CHAPTER 2

EXPERIMENT

2.1 Sampling site description and sample collection

2.1.1 Sampling site description

A pickling food factory in Hang Dong district of Chiang Mai province (Figure 2.1) was selected as study site. Eight sampling sites were selected inside and outside factory as shown in the diagram below (Figure 2.2). The pictures of site are shown in Appendix 2. The first site is water supply pond using as control site. The second site is the sediment pond. The wastewater from the processing unit is stored in this pond for slight treatment by evaporation and aeration. It's equipped with an aeration system. Then, the water is flowed to the second sediment pond also the third sampling point and to the discharged place to the small channel (site 4). The fifth site selected is the junction of the small channel to the big channel along the road. Site 6, 7 and 8 were selected along the road (following the water flow) with the different distances to the discharged place (site 5) of 50 m, 100 m and 200 m, respectively. It should be noticed that the flow was not continuous among the sampling times. This flow was changed may be by rain water and wind. Therefore, the water could be running water this time, but became standing water in another time. The water became less in near the end of the road and e.g. in dry season, there was no water in site 8. All of the remarks above should be paid attention to explain the achieved monitoring data.

Figure 2.1 The study site

Table 2.1 Summary of sites description

Site	Description	Remark
1	Supplied water pond	Control site
2	First sediment pond	Aeration system
3	Second sediment pond	
4	Discharged place to small channel	
5	Discharged place to road channel	
6	50 m far from site 5	
7	100 m far from site 5	
8	200 m far from site 5	

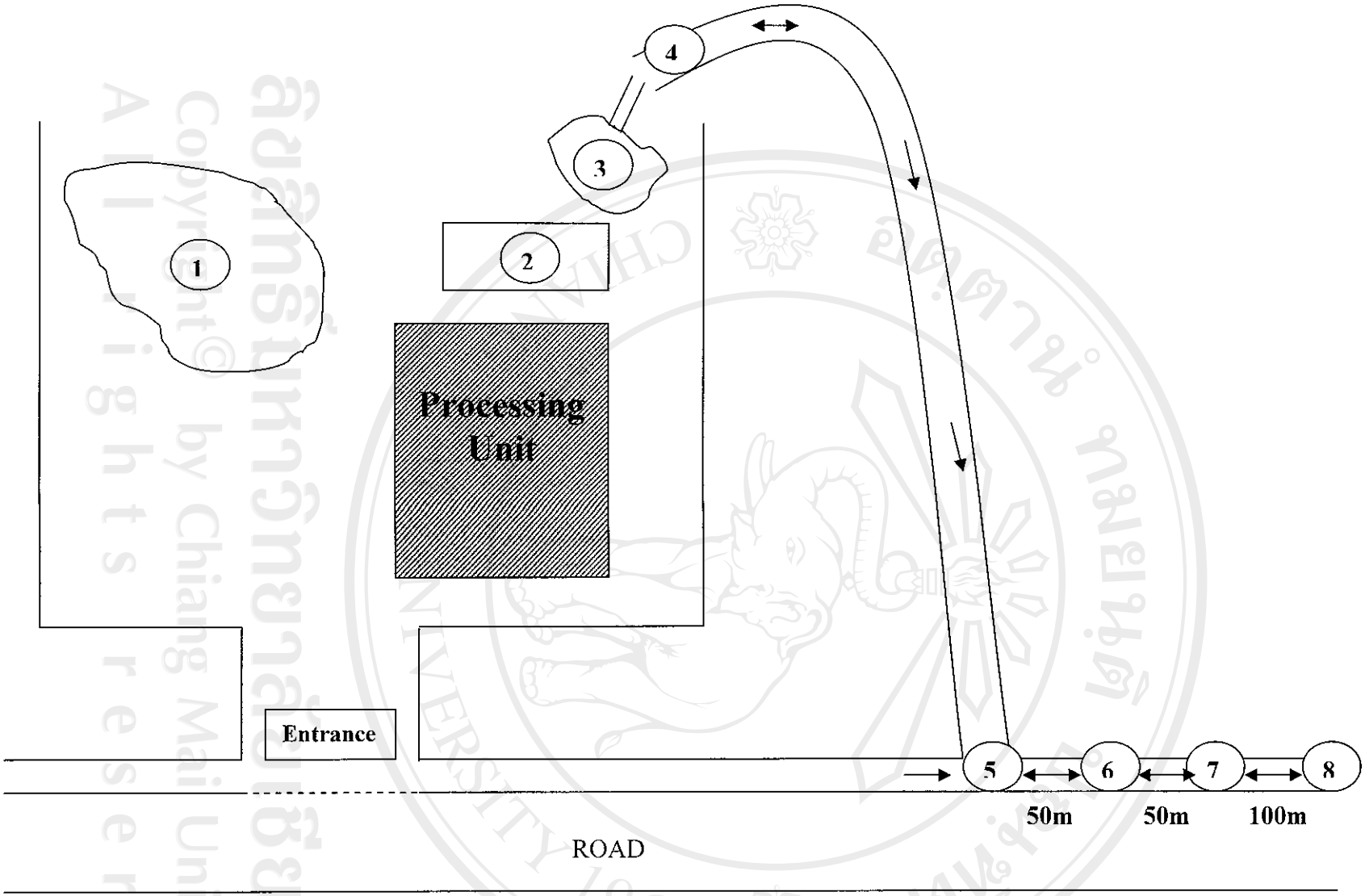

Figure 2.2 Diagram of sampling sites

2.1.2 Sample collection

The duration of monitoring period is 1 year with 4 sampling times divided into 2 times in rainy season (August, September/2003) and 2 times in dry season (December/2003 and January/2004). The parameters to be analyzed including: chloride, pH, conductivity, temperature, dissolved oxygen (DO) and total dissolved solids (TDS). All water samples were collected in pre-cleaned polyethylene bottles and preserved in ice box during the trip and in refrigerator at lab, except DO samples were collected in glass BOD bottles (300 ml). For chloride samples preservation, the suggested condition is at 4°C with maximum permissible storage time of 7 days (Bartram and Ballance, 1996). The summary of sample collection and using methods are as follows:

Table 2.2 Summary of sample collection and using methods

Parameter	Method	Replication	ml of sample	Instrument	Remark
pH	Electrode	2	-	pH meter	on field
Temp. (°C)	Electrode	2	-	pH meter	on field
DO (mg/l)	Winkler titration	3	300	DO kit	on field
Conductivity (mS/cm)	Electrode	2	-	Conductivity meter	on field
TDS (mg/l)	Electrode	2	-	Conductivity meter	on field
Chloride (mg/l; M)	Titration & SIA	3	-	Burette, SIA system	at laboratory

Field sampling and measurement procedures were followed those specified according to Bartram and Ballance (1996) for temperature, pH, conductivity, dissolved oxygen (see Appendix 3) and total dissolved solids. All meters were pre-calibrated according to manufacturers' instruction manual.

2.2 Instruments, chemicals and apparatus

2.2.1 Instruments

(1) SIA system analyzer comprises the following elements:

- Personal computer (PC) with software package (Labview, National Instruments Corporation, USA) for the system control;
- Syringe pump 665 Dosimat (Metrohm, Switzerland)
- Selection valve, 10 ports;
- Holding coil, tygon tubing I.D. 1.6 mm, long 460 cm;
- Interface card (National Instruments Corporation, USA)
- Ag/AgCl electrodes (laboratory made).

(2) Titration method instruments including:

- Burette 50 ml;
- Flask 250 ml.

(3) pH meter (WTW model 320, Germany) for measuring pH and temperature of water.

(4) Conductivity meter (ORION model 115, USA) for measuring conductivity, TDS of water.

(5) Dissolved Oxygen (DO) kit including:

- BOD glass bottles with 300 ml capacity;
- Pipettes 10 ml;
- Graduated cylinder 100 ml;
- Flask 250 ml.

2.2.2 Chemicals

(1) Sodium chloride, analytical grade, Carlo Erba, Italy

(2) Potassium nitrate, analytical grade, MERCK, Germany

(3) Potassium chromate, laboratory grade, M&B, England

(4) Silver nitrate, analytical grade, MERCK, Germany

(5) Ferrous chloride, AR grade, MERCK, Germany

(6) Manganese sulfate, analytical grade, MERCK, Germany

(7) Sodium hydroxide, GR grade, MERCK, Germany

(8) Sodium iodide, analytical grade, Carlo Erba, Italy

(9) Sulfuric acid, 95 – 97% (w/w), GR Grade, MERCK, Germany

(10) Sodium thiosulphate, Fluka, Switzerland

(11) Milli-Q water

2.2.3 Apparatus

The set-up of the SIA system recently developed by the Chiang Mai FBA research group is shown in the below Figure 2.3.

Figure 2.3 The SIA system for chloride determination

2.3 Preparation of solutions

2.3.1 Preparation of reagents for SIA method

a. Stock standard solution of 0.5 M chloride, 100 ml

The solution was prepared by dissolving 2.925 g of sodium chloride in Milli-Q water in 100 ml volumetric flask.

The working standard solution series were prepared by diluting the stock solution.

b. Solution of 0.01 M KNO_3

The solution was prepared by dissolving 0.101 g of potassium nitrate in Milli-Q water in 100 ml volumetric flask.

c. Reference electrode solution of 0.1 M chloride in 0.01 M KNO_3, 25 ml

The solution was prepared by dissolving 0.146g of sodium chloride in 0.01 M KNO_3 and made up to 25 ml in volumetric flask.

d. Reference electrode solution of 300 ppm chloride in 0.01 M KNO_3, 25 ml

The solution was prepared by dissolving 0.012 g of sodium chloride in 0.01 M KNO_3 and made up to 25 ml in volumetric flask.

2.3.2 Preparation of reagents for Argentometric method

a. Solution of 0.0141 M $AgNO_3$, 500 ml

The solution was prepared by dissolving 824 mg of $AgNO_3$ in deionized water in 1,000 ml volumetric flask.

b. Potassium chromate indicator

The solution was prepared by dissolving 5 g of K_2CrO_4 to 100 ml of deionized water, then added drop by drop of $AgNO_3$ solution to produce a slightly red precipitate of Ag_2CrO_4 and filtered.

2.3.3 Preparation of reagents for dissolved oxygen analysis

a. Manganous sulphate solution, 250 ml

The solution was prepared by dissolving 45.5 g of $MnSO_4.H_2O$ in deionized water in 250 ml volumetric flask.

b. Alkali-iodide-azide reagent, 250 ml

Dissolved 5 g NaN_3 in 250 ml deionized water. Added 240 g NaOH and 375 g NaI, stirred until dissolved.

c. Starch solution

Dissolved 2 g soluble starch and 0.2 g salicylic acid, as a preservative, in 100 ml hot deionized water.

d. Standard sodium thiosulphate titrant

Dissolved 6.205 g of $Na_2S_2O_3.5H_2O$ in deionized water. Added 1.5 ml 6 M NaOH or 0.4 g solid NaOH and diluted to 1,000 ml.

2.4 Determination of chloride by sequential injection potentiometric method

2.4.1 Schematic diagram

The schematic diagram of the SIA system is shown in Figure 2.4. The instruments used were described in 2.2.1.

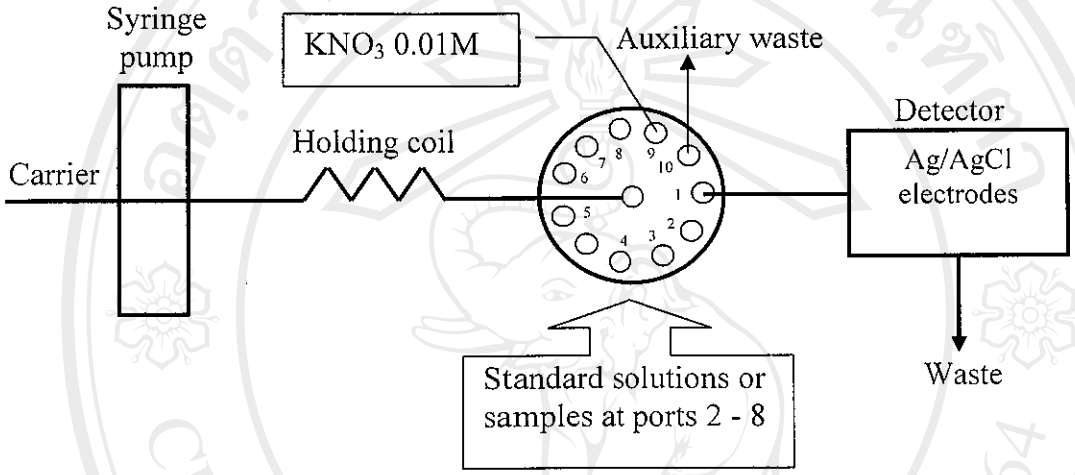

Figure 2.4 A schematic diagram of the SIA system for chloride determination

2.4.2 Procedure

Before using, chloride-selective electrode was prepared by surface oxidation of silver metal in 0.5M iron (III) chloride solution. This preparation is simpler and more efficient than the conventional anodic oxidation.

The software program used is an in-house developed by the Chiang Mai FBA research group using Labview (Laboratory Vitual Instrument Engineering Workbench, National Instruments, USA).

The measurement was repeated with 3 replications for each sample. The results were recorded in the data files, which could be used to plot and calculate by using Microsoft Excel program.

2.5 Determination of chloride by Argentometric method

Procedure

1. Samples were diluted to appropriate concentration.
2. Added 1 – 3 drops of K_2CrO_4 indicator into flask.
3. Titrate with 0.0141 M $AgNO_3$ until occurring of red precipitate, the colour of solution turns to pinkish orange.
4. Record the titration volume and calculate the chloride concentration as follows:

$$mg\ Cl/l = \frac{(A-B)\times M\times 35{,}450}{ml\ sample}$$

Where: A: ml titration for sample,

B: ml titration for blank, and

M: normality of $AgNO_3$

(APHA, AWWA, WPCF, 1985).

2.6 Data analysis

The data from the supporting data set (on field parameters) and chloride results were used for assess the general water quality in terms of salinity. The chloride results got from 2 methods were used to test the difference for comparison between 2 methods by t-test. The correlations among parameters; chloride, TDS and conductivity; chloride, DO and temperature; were tested by Mann-Whitney U test. The seasonal variation of chloride concentration among 4 sampling times was tested by repeated measures analyses of variance. The one-way ANOVA (analysis of variance) analysis (LSD test) was used to compare the chloride contents among the sites to check the statistical significant difference

(control site vs other sites), therefore it could be concluded whether the waters were contaminated by chloride (McBean and Rovers, 1998). All of the tests above were analyzed by statistical program SPSS (Statistics Package for Social Science) version 10.