administered in high doses in drinking water (Jorgenson *et al.*, 1985). Chloroform also produced kidney tumours in male rats and liver tumours in male and female mice when administered by gavage in corn oil (National Cancer Institute, 1976). Other THMs, including dibromochloromethane, bromodichloromethane and bromoform also caused various cancers (colon, kidney and liver) in both mice and rats (Mills *et al.*, 1998).

Mills *et al.* (1998) indicate that no single chlorinated by-product studied in toxicologic studies appears to be carcinogenic at human levels of exposure.

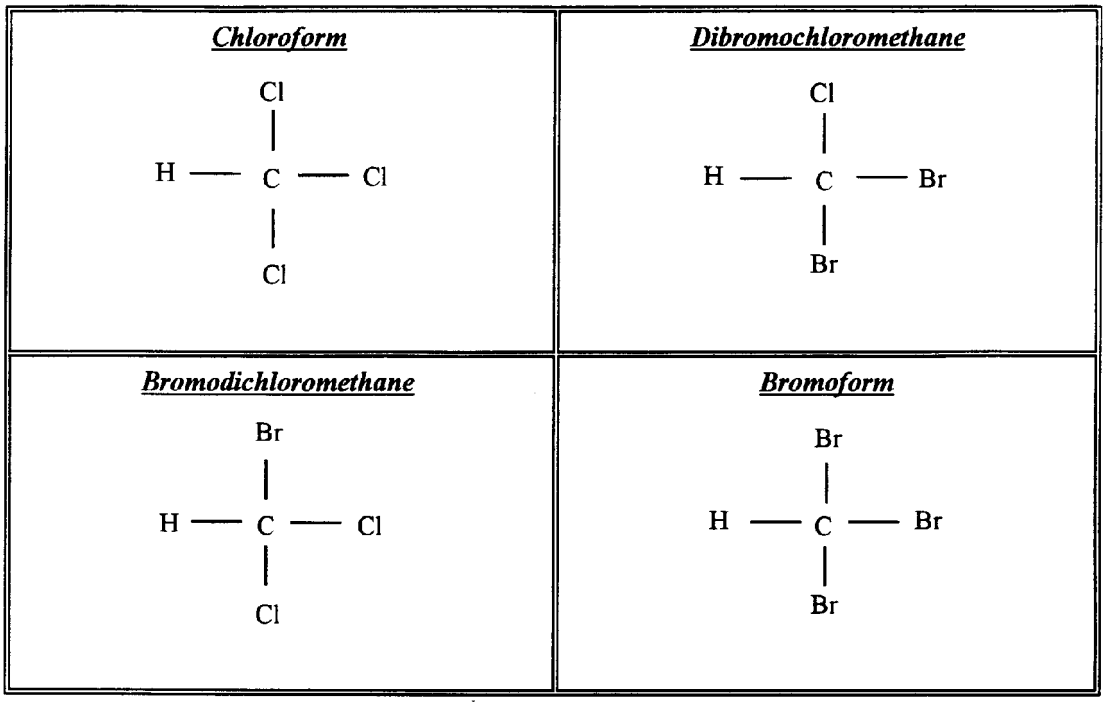


Figure 2.2: The Chemical Structure of each of the four forms of THMs

Most toxicology studies involving chlorination by-products focus mainly on carcinogenicity. However, recently there have been some animal studies focusing on developmental and reproductive health effects, with the most consistent developmental finding being soft tissue abnormalities in rats (Mills *et al.*, 1998).

The health risks associated with chlorinated drinking water cannot be ascertained solely by considering the toxicologic hazards found in animal studies. It still remains questionable whether it is appropriate to extrapolate findings from animal studies to humans. Toxicology findings should complement epidemiology findings when assessing the risk.

2.3.2 *Epidemiology Studies*

Throughout the past 20 years numerous epidemiology studies have examined possible associations between cancer and chlorinated by-products. The three cancers most frequently associated with chlorinated water are colon, rectal and bladder cancers.

A review of cancer epidemiology by an expert working group concluded that the evidence for increased risk of colon and rectal cancer from exposure to chlorinated by-products remains inconclusive (Mills *et al*, 1998). However, the evidence linking exposure to chlorination by-products and bladder cancer is much more consistent (Mills *et al.*, 1998). Essentially, there were five epidemiology studies that showed a significant positive association of risk of bladder cancer with chlorination by-products exposure (Mills *et al.*, 1998). It was estimated by King and Marrett (1996) that 14-16% of bladder cancers in Ontario may be attributed to chlorinated water. Mills, *et al*. (1998) state that "our understanding of this phenomenon however, remains limited by the fact that all studies relied on retrospective estimates".

Epidemiology studies have also been performed on the reproductive and developmental effects associated with the consumption of chlorinated drinking water. A number of studies indicate that chlorinated water is associated with health effects such as spontaneous abortion, low birth weight and birth defects (Mills *et al.*, 1998). A recent study by Waller *et al.* (1998) evaluated THM levels in tap water with pregnancy outcome. The authors concluded that there is an association between consumption of large amounts of tap water containing high levels of THMs and early-term miscarriage (Waller *et al.*, 1998). It is important to note that epidemiologic research concerning reproductive and developmental effects is still at an early stage. There is inadequate information to determine a cause/effect relationship, however, the evidence does suggest a weak association between chlorination by-products and adverse fetal growth and a moderate association with congenital malformations (Mills *et al.*, 1998).

It is important to reiterate that limits remain within epidemiology studies and thus both toxicology and epidemiology studies must complement one another when evaluating risk assessment.

Upon examination of all available toxicologic and epidemiologic evidence, an expert working group sponsored by Health Canada determined that on a site-specific basis, it was possible (60% of the group) to probable (40% of the group) that CDBPs pose a significant risk to the development of cancer, particularly bladder cancer (Mills *et al.*, 1998). On the issue of reproductive and developmental effects there was insufficient evidence to establish a causal relationship (Mills *et al.*, 1998).

Overall, it is evident from the research that there are potential health risks associated with chlorinated drinking water. Thus, both toxicologic and epidemiologic research must continue in order to warrant more in-depth evaluation and to improve the confidence in risk management decisions.

2.4 *Balancing Act*

In understanding the issue of THMs in drinking water, it is essential to balance the human health risks associated with the consumption of drinking water with high levels of THMs with the significant amount of risk associated with improper disinfection (CWRS Workshop Notes, 1995). Health Canada has recognized that the use of disinfectants has almost eliminated the threat of waterborne microbial diseases and saved millions of lives since the turn of the century (CWRS Workshop Notes, 1995). **Thus, it is known that the health risks from pathogenic microorganisms far exceed those potential health problems associated with THM production during water treatment (Health Canada, 1995).** However, the challenge must be to minimize the potential risks from CDBPs, including THMs, without compromising disinfection efficiency (Health Canada, 1995). A site-specific chlorine demand management survey and the development of seasonal guidelines for chlorine dose for various types of raw water would be the most appropriate step in this area.

2.5 *THM Guidelines*

Following the initial reports suggesting adverse health effects associated with THMs in drinking water, public concern increased dramatically thus, prompting regulatory bodies to define and implement THM guidelines for drinking water.

In Canada, drinking water guidelines are developed under the auspices of the Federal-Provincial Subcommittee on Drinking Water (DWS). “The Guidelines for Canadian Drinking Water Quality” identifies substances that have been found in drinking water and are known or suspected to be harmful. For each of these contaminants such as THMs, the guidelines establish the maximum acceptable concentration of the substance that can be permitted in water used for drinking or domestic purposes. The sixth edition of these guidelines is currently available

The Subcommittee itself is made up of representatives of provincial and territorial governments and a member from Health Canada acts as scientific advisors to the Subcommittee. The guidelines are used by all provinces and territories to develop their own measures of drinking water quality.

The original THM guideline in Canada was a Maximum Acceptable Concentration (MAC) of 350 g/L established in 1978. This being a one-time maximum value not to be exceeded (Holme & Bonk, 1993). Presently, the current acceptable level of THMs in Canada is **100 g/L** (micrograms per litre) or **100 ppb** (parts per billion) (Mills *et al.*, 1998). It is an interim guideline which is based on an annual running average of quarterly samples to account for seasonal variationt. This guideline of 100 g/L was established in 1993 by the DWS based on the risk of cancer reported in animal studies of chloroform (Health Canada, 1999). The development of 100 g/L THM guideline is based on the estimated lifetime cancer risk. It assumes that if an adult of 70kg consumes an average of 1.5 L of water with chloroform levels exceeding 100 g/L per day over a 70 year life span, they will have a 3.64 in 1,000,000 chance of developing cancer. This value of 3.64×10^{-6} is within a range that is considered to be "essentially negligible". The guideline is designated as interim until such time as the risks from other DBPs are ascertained. The guideline is intended to be both practical and protective of health (Holme & Bonk, 1993). The details of the development of "The Guidelines for Canadian Drinking Water Quality" are outlined in Appendix A (pg. 14-37).

Since that time, numerous strong scientifically-based epidemiologic studies have emerged with updated information thus, leading the DWS to re-visit the THM guidelines. In 1998, DWS reopened a review of the guidelines. In July 1998, Health Canada established a multi-stakeholder Chlorination Disinfection By-Products (CDBP)Task Group to oversee a comprehensive update of health risk information on THMs and to develop recommendations for controlling the risks (Health Canada, 1999). As part of the Task Group mandate, Health Canada has established a Health Effects Subgroup, an Economics Issues Subgroup and a Water Quality Subgroup under the CDBP Task Group. These subgroups are evaluating the epidemiologic and toxicologic evidence of health effects from chlorination disinfection by-products, drinking water quality data and water treatment facility characteristics for communities across Canada. This report, along with numerous others, will be submitted to the CDBP Task Group during 2000. Based on these reports, the CDBP Task Group will formulate recommendations to the Federal-Provincial DWS for managing health risks from chlorination disinfection by-products. Depending on the scientific findings and recommendations, the DWS may decide to revise the THM guidelines, if necessary. Additional information on the CDBP Task Group is included in Appendix A (pg. 38-46).

Presently, the work of numerous Federal and Provincial organizations is ongoing to minimize the potential risks associated with THMs in drinking water while maintaining adequate disinfection against microbial contamination.