CHAPTER III

METHODOLOGY

3.1 Source of Raw waters

Water samples from Aung-Keaw Reservoir, Mae-Kuang Reservoir, and Mae-Sa River were selected as raw water in this study. These waters were utilized daily as raw water to produce a water supply for distribution to consumers in Chiang Mai province, Thailand. The details of each water source are presented separately in the following sections.

3.1.1 Aung-Keaw Reservoir

Aung-Keaw Reservoir is located in Chiang Mai University, Tumbol Suthep, Amphur Muang, Chiang Mai province, Thailand. The pictorial view of Aung-Keaw Reservoir is depicted in Figure 3.1. Water from Aung-Keaw Reservoir is utilized as the raw water for the Aung-Keaw water supply plant. The Aung-Keaw water supply plant has the capacity to produce the water supply of approximately 500-800 m^3/day. The produced water from Aung-Keaw water supply plant was distributed for drinking, bathing, and household used for all the communities, facilities, offices and dormitories in Chiang Mai University, Chiang Mai province, Thailand.

Figure 3.1: The pictorial view of Aung-Keaw Reservoir

3.1.2 Mae-Kuang Reservoir

Mae-Kuang Reservoir is located near Wangtarn village, Tumbol Loungnueng, Amphur Doisaket, Chiang Mai province, Thailand. The pictorial view of Mae-Kuang Reservoir is illustrated in Figure 3.2. . Water from Mae-Kuang Reservoir was used as the raw water for producing a potable water supply. A capacity of approximately 52,800 m^3/day can be produced from the Mae-Kuang water supply plant. Water from the supply plant was distributed to consumers in Amphur Muang, Chiang Mai province, for drinking, bathing and household activities.

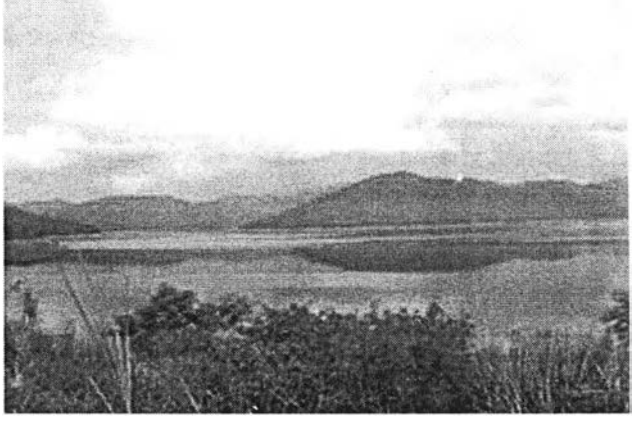

Figure 3.2: The pictorial view of Mae-Kuang Reservoir

3.1.3 Mae-Sa River

Mae-Sa River is located in Pongyak village, Tumbol Mae Ram, Amphur Mae Rim, Chiang Mai province, Thailand. The pictorial view of Mae-Sa River is demonstrated in Figure 3.3. Water from Mae-Sa River is utilized as the raw water for a water supply plant. Produced water from the Mae-Sa River water supply plant is distributed for drinking, bathing, and household use for the communities in Amphur Mae-Rim, Chiang Mai, Thailand.

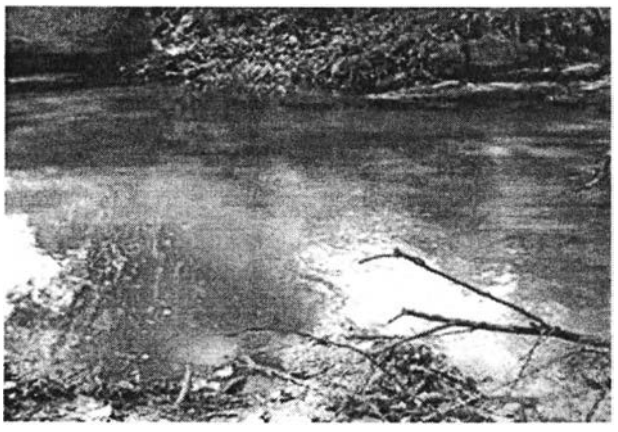

Figure 3.3: The pictorial view of Mae-Sa River

3.2 Sample collection and preservation

Water samples were collected from Aung-Keaw Reservoir, Mae-Kuang Reservoir, and Mae-Sa River in November and December, 2004, and February, 2005, respectively. 100 liters of samples were taken from each selected water source by grab sampling. 10 liters of samples were filtrated through a 0.7 μm glass fiber filter (GF/F) and stored in glass bottles with TFE screw caps. These filtered water samples were utilized to conduct resin fractionation process. 90 litters from each sources were utilized to conduct alum coagulation process. All water samples were kept in a refrigerator at 4°C.

3.3 Experimental procedure

The water samples from each selected sources were utilized to conduct the experiments as depicted in Figure 3.4, and these are described below

Raw waters were analyzed for pH, temperature, alkalinity, turbidity, and TOC. Raw waters were divided into 2 portions. For the first portion, raw waters were filtered through a 0.7 μm GF/F. The filter papers were combusted at 550 °C for 2 hours and used to filtered water sample. Filtered waters were fractionated by resin fractionation process (the resin fractionation process is separately presented in section 3.3.1) to obtain hydrophilic and hydrophobic DOM fractions. Filtered water, hydrophilic and hydrophobic DOM fractions were measured for UV-254, DOC,

SUVA, EEM, and THMFP. Filtered waters were also analyzed for DOC/TOC ratios. All parameters measurement were analyzed by duplicated sample. The results in the first portion represented the DOM and THMFP in raw water with and as well as the component of hydrophilic and hydrophobic DOM and their THMFP.

In the second portion, raw waters were used to conduct the coagulation in jar-test unit in order to determine the optimal condition (the coagulation process is separately presented in section 3.3.2). The coagulated waters at optimal conditions were filtered through a GF/F filter and the same experiment as for filtered waters in the first portion was conducted. The result in the second portion represented the DOM and THMFP in coagulated water with and the component of hydrophilic and hydrophobic DOM and their THMFP in such water.

The obtained results from the first and second portions could be used to represent the reduction of DOM fractions and their THMFP in water sources by alum coagulation.

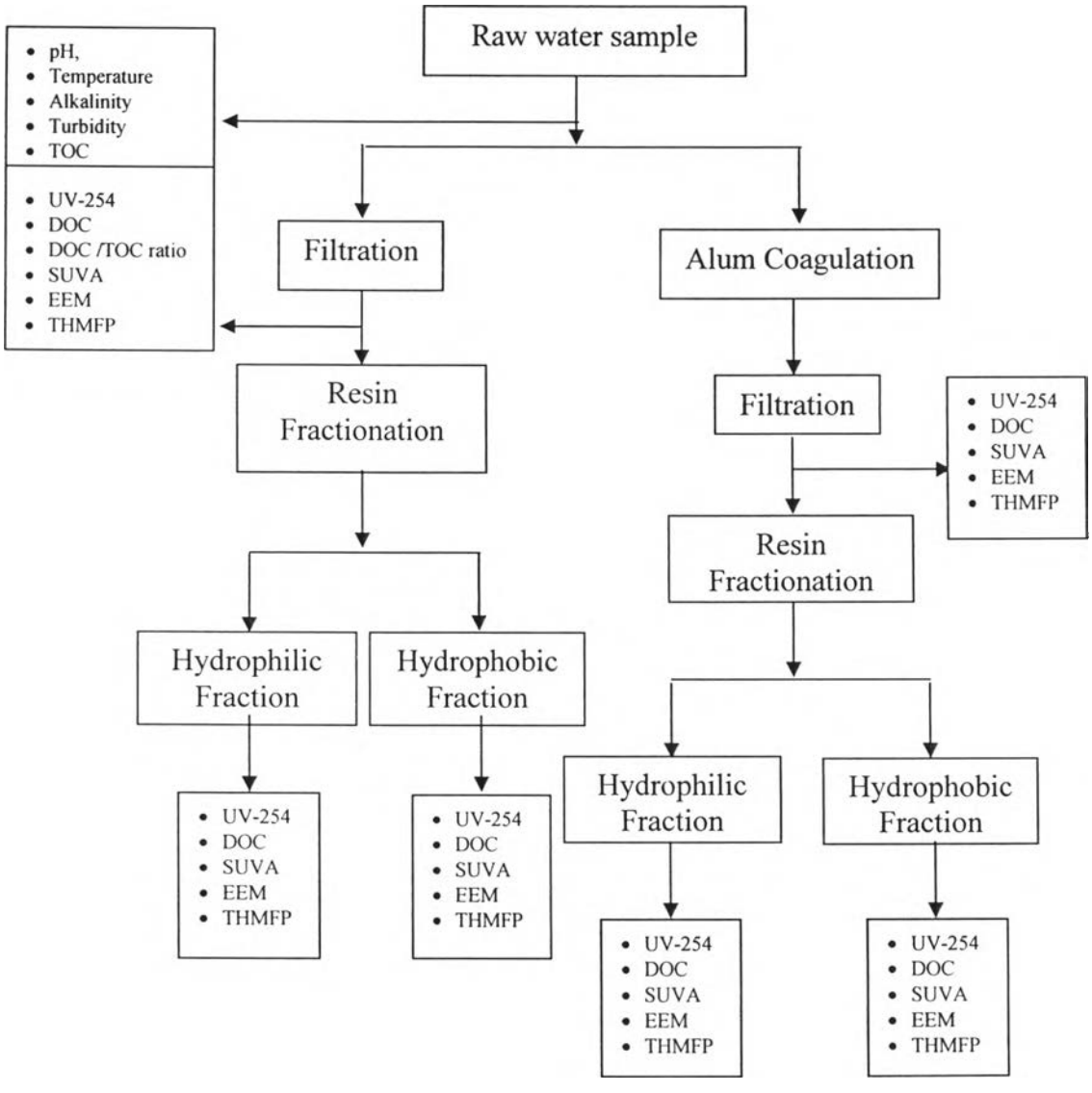

Figure 3.4: Overall diagram of experimental procedure

3.3.1 DOM Fractionation

The DOM fractionation procedure was based on the procedure followed by Thurman and Malcolm (Leenheer, 1981; Thurman and Malcolm, 1981; Marhaba, Pu, and Bengraine, 2003). The preparation of DAX-8 resin and fractionation procedure are described below.

3.3.1.1 Preparation of DAX-8 resin.

The preparation of DAX-8 resin procedure is described as follows

1. The amount of DAX-8 resin, a macroporous methylmethacrylate copolymer, was determined according to the Leenheer (1981) and Marhaba, Pu, and Bengraine (2003) method with the capacity factor of 50 (k'=50) and a porosity of 0.6.

2. The DAX-8 resin was purified with 0.1 N NaOH for 24 hr. Then, the DAX-8 resin was sequentially extracted with acetone and hexane for another 24 hr in a set of soxhlet extraction apparatus.

3. The purified DAX-8 resin was kept in methanol.

4. The DAX-8 resin was taken into a column in a slurry of methanol.

5. The 2.5 bed volume of 0.1 N NaOH and 0.1 N HCl, respectively, was rinsed with the resin in the column and then with milli-Q water until the conductivity and DOC of the effluent water was less than 10 μS/cm and 0.2 mg/L, respectively.

3.3.1.2 Fractionation procedure

The fractionation procedure diagram is illustrated in Figure 3.5.

1. The water sample was filtrated through filter paper pore size 0.7 μm GF/F and divided into 2 portions. The first portion was analyzed for DOC, UV-254, SUVA and THMFP. The second portion was fractionated into hydrophilic and hydrophobic dissolved organic matter fractions.

2. The water sample of the second portion had its pH adjusted to 2 by concentrated H_2SO_4 and was then pumped into the DAX-8 resin column with a flow rate of 12 bed volume/hr or less.

3. The effluence water from the DAX-8 resin column is the so-called hydrophilic DOM fractions whereas the hydrophobic DOM fraction was adsorbed on DAX-8 resin and eluted by base.

4. Before the elution, Milli-Q water was replaced immediately and then discarded.

5. The hydrophobic DOM fraction was eluted with 0.25 bed volume of 0.1 N NaOH and followed by 1.25 bed volume of 0.01 N NaOH at a flow rate 2 bed volume/hr or less.

6. The pHs of the hydrophilic and hydrophobic DOM fractions were adjusted to neutral prior to their being analyzed DOC, UV-254, SUVA and THMFP.

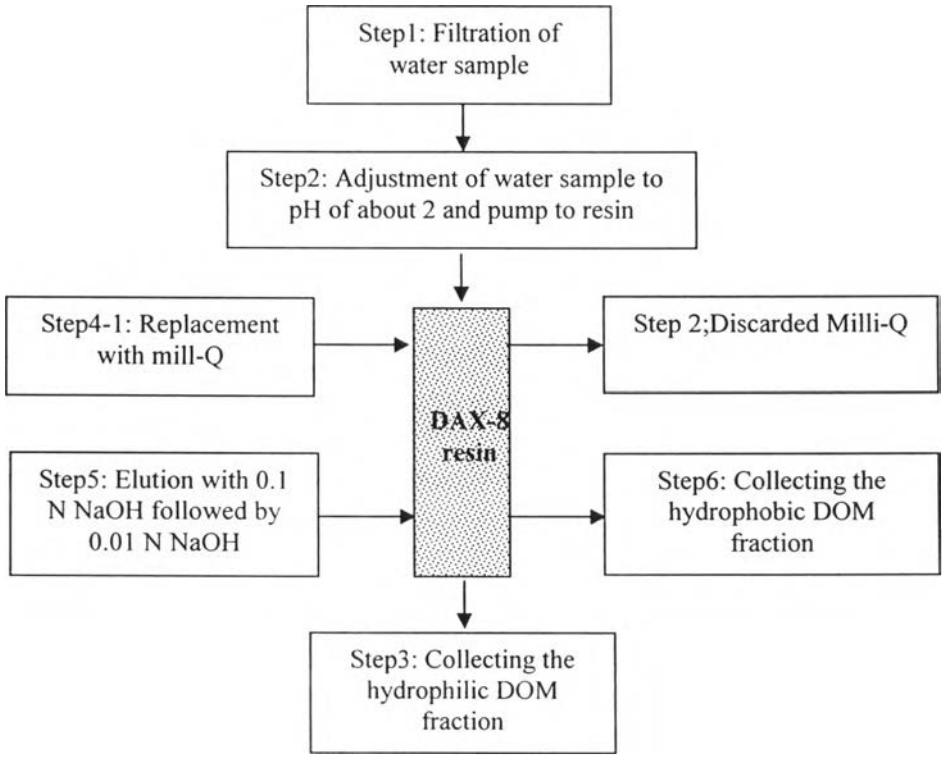

Figure 3.5: Schematic diagram of resin fractionation procedure

3.3.2 Coagulation Experiment

3.3.2.1 Coagulation procedure

The alum coagulation was performed using Jar-test apparatus. In case of low alkalinity, sufficient alkalinity was added to the water sample prior to adding coagulant. Then, the alum coagulation was performed by rapid mixing with the speed of paddle at 100 rpm for 1 minute which started immediately after addition of the coagulant. After this, slow mixing was conducted to form floc with the speed of the paddle fixed at 30 rpm for 30 minute. Then, the floc was allowed to settle for at least 1 hr or more. The supernatant was filtered through a combusted 0.7 μm GF/F filter prior to analysis.

The coagulation condition was carried out under controlled pH values by the addition of H_2SO_4 1.0 N and NaOH 1.0 N and a variation of alum dosage as can be seen in Table 3.1. The optimal condition was chosen as the condition in which greatest removal of DOC, UV-254 and SUVA was achieved and the most cost effectiveness was obtained.

Table 3.1 The coagulation condition

Coagulant	Coagulant dosage (mg/L)	Controlled pH
Alum (Aluminum sulfate)	0, 20, 40, 60, 80 and 100	5.0, 5.5, 6.0, 6.5 and 7.0

Reagent grade aluminum sulfate [$Al_2(SO_4)_3.14H_2O$] was used as a coagulant. The stock solution of 10 g/L of alum was prepared. Sodium carbonate (Na_2CO_3) was used as a sufficiency alkalinity. The stock solution of 10 g/L of sodium carbonate was prepared. According to the chemical reaction to produce floc in alum coagulation, 10 mg/L of alum dosage require 5.05 mg/L as $CaCO_3$ of sodium carbonate.

3.4 Analytical Method and Instrument

3.4.1 pH

The pH of water samples was directly measured by a Horiba pH meter, Model F-21 with an accuracy of ±0.01 pH unit.

3.4.2 Temperature

The temperature of water samples was measured by a Thermometer.

3.4.3 Alkalinity

The alkalinity of water samples was analyzed in accordance with standard method 2320 Alkalinity; section 2320 B, Titration Method.

3.4.4 Turbidity

The turbidity of water samples was directly measured by a HACH 2100, Turbidity Meter.

3.4.5 TOC and DOC

TOC and DOC of water samples were measured in accordance with standard method 5310 Total Organic Carbon (TOC); section 5310 D Wet Oxidation Method by O.I analytical 1010 TOC Analyzer.

3.4.6 UV-254

UV-254 of water samples was measured in accordance with standard method 5910 B Ultraviolet Absorption Method by a Jasco, Model UV-530. The water samples were filtered through 0.7 μm GF/F prior to measurement.

3.4.7 THMFP

According to analyzing THMFP, three analytical methods were used to analyze the water sample. The three analytical methods consist of free chlorine residual test, liquid-liquid extraction and THMs measurement. The detail of these analytical methods is described below.

3.4.7.1 Free Chlorine Residual

Free chlorine residual was measured in accordance with standard method 4500 Cl G. DPD Colorimetric Method. According to THMFP analysis, the free chlorine residual of water samples must be in the range of 3 to 5 mg/L.

3.4.7.2 Liquid-Liquid Extraction

THMs in water samples were extracted in accordance with standard method 6232 B. Liquid-Liquid Extraction Gas Chromatography Method.

3.4.7.2 Gas Chromatography

THMs were measured in accordance with standard method 5710, Formation of Trihalomethanes and Other Disinfection By-Product by Agilent 6890 Series Gas Chromatographic with ECD detector under the following condition:

Inlet condition

Mode: Split, Initial temp: 225 °C, Pressure: 31.33 psi, Split ratio: 10:1, Split flow 15.9 mL/min, Gas Type: Helium and Total flow: 20.5 mL/min.

Oven condition

The temperature programs of oven adjusted for analyzing THMs are shown in Table 3.2.

Table 3.2 Temperature programs for analyzing THMs.

Ramp	Rate (°C/min)	Final temperature (°C)	Holding time of final temperature (min)
1	15	100	1.00*
2	15	130	1.00
3	15	180	1.00

*Initial temperature: 75 °C, Initial temperature holding time: 1.00 min.

Detector Condition

Temperature: 300 °C, Mode: Constant make up flow, Makeup flow: 60 mL/min, Makeup Gas Type: Nitrogen.

3.4.8 Excitation-Emission Matrix (EEM)

EEM spectra were directly measured by fluorescence spectrometry using scanning the wavelength of both excitation and emission of fluorescent intensity. Fluorescent intensities were measured at every 5 nm increment of wavelength from 220 to 600 nm for both excitation and emission. All slit widths were set to 5 nm. EEM spectra were blank subtracted (to remove Raman scattering peak) and converted to quinine sulfate unit (QSU). The calibration curve was regularly established using 5 points of quinine sulfate in 0.1 M H_2SO_4, where 10 QSU is equivalent to the fluorescence spectra of 10 μg/L quinine sulfate solution at 450 nm with an excitation wavelength of 345 nm (Kasuga, Nakajima, and Furumai, ,2003).

The summary of parameters, analytical methods, standard, and instruments are presented in Table 3.3.

Table 3.3: Analytical methods, standards, and Instruments.

Parameter	Analytical Method	Standard	Analytical Instruments
pH	Direct Measurement	-	Horiba pH-meter, Model F-21
Temperature	Direct Measurement	-	-
Turbidity	Direct Measurement	-	HACH, 2100 Turbidity Meter
Alkalinity	Titration Method	Standard method 2320 B*	-
UV-254	Ultraviolet Absorption	Standard method 5910 B*	Jasco, Model UV-530, UV/VIS spectrometer.
TOC	Wet Oxidation Method	Standard method 5310 D*	O.I. analytical 1010 TOC analyzer
DOC	Wet Oxidation Method	Standard method 5310 D*	O.I. analytical 1010 TOC analyzer
Free chlorine residual	Colorimetric Method	Standard method 4500-Cl G*	Jasco, Model UV-530, UV/VIS spectrometer.
THMFP	Formation of Trihalomethane and Other Disinfection By-Products and Liquid-Liquid Extraction Gas Chromatography Method.	Standard method 5710 and 6232 B*	Agilent 6890 Series Gas Chromatography with ECD detector

(* APHA, AWWA, and WPCF, 1995)