CHAPTER 2

LITERATURE REVIEW

2.1 Precursors of disinfection by-products

Total organic carbon (TOC) is the term which is used to quantify the presence of organic matter (OM) in the aquatic system. TOC and natural organic matter, NOM are often synonymous because in aquatic system organic contaminants usually represent an insignificant fraction of the TOC (Leenheer, 2003). The subdivision of TOC are dissolved organic carbon (DOC) which diameter is smaller than 0.45 μm and particulate organic carbon (POC) which is retained in the filtrated paper 0.45 μm. NOM is a precursor forming disinfection by-product THMs, HAAs etc. Organic precursors in natural water are derived from various sources; for instance, agricultural drainage, surface runoff (including urban storm water runoff), wastewater treatment discharge, seawater intrusion etc. DOC can be characterized into humic (hydrophobic) and non-humic (hydrophilic) substances based on polarity. Details of each fraction are illustrated in the following subsections:

2.1.1 Humic substance (Hydrophobic fraction)

Humic substances are the organic portion of soil that remains after prolonged microbial decomposition, and that is formed by the decay of animal, leaves, wood, and other vegetable matters. They can impart a yellowish-brown to brownish-black color to water.

Humic material (also called humate or humus) is subdivided in an operational sense into three categories, VanLoon and Duffy,

- Fulvic acid (FA) is the fraction of humic matter that is soluble in aquatic solutions that span all pH value
- Humic acid (HA) is insoluble under acid conditions (< pH2) but soluble at elevated pH

- Humin (Hu) is insoluble in water at all pH values.

Humic molecules contain aromatic, carbonyl, carboxyl, methoxyl, and aliphatic units (Stevenson, 1982; Christman *et al.*, 1989; Perdue, 1985; Gjessing, 1976) with the phenolic and carboxylic functional groups providing most of the protonation and metal complexation sites. In the hydrosphere, humic substances were discovered a major portion (50-65%) of the DOC in surface water (Thruman, 1985; Collin *et al.*, 1986; Martin *et al.*, 1997 ; Marhaba *et al.*, 1999).

2.1.2 Non-humic substance (hydrophilic fraction)

Hydrophilic fractions mainly contained carboxylic acids, carbohydrates, amino acids and amino sugars, and proteins (Marhaba and Van, 1999) and are enriched in organically bound nutrients. Moreover, hydrophilic fractions were also discovered to have higher COOH, phenolic-OH, and organic –N content compared to the hydrophobic fractions. The present of phenolic-OH on the other hand could lead to THM formation due in part to –OH, an electron-donating substituent. The -OH activates the ring that favors reaction with chlorine resulting in the formation of THM and other chlorinated by-products (Rockwell and Larson, 1978).

2.2 Disinfection by-products

Chlorine, when added to water, reacts with various substances or impurities in the water (e.g., organic materials, sulfides, ferrous iron, and nitrites), creating a chlorine demand. Chlorine demand is a measure of the amount of chlorine that will combine with impurities and is therefore available to act as a disinfectant.

The chlorination of water containing NOM produces disinfection by-products (DBPs). The order of dominance DBPs from chlorination is generally trihalomethanes (THMs), haloacetic acid (HAAs), haloacetonitriles(HANs), respectively. Total trihalomethanes are not a single chemical but a group of compounds which includes chloroform ($CHCl_3$), bromoform ($CHBr_3$), dichlorobromomethane ($CHCl_2Br$), dibromochloromethane ($CHClBr_2$). The general reaction of NOM with chlorine is as follows (Marhaba and Washington, 1998):

DOM + free chlorine $\longrightarrow$ THMs + HAAs + cyanogen halides + other DBPs (2-1)

2.3 Trihalomethanes Health Issues

Some scientific studies (Cantor *et al.,* 1998; McGeehin *et al.,* 1993; Hildesheim *et al.,* 1979; Lawrence *et al.,* 1984; Flaten, 1992; Hsu *et al.,* 2000) have linked THMs to increase risk of cancers. Several studies suggest a small increase in the risk of bladder cancer and colorectal cancer. Beyond the 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 as shown in Table 2-1. Other studies have linked THMs 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 THMs, compared to a miscarriage rate of 9.5% for women with a low THMs exposure. A North Carolina study investigating the same question but found no strong relationship between THMs and problem pregnancies. Exposure to THMs is not limited only to drinking water. An article in the Washington Post Health Section on (March 12, 2002) stated that one study showed that a 10-minute shower produced more absorption of THMs through the skin than drinking 5 glasses of water. When taken in total, the cancer evidence is probably the strongest among the possible THMs health risks (John, 1998).

Of the THMs compounds, Dibromochloromethane may 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 (John, 1998).These distinctions among the specific chemical by-products is a result of toxicological, not empidemiological studies. 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.

Table 2-1 United State Primary Drinking Water Regulations Establishing Maximum Contaminant Levels (MCLs) and Maximum Contaminant Level Goals (MCLGs) Related to DBPs

Compound	MCLG (mg/L)	MCL (mg/L)	Potential Health Effects	Sources of Water Contamination
Bromodichloromethane	Zero[b]	see TTHMs	Cancer,liver,kidney, Reproductive effects	Drinking water chlorination and chlorination by-product
Bromoform	Zero[a]	see TTHMs	Cancer,nervous system, liver,kidney effects	Drinking water ozonation, chlorination chloramination,and by-product
Chloroform	Zero[a]	see TTHMs	Cancer,liver,kidney, reproductive effects	Drinking water chlorination and chloramination by-product
Dibromochloromethane	0.06[a]	see TTHMs	Nervous system,liver, kidney,reproductive	Drinking water chlorination and chloramination by-product
Total trihalomethanes[c] (TTHMs)	N/A	0.08[b]	Cancer and other effects	Drinking water chlorination and chloramination by-product

Source: 63 Federal Register 69390

[a] Finalized on December 16,1998 (*63 federal Register 69390*) as established in 40 CFR 141.53.

[b] Finalized on December 16,1998 (*63 federal Register 69390*) as established in 40 CFR 141.64.

[c] Total trihalomethanes are the sum of the concentrations of bromodichloromethane, dibromochloromethane, bromoform, and chloroform in mg/L

2.4 Factor Influencing Trihalomethanes Formation Potential

The factors influencing the formation of THMs are a function of pH, precursor concentration, contact time, chlorine dosage, bromide concentration, temperature, and type of disinfectant. The effect of each of these factors is discussed herein.

2.4.1. pH

Form the previous research works may lead to the conclusion that THMs formation levels increase with pH. This supports the hypothesis that THM formation via the haloform reaction is basic-catalyzed. Supposing by the study of Lin and Philip, 2003 who noted that the increasing of pH from 6 to 8 due to the higher forming of trihalomethanes and also, those results, accords with Hossein and Alan, 1995 ' s study; at pH 9.4 TOC is more related to THMs than at the other pH 5 and 7.

Rook (1976) examined an influence of pH on THM formation: the higher the pH, the more THMs was produced. This observation would lead one to believe that a reduction of THM formation could be achieved by maintaining a low pH during chlorination and than raising the pH once free chlorine was disappeared. Nevertheless, the research by Trussell and Umphres (1978), AWWA (1999) reported that THM can form in none existing of chlorine residual once the pH is raised. They suggested that chlorinated intermediates form at low pH and hydrolyze to form THMs once the pH is raised.

2.4.2. Precursor concentration

A positive correlation between TOC (THMs precursors) and THMFP is demonstrated by several researchers. Refer to the chemical reaction of NOM with chlorine; it is a forward reaction, THMs increase along with DOM and free chlorine increase. Confirming by experiment, with varying concentration of TOC, at 10 mg/L chlorine dosage, temperature 20 °C , and contact time 24 hours, has potential to form THMs in different rate. THMs concentration levels increase as TOC concentration, Natural Environment (Borad, 1984).

Species of NOM is also an important factor in forming THMs. Herein divided Species of NOM into 2 groups; hydrophobic and hydrophilic. Hydrophobic fractions have more potential to form THMs than that of hydrophilic fractions, but in water having low humic content, hydrophilic carbon also played an important role in DBP formation (Lin and Philip, 2003). More clearly illustrated by the study of Reckhow et al., reported the halogenated DBP formation increases with the 'activated aromatic'.

Chang *et al.* (2001) indicated that disinfection by-product precursors in the Pan-Hsin, Taiwan water were small compounds with a molecular weight less than 1 kDa. Since most of the DBPFPs are distributed in the low molecular precursors will play an important role in forming DBPs. Hydrophobic acids displayed the greatest ability to produce DBPs. Total organic concentration in various sources are different base on the study of Kavanaugh (1978) in Table 2-2.

Table 2-2 Total organic carbon in natural waters

Source	Total organic carbon (mg C/L)
Sea water	0.5-5
Groundwater	0.1-2
Surface waters	1-20
Swamps	80-300
Effluents, Biological treatment	10-20
Wastewater	50-100

Source: Kavanaugh (1987)

2.4.3 Chlorine contact time

An increasing chlorine contact time means chlorine efficiency increase due to free chlorine has more time to react with NOM as a result of producing more THMs.

Hossein and Alan (1995) showed the observation of chlorinated reaction time at 6, 48 and 168 hours, 70% of THMs was formed during 6 h. but no significant differences between 48 and 168 h.

2.4.4 Chlorine dose

Samorn *et al.*,(1995) showed the relationship between THM concentrations and chlorine dosage. THM concentrations increased as the chlorine dosage increased. At chlorine dosages of 7 and 10 mg/L, the total THM concentrations at the end of the test run were found to be 124.5 μg/L and 158.3 μg/L, respectively.

The chloroform levels increase from 20 μg/L to 220 μg/L after chlorine dosages were varied from 4 mg/L to 30 μg/L. At chlorine dosage 22 mg/L, chloroform level was the highest (Trussell, 1978).

The mechanism of the reaction of chlorine and NOM can be divided into 3 phases. Firstly, immediated chlorine is exerted. Generally this demand is inorganic rather than organic. Sulfide, Fe (II), and ammonia are substances that perhaps associated with this phase. Owing to the fact that these substances can rapidly use the chlorine dosage, few THMs are formed at this phase. Since this immediate chlorine demand has been satisfied, the residual chlorine began to react with available organic materials. This is a short time phase and its correlation between chlorine dose and THMs level present a linear relation. Providing enough chlorine to satisfy both the immediate and short-term phase, long term chlorine residual is obtained and further formation of THMs level seem fairly small amount. At the time of chlorine demands were satisfied, increasing of chlorine residual had little to no effect on THMFP(Kajino and Yagi, 1980 , AWWA,1999).

2.4.5 Bromide

The type and relative amount of the chlorination by-products varies not only with the organic content of the source water but also with the inorganic species present. As having been known that one species of trihalomethanes is brominated trihalomethans or bromoform. Water with the existing of bromide concentration produces mostly bromoform, while water with low or no initial bromide concentration produces mostly chloroform. During chlorination, bromide is oxidized by chlorine to bromine and chlorination and bromination become competitive reactions. With bromide in water at equal carbon content and chlorine dose, THMs tends to form higher level than those without bromide (Minear and Bird, 1980; AWWA,1999)

Bromide was more reactive with the hydrophilic fraction than with the corresponding hydrophobic fraction in the formation of THMs and HAAs, while chlorine was more reactive with the hydrophobic fraction than with the corresponding hydrophilic fraction. Since hydrophobic organic material usually contains larger amounts of activated aromatic moieties compared to hydrophilic organic material which is rich in aliphatic structures such as aliphatic ketones and alcohols, it can be concluded that bromine is more reactive with aliphatic precursors than with aromatic precursors, and the reverse is true for chlorine.

Hong *et al.*, (2003) studied the occurrence and fate of THMFP in water supply system of Hanoi city, Vietnam In type (I) water, high bromide, more than 80 % were brominated THMs due to the noticeable high bromide level ($\leq$ 140 µg/L), while in type (II) water, low bromide, the brominated THMs still accounted for some 40% due to the lower bromide level ($\leq$ 30 µg/L). On the other hand, only 5% of brominated THMs were formed in type (III) water ,high bromide combined with high ammonia and high dissolved organic carbon (DOC) concentrations, despite bromide levels were considerably high ($\leq$ 240 µg/L). These could be explained by competition kinetics of chlorine reacting with ammonia and bromide.

Hossein and Alan (1995) investigated the relationship between bromide, pH and THMFP. This observation suggested that both a higher bromide concentration and pH cause the formation of brominated trihalomethanes

Chang *et al.*,(2001) stated the molar ratio of applied chlorine to bromide dosage was an important factor in examining DBP formation and speciation. For instance, as Cl_2/Br^- molar ratio increased, the concentrations of $CHClBr_2$, $CHCl_2Br$ and $CHCl_3$ increased. $CHBr_3$ was the only species that decreased with increasing Cl_2/Br^- ratios. In halogen substitution for THM, HOBr was 25 times stronger than HOCl.

Ruud J.B. Peters *et.al.*, (1994) the formation of halogenated compounds by chlorination of humic acid with and without bromide present was studied. The result show that many of chloro-bromo compounds were produced when bromide ion present. The most prevalent products were trihalomethanes, halogenated aliphatic acids and diacids, and trihalomethanes precursors. The mutagenic activity was shown to be 2-3 times high when bromide is present during chlorination.

2.4.6 Temperature

The concentrations of THMs were higher during summer and autumn than in winter and spring. Spyros *et al.*,(1997).

El-Shahat *et al.*, (2001) investingating THMs in the water treatment plants in Tebbin , Rod El-Farag, and Mostorod during summer and winter seasons. The results conclude that the highest THMs concentrations were in finished water occurred in the range of 41.70 and 54.40 μg/L in summer , 29.00 and 34.90 μg/L in winter.

The concentrations of humic substances were high in the summer and low in the winter. The trends for the seasonal and annual changes in the concentration of the trihalomethane formation potential in Yodo River were almost consistent with those of humic substance concentration (Etsu, 1998).

Michael (2000) Seasonal variation and the variability of DOC (humic and nonhumic) ultimately a ffected the g eneration of disinfection by-products during chlorination and regulatory levels could be exceeded.

Chlorine efficiency increased as w ater temperature increased. Stevens (1976) at 3, 5, and 40 ˚C / at 40 ˚C and long contact time, the concentration of chloroform was approximately 150 – 225 μg/L.

*2.4.7 **Disinfectants***

Pre-oxidation with ozone leads to a lower THM formation and chlorine demand with an unaltered chlorine demand and peroxide with chlorine dioxide.

Jean *et al.*, (2003) noted the different types of disinfectants mainly due to the contribution of DBPs. In Sainte Foy, the pre-ozonation and subsequent physico-chemical treatment, was the utility which was found the lowest THMs concentrations with minimum, average, maximum value being 15, 32, and 74 μg/L. While in Quebec average concentrations of T HMs w ere h igher, t his s hould b e c losely related t o p re-chlorination of raw waters.

Marhaba and Van (1999) studied the disinfection by-product formation potential of DOC at an ozonation water treatment plant. They found that pre-ozonation was most effective in reducing the chlorinated THMs DBPFP of the hydrophobic base, hydrophobic acid and hydrophobic neutral fraction. It was less effective in the case of the hydrophilic base and essentially non-effective in the case of the hydrophilic acid and hydrophilic neutral precursors.

According to the Table 2-7, natural water consisted of both hydrophobic and hydrophilic organic material originating from the degradation and leaching of organic detritus within the watershed. The nature and distribution of these hydrophobic and hydrophilic materials differed, depending on the source materials and the biogeochemical processes involved in carbon cycling within the terrestrial and aquatic systems.

Table 2-8 showed the previous research works may lead to the conclusion that

- THMs formation levels increase with pH.
- THMs concentration levels increase as TOC concentration.
- An increasing chlorine contact time means chlorine efficiency increase due to free

chlorine has more time to react with NOM as a result of producing more THMs.

- THM concentrations increased as the chlorine dosage increased.
- THM concentration was high during summer.
- Water with the existing of bromide concentration produces mostly bromoform, while water with low or no initial bromide concentration produces mostly chloroform.
- Pre-oxidation with ozone leads to a lower THM formation and chlorine demand with an unaltered chlorine demand and peroxide with chlorine dioxide.

2.5 Shrimp Farm Situation in Thailand

The increased demand for shrimp in world markets has encouraged many developing countries to enter into the practice of shrimp farming. Without proper measures to protect the areas brought on a significant impact on water quality.

2.5.1 Shrimp culture in Thailand

The Countries dominating the production of cultured marine shrimp in Southeast Asia are Thailand, Indonesia, Vietnam and the Philippines (see Table 2-3). Thai shrimp farming started in the early 1980s and really began to expand in the mid 1980s. Before 1984, Thailand harvested as much as 90% of its shrimp from natural resources, mainly the gulf of Thailand (Michael, 1997).

Table 2-3 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

Source: Kongkeo (1997); Rosenberry (1999)

[a] *Figures in metric tons*

Thailand produced more cultured shrimp than any other country in the world (FAO, 1999). The estimated total area of productive Thai shrimp farms are presently estimated at 80,000 hectares, which are managed by about 20,000 farmers (see Table 2-4). In the 1990s, there was a rapid development of saltwater shrimp farming in freshwater areas of Thailand. This practice depends on the transportation of seawater to ponds inland, where it is diluted with freshwater from irrigation canals or nearest river to relatively low salinities tolerable for *Penaeus monodon* (or commonly known as black tiger prawn)(Rosenberry,1999). This new discovered method is both practical and profitable so that it has been becoming popular recently.

Table 2-4 Shrimp farm areas in Thailand

	1980	1985	1990	1995	1996	1997
No. farms	3600	5,000	15,100	26,200	26,000	25,000
Area of farms (ha)	26,000	40,800	64,600	74,900	84,000	80,000

Source: department of Fisheries(1995, 1996) ; Rosenberry (1998)

Table 2-5 Inland shrimp farms in the central region of Thailand

Province	Area (ha)	Province	Area (ha)
Chachoengsao	8375	Ang Thong	193
Prachinburi	4577	Khrung Thep	51
Nakhon Pathom	2204	Lopburi	48
Nakhon Nayok	1752	Chai Nat	46
Chonburi	1631	Nakhon Sawan	44
Suphanburi	1359	Nonthaburi	22
Samut Prakan	518	Kanchanaburi	19
Ayutthaya	451	Saraburi	16
Ratchaburi	350	Singburi	12
Phetchaburi	322	Uthaithani	10
Pathum Thani	244	Samut Songkhram	5
Samut Sakhon	206		= 22455

Source: Department of Land Development (1999a), Szuster and Flaherty (1999)

2.5.2 Chemicals Used in Shrimp Farming

In 1995, approximately US $ 100 million was spent on chemicals for use in shrimp farming in Thailand alone (Tonguthai, 1996; Sara, 2001). The most common p roducts u sed i n p ond a quaculture a re f ertilizers o r p alletized f eed, l iming material, and oxidants.

Fertilizers have a widespread use in shrimp ponds to increase the growth of natural food. Although the addition of fertilizers can increase shrimp production, it may also cause soil and water conditions to deteriorate if applied indiscriminately. There are two groups of fertilizers which are generally used -organic and inorganic. The organic fertilizers, mainly chicken manure, but cow, water buffalo carabao and pig manure (Primavera *et al.*, 1993; GESAMP, 1997; Sara, 2001) while, another one is a combination of inorganic fertilizers, ammonium phosphate, diammonium phosphate, ammonium sulfate, calcium nitrate and calcium sulfate. Daily adding these substances mean to enlarge the amount of organic in shrimp ponds. The compositions of feed were showed in Table below.

Liming material is applied to pond waters to neutralize acidity and increase total alkalinity (Boyd and Tucker, 1998). Increased alkalinity buffers water against drastic daily changes in pH common in eutrophic ponds with soft water.

Disinfectants, antibiotics, algaecides, herbicides, and probiotics are also applied to improve the production and to control phytoplankton, to kill disease organisms or to oxidize the bottom soil. Chlorine is sometimes used as an algaecide, a herbicide, or to regulate the pH of the pond water or to kill bacteria and viruses (Primavera *et al.*, 1993; Dierberg and Kiattisimkul, 1996; Boyd, 1997; GESAMP, 1997; Boyd and Clay, 1998; Chang *et al.*, 1998; Funge- Smith and Briggs, 1998; Sara, 2001). Peroxides and chlorine compounds are powerful oxidizing agents. Calcium hypochlorite is sometimes applied to ponds to oxidize organic matter. Only small doses of calcium hypochlorite added in to the ponds during the production cycle do not improve water quality. However, treatment of pond waters with large doses of chlorine might form DBPs such as THMs.

Table 2-6 Composition of shrimp and feed showing assimilation and loss to environment

Nutrient	Proximate analysis (% dry weight)		Composition of 1 kg dry feed (g kg^{-1} dry feed)
	Feed	Shrimp	
Protein	45.4±2.6	54.2±2.5	454
Lipid	6.1±0.5	4.9±0.5	61
Ash	12.8±0.8	19.3±0.8	128
Fibre	3.1±0.4	2.3±0.2	31
Carbohydrate	23.0±2.4	19.3±1.5	23
Dry matter	90.3±1.1	24.6±1.2	-
Nitrogen	7.08±0.59	11.50±0.18	70.8
Phosphorous	1.34±0.20	1.19±0.15	13.4
Carbon	43.16±1.71	41.2±1.3	43.16

Source Funge-Smith and Stewart (1996)

2.5.3 Water consumption

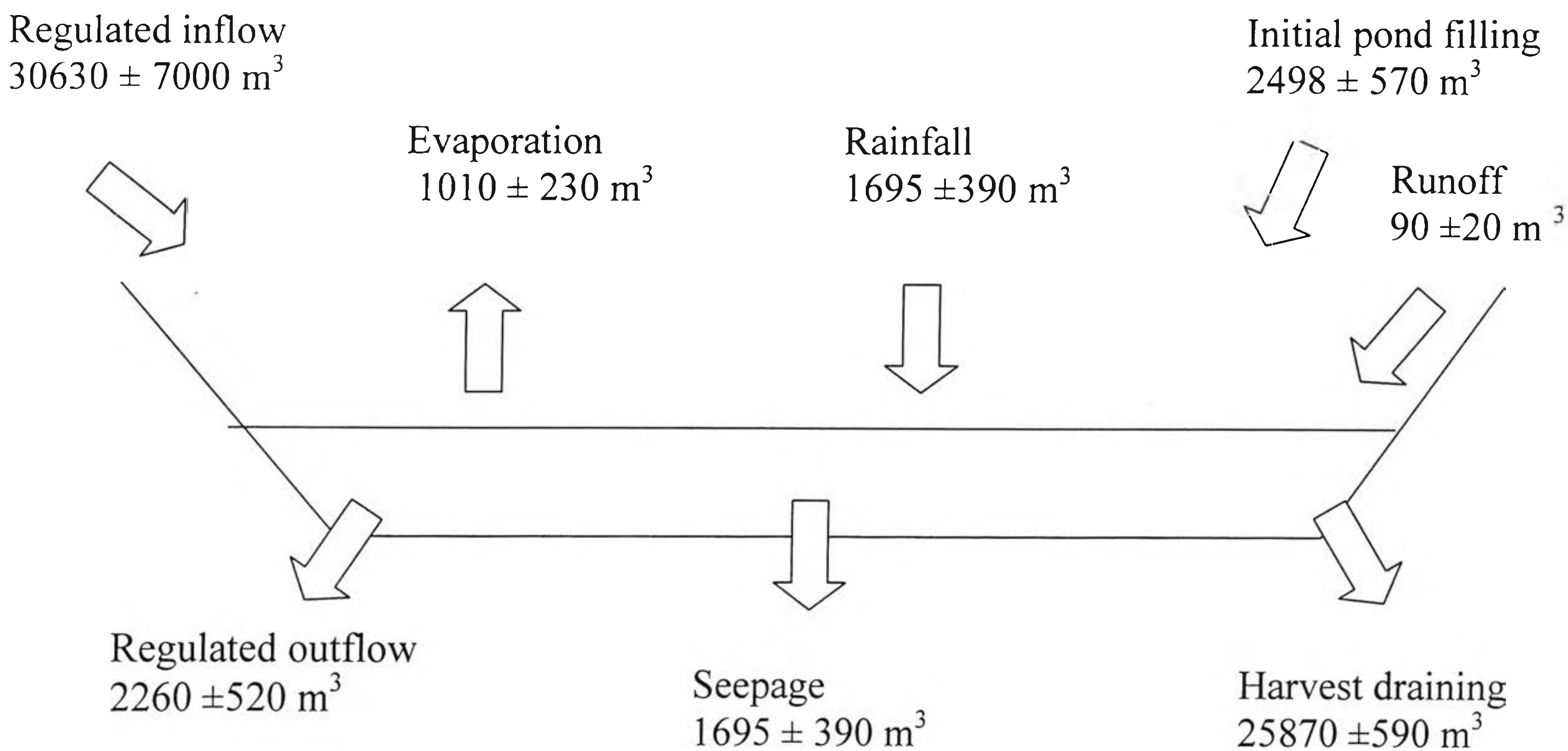
There was considerable variation in freshwater used from farm-to-farm owing to differences in management practices. Figures 2-1 and 2-2 show the hydrology of shrimp farm. Table 2-7 summarizes the studies of water consumption in shrimp farms per one ha from previous research works. As a rough estimate, water used in shrimp farming was equal to 21,000 m^3/ha. Nevertheless, total freshwater consumption was likely to be considerably higher than estimation because many farmers who have problems with disease would flush their ponds and refill them for the next crop and also would add water during algae booms to improve pond water conditions.

Table 2-7 The measured amount of used water in shrimp ponds

Inflow (ha^{-1} per one crop)	Outflow (ha^{-1} per one crop)	References
9,000 m^3	2,600 m^3	Brian W. Szuster, 2000
33,000 m^3	-	Mark, 1999

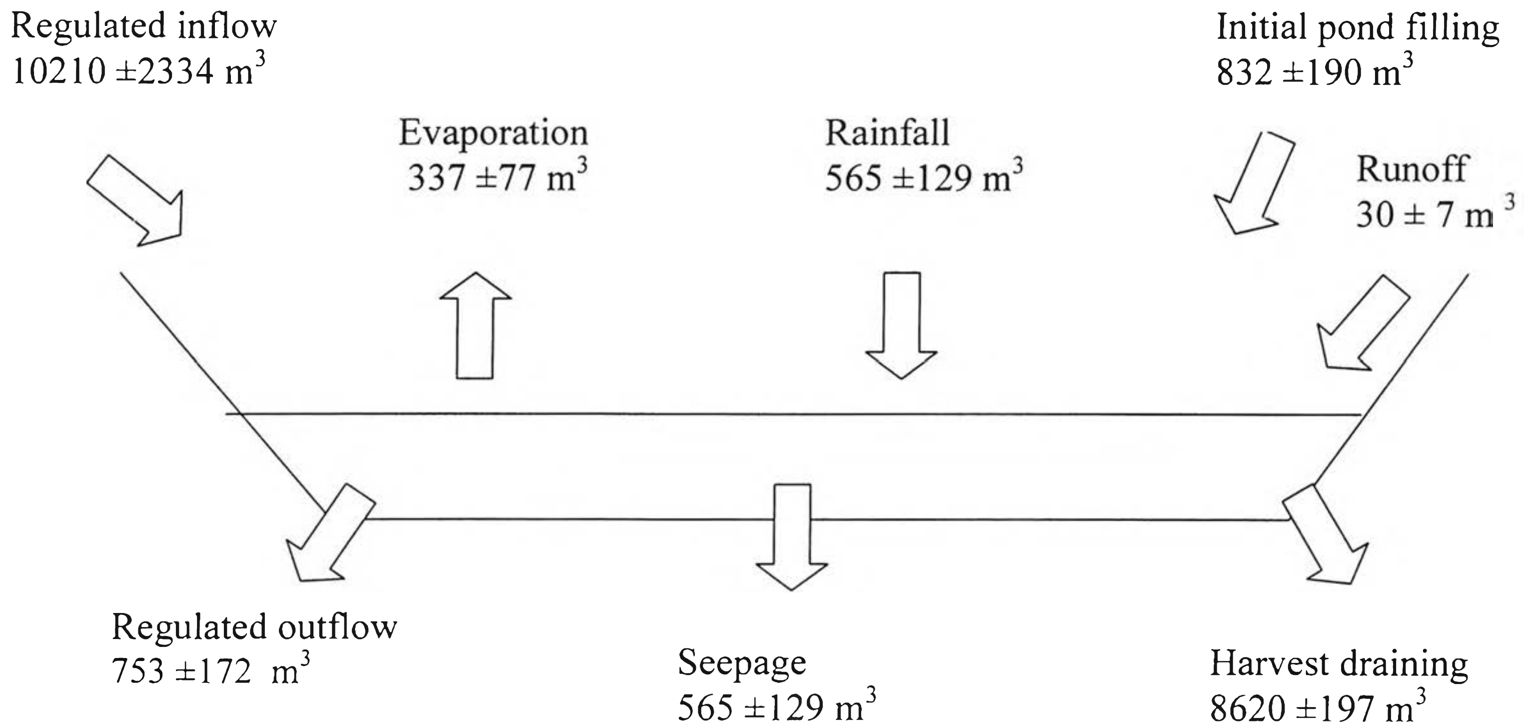
2.5.4 Organic loading

The character of the accumulated organic in ponds was depended upon culture intensity, pond soil organic content, and water exchange practices. The accumulated organic substances in the pond bottoms and effluents were derived from pond soil, plankton, shrimp faeces and uneaten feed. According to previous studies, the total discharge of organic matter in the effluent was estimated as 4.8 t ha^{-1}, the total solids were approximately 12.6 t ha^{-1}(Simon, 1998) and salt loading per ha for one crop of shrimp was 3,048 kg $^{-1}$(Mark, 1999). Figure 2-3 shows nutrient budget shrimp pond.



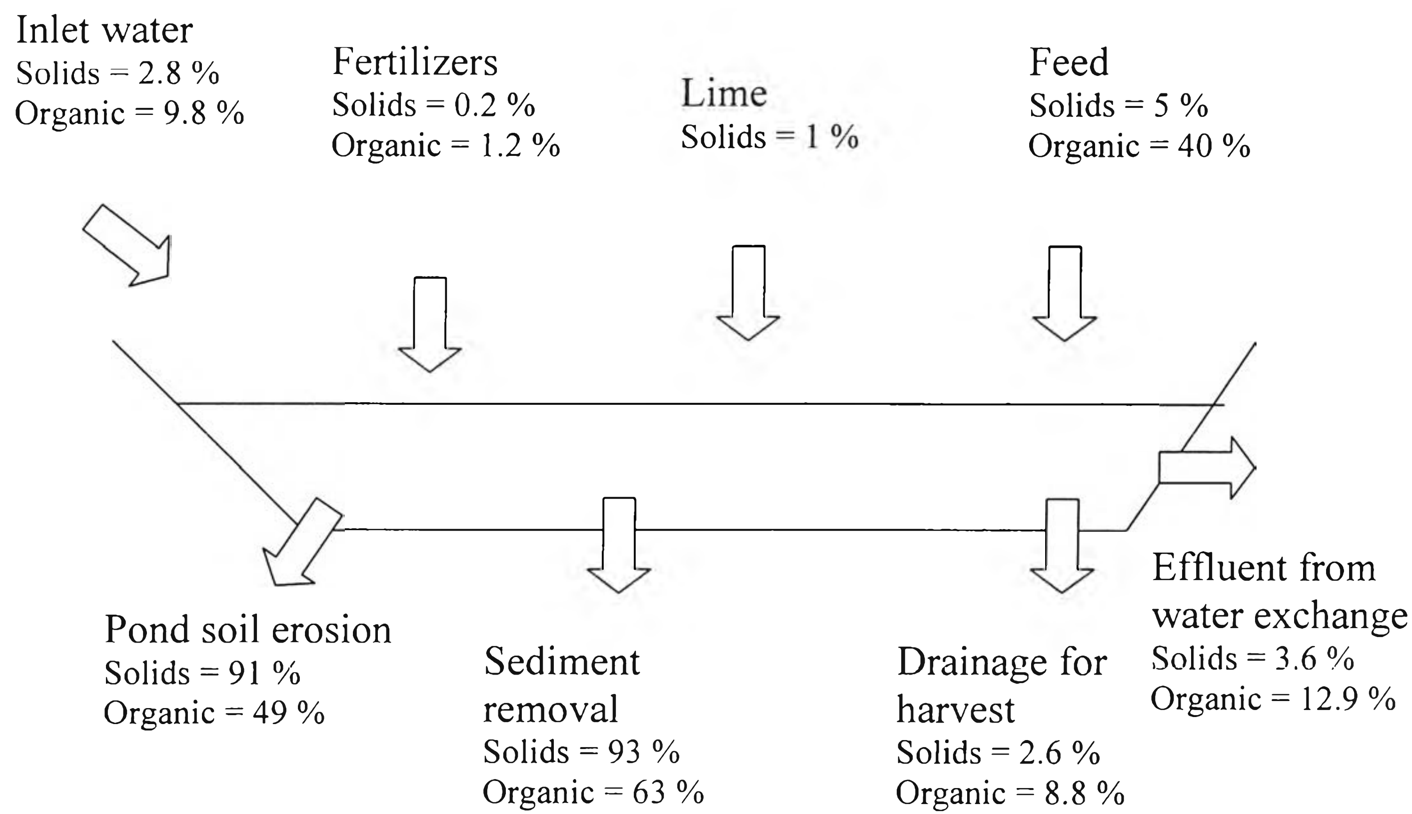
Source: Braaten and Flaherty, 2000

Figure 2-1 Estimates water budget for an inland shrimp pond over crop cycle (area 2974±680 m^2).



Source: Braaten and Flaherty, 2000

Figure 2-2 Estimates water budget for an inland shrimp pond over crop cycle per one ha.



Source: Funge-Smith and Briggs, 1998

Figure 2-3: Total and organic solids budgets for intensive Thai shrimp ponds

2.5.5 Potential impact on the environment

Rapid extension of inland shrimp cultures over fresh water areas may face the consequence of environmental impacts such as soil salinization, poor water quality as an outcome of high nutrient and chemical contamination in effluents.

One obvious problem is the effect from salty water which can direct accumulation in soils located beneath the ponds or seepage to near agricultural areas (sodium, chloride, bromide), thus, agricultural product will reduce. The problem of increasing salty areas should pay attention in short and long term. Traditionally high productive rice fields were replaced by shrimp ponds, and the cost of returning this land to fruitful areas if shrimp farming fails could be very expensive.

Chemicals 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. The dispersion of antibiotics, oxytetracycline, after treatment in shrimp ponds or hatcheries can cause resistance among the pathogens, and a changed microorganism composition in the aquatic environment.

The organic discharged, e.g. erosion of soil, shrimp faeces and uneaten feed etc., from the ponds from a minor but significant part of total solids in the system. The total discharge of organic matter in the effluent was 4.8 t ha $^{-1}$ and the total solids approximately 12.6 t ha^{-1}(Funge-Smith and Briggs, 1998). Nutrient enriched effluents which most small shrimp farms usually totally drain out into adjacent canal or river without pretreatment may due to the reducing of dissolved oxygen levels, can suffocate aquatic lives, and producing toxic chemical such as ammonia and hydrogen sulfide (Primavera,1998; Szuster, 2000).

The untreated effluents discharged directly in the river, where next time it has to use as a source water to grow the next crop. The organic contribution of the influent water was significant (7-13%), but so less than feed and soil erosion. The accumulated sediment was the sink of the organic matter in the system (58-70%); however, it depends upon culture intensity, pond soil organic content, and water exchange practices. Routine water exchange accounted for 4% of solids discharge and pond drainage for a further 3%. The organic content of these discharged solids were 13% and 9% respectively (Funge-Smith and Briggs,1998).

Hardly remove shrimp ponds' suspended solids by settling under gravity. In trials on shrimp pond waters one hour settlement achieved 22-44%

settlement of suspended solids. There was no significant difference between setting times of 1, 2 and 3 hours. Thus, the use of settling ponds for removal of this fraction is ineffective unless enhanced sedimentation is practiced (e.g. flocculation).

2.5.6 Disinfection by-products

Base on the existing data, DBPs relate to shrimp cultures in two ways; firstly, directly use as disinfection in ponds. In Southeast Asian shrimp farming, chlorine (usually calcium or sodium hypochlorite) is widely used and recommended as disease-preventing (Kongkeo, 1997; Rosenberry, 1999). In Thailand alone, approximately 50,000 tons of chlorine is used annually for disinfection in shrimp farms (Lin, personal conmunication; Sara, 2001). Aquaculture ponds contain a considerable amount of organic substances and ions such as bromide. It can be concluded that there is a clear risk that toxic chlorinated and brominated hydrocarbons form following the chlorination of shrimp ponds. After disinfection of a shrimp pond, the oxidizing agent itself disappears from the pond water within a few hours while the by-products that formed may be persistent.

Secondly, Untreated and directly released shrimp effluents into water bodies might be eventually discharged to surface waters or seepage to groundwater which could later be utilized as sources of drinking water supply after undergoing a series of treatment and disinfection processes can then be form THMs.

Formation of disinfection by products from oxidizing agents other than chlorine has not been as thoroughly studied. However, all oxidizing agents that are effective in water treatment will create oxidant by products that are potentially toxic.

2.5.7 Bang pakong watershed

The study area is located at Bangpakong watershed in the eastern part of Thailand located in Chacherngsao and Chonburi province. (Figure 2-4)

Bang Pakong River is originated from Khao Yai mountain range, the biggest national park of Thailand. Two branches of Bang Pakong Rivers, Nakhon Nayok and Prachinburi River, merge at Bang Nam Preaw district, Chachoengsao province. The river then, flows down passing Muang and Bang Pakong districts to its estuary at the upper Gulf of Thailand.

Bang Pakong watershed covers areas about 5,424,380 rai or 867900 ha or which are agriculture 77.16%, forest 20.13%, resident 1.10%, water supply 0.94% and other 0.67% Bang Pakong River is the most important river in the eastern region as water supply for industries, municipality, and inland culture both shrimp and fish farms (Office of environmental policy and planning, 2001).

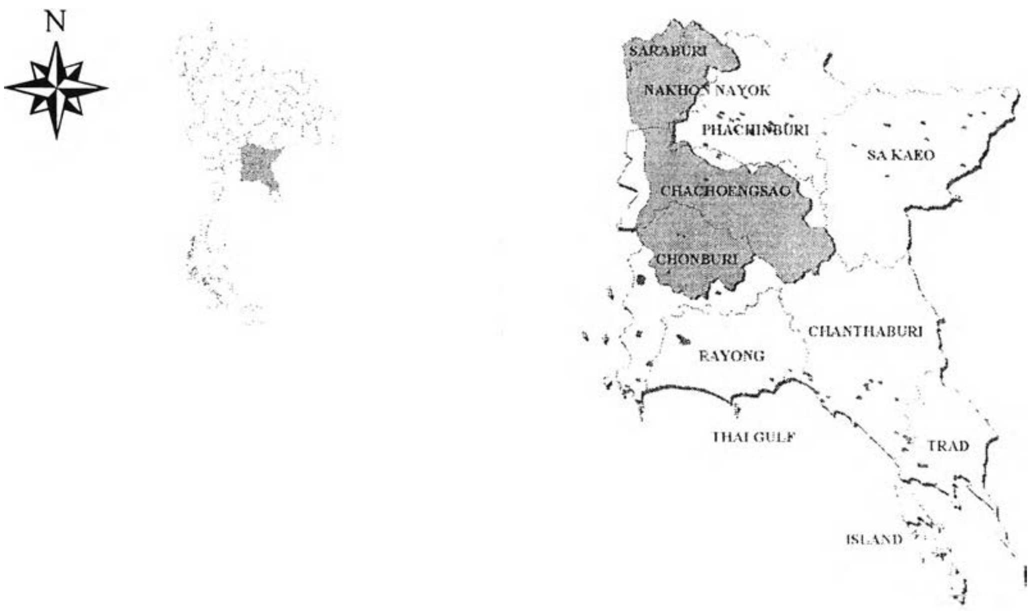
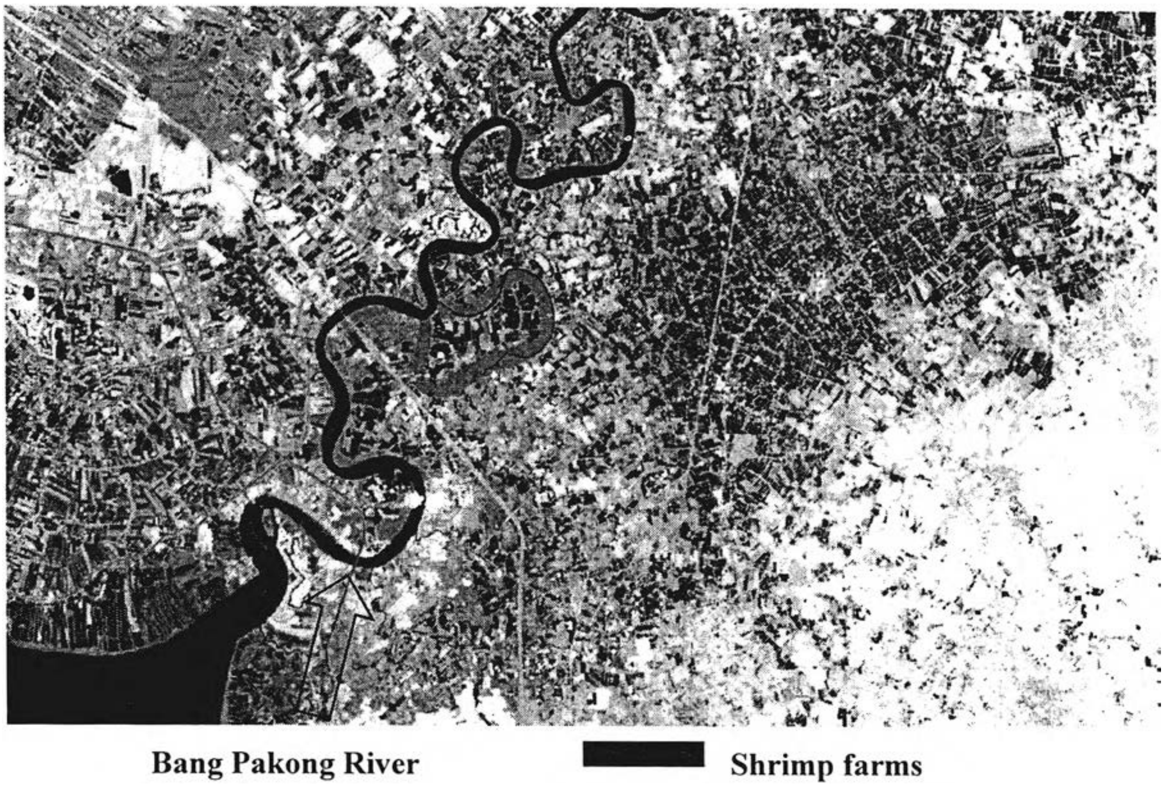


Figure 2-4 Bangpakong watershed

2.5.7.1 Land Use

Topography of the study area is flat with some low terrace. This type of topography is most suitable for paddy field; however, aquaculture including shrimp and fish farms are also found in flat terrain near the river (Figure 2-5: land use of Bang Pakong watershed) In addition, this area is famous for mango productions, which are mostly found in the levee along Bang Pakong River as well as in gentle terrain. On low terrace and rough terrain, land use is devoted to field crops, such as cassava, sugar cane and cornfield. There are many mixed orchards scattered in low terrace area.



Source: Landsat 7 ETM+ part: 129 row: 051 band combination R:4 G:5 B:3

Figure 2-5 Satellite imagery of Bangpakong watershed

2.5.7.2 Water quality problem

A number of farmers rapidly converted the utilization of their lands from paddy fields to shrimp farms. As a consequence, the number of saltwater shrimp farms in this zone has been increased. Unplanned or mismanagement in this situation induced severe effect on surface water because of high organic matter contamination.

On July 1999, Pre-development Consultant and Progress Technology Consultants investigated water quality at 91, 70 and, 68 km. from river's delta and found that Bangpakong River was under the surface water quality standard class 3 : medium clean fresh surface water resources used for (1) consumption, but with an ordinary pretreatment process, and (2) agriculture.

Table 2-8 Disinfection by-product precursors in various sources

Sources	Disinfectants	Potential reactive precursors	The most reactive precursor	References
Katsura, Uji, Kidzu and Yodo Rivers,Japan	Chlorine	-	Fulvic acid	Etsu (1998)
Water treatment plant in Central New Jersey, USA	Preozone and chlorine	-	Hydrophobic material	Marhaba and Van (1999)
Water treatment plant in Northern New Jersey, USA	Chlorine	Hydrophobic acid (HPOA) 12% Hydrophobic neutral (HPON) 10% Hydrophobic base (HPOB) 7% Hydrophilic acid (HPIA) 53% Hydrophilic neutral (HPIN) 13% Hydrophilic base (HPIB) 5%	Hydrophilic acid	Marhaba and Van (2000)
Fung Yuan treatment plant, Korea	Chlorine dioxide (ClO_2)	Hydrophobic substance (43%), Hydrophilic acid (41%), Non-acid hydrophilic (16%).	Non-acid hydrophilics.	Chang *et al.* (2001)
Pan-Hsin water, Taiwan	Chlorine	-	Hydrophobic acids	Chang *et al.* (2001a)

White River, Lake Manatee, Mississippi River, Poquonnock, South Fork Tolt River	Chlorine	-	Hydrophobic fraction	Lin and Philip (2003)
Treated industrial wastewater (domestic, Laundrary/dry cleaning, pickled vegetables, packed meals, pharmaceuticals, bean curd, becerage, dairy, rice wine), Japan		-	Hydrophilic fraction	Galapate et al., 1998

Table 2-9 Effect of various parameters on THMFP

Sources	Factors	Detail	References
Clinton Lake	Organic	Greater amounts of carbon attributable to tannin derived chemical structures might correspond with higher THMs.	Michael (2000)
Fung Yuan treatment plant	Organic	Larger molecular organic precursors had larger consumption of disinfectant.	Chang *et al.* (2001)
Pan-Hsin water	Organic	Most of the DBPFPs are distributed in the low molecular precursors played an important role in forming DBPs.	Chang *et al.* (2001a)
White River, Lake Manatee Reservoir, Mississippi River, Poquonnock Reservoir, and South Fork Tolt River .	Organic	Hydrophilic fractions trend to react with bromine more than hydrophobic fractions.	Lin and Philip (2003)
Galatsi Treatment Plant of Athens	Season	The concentrations of THMs were higher during summer and autumn than in winter and spring.	Spyros *et al.* (1997)
Katsura, Uji, Kidzu and Yodo Rivers	season	The c oncentrations o f humic substances were high in summer and low in winter. The trends for the seasonal and annual changes in the concentration of the trihalomethane formation potential in Yodo river were almost consistent with	Etsu (1998)

		those of humic substance.	
Clinton Lake	season	Seasonal variation and the variability of DOC (humic and nonhumic) ultimately affected the generation of disinfection by-products during chlorination.	Michael(2000)
Water treatment plants in Tebbin , Rod El-Farag and Mostorod,	Season	Investingating THMs in the during summer and winter seasons. The results conclude that the highest THMs concentrations were in finished water occurred in the range of 41.70 and 54.40 ug/L in summer , 29.00 and 34.90 ug/L in winter.	El-Shahat *et al.*, (2001)
Kizu River and the Yodo River	chlorine	The formation of THMs concentration range between 45.9 and 111 µg/L was evaluated.	Satoshi(2001)
Water treatment plant in central New Jersey	Ozone	Preozonation was most effective in reducing the chlorinated THMs DBPFP of the hydrophobic base, hydrophobic acid and hydrophobic neutral fraction.	Marhaba and Van,(1999)
Limmat River, Lake Zürich, Seine River (Switzerland)	Ozone	Preoxidation with ozone leads to a lower THM formation with an unaltered chlorine demand and peroxide with chlorine dioxide reduces THM formation and the chlorine demand.	Hervé and Urs (2002)

White River , Lake Manatee Reservoir , Mississippi River , Poquonnock Reservoir , and South Fork Tolt River.	pH	The result showed that the increasing of pH from 6 to 8 due to the higher forming of trihalomethanes but lower formation of trihaloacetic acid.	Lin and Philip (2003)
ultrapure water containing commercial humic acid	Bromide	with increasing Br^- concentration and the formation of THMs trended to be higher than at lower bromide concentration.	Hossein and Alan (1995)
	pH	At pH 9.4 the TOX is more related to THMs than at the other pH 5 and 7.	
	Reaction time	The observation of chlorinated reaction time at 6, 48 and 168 h. showed that 70% of THMs were formed during 6 h. but no significant differences between 48 and 168 h.	
water supply system of Hanoi city, Vietnam	Bromide and ammonia	Three types of water were divided in to (I) High bromide level (≤ 140 μg/L), (II) Low bromide(≤ 30 μg/L) (III)High bromide(≤ 240 μg/L) combined with high ammonia and high dissolved organic carbon (DOC) concentrations.	Hong *et al.*, (2003)

		Type (I) more than 80 % were brominated THMs, while in Type (II) water, the brominated THMs still accounted for some 40%. On the other hand, only 5% of brominated THMs were formed in Type (III) water.	

Table 2-10 THMFP of various sources

Sources	types	THMFP (µg/L)	References
Northern Region Industrial Estate in Lumphoon, Thailand	Wastewater treatment plant	480.68	Musikawong, 2002
León, Mexico	Wastewater site/ Contaminated groundwater	362-673/ 120-397	M.E.Stuart, 2001
Mezguital, Mexico	Wastewater site/ Contaminated groundwater	719-1107/ 61-218	
Wadi Dhuleil, Jordan	Wastewater site/ Contaminated groundwater	320-370/ 25-620	
Hat Yai, Thailand	Wastewater site/ Contaminated groundwater	238-786/ 66-155	
Dzitya, Mexico	Contaminated groundwater	170-514	
Mérida, Mexico	Landfill sites/ Contaminated groundwater	193-4551/ 93-2892	
Tha Muang, Thailand	Contaminated groundwater	18-24	
Mai Hai, Thailand	Contaminated groundwater	9-428	
San Gabriel River and Rio Hondo, USA.	Ponded water in Research Basin geoprobes	358.8	Leenheer J.A., 2001
	1-foot	286.7	
	2-foot	318	
	3-foot	257.6	
Alaskan water supplies	surface and ground water	37-1050	Danial M.W.,2003
Sabak Bernam district	water distributing system	54.64-89.83	Abdullah *et al.*, 2003
Katsura River		51.7-92.9	Yamada *et al.*, 1998
Uji River		45.4-163.2	
Kidza River		95.4-110.1	
Yodo River, Japan		67.9-292.8	

Galatsi Treatment Plant (GTP) of Athens	Coagulation channel to finish water reservoir	15 -82	Spyros K. Golfinopoulos *et al*, 1998
Wastewater treatment plants, Japan	Treated industrial wastewater (domestic, Laundrary/dry cleaning, pickled vegetables, packed meals, pharmaceuticals, bean curd, becerage, dairy, rice wine)	15-211	Galapate et al, 1998