



CHAPTER II

THEORY AND LITERATURE REVIEW

Chlorination

Chlorination of water supplies on an emergency basis has been practiced since about 1850. With definite evidence at hand that certain diseases were transmitted by water, emergency treatments with hypochlorites become quite common during periods of epidemics.

It was not until 1904 that continuous chlorinating of public water supply was attempted in England. Shortly thereafter, in 1908, George A. Johnson initiated treatment with calcium hypochlorite of the water at the Bubbly Creek filter plant of the Union Stock Yards in Chicago. In 1909, Jersey City, New Jersey, started hypochlorite treatment of its Boonton supply. This was the first attempt to chlorinate a public water supply in the best interests of public health. From that day, chlorinating for disinfection of public water supplies has spread so that today it is almost routine practice (Sawyer and McCarley, 1985)

Chlorination is the most widely used method for disinfecting drinking water and other type of water, such as swimming pool and treatment plant effluent. It is easy to apply, measure and control and it is relatively inexpensive. In the 1970's, it was discovered that chlorine reacted with naturally occurring organic constituents to yield small quantities of chlorinated by-products such as trihalomethane (mainly chloroform) for which regulations were subsequently developed.

1. Alternate Forms of Chlorine

For purpose of disinfection of water, chlorine is primarily used in the form of either as a gaseous element or as a solid or liquid chlorine-containing hypochlorite compound. As shown in Table 2.1, there are many forms of chlorine compounds. The

appropriate compounds used depend on several factors such as site of the system, location of the treatment facility, safety consideration and requirement for chlorine residual in the distribution system.

Table 2.1 Percent available chlorine of various chlorine materials.

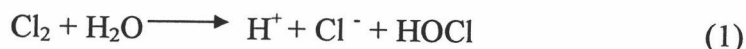
Material	Available chlorine(%)
Cl ₂ , Chlorine	100(by definition)
Bleaching Powder (chloride of lime, etc.)	35-37
Ca(OCl) ₂ , Calcium Hypochlorite	99.2
Commercial Preparations	70-74
NaOCl, Sodium Hypochlorite (unstable)	95.2
Commercial Bleach (industrial)	12-15
Commercial Bleach (household)	3-5
ClO ₂ , Chlorine Dioxide	263.0
NH ₂ Cl, Monochloramine	137.9
NHCl ₂ , Dichloramine	165.0
NCl ₃ , Nitrogen Trichloride	176.7
HOCC ₆ H ₄ SO ₂ NCl ₂ (Halozone)	52.4
NC(=O)NC(=O)NC(=O)CO, Trichloroisocyanuric Acid	91.5
NC(=O)NC(=O)NC(=O)NH ₂ , Dichloroisocyanuric Acid	71.7
NC(=O)NC(=O)NC(=O)Na, Sodium Dichloroisocyanurate	64.5

Source : Handbook of Public water Systems, 1986.

Gaseous chlorine is used for large volumes of municipal and industrial waters. Small-scale facilities frequently apply calcium and sodium hypochlorite (Culp *et al.*, 1986)

2. Chemistry of Chlorination

When chlorine is added to water, it rapidly hydrolyzes according to the following reaction.



Hypochlorite chlorine forms also ionize in water and yield hypochlorite ions which establish equilibrium with hydrogen ion ;



2.1. Chemistry of Hypochlorous Acid

The most important reaction in the chlorination of an aqueous solution is the formation of hypochlorous acid. This species of chlorine is the most germicidal of all chlorine compounds with the possible exception of chlorine dioxide.

Hypochlorous acid, HOCl, is a weak acid which means it tends to undergo partial dissociate as follows :



to produce a hydrogen ion and a hypochlorite ion. In waters of pH between 6.5 and 8.5 the reaction is incompleted and both species are present to some degree. The extent of this reaction can be calculated from the equation

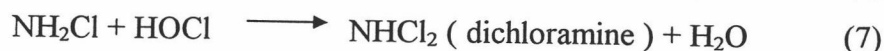
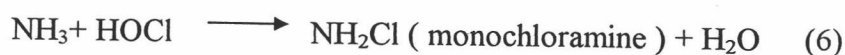
$$K_i = \frac{(\text{H}^+)(\text{OCl}^-)}{(\text{HOCl})} \quad (5)$$

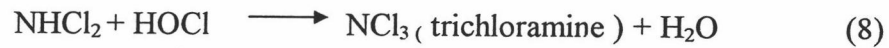
K_i , the ionization constant, varies in magnitude with temperature. (White, 1992)

The two chemical species formed by chlorine in water, HOCl and OCl⁻, are known as free available chlorine.

2.2 Reaction with Ammonia

In aqueous systems, chlorine reacts with ammonia (NH₃) to form the chloramine.





These chloramines have many different properties from those of the HOCl and OCl⁻ forms of chlorine. They exist in various proportions, depending on the relative rates of formation of monochloramine and dichloramine, which change with the relative concentrations of chlorine and ammonia as well as with pH and temperature. Above about pH 9, monochloramines exist almost exclusively; at about pH 6.5, monochloramines and dichloramines coexist in approximately equal amounts; between pH 6.5 and pH 4.5, dichloramines predominate; while trichloramines exist below pH 4.5.

The point where all ammonia is converted to trichloramine or oxidized to free nitrogen is referred to as the breakpoint. Chlorination below this level is combined available residual chlorination; that above this level is free available residual chlorination. Figure 2.1 shows a graphical illustration of the breakpoint reaction. The breakpoint curve results from the reaction shown on equation (6), (7), and (8). (Culp *et al.*, 1986)

3. Chlorination Byproducts

Chlorination byproducts have been much thoroughly studied. Many of the chemical that have been clearly identified as byproducts of chlorination and provide some indication of the concentrations that have been encountered in drinking water. In terms of the concentrations found in a chlorinated water, the trihalomethane (THM) is the most important group of byproducts.

Trihalomethane are formed by the reaction of free chlorine with certain naturally occurring organic compounds. The generalized formular for the reaction is:



The rate of THM formation and the concentration are influenced by a number of factors. Among the more important ones are :

- * Temperature : Higher water temperature increases the rate of THM formation.

- * pH : pH increase, the rate of THM formation increases.

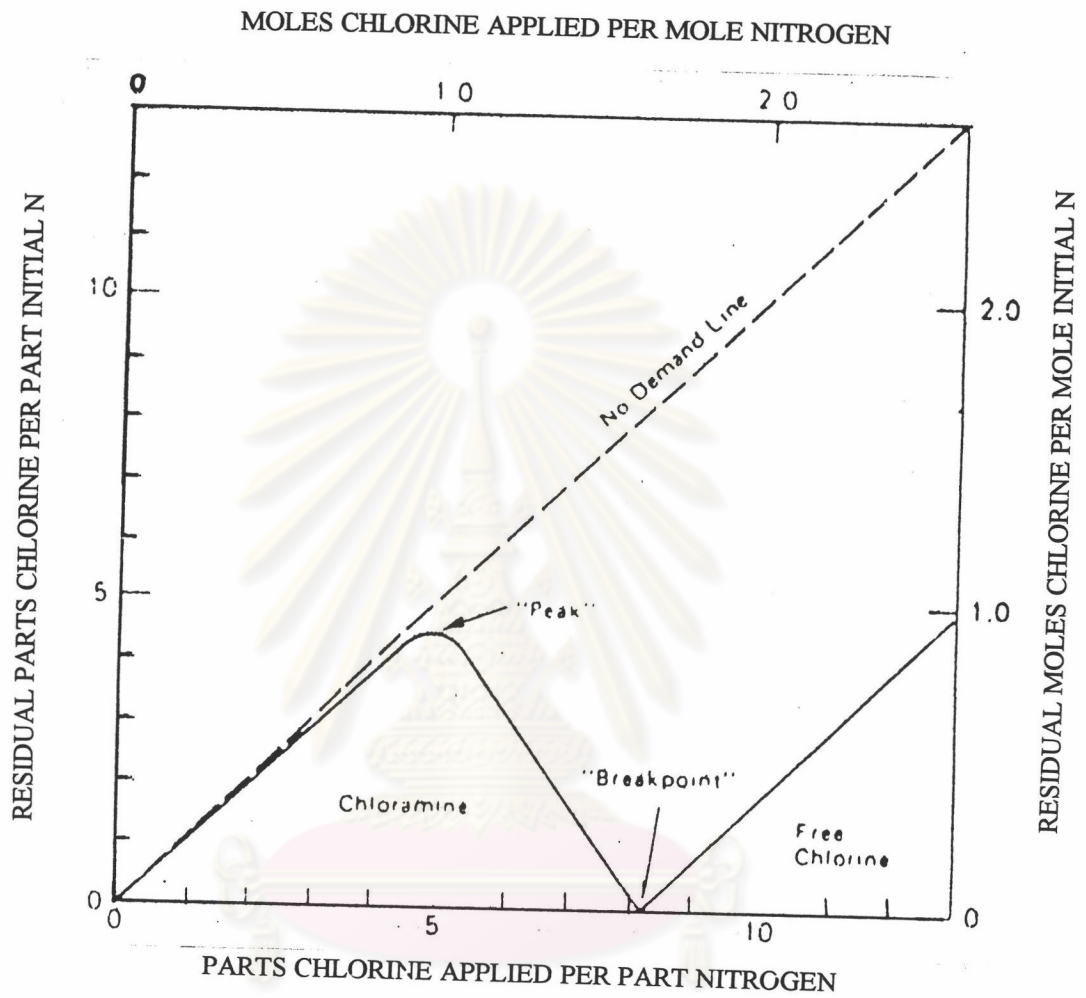


Figure 2.1 Diagrammatic representation of completed breakpoint reaction
(Culp, 1986)

* Organic precursors : The type and concentration of organic precursors influence the reaction rate of THM formation.

* Free chlorine concentration

* Bromide concentration

Beside of THM, volatile organic compounds are increasing being detected in drinking water source (Culp *et al.*, 1986). Many compounds which have been detected in drinking water, are recommended by EPA and WHO such as trichloroethylene, 1,1,1-trichloroethylene, carbon tetrachloride etc. The pattern of the haloform reaction is shown in Figure 2.2.

Chemistry of some Halogenated Hydrocarbons

1. Methylene chloride

Chemical Formular : CH_2Cl_2

Description : CH_2Cl_2 , methylene chloride, is a nonflammable, colorless liquid with a pleasant aromatic odor noticeable at 300 ppm. (This, however, should not be relied upon as an adequate warning of unsafe concentrations.) It boils at 40°C .

Synonyms: DCM, methane dichloride, methylenum chlratum, dichloromethane, methylene dichloride, methylene bichloride.

Uses and Sources of Exposure : Methylene chloride is widely used as a solvent, as a degreasing and cleaning reagent, in paint removers, and in extractions of organic compounds from water for analysis.

Few reports contained data concerning the occurrence of methylene chloride in natural waters. In a survey in the USA, 8 % of finished-water supplies tested contained methylene chloride, but only 1% of the raw water supplies. Water from a sewage treatment plant contained a methylene chloride concentration of $8.2 \mu\text{g/litre}$ before treatment, $2.9 \mu\text{g/litre}$ after treatment but before chlorination, and $3.4 \mu\text{g/litre}$ after chlorination. These results show that methylene chloride is formed during the chlorination of water. Concentration of $1\text{-}2 \mu\text{g/litre}$ and $5 \mu\text{g/litre}$ were reported at the same point in the River Rhine (Environmental Health Criteria 32, 1984).

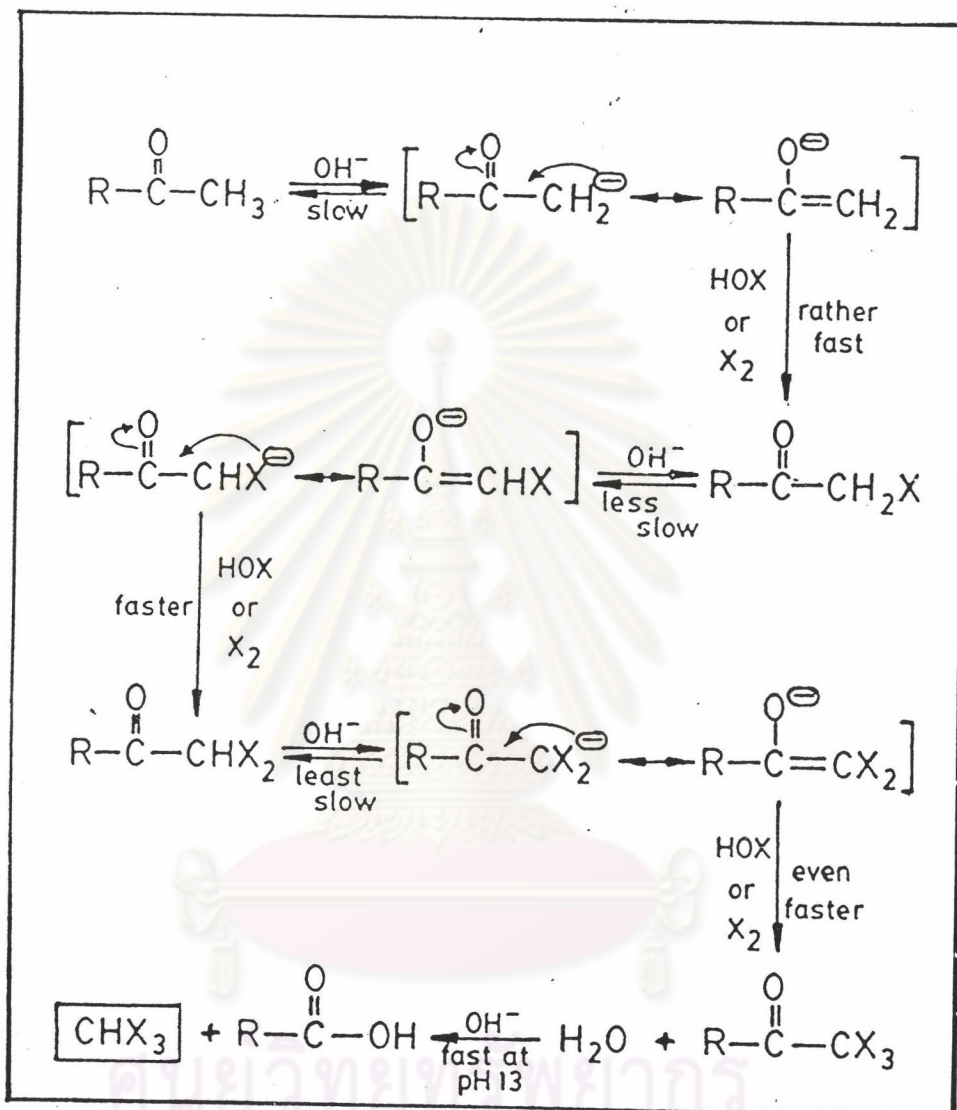


Figure 2.2 Detailed reaction mechanism for the haloform reaction

Physical properties : Colorless liquid; density 1.3255 at 20° C; boils at 39.7 ° C; freezes at -95° C; slightly soluble in water(1.3%), miscible with organic solvents; vapor pressure 350 torr at 20° C.

Health Hazard : Methylene chloride is a low to moderately toxic compound, toxicity varying with the animals species. It is less toxic in small animals than in humans. The toxic routes of exposure are inhalation of its vapors, ingestion, and absorption through the skin.

Limits in Drinking Water

USA (EPA) recommendation : not exceed 5 µg/litre

2. Chloroform

Chemical Formular : CHCl_3

Description : CHCl_3 , chloroform, is a clear, colorless liquid with a characteristic odor. Though nonflammable, Chloroform decomposes to form hydrochloric acid, phosgene, and chlorine upon contact with a flame.

Synonyms : trichloromethane, methenyl trichloride, methane trichloride, trichloroform, methyl trichloride

Uses and Sources of exposure : Information on the natural occurrence of chloroform has not been identified. Most of chloroform occurrence is from anthropogenic source. Direct production of chloroform was prepared by the action of alkali on chloral (Liebig, quoted in Environmental Health Criteria 163, 1994) and by treating bleaching powder with ethanol or acetone.

There are many sources of indirect production of chloroform. In particular the reaction of chlorine with organic compounds may produces substantial quantities of chloroform. The following sources are known to contribute to the formation and emission of chloroform:

- Paper bleaching with chlorine
- Chlorination of drinking water
- Chlorination of swimming pool water

- Chlorination of cooling water: The quantity of chloroform formed depends on a vast range of factors, such as acidity and the concentration of organic materials.

- Chlorination of waste water

- Exhaust emission from traffic

- Decomposition of 1,1,1-trichloroethane has also been suggested as a source.

Physical Properties : Colorless liquid with a pleasant sweet odor; sweet taste; volatile, vapor pressure 158 torr at 20° C; density 1.484 at 20 °C; boils at 61.2 °C; solidifies at -63.5°C; slightly soluble in water (0.82 mL/100 mL water at 20°C), miscible with organic solvents; sensitive to light.

Health Hazard : The inhalation toxicity of chloroform in animals and humans is low. It is moderately toxic by ingestion. Toxic symptoms include dizziness, lightheadedness, dullness, hallucination, nausea, headache, fatigue, and anesthesia.

Chloroform produced embryo toxicity in experimental animals, causing a high incidence of fetal resorption and retarded fetal growth. Animal experiments indicate this compound to be carcinogenic, causing cancers in the kidney, liver and thyroid. It is a suspected human carcinogen for which there is limited evidence. But there have been reports about the evaluation of the relationship between chlorinated water and the incidence of cancer.

Kramer *et al.* (1992) studied the association between exposure to trihalomethanes in the water supply and adverse reproductive outcomes in the state of IOWA (USA). Estimations of chloroform exposure were based on municipal water surveys. After adjustment for maternal age, parity, prenatal care, marital status, education and maternal smoking, an increase risk for intrauterine growth retardation (abnormally low birth weight) was associated with chloroform concentrations above 10 µg/litre. Limitations of the study involve the ascertainment and classification of exposure to trihalomethanes (such as fluctuation of levels and exposure at individual level) and the influence of potential confounding influences of unmeasured contaminants.

Morris *et al.* (1992) conducted a meta-analysis which attempted to integrate quantitatively the results of previously published studies in which individual exposures were evaluated (i.e. case control and cohort studies). They identified increased rates of bladder and colo-rectal cancer in individuals exposed to chlorinated surface water, which appeared to exhibit a dose-related trend. Although this study was confound by substantial differences in exposure variables that occurred in difference water supplies, higher risk rates were estimated when the analysis was restricted to those studied which were judged to have the highest quality exposure assessments. Because of the results confound by chlorine residual levels and multiplicity of other chemicals which are carcinogenic and mutagenic to animals, none of the drinking-water studies specifically implicates chloroform as a human carcinogen.

Limit in Drinking Water

WHO recommendation : not exceed 30 µg/litre

USA(EPA) recommendation : not exceed 5.7 µg/litre (Marshell, 1994)

3. 1,1,1-trichloroethane

Molecular formular : CH_3CCl_3

Description : CH_3CCl_3 , 1,1,1-trichloroethane, is a colorless, nonflammable liquid with an odor similar to chloroform. It boils at 74 °C.

Synonyms : Methyl chloroform

Uses and Sources of Exposure : 1,1,1- trichloroethane is used as a cleaning solvent for cleaning metals and plastic molds.

Physical Properties : Colorless liquid with a mild chloroform-like odor ; density 1.338 at 20° C : boils at 74° C ; melting point -32.5 °C; very slightly soluble in water (0.07%), soluble in organic solvents : vapor pressure 100 torr at 20 °C.

Health Hazard :The oral and inhalation toxicity of 1,1,1-trichloroethane is of low order in animals and humans. Exposure to its vapors at 1.5 % concentration in air may be lethal to humans. Prolonged skin contact may cause defatting and reddening of eyes.



Limit in drinking water

USA(EPA) recommendation :not exceed 200µg/litre

4. Carbon tetrachloride

Molecular formular : CCl_4

Description : CCl_4 , carbon tetrachloride, is a colorless, nonflammable liquid with a characteristic odor, Oxidative decomposition by flame causes phosgene and hydrogen chloride to form.

Synonyms : tetrachloromethane, perchloromethane.

Uses and Sources of Exposure : Carbon tetrachloride is used as a solvent in fire extinguishers, in dry cleaning, and in the manufacture of fluorocarbon propellents.

Physical Properties : Colorless, heavy liquid with characteristic odor; density 1.589 at 25 °C ; boiling point 76.7° C : melting point -23 °C ; insoluble in water (0.05 mL dissolves in 100 mL of water). miscible with organic solvents ; vapor pressure 89.5 torr at 20° C.

Health Hazard : Exposure to high concentrations of carbon tetrachloride results in depression of the control nervous system(CNS). If the concentration is not high enough to lead to rapid loss of consciousness, other indication of CNS effects such as dizziness, vertigo, headach, depression, mental confusion, and incoordination are observed. The International Agency for Research on Cancer (IARC) reviewed the available carcinogenicity data in 1972 and again in 1979. Carbon tetrachloride is grouped with 18 chemicals considered “probably carcinogenic for humans”.

Limit in Drinking Water

WHO recommendation : not exceed 3 µg/litre

USA(EPA) recommendation : not exceed .0.25 µg/litre

5. Trichloroethylene

Molecular Formular : $\text{ClCH}=\text{CCl}_2$

Description : $\text{ClCH}=\text{CCl}_2$, trichloroethylene, a colorless, nonflammable, non corrosive liquid has the “sweet” odor characteristic of some chlorinated hydrocarbons. It boils at 86°C to 87°C .

Synonyms : Ethylene trichloride, ethinyl trichloride, trichloroethene, TRI, TCE

Uses and Sources of Exposure : A major use of trichloroethylene is in metal degreasing, other significant uses are in textile cleaning, solvent extraction processes, and a carrier solvent. It is in limited use as a surgical anesthetic.

Physical Properties : Colorless liquid with a chloroform-like odor ; density 1.465 at 20°C ; boils at 87°C ; solidifies at -85°C ; very slightly soluble in water ; (0.1%), miscible with organic solvents ; vapor pressure 58 torr at 20°C .

Health Hazard : The toxic effects manifested in humans from inhaling trichloroethylene vapors are headache, dizziness, drowsiness, fatigue, and visual disturbances. Trichloroethylene exhibited evidence of carcinogenicity in laboratory animals. Oral administration produced liver tumors, while inhalation caused lung and blood tumors in mice and rats.

Limit in Drinking Water

WHO recommendation : not exceed $30\ \mu\text{g}/\text{litre}$

USA(EPA) recommendation : not exceed $2.7\ \mu\text{g}/\text{litre}$ (Marshall, 1994)

Disinfection in Swimming Pool

There are many kinds of chemical used as disinfectant such as bromine, chlorine, iodine and ozone. The most widely used is chlorine because it is effective, widely available, reasonably inexpensive, easy to use and has good staying power. Chlorination in swimming pool is not only used to against the diseases that may be abound in a swimming pool, but also against algae and undesirable element. Chlorine is the most often used in the following forms:

1. Calcium hypochlorite is available as a granular powder and in tablet form. Containing 70 percent available chlorine, it is a potent enemy of bacteria and algae if the pH of the pool is between 7.2 and 7.6 and it is economical in use.
2. Sodium hypochlorite is a colorless clear solution. The commercial product is available in various strengths, the most common being 5, 10, 15 percent available chlorine.
3. Lithium hypochlorite is a granular material with 35 percent available chlorine.
4. Chlorinated iso-cyanurates are concentrated organic chemicals (as opposed to the above inorganic materials) which disinfect pool water and simultaneously protect the chlorine from destruction by the sun. They are long lasting(residuals do not dissipate quickly) and need not be added to the pool so often as hypochlorites. (Schuler,1974.).The most widely used form of iso-cyanurate is trichloroisocyanuric acid containing 90 percent available chlorine.
5. Chlorine gas is supplied in various size steel cylinders as a liquid under pressure (Swimming pool annual, 1964).
6. Calcium hypochlorite is in powder or tablet form with 70% available chlorine.

Literature Review

Beech *et al.* (1980) studied water from swimming pools in the Miami area. Samples were analysed for nitrates, chlorates and trihalomethanes. The average concentrations of nitrate and chlorate found in freshwater pools were 8.6 mg/liter and 16 mg/liter respectively, with the highest concentrations being 54.9 mg/liter and 124 mg/liter respectively. The average concentration of total trihalomethanes found in freshwater pools was 125 µg/liter (mainly chloroform) and in saline pools was 657 µg/liter (mainly bromoform); the highest concentration was 430 µg/liter in freshwater and 1287 µg/liter in saltwater. The possible public health significance of these results is briefly discussed.

Lahl *et al.* (1981) studied the chlorination practice of swimming pool waters. The subjects were 8 swimming pools in Bremen-a city in the north of West Germany. This study estimated the risk for a pool visitor and discuss alternative methods to the observed chlorination practice. The study showed that the mean concentration of chloroform in different swimming pool waters at various time and locations is between 88-407 $\mu\text{g/l}$. Mean concentration of CHCl_3 and CHCl_2Br in the air of 8 covered swimming pools are between 36-241 $\mu\text{g/l}$ and 0.2-22 $\mu\text{g/l}$ respectively. The study concluded that the application of chlorine for disinfection should be minimized

Chambon *et al.*(1983) evaluated haloforms occurrence in various water samples in Rhone-Alps region. The study found drinking water contained very low levels of haloforms. Whereas surface water and water at the outlet of wastewater treatment plants had significantly higher haloforms levels, both around 6 times more than drinking water. As for swimming pools, where high levels of haloforms were found. The study found that chloroform levels in 42 samples tested were 83-665 $\mu\text{g/L}$ (mean = 271 $\mu\text{g/L}$). It can be postulated that haloforms originate from human biological products, such as sweat, traces of urine, and human grease or from cosmetics might serve as precursors.

Aggazzotti and Predieri (1986) studied levels of volatile halogenated hydrocarbons(VHO) in drinking water, surface water and swimming pool water. Swimming pool samples were showed the high level of chloroform (max = 179 $\mu\text{g/L}$) as a consequence of chlorination with sodium hypochlorite.

Benoit and Jackson (1987) studied 25 whirlpool spas using halogen disinfectants, the only organohalide contaminant observed in the water and in the air at concentrations in excess of 1 $\mu\text{g/L}$ (water) and 1 $\mu\text{g/m}^3$ (air) was the trihalomethane corresponding to the disinfectant used. The levels of trihalomethane observed in the water in thermal spas were comparable to levels reported for swimming pools. The study was concluded that the heat, agitation and aeration of the spas do not produce

higher residual levels of trihalomethanes in the water and do not promote the formation of novel volatile organohalide. The concentration of trihalomethane in the water appeared to be related to the combination of high total dissolved solids and high disinfectant levels. The trihalomethane levels in the air though dependent on the concentration of trihalomethane in the water were modified by the variety of room sizes, ventilation rates, water surface areas and aeration rates associated with each individual spa.

Coates (1991) studied the level of trihalomethanes produced by the chlorination of swimming pool in the Las Vegas Valley. The results showed that the public swimming pools produced more trihalomethanes, specifically chloroform, than the private swimming pool. The average level of chloroform found in private pools was 20.1 µg/l. For the public pools, the average chloroform level was 65.3 µg.

Dietz and Singley (1979) compared the headspace method with the purge and trap method that used for determination of volatile organics in drinking water, well water, industrial water and lake water. The obtained results were equivalent but the chromatograms provided from the purged and trap method were of much poorer quality than those observed using headspace technique, e.g. peak tailing and detector base line noise. In addition, only 8-12 samples per day (8 h) could be analyzed using purge and trap method while 25 samples per day (8 h) were routinely examined by headspace method. Therefore the headspace technique was preferable to purge and trap method for routine sample analyses of volatile halocarbons.

Wutichai Yentongchai (1992) developed the headspace technique for determination of some volatile chlorinated hydrocarbons i.e., methylene chloride, chloroform, carbon tetrachloride, 1,1,1-trichloroethane and trichloroethylene in water samples. Various factors having effect on the sensitivity and the percent recovery i.e., equilibration time, temperature, liquid to gas phase volume ratio, injection volume and salting out with sodium chloride, sodium sulfate and calcium carbonate were studied

and evaluated. The temperature of 60 °C, equilibration time of 60 minutes, the liquid to gas phase volume ratio 30:30 in 60 mL serum vial, 1.50 mL of injection volume, and salting out with 13.00 g of anhydrous sodium sulfate were chosen as the optimal headspace analysis condition for the analysis of the volatile chlorinated hydrocarbons in water samples. The minimum detectable level of this technique was lower than 0.50 ppb for all studied compounds and percent recoveries of the chlorinated hydrocarbons were in the range of 54.22 - 90.81% with $\pm 1.04 - 4.81\%$ RSD.

Dunnick and Melnick (1993) investigated the carcinogenic potential of chlorinated or chloraminated drinking water and of four organic trihalomethane by products of chlorination (Chloroform, bromodichloromethane, chlorodibromomethane and bromoform) in rats and mice. The result showed that trihalomethanes were carcinogenic in the liver, kidney, and/or intestine of rodents. These studies suggest that organic byproducts of chlorination are the chemicals of greatest concern in assessment of the carcinogenic potential of chlorinated drinking.

Beech (1980) estimated worst case trihalomethane body burden of a child using a swimming pool. The results showed that the amount of trihalomethane (as chloroform) absorbed over a three hour period by a six-year-old boy when using a chlorinated freshwater swimming pool containing 500 $\mu\text{g/liter}$ of trihalomethanes, has been estimated to be 2.82 mg.

Aiking *et al.* (1994) reported a pilot study that addressed potential effects of long-term exposure to chlorination products in swimming pools. The indicator compound chloroform was detectable in blood from competitive swimmers in an indoor pool (mean=0.89 \pm 0.34 $\mu\text{g/l}$; N=10), but not in outdoor pool swimmers. The concentration of chloroform in pool water was between 18.4-28.7 $\mu\text{g/l}$. No hepatotoxic effect was indicated by serum glutamate oxaloacetate transaminase (SGOT), serum glutamate pyruvate transaminase (SGPT) or gamma-glutamyl transpeptidase (γ -GT) enzyme levels β -2-microglobulin, an indicator of renal damage,

was significantly elevated in urine samples of the slightly, but significantly, younger indoor swimmers. The precise ratio between these two possible causes, age and chloroform exposure, as well as the mechanism of the former, remain to be elucidated.

Biziuk, Czerwinski and Kozłowski (1993) determined volatile organohalogen compounds in a swimming pool using three methods: determination of volatile organic haloform (VOH) after sorption on XAD solid sorbent, thermal adsorption and coulometric titration of the halides formed; identification and determination of the individual organohalogen compounds after sorption on XAD-4, solvent extraction and chromatographic determination; direct injection of aqueous sampled to the chromatographic column. The concentration of organohalogen compounds varied from 35.9 to 99.7 $\mu\text{g}/\text{dm}^3$ for trichloromethane, 22.0 to 57.7 $\mu\text{g}/\text{dm}^3$ for dichloromethane, 2.4 to 27.4 $\mu\text{g}/\text{dm}^3$ for trichloroethylene 2.3 to 14.7 $\mu\text{g}/\text{dm}^3$ for bromodichloromethane and 4.2 to 7.6 $\mu\text{g}/\text{dm}^3$ for tetrachloromethane. The results obtained by the three methods were consistent in principle.

Clemens and Scholer (1992) studied 18 different swimming pool waters in the Bonn-Rhein-Sieg area. Trihalogenmethanes, halogenated acetic acids, 2,2-dichloropropionic acid, dihalogenacetonitriles and chloral hydrate were analysed. Most substances mentioned above were determined in almost every sample reaching total concentrations up to 538 $\mu\text{g}/\text{l}$. Considering the results one can see that some of the main pollutants are polar organic compounds like di- and trichloroacetic acid as well as chloral hydrate.