CHAPTER 3

RESULTS AND DISCUSSION

3.1 Supporting data set

The supporting data set includes: pH, temperature (^{o}C), conductivity (mS/cm), total dissolved solids TDS (mg/l) and dissolved oxygen DO (mg/l). All of these data were measured on field through four monitoring times and shown in the Tables 3.1, 3.2, 3.3, 3.4.

Table 3.1 Supporting data - sampling date 7 August, 2003 (Rainy season) -- the 1st time

Site	Temp. (^{o}C)	Cond. (mS/cm)	TDS (mg/l)	pH	DO (mg/l)	Time	Remarks
1	30.2	0.91	440	6.84	4.2	10:00	
2	29.9	7.82	4,240	7.10	12.2	10:15	Aeration process
3	29.8	8.08	4,390	7.17	5.0	10:30	
4	29.6	8.22	4,470	7.05	2.1	10:45	standing water
5	29.6	3.39	1,720	7.16	2.7	11:05	
6	30.3	5.22	2,730	7.31	14.4	11:30	high flow rate
7	28.7	7.50	4,020	7.18	2.9	11:45	
8	31.9	7.78	4,200	7.92	15.0	12:00	high flow rate

General observation: It should be noticed that the aeration system was working in first sediment pond (site 2) during the sampling time, thus, the DO data was affected with very high value even to the third site. From the site 4 to site 8, the flow was un-continuous (standing or running water), so it also influenced on the DO value.

Table 3.2 Supporting data - sampling date 16 September, 2003 (Rainy season) – the 2nd time

Site	Temp. (°C)	Cond. (mS/cm)	TDS (mg/l)	pH	DO (mg/l)	Time	Remarks
1	29.2	0.29	141	5.96	2.6	9:05	
2	28.2	7.55	4,050	5.93	1.2	9:15	Aeration system not worked
3	29.1	7.48	4,070	6.16	2.6	9:25	
4	31.0	7.28	3,890	6.03	3.3	9:35	
5	31.0	4.05	2,070	6.19	0.9	9:50	
6	31.3	2.78	1,370	6.19	0	10:20	standing water
7	29.0	3.52	1,800	6.38	1.4	10:35	
8	33.0	2.84	1,420	6.21	1.8	10:50	

General observation: For this sampling time, it was heavy rain all last week, therefore, the data were better due to the dilution of rainwater. The aeration system in site 2 did not work for this time, so the DO value was so low (only 1.2

mg/l). Site 6 was seemed to be standing water with densely covering vegetation, thus, the DO value was 0.

Table 3.3 Supporting data - sampling date 2 December, 2003 (Dry season) – the 3rd time

Site	Temp. (°C)	Cond. (mS/cm)	TDS (mg/l)	pH	DO (mg/l)	Time	Remarks
1	24.7	0.30	141	7.63	6.1	9:05	
2	24.3	8.65	4,710	7.69	7.1	9:20	Aeration process
3	24.5	9.21	5,060	7.65	6.4	9:30	
4	24.3	9.24	5,050	7.79	7.2	9:35	Running water
5	24.1	9.31	5,080	7.58	2.8	10:00	
6	23.3	9.40	5,160	7.54	2.4	10:15	
7	23.3	9.45	5,180	7.59	3.8	10:30	
8	- Dry channel -						

General observation: The supporting data for this time were seemed to be worse due to the dry season, the water in the channel along the road was less (site 5, 6, 7 and site 8 no water). The conductivity and TDS data were higher than two rainy-season sampling times. It was expected that the chloride content were also higher.

Table 3.4 Supporting data - sampling date 6 January, 2004 (Dry season) – the 4th time

Site	Temp. (°C)	Cond. (mS/cm)	TDS (mg/l)	pH	DO (mg/l)	Time	Remarks
1	21.8	0.21	101	6.85	6.4	9:04	
2	22.1	11.89	6,650	6.57	7.3	9:14	Aeration process
3	22.2	10.72	5,950	6.42	4.2	9:25	
4	22.2	10.89	6,040	6.38	6.0	9:34	Running water
5	21.8	10.94	6,070	6.26	5.1	9:50	
6	20.6	10.55	5,810	6.37	2.2	10:00	Vegetation densely covering
7	22.0	9.69	5,340	6.25	3.0	10:10	
8	- Dry channel -						

General observation: The climatic condition for this sampling time was cooler with the lower in water temperature. With the long of dry period, the water was less with more high in conductivity and TDS. Hence, it was expected that the chloride contents were also higher. The DO values were still fluctuated due to the unstable of water stream. There was no water in site 8 liked in 3rd sampling time.

3.1.1 Water temperature

The average of water temperature during four sampling times of 8 sampling sites is shown in Figure 3.1. The result can be clearly divided into 2 ranges of seasonal variation. The first group was rainy-season sampling times (1

& 2) with the higher water temperature variation of 28.2 – 33°C. And the second group was dry-season sampling times (3 & 4) with the lower water temperature variation of 21.8 – 24.7°C. Figure 3.1 shows the average temperature variation of sampling sites with not much difference among eight sites.
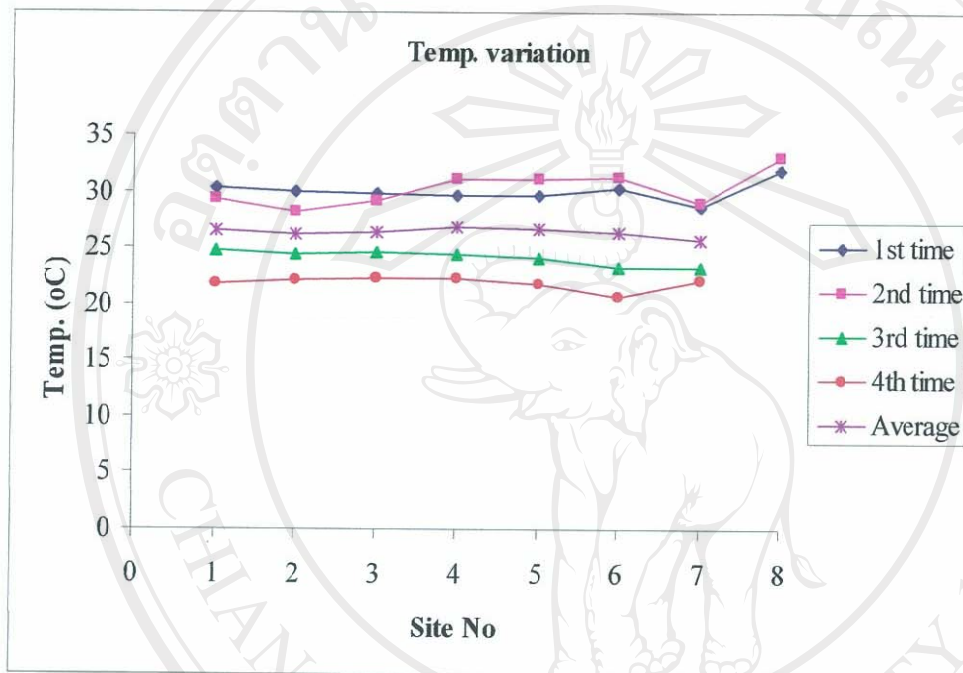

Figure 3.1 Water temperature variation among sampling times and sites (see Tables 3.1 – 3.4)

3.1.2 Conductivity

The average of conductivity of 8 sampling sites is shown in Figure 3.2. It was clearly to see the low of conductivity in the first site as control site, this result is also used to compare with other sites in terms of contamination. The data got from dry season was higher than those in rainy season due to the dilution of rainwater. The upper layer of average line is 3rd and 4th sampling times in dry season and lower layer of average is from rainy season. It can be observed that the conductivity along the distance far from the factory was reduced but not too much. It was lower in site 4, 5 but increased a little bit again in site 6 and 7. The

reason could be explained that the water stream was not much in the channel, therefore the flow movement was less. Thus, the water in site 6 and 7 was mainly standing water with long-standing water. The conductivity was lower in site 8 due to the data was just come from only rainy season.
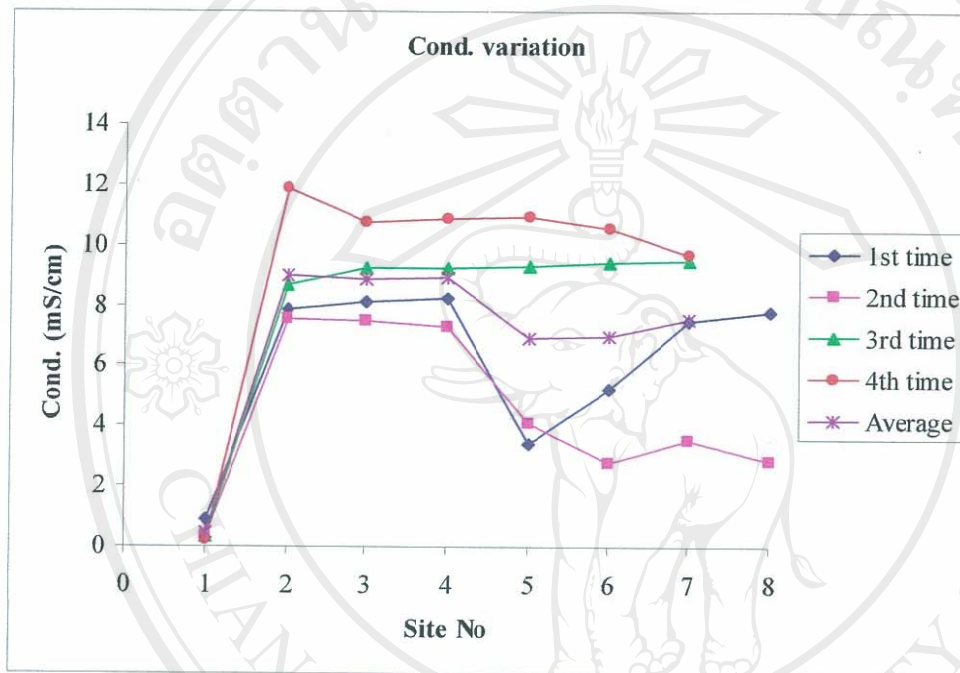

Figure 3.2 Conductivity variation among sampling times and sites (see Tables 3.1 – 3.4)

3.1.3 Total dissolved solids

Total dissolved solids data of 8 sampling sites is shown in Figure 3.3. As similar as above condition of conductivity, the TDS variation is also expressed the low level in site 5 and increased a little bit again in site 6 and 7. It should be noticed this variation among the sites for comparing in the chloride results among the sites. It could be seen clearly that the high TDS content in site 2 - 8 in comparison with site 1 (control site) due to the contamination from the factory.
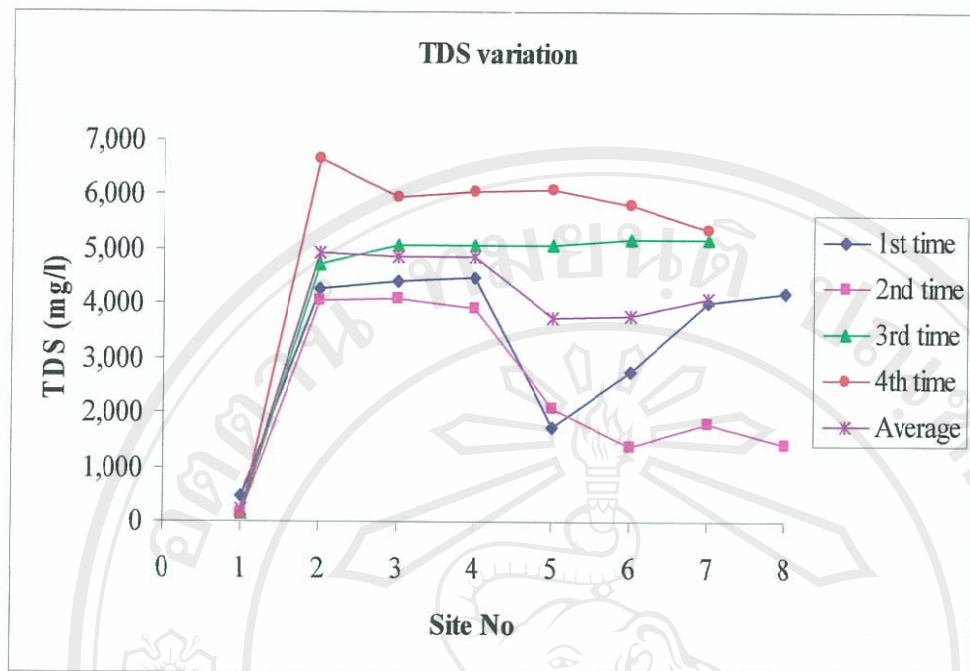
Figure 3.3 TDS variation among sampling times and sites (see Tables 3.1 – 3.4)

3.1.4 pH

The pH results of 8 sampling sites are shown in Figure 3.4. The characteristic of the pickling wastewater is acidic property due to the fermentation process. However, in this result, the pH data were neutral with the range of 5.93 – 7.79 and there were no any difference among sites and seasons.
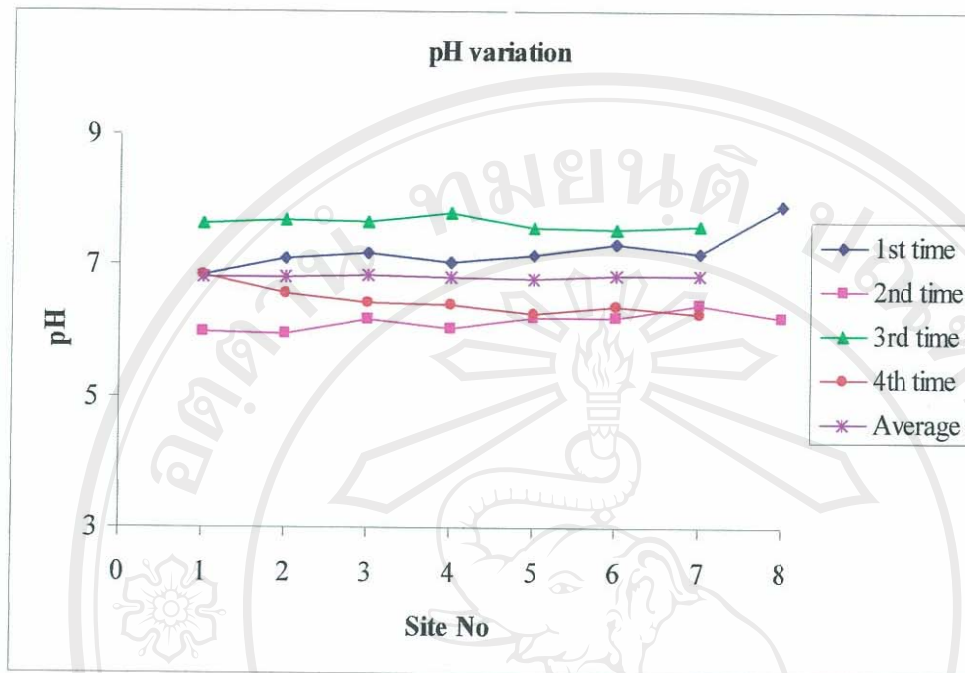
Figure 3.4 pH variation among sampling times and sites (see Tables 3.1 – 3.4)

3.1.5 Dissolved oxygen

The average of dissolved oxygen of 8 sites is shown in Figure 3.5. As mentioned in the experiment part (Chapter 2), the water flow was not stable during the times, and among the sites. It can be standing water for this time and running water for next time. However, it also could be noticed that, with standing water (without the movement), the DO value was so low in comparison with control site (also standing water), the reason may be the effect from chloride content. Figure 3.5 is expressed clearly about the fluctuation by the sampling times of data such as site 6 with 14.4 mg/l for 1st time and 0 mg/l for 2nd time. Therefore, it is difficult to discuss about the effect of chloride content on the oxygen solubility in water due to the un-homogeneous conditions.
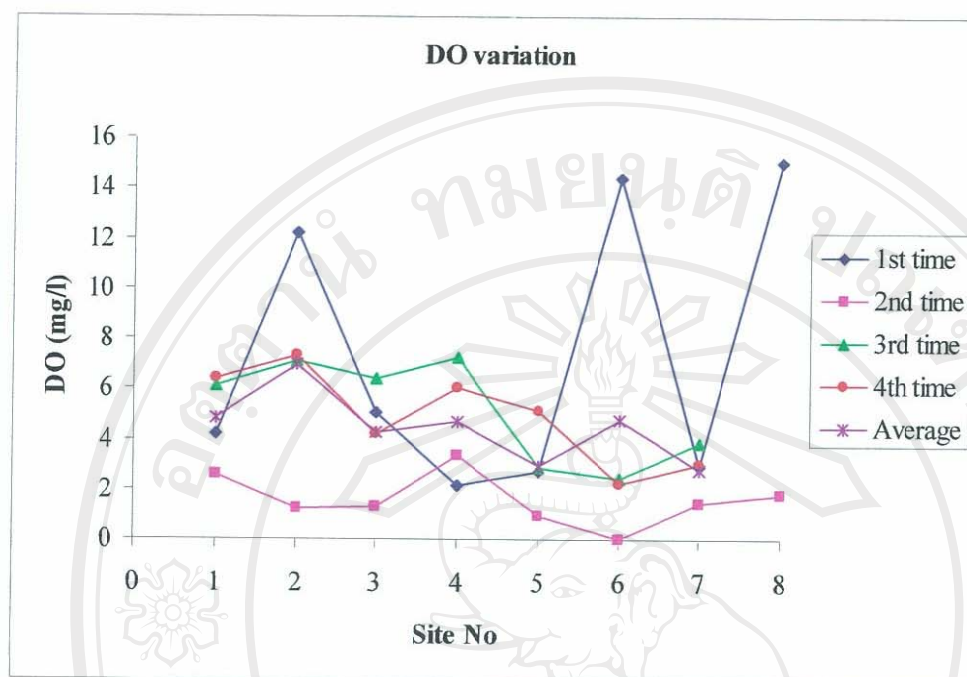
**Figure 3.5** DO variation among sampling times and sites (see Tables 3.1 – 3.4)

3.2 Chloride analysis

3.2.1 Calibration graph for chloride

Calibration graph for chloride was established by injection a series of standard solutions at different concentrations, recorded the measured voltages and plotted the trend graph of concentration vs voltage. Two ranges of chloride concentration have been investigated, which were suitable with the range of chloride contents in control site and remaining sites. Table 3.5 shows the recorded voltages with each concentration. Two calibration graphs are shown in Figure 3.6.

Table 3.5 Voltages of chloride standard solutions

Chloride concentration (ppm)	Voltage (mV)	Chloride concentration (mol/l)	Voltage (mV)
30	0.110	0.01	0.085
50	0.095	0.04	0.048
100	0.080	0.06	0.038
150	0.071	0.08	0.031
200	0.064	0.10	0.025
250	0.057	0.12	0.020
300	0.053		
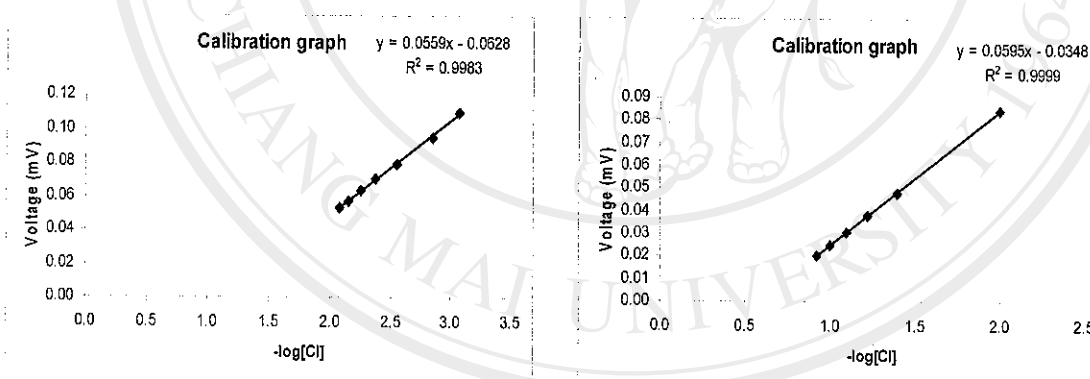
(A)   (B)

Figure 3.6 Calibration graphs for chloride:

(A) Concentration in range of 30 – 300 ppm

(B) Concentration in range of 0.01 – 0.12 M

The equations of the above calibration graphs are y = 0.0559x – 0.0628 and y = 0.0595x – 0.0348 for (A) and (B), respectively.

In comparison with theoretical Nerstian slope of 0.0591 for a monovalent ion at 298K (Rouessac, 2000), the relative error from above achieved slopes has been calculated by the below formula:

$$Relative\ Error\ = \frac{(slope - 0.0591) \times 100}{0.0591}$$

Table 3.6 The relative error of the achieved slopes

Equation	Relative Error
y = 0.0559x – 0.0628	- 5.41 %
y = 0.0595x – 0.0348	+ 0.68 %

3.2.2 Chloride results

Figure 3.7 shows the chloride variation among eight sites. It can be noticed that the chloride contents were also reduced in site 5 and increased a little bit again in site 6 and 7. This attention is suitable with the results of conductivity and TDS discussed before. The chloride contents in dry season were also higher than those in rainy season.

Table 3.7 Chloride concentration (mol/l) of 8 sampling sites during 4 sampling times by SIA method

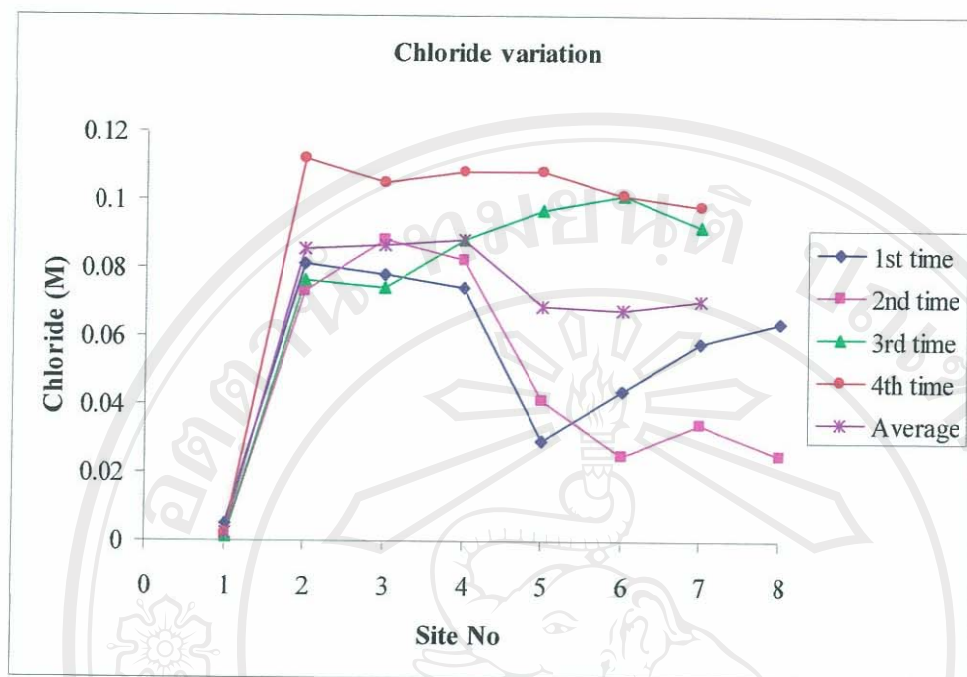| Sampling time	Site 1	Site 2	Site 3	Site 4	Site 5	Site 6	Site 7	Site 8
1st	0.005	0.081	0.078	0.074	0.029	0.044	0.058	0.064
2nd	0.001	0.073	0.088	0.082	0.041	0.025	0.034	0.025
3rd	0.001	0.076	0.074	0.088	0.097	0.101	0.092	-
4th	0.002	0.112	0.105	0.108	0.108	0.101	0.098	-

Figure 3.7 Chloride variation among sampling times and sites (see Tables 3.1 – 3.4)

It can be seen clearly that the chloride contents in other sites were higher than in control site due to the contamination with at least 25 to 80 times higher.
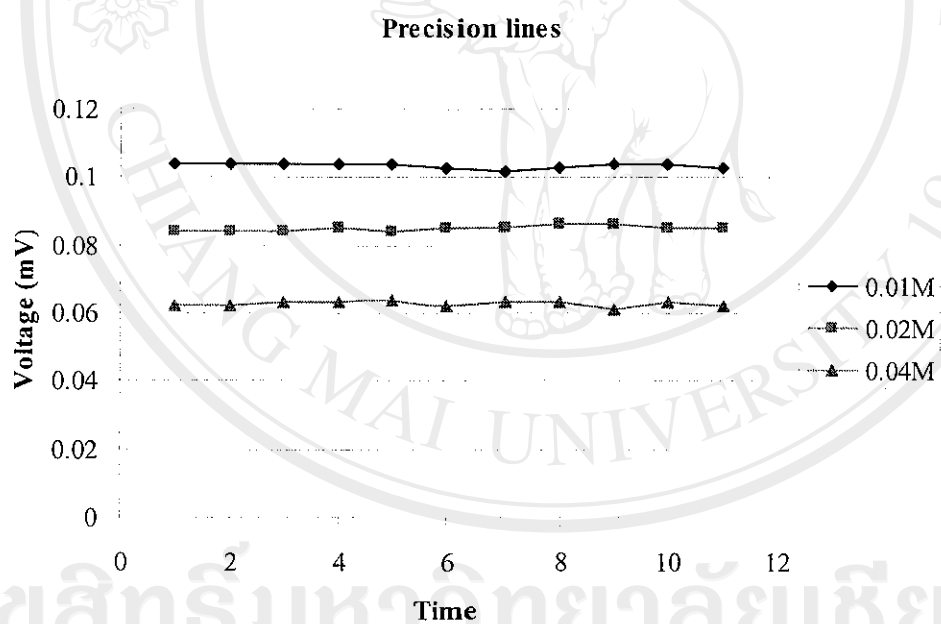
3.3 Precision study of the SIA method

To study the precision of this method, 11 aspirations of standard solution with 0.01, 0.02 and 0.04M of chloride were repeated and recorded the voltages. Table 3.8 shows the Mean, SD. and %RSD of 11 replications of each solution. Figure 3.8 shows the precision lines of 0.01, 0.02 and 0.04M, respectively.

Table 3.8 Precision study of chloride standard solutions

Concentration	Mean (Voltage, mV)	SD	%RSD
0.01M	0.104	0.001	0.7%
0.02M	0.085	0.001	0.9%
0.04M	0.063	0.001	1.3%

Figure 3.8 Precision study of the SIA method

3.4 Accuracy study of the SIA method

In parallel with chloride analysis by SIA method, the standard Mohr titration method was also used as the reference method for comparison. Table 3.9 below shows the chloride results by titration method with the same samples.

Table 3.9 Chloride concentration (mol/l) of 8 sampling sites during 4 sampling times by Mohr method (cf. Table 3.7)

| Sampling time	Site 1	Site 2	Site 3	Site 4	Site 5	Site 6	Site 7	Site 8
1st	0.007	0.074	0.077	0.079	0.031	0.048	0.070	0.074
2nd	0.001	0.072	0.070	0.068	0.036	0.024	0.031	0.026
3rd	0.002	0.082	0.087	0.089	0.089	0.091	0.091	-
4th	0.002	0.116	0.104	0.106	0.106	0.101	0.092	-

In order to compare the achieved results of two above methods to test whether there was good agreement between two methods, the statistical t-test was analyzed at 0.05 significant level. The result of $P > 0.05$ pointed out there was no significant difference between two methods (see Appendix 4).

The averages of chloride in each site measured by two methods are shown in Table 3.10 and the comparison in Figure 3.9. The linear correlation between 2 methods is plotted in Figure 3.10, which is expressed relative equation with the slope is nearly 1 (0.9573) and the low intercept (0.0025).

Table 3.10 Average chloride of each site by two methods

Sample	Average chloride (M)		Difference (%)
	Titration	SIA	
1	0.003	0.002	-33.333
2	0.086	0.086	0.000
3	0.085	0.086	1.176
4	0.086	0.088	2.326
5	0.066	0.069	4.545
6	0.066	0.068	3.030
7	0.071	0.071	0.000
8	0.050	0.045	-10.000
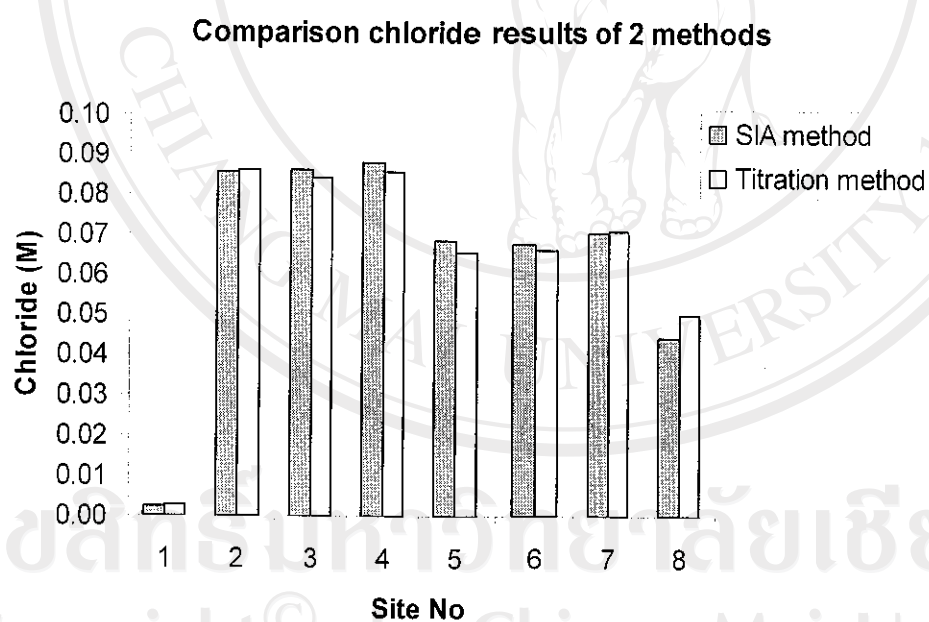
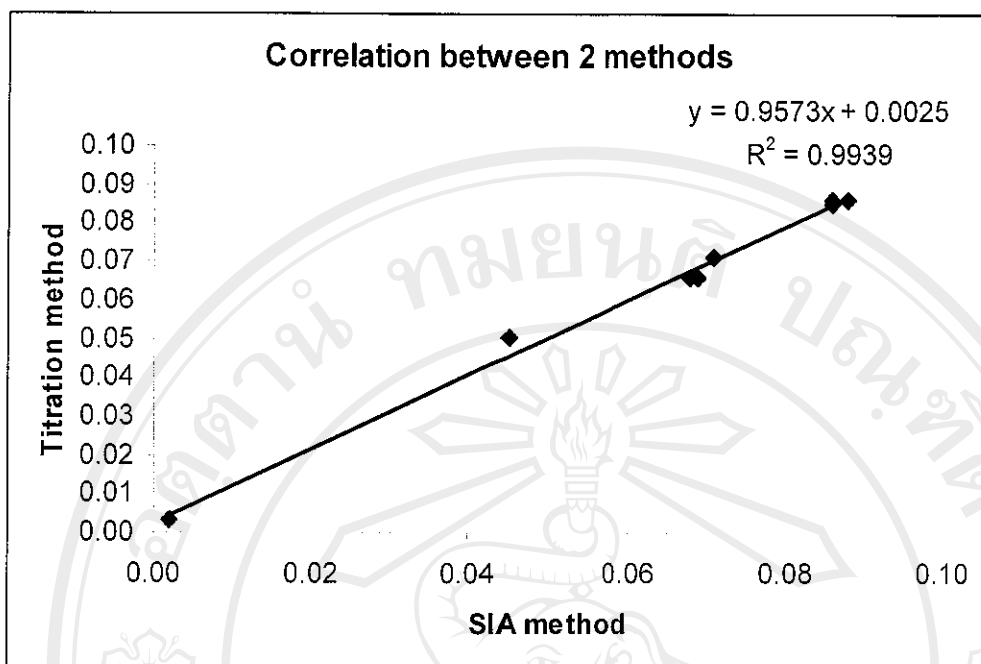Figure 3.9 Comparison chloride results of two methods

Figure 3.10 Linear correlation between the two methods

3.5 General assessment of water quality in terms of salinity

3.5.1 The relationship among parameters

As mentioned in the introduction part (Chapter 1), there is relationship among the parameters that selected as supporting data for chloride results. Therefore, the Correlation test (Man-Whitney U test) was used to find out the correlation of 1st group (chloride, TDS and conductivity) and 2nd group (chloride, temperature and DO), see the output in Appendix 4. The significant relationships were found in chloride with TDS and conductivity at $P < 0.01$. Whereas, the significant relationship was found in chloride with temperature at $P < 0.01$. However, there was no statistical relationship between chloride and DO. It could be explained by the fluctuated DO data due to unstable water flow. Hence, it could not be concluded the effect of chloride on the oxygen solubility in this case.

3.5.2 Chloride variation among sampling times

As discussed in chloride result part (3.2.2), it was observed that the chloride content in dry season was higher than in rainy season. The repeated measures analysis of variance on the sampling sites and times was tested (see Appendix 4).

The results are shown there was significant differences of chloride results among sampling times and sites by times interaction (P < 0.001, highly significant). It means that there was seasonal variation of chloride content within 4 sampling times.

3.5.3 Comparison of control site with other sites

The control site was selected to test whether there was the chloride contamination in other sites. The one-way ANOVA analysis and LSD test were selected to test this hypothesis. The result of P < 0.05, which mean that there was significant difference within groups (see Appendix 4). The LSD test result clearly found out the significant difference of control site (site 1) vs other sites except site 8 because this site got only the rainy season data (lack of evidence to prove the difference).

3.5.4 General assessment

The chloride data revealed very high concentration in seven sites except control site. The statistical test confirmed the chloride contamination in these sites. With along the distance far from factory (follows with the site's number), the concentration was not reduced much due to the status of water stream, which had less movement. Therefore, with the water evaporation day by day, the chloride content was higher and gradually absorbed in the soil and finally to ground water, which will be more difficult to assess the effect. In comparison with Table 1.3 in salinity classes for irrigation waters, the salinity class for water here

was in range of class 4 to 5, it means that from *"saline"* to *"highly saline"* for irrigation water can be caused the severe crop problem. Additionally, according to the Industrial Effluent Standards of Thailand (Department of Environmental Quality Promotion, Ministry of Natural Resources and Environment – see Appendix 3), the maximum chloride standard value is 2,000 mg/l and the TDS value is not over 5,000 mg/l. However, the chloride data got from here is in range of 887 – 3,976 mg/l and the TDS data is up to 6,650 mg/l. There was significant difference of chloride results among 4 sampling times due to the seasonal changes (P < 0.001). The ANOVA analysis also confirmed the significant difference between site 1 (Control site) vs other sites, it mean that, there was the contamination of chloride along the stream discharged from factory as shown in Figure 3.11.

Figure 3.11 Wastewater from factory discharges to around channel