สำนักงานวิทยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย

CHAPTER III

METHODOLOGY

3.1 Study area: Bangkhen Water Treatment Plant

Bangkhen Water Treatment Plant (WTP) was selected in this study as it is the main water supply facility with a design capacity of 3,1000,000 m^3/d potable water production delivered to more than a million people in Bangkok. This facility receives water mainly from Chao Phaya River. Major unit operations include pre-chlorination, coagulation, flocculation, sedimentation, filtration, and disinfection.

3.2 Sample collection

Water samples were collected at the common intake at the Bangkhen WTP. A total of seven water samples were collected on Mar 23, May 13, May 30, Jun 21, Jul 27, Aug 5, 2003 and Sep 1, 2004. All samples were filtrated by sequence with three filter paper types; Whatman#40, GF/C, and 0.45-μm-cellulose membrane, respectively, to remove fine particles and stored in a 4°C container in the dark to minimize interferences from the environment. During the first five sampling dates (Mar 23, May 13, May 30, Jun 21, Jul 27, 2003) only 6 liters of sample was fractionated to observe the variation of organic species. Approximately 50 liters from the sampling date of Aug 5, 2003 was fractionated, and determined for its formation potential of HAAs. The corresponding functional groups for each organic fraction both before and after the chlorination were determined with Fourier Transform InfraRed. The sample from the last sampling date (Sep 1, 2004) was also examined for its HAAFP. This was to validate the predictive capability of the empirical model for the estimate of HAAs from this water source. It is noted that Milli-Q water (ELGA, Ultra Analytical) was used for all dilutions, sample preparation, and final glassware cleansing in this work.

3.3 Parameter measurement

Basic physico-chemical parameters, i.e. pH, turbidity, and alkalinity were measured according to the methods as indicated in Table 3-1.

3.4 Fractionation

The fractionation of DOC was performed through the adsorption using three types of resin adsorbent, i.e. DAX-8 (SUPELCO), AG-MP-50 (BIO-RAD), and WA-10 (SUPELCO), according to Marhaba *et al.* (2003). DAX-8 resin was initially employed to fractionate the hydrophobic fractions where the fractionation at neutral pH resulted in the separation of hydrophobic neutral (HPON) components, at high pH (approx. 10) the separation of hydrophobic base (HPOB) components, and at low pH (approx. 2) the hydrophobic acid (HPOA) components. AG-MP-50 cationic resin was then used to separate hydrophilic base (HPIB) components, and WA-10 weak anionic resin was finally applied to fractionate hydrophilic acid (HPIA) and hydrophilic neutral (HPIN) components. The fractionation method is shown in Figure 3-1 and described below.

3.4.1 Resin preparation

3.4.1.1 DAX-8

1) Soak the resin with 0.1 N NaOH for 24 h.
2) Rinse the resin with Milli-Q water to remove NaOH.
3) Purify the resin by sequential soxhlet extraction with acetone and hexane for 24 h.
4) Rinse the resin with methanol until the effluent was free of hexane.
5) Pack the resin into the column with glass wool packed at a bottom as a support, and rinse with more than 2.5 bed volume (BV) of 0.1 N NaOH, followed with 0.1 N HCl and Mill-Q water, respectively, until DOC and conductivity of the effluent are less than 0.1 mg/L and 10 μs/cm, respectively.

3.4.1.2 AG-MP-50

1) Purify the resin by soxhlet extraction with methanol for 24 h.
2) Pack the resin into the column, with glass wool packed at a bottom as a support, and rinse with more than 2 BV of 1 N NaOH, followed by more than 2 BV of 2 N HCl, and Mill-Q water, respectively, until DOC and conductivity of the effluent are less than 0.1 mg/L and 10 μs/cm, respectively.

3.4.1.3 WA-10

1) Soak the resin with methanol for 24 h.
2) Pack the resin into the column, with glass wool packed at a bottom as a support, and rinse with more than 1 BV of 1 N HCl, followed by more than 2.5 BV of 1 N NaOH, and Mill-Q water, respectively, until DOC and conductivity of the effluent are less than 0.1 mg/L and 10 μs/cm, respectively.

Note that glass wool used in this investigation was purified by soxhlet extraction with methanol for 24 h prior to packing into the column.

3.4.2 Fractionation procedure

3.4.2.1 Hydrophobic neutral (HPON)

1) Adjust the water sample to pH 7±2 with H_2SO_4 or/and NaOH and pump the sample through the first DAX-8 column with a flow rate of less than 12 BV/h.
2) Displace quickly with 1 BV of Milli-Q water.
3) Turn the column up side down and the resin is air-retrieved, stored, and dried in a descicator.
4) Extract HPON fraction with methanol by rotary vacuum evaporator approx. 20 minutes at 5 bar, 60°C.

3.4.2.2 Hydrophobic base (HPOB)

1) Adjust the sample to pH 10 with NaOH and pump the sample through the second DAX-8 column with a flow rate less than 12 BV/h.
2) Displace quickly with 1 BV of Milli-Q water.

3) Elute HPOB fraction with 0.25 BV of 0.1 N HCl followed by 1.5 BV of 0.01 N HCl at a flow rate of less than 2 BV/h.

3.4.2.3 Hydrophobic acid (HPOA)

1) Acidify the sample to pH 2 with H_2SO_4 and pump the sample through the third DAX-8 column with a flow rate of less than 12 BV/h.
2) Displace quickly with 1 BV of Milli-Q water.
3) Elute HPOA fraction with 0.25 BV of 0.1N NaOH, followed by 1.25 BV of 0.01 N HCl at a flow rate of less than 2 BV/h.

3.4.2.4 Hydrophilic base (HPIB)

1) Pump the water sample through the fourth column containing AG-MP-50 resin with a flow rate of less than 5 BV/h.
2) Displace quickly with 1 BV of Milli-Q water.
3) Elute for the HPIB fraction with more than 1 BV of 1 N NaOH at a flow rate of less than 2 BV/h.

3.4.2.5 Hydrophilic acid (HPIA)

1) Pump the water sample through the fifth column containing WA-10 resin with a flow rate less than 8 BV/h.
2) Displace quickly with 1 BV of Milli-Q water.
3) Elute the HPIA fraction with 1.5 BV of 0.1 N NaOH followed by 1 BV of 0.01 N HCl at a flow rate of less than 4 BV/h.

Note that the ratios between the resin volume and the water sample were 15mL:1L, 4mL:1L, and 85mL:1L for DAX-8, AG-MP-50, and WA-10, respectively.

3.5 Dissolved organic carbon measurement

Dissolved organic carbon (DOC) in samples was measured with a TOC analyzer (model 1010 O.I. Corp.) with an autosampler (model 1051), persulfate-ultraviolet oxidation. Potassium hydrogen phthalate (KHP) (CARLO ERBA brand) solutions at 0, 1, 2.5, 5, and 10 mg/L were used as standard solutions. The two reagents, i.e. phosphoric acid and sodium persulfate, were used as an acid and an

oxidant, respectively. These standard chemicals were recommended to be re-prepared every other week. Each sample was diluted and prepared properly prior to analyze. The programs were appropriately set following the recommendation from manufacturer. The pH of all fractionated samples was adjusted to 7 prior to the TOC measurements. At least three replications of each measurement were carried out, and more replications were performed in the cases where the variation between each measurement exceeded 5%.

3.6 Ultraviolet absorbance

UV absorbance was measured with spectrophotometer (Helios Alpha, Beta) at a wavelength of 254 nm using a quartz cell. This was to investigate the relationship between the adsorbent and the quantity of organic matters in the water sample as a rough indication of overall DOC concentration. All samples were adjusted to pH 7 prior to measurement. Milli-Q water was used as a blank sample.

3.7 Disinfection by-product formation potential (DBPFP)

A 7-day chlorination DBPFP test was carried out in accordance with the Standard Method 5710B. Chlorine solution was prepared in a form of concentrated sodium hypochlorite (100 mgCl/L). The chlorine dosage for each water sample was determined such that a final residual chlorine concentration of 3-5 mg/L was remained in the sample after the 7 days test. All samples were adjusted to a pH 7±0.2 using H_2SO_4 and NaOH. The neutralized solution was then buffered with a phosphate solution prior to the incubation at 25±2°C in amber bottles for 7 days. At the end of the incubation, samples were dechlorinated using sodium sulfite (Na_2SO_3) as the sole dechlorinating agent as recommended by the EPA 552.2 method. The samples were then evaluated for their HAAs (see Section 3.7). The difference between concentrations of HAAs before and after the chlorination was taken as DBPFP, or in this case, HAAFP.

3.8 Haloacetic acids (HAAs)

Five species of HAAs, i.e. monochloroacetic acid (MCAA), dichloroacetic acid (DCAA), trichloroacetic acid (TCAA), monobromoacetic acid (MBAA), and dibromoacetic acid (DBAA), were analyzed in accordance with the EPA method 552.2. Methyl-tert-butyl-ether (MtBE) was used as an only extracting solvent in this method. All extracts were analyzed within 24 hours of the completion of the liquid-liquid extraction (LLE) procedure (see the EPA 552.2 method). HAAs analyses were conducted using the 6890N Gas Chromatograph (Agilent Technologies) equipped with two fused silica columns (DB-XLB, 0.32mm x 30m), a micro electron capture detector (μECD), and an autosampler (Agilent Technologies 7683 Series). The operating conditions of Gas Chromatography are as follows:

3.8.1 Inlet condition

Mode: Splitless,

Initial temp: 250°C

Pressure: 12.65 psi

Purge flow: 20 mL/min

Purge time: 0.50 min

Total flow: 25.9 mL/min

Gas Type: Helium

3.8.2 Oven condition

Initial temp: 40°C

Initial time: 0.50 min

Ramps#1: Rate 15°C/min, Final temp 200°C, Final time 2 min

Ramps#2: Rate 20°C/min, Final temp 300°C, Final time 5 min

Run time: 23.17 min

3.8.3 Detector condition

Temperature: 350°C

Mode: Constant column + make up flow

Combined flow: 30 mL/min

Makeup gas type: Nitrogen

I 3224055X

The internal standard was 1,2,3-trichloropropane (Supelco) and the surrogate standard was 2,3-dibromopropionic acid (Supelco). At the beginning of each analytical run, solvent blanks and solvent samples containing the internal standard were injected to condition the GC and to verify that interferences were insignificant. Other quality assurance/quality control (QA/QC) procedures, such as preservation techniques, detection limits, internal standards, surrogate standards, and matrix spikes, were taken through the analysis.

3.9 Functional groups

FTIR spectrometry is used to determine the functional chemistries of unknown materials. DOCs of the organic isolates both before and after the 7-day reaction period were freeze-dried and kept in a desiccator over silica gel prior to the FTIR analysis by Perkin Elmer 1760X. Infrared spectra were obtained using 2 to 4 mg of filtrated sampling isolates in 150 mg of potassium bromide pellets. FTIR was set to scan from 4,000 to 400 cm^{-1}, averaging 8 scans at 1.0 cm^{-1} interval. All spectra were normalized after acquisition to a maximum absorbance of 1.0 for comparative purposes. FTIR libraries were referenced from (Pavia *et al.*, 1979 and Fiveash Data Management, Inc. 2003).

3.10 Statistical analysis

The experimental data were statistically evaluated to determine a suitable mathematical form of the formation of HAAs using the commercial available SPSS (Statistical package for social sciences) program version 11 and Microsoft Excel version 2002 (XP).

3.11 Quality control

QA/QC plans were set for all steps of the experiments to obtain accurate and reliable results. The QA/QC measure includes the following area.

1) All chemicals in this work were analytical grade.

2) The entire stock of glassware was of high quality grade. Every piece was neatly cleaned with a particular washing liquid for laboratory purposes, and was rinsed with Milli-Q water, and heated at 105°C for more than 2 hours before use.
3) TFE-screw cap with amber glass bottles were used to store samples for HAAFP.
4) The instruments were regularly calibrated step by step as noted in instrument guideline: this applies to all measurement including pH, conductivity, turbidity, UV spectroscopy etc.
5) During the fractionation process, resins and glass wool were cleaned and purified by soxhlet extraction as described in the approved research paper of Leenheer 1979 and Leenheer 1981.
6) 1,2,3-trichloropropane (internal standard) and 2,3-dibromopropionic acid (surrogate standard) were used in accordance with the QA/QC mentioned in the EPA method (AWWA).

Table 3-1 Analytical methods and instruments

Parameter	Analytical method	Method	Analytical instrument
pH			pH meter
Turbidity			Turbidity meter
Temperature			pH meter
Conductivity			Conductivity meter
Alkalinity	Titration method	Standard method 2320B	
DOC/TOC	Persulfate-ultraviolet oxidation method	Standard method 5310C	O.I. analytical 1010 TOC Analyzer
Free chlorine residual	Colorimetric method	Standard method 4500-Cl G	Perkin-Elmer Model Lambda 25, UV/VIS spectrometer
HAAs	Formation of haloacetic acids and other disinfection by-products and liquid-liquid extraction gas chromatography method	Standard method 5710B and EPA method 552.2	Agilent 6890 Series, Gas Chromatography with μECD detector
Functional groups	-	-	Perkin Elmer 1760X, Fourier Transform InfraRed (FTIR)

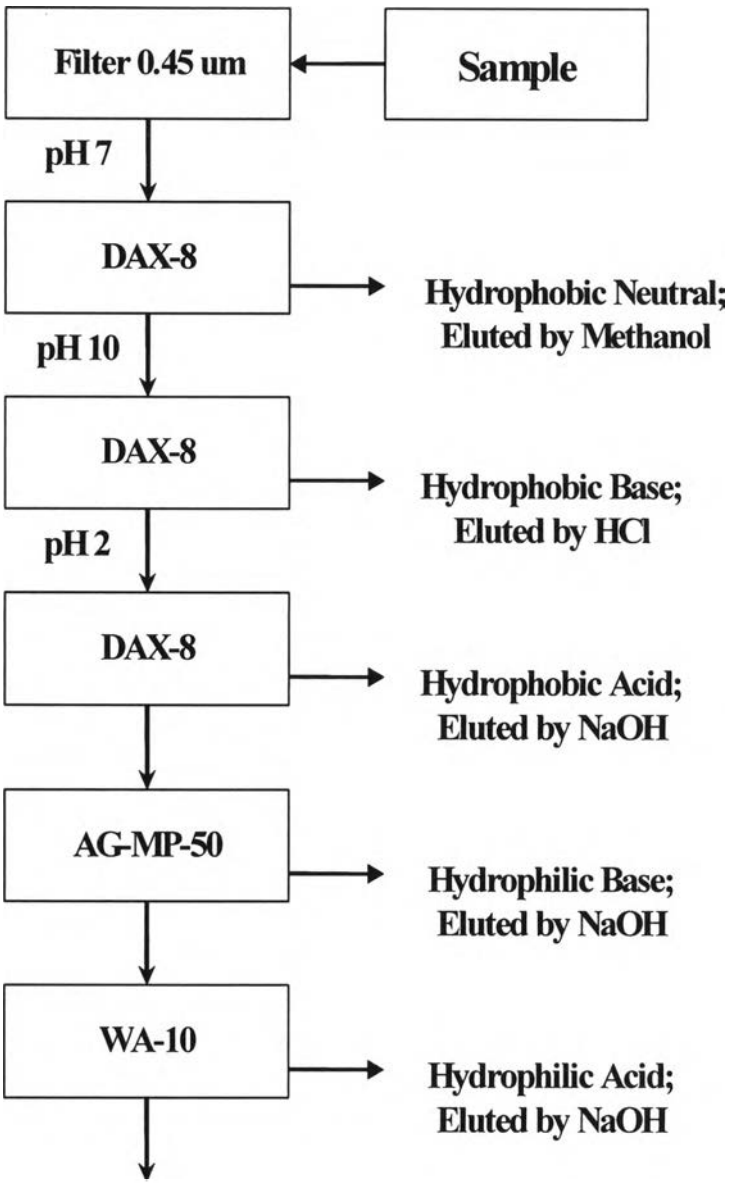

Figure 3-1 Fractionation method