CHAPTER 2

LITERATURE REVIEW

This part describes the background of trihalomethane including its formation mechanism, and general structure, a definition of trihalomethane formation potential, its health effects, factors influencing trihalomethanes formation. In addition, it also shows data regarding shrimp farming in Thailand.

2.1 Formation of trihalomethanes (THMs) and other disinfection by-products

Trihalomethanes belong to a group of organic chemicals formed in water when chlorine reacts with natural organic matter. Total trihalomethanes (TTHMs) include the sum of the concentrations of compound numbers 1, 2, 3 and 4 in Figure 2.1.

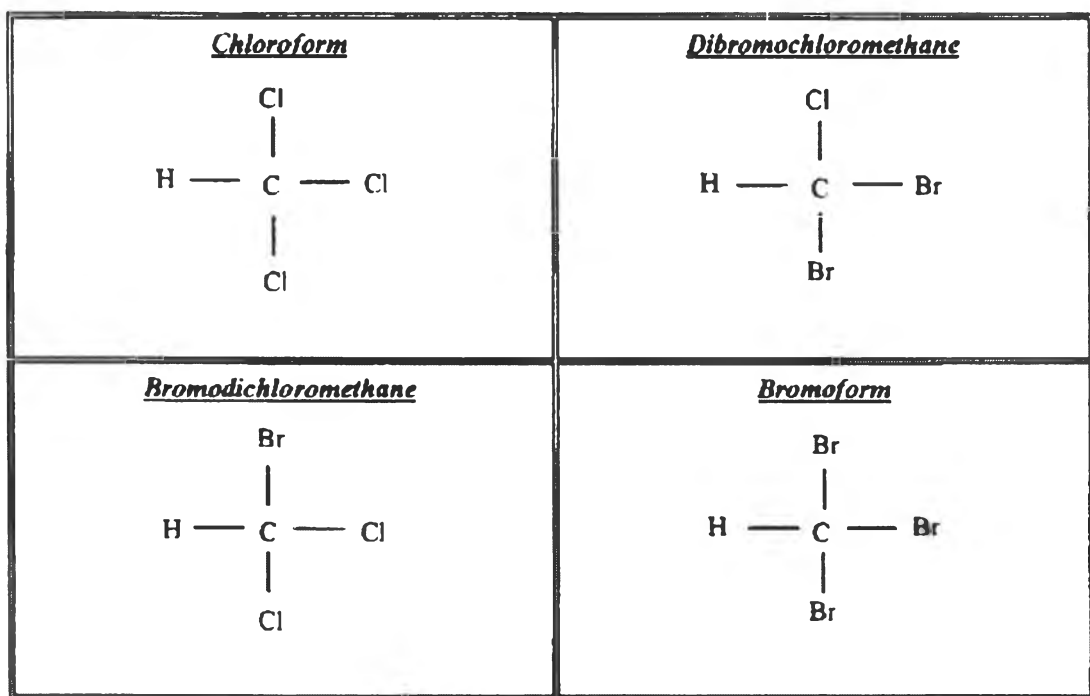| *Chloroform*	*Dibromochloromethane*
Cl | H — C — Cl | Cl	Cl | H — C — Br | Br
Bromodichloromethane	*Bromoform*
Br | H — C — Cl | Cl	Br | H — C — Br | Br

Figure 2.1 The chemical structure of each of the four forms of THMs

The formation of trihalomethanes during the free chlorination of drinking water results from a complicated mechanism of attack by aqueous halogen species on

natural aquatic humic substances, i.e., humic acid and fulvic acids. The generalized equation describing the formation of the trihalomethanes is as follows:

$$HOCl + Br^- + NOM \longrightarrow \text{THMs and Other Halogenated DBPs} \quad (2.1)$$

NOM is a complex matrix of organic material present in all natural surface waters (CWRS Workshop Notes, 1995). NOM is result of the decomposition of matter from the environment surrounding a watershed, such as leaves and aquatic plants. Water quality parameters such as water color and total organic carbon (TOC) are considered to be a good indicators 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). Often, an increasing level of water color 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 the disinfectant used to disinfect the water.

The major halogenated DBPs that are commonly identified as a result of chlorine treatment are THMs, HAA, HANs, cyanogen halides and halopicrins (Krasner et al., 1989)

2.2 Trihalomethane formation potential (THMFP)

Trihalomethane formation potential is the difference between the final $TTHM_T$ and the initial $TTHM_0$ concentration. Usually $TTHM_T$ is reported in terms of $TTHM_7$ which is the TTHM after the sample is left for 7 days. If a sample did not contain chlorine at the time of collection, $TTHM_0$ would be close to zero and the term Δ THMFP would be equal to $TTHM_7$ (Figure 2.2). If a sample does contain chlorine at the time of collection, The initial TTHM is not zero and the $\Delta THMFP$ would be equal to the difference between the final and initial concentration (Figure 2.3).
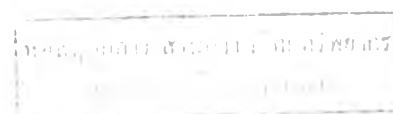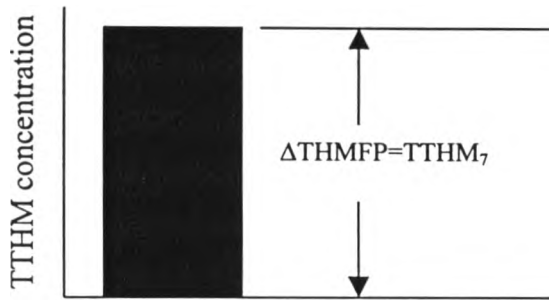
Figure 2.2 Relationships between definitions used in the formation potential test, for a sample that did not contain free chlorine at the time of sampling.
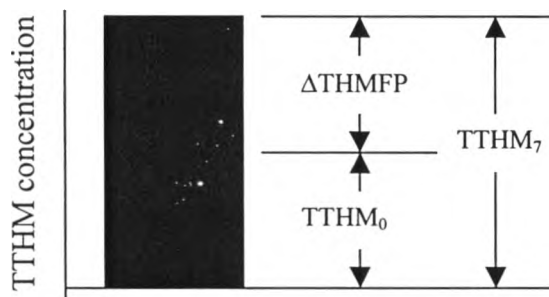

Figure 2.3 Relationship between definitions used in the formation potential test, for a sample that already contained free chlorine at the time of sampling.

Note that the term "THMFP" is often equal to the final TTHM concentration, even if the sample contains chlorine when collected. (APHA, AWWA and WEF, 1995).

2.3 Factors influencing THMs formation

Many studies have concluded that THM formation in drinking water depends upon various factors, such as pH, concentration and properties of NOM, concentration of chlorine and residual chlorine, temperature, reaction time, turbidity and bromide concentration.

2.3.1 pH

Rook (1976) suggested that THM formation increased evidently at pH values from 8 to 10, whereas in a range of pH 1 to 7 had less influence on the THM formation, a feasible variation range during chlorinating.

Stevens et al. (1976) conducted an experiment with a wider pH range from 6.5 to 11.5. The results showed that the rate of formation of chloroform increased as the pH increased. They explained that this was due to an increase in the humic acid reaction rate, since the rate-determining step of the classical haloform reaction was enolization (mechanistic interpretation of the bromination) of a ketone.

Krasner et al. (1989) observed that at high pH values, the hydrolysis of many halogenated DBPs occurs. It can be concluded that as the pH increases, trihalomethanes formation also increases.

According to Adin et al. (1991)'s study on pH had two effects: a decrease in pH resulted in low THM formation and similarly, an increase in pH led to high THM formation. This was due to the fact that the initial attack was dependent on the HClO concentration, w hich w as r elated t o t he p H. Lower l evels o f pH resulted in higher concentrations of humics.

Furthermore, Singer (1993) studied the role of pH to the formation of chlorinated DBP and found that, increasing the pH led to a decrease in the formation of total organic halides (TOX), but at the same time THM formation also increased.

In conclusion, this effect was also noted by other investigators (Peter et al., 1980; Sandler, 1977), who reported that a decrease in THM formation was a result of lowering the pH. Gracia-Villanova et al.(1997) reported that there was a linear relationship between pH and THM formation. This parameter seemed to be very important in controlling THM formation.

2.3.2 Concentration and properties of NOM

With increasing NOM concentration, DBP formation increases. Properties of NOM play an important role as well, since activated aromatic content of NOM increases DBP formation (Reckow et al., 1990). In addition, NOM contains hydrophobic and hydrophilic materials, the nature and distribution of which may vary with different types of vegetation in the watershed and different species of algae in water. This results in varying the influence of NOM on DBP formation (Singer, 1994).

2.3.3 Chlorine concentration and residual chlorine

By increasing the chlorine dose, and the residual formation of haloactic acids becomes more prevalent than trihalomethane formation. Also, more trihalogenated

species are formed in comparison to mono- and di-halogenated species, and more chlorinated than brominated species are formed (Singer, 1994). Depletion of the free chlorine residual ceases THM and haloacetic acid formation. However, the limited formation of some other DBPs continues due to hydrolysis reactions (Singer, 1994).

2.3.4 Temperature and season

Generally, temperature has an effect on most chemical reactions that occur in natural water systems. In the studies on the effect of temperature on THM formation, Kohei et al. (1983) and Peter et al. (1980) found an Arrhenius dependency between the rate constant and temperature with an activation energy of $10 - 20$ kJ mol^{-1}.

Gracia-Villanova et al.(1997) reported that there was no linear relationship between temperature and THM formation. However, they found that the critical temperature value (Tc) for THM formation was 18.97 °C. THM level was reduced drastically when the temperature was above the Tc value. This could be accounted for due to a shift in the extent of two phenomena: temperature increases the rate of formation up to Tc, at which the rate of removal of THMs (most likely because of their volatility) becomes higher than their formation rate in the open system.

As with most other chemical reactions, the formation rate of trihalomethanes in the chlorination of drinking water exhibits a temperature dependence. Stevens and co-workers (1976) demonstrated that the rate of formation of chloroform in raw water treated with a chlorine dose of 10 mg/L increased threefold between 3 °C and 25 °C.

Subsequently, DBP concentrations are expected to be higher in the summer than in the winter (Williams et al., 1997; Golfinopoulos et al., 1993) However, influence of season and weather on the nature of NOM and on bromide concentrations must be taken into account.

2.3.5 Reaction time

Reaction time is among the major factors influencing THM formation. Reckhow and Singer (1984) found that by varying the chlorine contact time, chloroform and total THM increased rapidly in the first few hours and then the rate of the increase dropped.

Furthermore, Singer (1994) found that with increasing contact time, trihalomethane and haloacetic acid formation increased. On the other hand, DBPs

such as haloacetonitriles and haloketones, which were initially formed, decayed as a result of hydrolysis and reactions with residual chlorine.

2.3.6 Turbidity

Turbidity in water is caused by suspensed matter, such as clay, silt, finely divided organic and inorganic matter, soluble coloured organic compounds, plankton and other microscopic organisms (APHA, AWWA, WPCF, 1989).

In the water treatment process, Chlorine (as hypochlorous acid) reacts readily with organic matter containing unsaturated linkages, phenolic groups and nitro groups, giving rise to taste and odour producing compounds (Sawyer and McCarty, 1978) as well as trihalomethanes (Rook, 1977).

2.3.7 Bromide concentration

Bromide can enter source waters through natural or anthropogenic processes. Natural mechanisms include bromide contributions from geologic sources and from the saltwater instrusion of aquifers. Bromide may also appear as a trace impurity in the chlorine used for water disinfection.

Once bromide is present in source water, there are no known treatment techniques available for economically removing it. If chlorination is used for disinfection, the possibility exists that THMs, especially brominated ones, may increase. Much less is known about brominated THMs than chloroform, and it is possible that the health effects of brominated conpounds may pose more serious problems than chloroform.

Rook (1977) found that the ratio of total bromide to total chlorine in the THMs of finished water was much greater than the bromide-to-chlorine ratio of the raw water, even if the quantitative oxidation of all bromide was assumed. Later work offered that in the presence of bromide ions (Br^-), produced more brominated and mixed chloro-bromo derivatives are formed (Krasner et al., 1989). This was a result of bromide oxidation to hypobromous acid (HOBr) and residual HOCl with NOM. In waters with very high bromide concentrations, the brominated species -bromoform, dibromoacetic acid may be the major species formed (Singer, 1994).

2.4 Health effects on trihalomethanes

Although short-term toxic responses to trihalomethanes in drinking water are not well documented, the potential effects of chronic exposure to trihalomethanes should be a matter of concern. The prolonged administration of chloroform at relatively high dose levels, 100 to 133 mg/kg, to rats and mice manifested oncogenic effects. Oncogenic effects were not observed at the lowest dose levels, 17 mg/kg, in three experiments. Since methods of establishing a "threshold no effect" level of

exposure to carcinogens, currently do not exist the preceding data does not imply that a "safe" level of exposure can be established for humans.

Some scientific studies have linked TTHM to an increased risk of cancer. Several studies suggest a small increase in the risk of bladder cancer and colorectal cancer. Beyond cancer and reproduction concerns, some investigations have found that chlorination by-products may be linked to heart, lung, kidney, liver, and central nervous system damage. Other studies have linked TTHM to reproductive problems, including miscarriage. A California study found a miscarriage rate of 15.7% for women who drank 5 or more glasses of cold water containing more than 75 ppb TTHM, compared to a miscarriage rate of 9.5% for women with a low TTHM exposure. A North Carolina study investigating the same question, but found no strong relationship between TTHM and problem pregnancies. When taken in total, the cancer evidence is probably the strongest among these possible health risks. For these reasons, total trihalomethanes (TTHM) in public water supplies are limited to 0.08 ppm (80 ppb) (Symons et al., 1981).

Of the TTHM compounds, dibromochloromethane was the most closely associated with cancer risk, (0.6 ug/l to cause a one in one million cancer risk increase) followed in order by bromoform, chloroform, and dichlorobromomethane. These distinctions among the specific chemical by-products is a result of toxicological, not empidemiological studies (Symons et al., 1981). TTHM can be found in chlorinated water supplies and in the air of buildings where running water and showers release the chemicals into the room, however, the EPA has determined that this airborne exposure is minimal compared to that from consumption (Capece, 1998).

In addition, The US Environmental Protection Agency (USEPA) has set a maximum contaminant level (MCL) of 100 ug/L for total trihalomethanes (or THMs,

equal to the sum of chloroform, bromoform, dibromochloromethane, and bromodichloromethane) and has set a new MCL of 80 ug/L in stage 1 of the disinfection by product rule (D/DBP Rule ; USEPA 1998). Stage 2 of the D/DBP Rule may lower the MCLs for THMs to 40 ug/L.

2.5 Shrimp farming
2.5.1 Shrimp farming in Thailand

The countries dominating the production of cultured marine shrimp in South-East Asia are Thailand, Indonesia, Vietnam and the Philippines (see Table 2.1).

Thailand produces more cultured shrimps than any other country in the world (FAO, 1999). The estimated total area of productive Thai shrimp farms is presently 80,000 hectares, managed by some 20,000 farmers (Rosenberry, 1999). Since 1992, the country has annually produced 150,000-220,000 tons of cultivated shrimp, of which 90% are exported (Rosenberry, 1996; Kongkeo, 1997; Bangkok Post, 1998 and Rosenberry, 1998). *Penaeus monodon* constitutes 90% of the cultured shrimps in Thailand (Rosenberry, 1998). The exportation of shrimp is of great significance to the Thai economy. Since 1992, shrimp export competed with rice as the agricultural product that gained the most foreign currency into the country (Fish Farming International, 1994).

Table 2.1 Production of cultured shrimp in the countries dominating the South-east Asia shrimp farming industry [a]

Year	Thailand	Indonesia	Vietnam	Philippines
1995	220,000	80,000	50,000	30,000 – 50,000
1997	150,000	80,000	30,000	10,000
1999	200,000 – 210,000	100,000	40,000	40,000

[a]Figures in metric tons. Kongkeo (1997), Rosenberry (1995;1997 and 1999) and Graslund and Bengtsson (2001)

2.5.2 Chemical products used in shrimp farming

In 1995, approximately US $100 million was spent on chemicals for use in shrimp farming in Thailand alone (Tonguthai, 1996). Major reasons for the use of chemical products in shrimp farming are to correct water quality problems, and reduce the high risk of disease. Some of the products have environmental impacts.

The most common products used in pond aquaculture are fertilisers and liming material. Disinfectants are also used to improve water quality (Boyd and Massaut, 1999).

2.5.3 Potential impacts on the environment

Concern is being expressed regarding the potential impact of aquaculture chemicals on the aquatic environment, adjacent terrestrial ecosystems and human health (Redshaw, 1995; FAO, 1997 and Bangkok Post, 2000). There is a lack of information about the quantities of chemicals used in shrimp farming in the different Southeast Asian countries. The absence of such quantitative information makes it very difficult to assess the impact of shrimp farming chemicals on the environment. However, with the available information on the types of chemicals that are used, the main aspects regarding their environmental fate may be discussed.

There are three main groups of substances used in shrimp farming that can affect the environment in different ways; they are toxic chemicals, antibiotics and nutrients. The chemicals that spread in the environment as a result of their use in aquaculture can be acutely toxic, mutagenic or have other negative sub-lethal effects on the wild flora and fauna (Graslund and Bengtsson, 2001). The dispersion of antibiotics after treatment in shrimp ponds or hatcheries can cause resistance among the pathogens, and a changed microorganism composition in the aquatic environment. Effluent with a high nutrient content can cause local or regional eutrophication and trihalomethane precursors, such as humic and fulvic acids.

2.5.4 Disinfection by-products

Disinfection using chlorine compounds, such as calcium or sodium hypochlorite, is common and actually a recommended disease preventing measure in shrimp farming (Kongkeo, 1997; Rosenberry, 1998). In Thailand alone, approximately 50,000 tons of chlorine is used annually for disinfection in shrimp farms (Graslund and Bengtsson, 2001).

Chlorine added to natural waters can react with different organic substances and result in significant concentrations of halogenated hydrocarbons. Humic substances and bromine are significant precursors in this process (Hanna et al., 1991; Italia and Uden, 1992; Xie and Reckhow, 1993; Peters et al., 1994; Tretyakova et al., 1994; White, 1998). The observed substances formed after the experimental chlorination are as follows: chlorinated and brominated trihalomethanes and haloacetates, chloral hydrate, benzaldehyde, trichlorophenols, halogenated furanones, haloacetonitriles, halogenated, fatty acids, organic chloramines and many more (Christman et al., 1983; Urano et al., 1983; Bauman and Stenstrom, 1990; Kristiansen et al., 1992; Jimenez et al., 1993; Kristiansen et al., 1994; Bull et al., 1995; Nordic Council of Ministers, 1997; Abia et al., 1998).

Marine aquaculture ponds contain a considerable amount of organic substances and ions such as bromide. It can be concluded that there is a clear risk of the formation of toxic chlorinated and brominated hydrocarbons following the chlorination of shrimp ponds. Chlorate is an inorganic by-product found in drinking water disinfected with chlorine dioxide. Small quantities are also present in water treated with hypochlorite (Bolyard et al., 1992; White,1998). Chlorate is highly toxic to m arine m acrobrown a lgae, b ut n on-toxic t o o ther g roups of investigated aquatic organisms (Van Wijk and Hutchinson, 1995).

Untreated a nd directly released shrimp e ffluents i nto w ater b odies m ight b e eventually discharged to surface waters or may seep into groundwater, which could later be utilized as sources of the drinking water supply after undergoing a series of treatment and disinfection processes can then be form THMs.

2.6 Literature reviews

A large number of investigations on trihalomethane formation potential are available in literature. One interesting subject among the literature is on the study of the relationship between functional groups in NOMs and the formation of THMs.

Table 2.2 summarizes the work done on the investigation of functional groups reactive to trihalomethanes formation in various sources of water. The functional groups, which were often found to chlorine and NOM in the formation of trihalomethane were dihydroxyaromatic compounds (Boyce and Hornig, 1983; Gallard and Gunten, 2002), phenolic-OH(Galapate et al.,1999; Galapate et al.,2001; Lin et al., 2001; Leenheer et al., 2001), organic nitrogen (Galapate et al.,1999),

carboxyl group (Lin et al., 2001), β-diketone (Gallard and Gunten, 2002), and β-ketoacids (Gallard and Gunten, 2002). Some work focused on the development of a mathmatical model for predicting THMs, and these works are summarized in Table 2.3. The parameters which were used for determining trihalomethanes were chlorine concentration, bromide concentration, pH, TOC, temperature, chlorophyll, UV260, functional groups, and reaction time.

Table 2.2 Functional groups which are reactive to trihalomethanes formation in various sources of water

Source	Functional groups	Results	Reference
Dilute aqueous solution	Dihydroxyaromatic compounds	- The 1,3-dihydroxyaromatic model compounds were most reactive with maximum yields of $CHCl_3$ (>90%) and $CHBr_3$ (>70%) at pH 8-10.	Boyce and Hornig (1983)
Various treated industrial wastewaters	Organic nitrogen Phenolic-OH	- Organic nitrogen and phenolic-OH influenced the formation of THMs. - Organic nitrogen and phenolic-OH could not predict THMFP.	Galapate et al. (1999)
Minaga reservoir water	Phenolic-OH	- Decrease in phenolic-OH indicating the oxidation of some reactive sites like resocinol or meta-dihydroxy benzene ring structures, which were prone to chlorine substitution, consequently decreasing the reactivity of the organic carbon to form THM.	Galapate et al. (2001)
Diluted humic acid solution	Phenolic group Carboxyl group	- A complete separation of the phenolic and carboxyl groups was not possible. The fraction with a higher content of the phenolic OH group exhibited the highest THMFP (190µg/mg C), whereas the fraction with a higher content of the carboxyl groups exhibited more flux decline.	Lin et al. (2001)
Reclaimed water in ground water, Los Angeles County, California	Phenol structures	- Phenols structures in natural fulvic acids in DOM isolated from the groundwater produced significant trihalomethanes and total organic halogen (TOX) yields upon chlorination.	Leenheer et al. (2001)
Surface water and Humic material solutions	Dihydroxyaromatic compounds(Resorcinol-type structures) β-diketone β-ketoacids phenolic-OH	- Resorcinol-type structures could possibly be responsible for the fast reacting THM precursors, which represented 15-30% of the THM precursors. - β-diketone and β-ketoacids might contribute to the initial THM formation. - Phenol showed that slow reacting THM precursors may consist of phenolic compounds.	Gallard and Gunten (2002)

Table 2.3 Models for predicting trihalomethanes in various sources

Source	Parameter	Result	Equation	Reference
Seawater distillation process	Cl_2 (mg/l) TOC(mg/l)	- THMs level increased with the increase of both chlorine and initial humic substances concentrations. - Increase in temperature and contact time also increased THM concentration. - Pre-chlorination and aeration step of the seawater resulted in a reduction of THMs.	$Log(THM) = A*Log (Cl_2)+B*Log(TOC)+C$ A, B and C = estimated parameters which depend on seawater chlorine dose.	Tawabini et al. (1987)
Finished water	Br(mg/l) Cl_2(mg/l) pH TOC(mg/l) Summer(S) Spring(Sp) Winter(W) Temperature(°C) Chlorophyll(Chla)(mg/m^3)	- 82% of the predicted values were within +/- 20% of the measurements - TOC was not included in the model because the results obtained were reliable. The TOC analyzer used was not appropriate for samples of drinking water with low organic concentrations of raw water because of lack of the desired sensitivity.	$TTHM= 13.54ln[chla]-14.47pH+230.25[Br]$ $-139.62[Br]^2-25.28S+110.55Sp$ $- 6.59(T*Sp)+1.48(T*[Cl])$	Golfinopoulos et al.(1998)

Table 2.3 Models for predicting trihalomethanes in various sources (cont.)

Source	Parameter	Result	Equation	Reference
Various treated industrial wastewaters	DOC(mg/l) UV260(1cm cell) COOH(meq/l) Phenolic-OH(meq/l) Organic-N(mg/l)	- The hydrophobic DOC had a higher potential to form THM compared to the hydrophilic DOC. - DOC and UV260, as well as specific chemical functional groups COOH, phenolic-OH, and organic nitrogen could not predict the bulk THMFP.	$Log[THMFP] = 2.17 + 0.20*UV260(nonhumic)$ $+ 0.30*organic\text{-}N(nonhumic)$ $+ 0.29*phenolic\text{-}OH$ $(nonhumic)$ $+ 0.59*log[UV260](humic)$ $+ -0.36*Log[Org.\text{-}N]\ (humic)$	Galapate et al. (1999)
Water distribution systems	Cl_2(mg/l)	- The model was capable of modeling chlorine, TTHM, and the four THM species in water distribution systems subjected to different varying loading conditions.	$[TTHM]_{(t+\Delta t)} = [TTHM]t + F*(Cl_{(t+\Delta t)} - Cl_t)$ F is a chlorine demand proportionality coeffiecient	Elshorbagy et al.(2000)
Drinking water	Br(mg/l) Cl_2(mg/l) pH TOC(mg/l) Summer(S) Spring(Sp) Winter(W) Temperature(°C) Chlorophyll(Chla)(mg/m^3)	- The hydrophobic DOC had a higher potential to form THM compared to the hydrophilic DOC - DOC and UV260, as well as specific chemical functional groups COOH, phenolic-OH, and organic nitrogen could not predict the bulk THMFP.	$TTHM = -0.26[chla] + 1.57pH + 28.74[Br]$ $- 66.72[Br]^2 - 43.63S + 1.13Sp$ $+ 2.62T*S - 0.72T*[Cl]$	Golfinopoulos et al.(2002)

Table 2.3 Models for predicting trihalomethanes in various sources (cont.)

Source	Parameter	Result	Equation	Reference
Water treatment plant	TOC (mg/L) pH Chlorine dose(mg/L) Contact time (h)	- A non-linear model was slightly better than a linear model in terms of percentage prediction errors. The model developed was site specific and the predictive capabilities in the distribution system varied with different environmental conditions.	$THM = a(TOC)^b (pH)^d (D)^e$ $THM = a + b(TOC) + c(t) + d(pH) + e(D)$ Where TOC = total organic carbon t = contact time D= chlorine dose a,b,c,d,e = the estimated values of statistical coefficients	Abdullah et al. (2003)
Drinking water plants	Chlorine dose Cl_2(mg/l) pH Reaction time(h)	- The percentage of observed values within 20% of the values ranged from 84% to 88%	$Log\ THM = 0.33pH - 0.02pH^2 + 0.12time$ $- 0.004time^2$(Tsinkias river) $Log\ THM = -0.44pH + 7.53logpH - 0.01time$ x Cl dose + 1.59logCl dose (Mylopotamos river)	Nikolaou et al. (2004)