CHAPTER 3

RESULT AND DISCUSSION

3.1 Optimization parameters for AAnalyst 800

3.1.1 Optimization of pyrolysis and atomization temperature

In trace metal determination by GFAAS, one of the important steps is a pyrolysis step which removed the matrix prior the atomization step. This step is decrease the possibility of chemical interference and reduces the magnitude of the background signal. The temperature for atomization step need to be adjusted in order to get the complete volatilization of the analyte.

The pyrolysis and atomization temperature plots were showed in Figure C-1 in Appendix C, the peak profiles were illustrated in Figure C-2(a) to Figure C-2(d) in Appendix C, and the detail of the data from was presented in Table C-1 in Appendix C.

A summary of the temperature program of GFAAS for determination of Cd, Cu, Pb, Zn were list in Table 3-1.

Table 3- 1 The optimum temperature program of AAnalyst 800 for determination of Cd, Cu, Pb and Zn

Element	**1st Drying**			**2nd Drying**			**Ashing**			**Atomizing**			**Cleaning**	
	T	R	H	T	R	H	T	R	H	T	R	H	T	R
Cd	110	1	30	300	15	30	600	10	20	1400	0	5	2200	1
Cu	110	20	30	130	10	15	800	10	10	2100	0	5	2200	1
Pb	110	15	35	130	10	15	750	10	20	1500	0	5	2300	1
Zn	110	1	30	130	15	30	700	10	20	1700	0	5	2200	1

T: Temperature (°C); R: Ramp time (s); H: Hold time (s)

3.1.2 Effect of matrix modifier

The matrix modifier is a chemical reagent, usually an inorganic salt used in GFAAS technique. The reagent caused either the interfering concomitant to become more volatile and thus more easily separated, or the analyte element to be converted to a less volatile form (Welz, 1985). Thus, it allowed the reduction or elimination of concomitants in complex matrices prior to atomization. The study of the matrix modifier was performed by using 2.0 μg/L of Cd, 25 μg/L of Cu, 50.0 μg/L of Pb and 2.0 μg/L of Zn standard solutions. The results were showed in Table C-2 in Appendix C. The absorbance signals for Cd and Pb were increased when using modifier while the signal of Cu and Zn were the same. Thus further investigation of various matrix modifiers was performed for Cd and Pb. The results were showed in Table C-3 and Table C-4 in Appendix C. It was found that lanthanum nitrate was suitable for both Cd and Pb standard solution. The effects of these matrix modifiers were also performed with extracted samples. It was found that these matrix modifiers had no influence to the peak area and peak shape for all metals in real samples. The shape of the peak of all metals showed minimized peak tailing. Thus in this study, the matrix modifier was not necessary for the analysis of metals in the samples.

3.2 Quantification of the analysis: calibration curve and standard addition curve

Metal concentration in the sample was quantified by calibration curve or standard addition curve. The slopes of standard addition curve and calibration were compared in order to know whether the matrix would interfere with measurement of all metals or not. The results showed that no interference from the sample matrix for Cd, Cu, Zn, Al, Fe and Mn as showed in Figure C-3(a) to Figure C-3(b) and Figure C-3(d) to Figure C-3(g) in Appendix C. However, the slope of standard addition and calibration curve was different for Pb in extracted sample as showed in Figure C-3(c) in Appendix C. Thus only Pb would be quantified by standard addition curve while Cd, Cu, Zn, Al, Fe and Mn were quantified by calibration curve.

3.3 Methods of validation

3.3.1 Detection Limits of method

The detection limit is the concentration which will give an absorbance signal three times the magnitude of the baseline noise. The procedure to evaluate limits of detection was undertaken by using ten replicate of procedural blank. In this study, there are two procedural blanks; extraction blank and particulate digestion blank. The procedural blanks were performed in the same manner as the sample described in section 2.7.1.-2.7.2. The detection limit of method was calculated by $3\sigma/m$ (section 2.8.1) for each metal. The detail of the data was presented in Table C-5 and Table C-6 in Appendix C and the results were summarized in Table 3-2.

Table 3- 2 The detection limit of Cd, Cu, Pb, Zn, Al, Fe and Mn

	Cd (µg/L)	Cu (µg/L)	Pb (µg/L)	Zn (mg/L)	Al (mg/L)	Fe (mg/L)	Mn (mg/L)
Dissolved phase	0.1	0.6	3.2	0.1	5.5	0.7	0.3
Particulate phase	0.1	2.3	0.7	0.8	35.9	0.3	0.1

3.3.2 Accuracy and precision

The accuracy of this technique was evaluated from the % Recovery and %RSD as mentioned in section 2.7.2. The result is shown in Table 3-3 and the detail of the data was presented in Table C-7 to Table C-9 in Appendix C. The accuracy of this method was in the range of 97-102 % for dissolved metal and 92-111% for particulate metal. The precision of the method for both dissolved and particulate metals was less than 10 %.

Table 3-3 The %Recovery and %RSD of Cd Cu, Pb, Zn, Al, Fe and Mn in dissolved and particulate phases

Metal	%Recovery		%RSD	
	Dissolved phase	Particulate phase	Dissolved phase	Particulate phase
Cd	101.5	91.9	6.3	9.7
Cu	97.2	110.7	3.3	6.8
Pb	102.1	94.3	6.2	4.1
Zn	99.8	92.9	4.1	9.3
Al	98.9	105.7	9.2	3.8
Fe	99.2	104.1	4.3	7.7
Mn	99.8	105.7	10.0	1.2

3.4 Trace metals in surface water of Songkhla Lake System

3.4.1 Trace metals in dissolved phase

Trace metals in filter samples collected from 74 stations in Songkhla Lake System (Thale Noi, Inner Lake, Middle Lakes and Outer Lake) were pre-concentrated by solvent extraction method and analyzed by GFAAS and ICP-AES.

Average dissolved trace metals (Cd, Cu, Pb, Zn, Al, Fe and Mn) in surface water of Songkhla Lake system in wet and dry season in Thale Noi, Inner Lake, Middle Lakes and Outer Lake were summarized and presented in Table 3-4. The details in concentration data were presented in Table C-10 to Table C-13 in Appendix C. The lowest concentration of Cd and Cu were found at Thale-Noi, while Fe and Zn were found at Inner Lake and Pb in the Outer Lake.

Table 3- 4 The average concentration (in µg/L) for dissolved metal in wet and dry seasons of Songkhla Lake System

Metal	Thale noi		Inner Lake		Middle Lake		Outer Lake	
	wet	dry	wet	dry	wet	dry	wet	dry
Cd	0.055	0.004	0.392	0.014	0.130	0.033	0.039	0.010
Cu	0.64	0.10	0.65	0.30	0.63	0.25	1.01	0.35
Pb	0.005	0.005	0.002	0.003	0.004	0.007	0.005	0.002
Zn	17.0	37.0	13.6	22.9	16.3	34.5	19.4	21.2
Al	167.0	12.5	55.9	16.8	43.0	10.5	79.9	113.5
Fe	163.3	133.0	29.8	5.1	19.9	24.3	74.3	40.8
Mn	164.0	106.2	210.8	166.1	9.5	64.4	2.3	21.5

In comparison with other natural waters and World average (Table 3-7), the dissolved Cd, Cu and Pb concentrations in Songkhla Lake System were in the same range while the dissolved Zn concentrations were higher than other natural waters and World average (Martin and Windom, 1991; Paucot and Wallast, 1997; Munksgaard and Parry, 2001; Nguyen *et al.,*2005) but it was in the same range as in Mersey Estuary (UK) (Comber *et al.,* 1995) and Lake Taxoma marinas (USA) which was a multi-used reservoir and had boat repairing activities (An and Kampbell, 2003).

Table 3- 5 The average dissolved metal concentrations (in µg/L) of other natural water

	Cd	Cu	Pb	Zn	Al	Fe	Mn	Ref
World Average	0.01	1.5	0.03	0.6		40		Martin and Windom (1991)
Chang jiang	0.003	1.7	0.1	0.1		0.6		Elbaz-Poulichet (1988)
Mekong	0.02	0.4	0.05	2.2				Hungspreugs *et al.* (1998)
Balaton	0.002	0.475	0.09	0.85				Nguyen *et al.*(2005)
DarwinHarbour	0.006	0.3	0.008	0.1				Munksgaard and Parry (2001)
Lake Taxoma	20	24	<15	59	92	119	7	An and Kampbell (2003)
Mersey	0.04	2	1.5	15				Comber *et al.* (1995)
Scheldt estuary	0.1	1.9		0.02			219	Paucot and Wollast (1997)

Dissolved trace metals in the Outer Songkhla Lake were examined two decade ago by Sirinawin *et al*. (1998). The comparison of trace metal concentration from this study with Sirinawin *et al.* (1998) was presented in Table 3-6. It should be noted that only dissolved Pb and Zn concentrations were elevated (2 to 10 folds higher than those collected in 1987). This may cause by anthropogenic input into the Outer Lake during two decades such as boats and fish waste, near shore drainage and municipal waste.

Table 3- 6 The comparison of dissolved trace metal concentrations (in µg/L) in the Outer Songkhla Lake collected in 1987 and 2004

Metals	1987 (Sirinawin *et al.*, 1998)	2004 (This study)	
		Wet season	Dry season
Cd	0.008 ± 0.007	0.039 ± 0.058	0.010 ± 0.009
Cu	0.358 ± 0.126	1.010 ± 0.692	0.351 ± 0.382
Pb	0.022 ± 0.045	0.005 ± 0.004	0.002 ± 0.003
Zn	0.43 ± 0.32	19.4 ± 9.5	21.2 ± 13.9
Fe	6.2 ± 10.5	74.3 ± 163.9	40.8 ± 102.4
Mn	11.2 ± 21.9	2.3 ± 4.2	21.5 ± 34.2

3.4.2 Trace metals in particulate phase

Trace metals in particulate phase were extracted by acid digestion and analyzed by GFAAS for Cd, Cu, Pb and Zn and FAAS for Al, Fe and Mn.

Average Cd, Cu, Pb and Zn concentrations in particulated form in Thale Noi were 0.4±0.7, 21±23, 60±61 and 84±157 µg/g, respectively; Inner Lake were 0.2±0.2, 37±54, 18±18 and 84±148 µg/g, respectively; Middle Lake were 0.07±0.07, 57±148, 22±18 and 61±67 µg/g, respectively; Outer Lake were 0.1±0.3, 19±17, 41±51and 68±101 µg/L, respectively. For Al, Fe and Mn in Thale Noi were 155±403, 150±154 and 3.5±5.6 mg/g, respectively; Inner Lake 123±218, 34±47 and 2.3±2.0 mg/g, respectively; Middle Lake 95±86, 24±22 and 2.2±2.4 mg/g, respectively; Outer Lake 140±186, 27±12 and 1.7±2.6 mg/g, respectively.

The average concentration of Cd, Cu, Pb, Zn, Al, Fe and Mn in wet and dry season in Thale Noi, Inner Lake, Middle Lakes and Outer Lake were summarized in Table 3-7. The detail in concentration data was presented in Table C-14 to Table C-17 in Appendix C. In Thale-Noi, the concentrations of Cd, Cu, Pb and Zn in particulate matter were higher than in other areas. However, all metals in Songkhla Lake System were at a same level as in other natural waters and World average (Table 3-8) (Martin and Whitfield, 1983; Cambell *et al*., 1988; Regnier *et al*., 1990; Chiffoleau *et al*, 1994; Paucot and Wollast, 1997).

Table 3 -7 The average concentration of Cd, Cu, Pb and Zn in mg/kg and Al, Fe and Mn in g/kg in particulate matters of Songkhla Lake water in wet and dry season

Metal	Thale Noi		Inner Lake		Middle Lake		Outer lake	
	wet	dry	wet	dry	wet	dry	wet	dry
Cd	0.6	0.5	0.3	0.1	0.1	0.1	0.1	0.3
Cu	20.2	21.6	50.5	20.6	103.7	10.6	22.5	16.0
Pb	41.2	78.5	9.8	23.3	9.9	34.8	11.1	71.7
Zn	97.3	71.6	131.9	30.7	98.9	23.4	65.5	70.7
Al	35.7	332.8	92.5	111.2	88.2	101.8	77.4	202.2
Fe	181.3	120.0	50.5	13.8	36.0	12.5	26.8	26.6
Mn	4.5	2.7	3.2	1.6	1.5	3.0	0.4	3.0

Table 3 -8 Comparison of metal concentrations (mg/kg) in particulate matters of this study to other estuaries

	Cd	Cu	Pb	Zn	Ref.
World Avg	1.2	100	35	250	Martin and Windom (1991)
Scheldt estuary	9.4	158.5	178.5	836.5	Paucot and Wollast (1997)
Seine	3	47	55	220	Chiffoleau *et al.* (1994)
Ebro	5.7	68	52.5	197.5	Guien *et al.* (1992)
Rhone	1.3	51.5	54	196.5	Paucot unpublished data
This study	0.3	33.2	35	73.7	

Trace metals in particulate phase in the Outer Songkhla Lake were reported by Sirinawin *et al*. (1998). The comparison of trace metal concentration from this study with Sirinawin *et al.* (1998) was presented in Table 3-9. All metals in particulate phase collected in 2004 (this study) were 1 to 2 order of magnitude higher than those collected in 1987. This is not surprising, since the elevated metal concentration can be resulted from strong acid digestion method (aqua regia and HF) which can extract metals in silicates lattice and other refractory oxides and giave the complete digestion solution while Sirinawin *et al.* (1998) used 0.3M HNO_3 and 0.3M H_2O_2 which was a mild digestion method.

Table 3- 9 The comparison of particulate trace metal concentrations (in mg/kg) in the Outer Songkhla Lake collected in 1987 and 2004)

Cd	Cu	Pb	Zn	Fe	Mn	Al	Ref.
0.00002	0.004	0.004	0.02	12.5	0.4	15.5	Sirinawin *et a1.* (1998)
0.001	0.7	0.2	1.9	1296.7	16.8	5524.2	This study

3.4.3 Total metals concentration in Box and outlier plot

Total metal concentration was a summation of dissolved and particulate fractions which were calculated in the same unit. The box plot and outlier is a graphically display a variable's location and spread at a glance. It also provides some indication of data's symmetry, skewness and outlier value. The box contains the middle 50% of the data, the upper edge of the box indicates the 75th percentile of the data set, and the lower edge indicates the 25th percentile. The line in the box indicates the median value of the data, while a whisker indicates the minimum and maximum values. The outlier is presented in which case the whiskers extend to a maximum of 1.5 times the inter-quartile range. Box plots of Cd, Cu, Pb, Zn, Al, Fe and Mn were illustrated in Figure 3-1 and Figure 3-2.

It was found that the median value of total Cd and Cu concentrations during wet and dry seasons in Thale Noi, Inner Lake, Middle Lake and Outer Lake were in the same range. The total Cd and Cu concentrations in each area in both seasons showed narrow distribution

The pattern of Pb, Zn, Al and Fe box plots showed similar trends in wet seasons which had a tendency to increase seaward. In dry season, the median values of these metals were quite consistent except Al in Thale Noi showed slightly lower value than other areas. However, Mn behaved differently from other elements. It was found high concentration and high variation in the Inner Lake in both season, this may indicate that the authigenically formed particles in this area are rich in Mn.

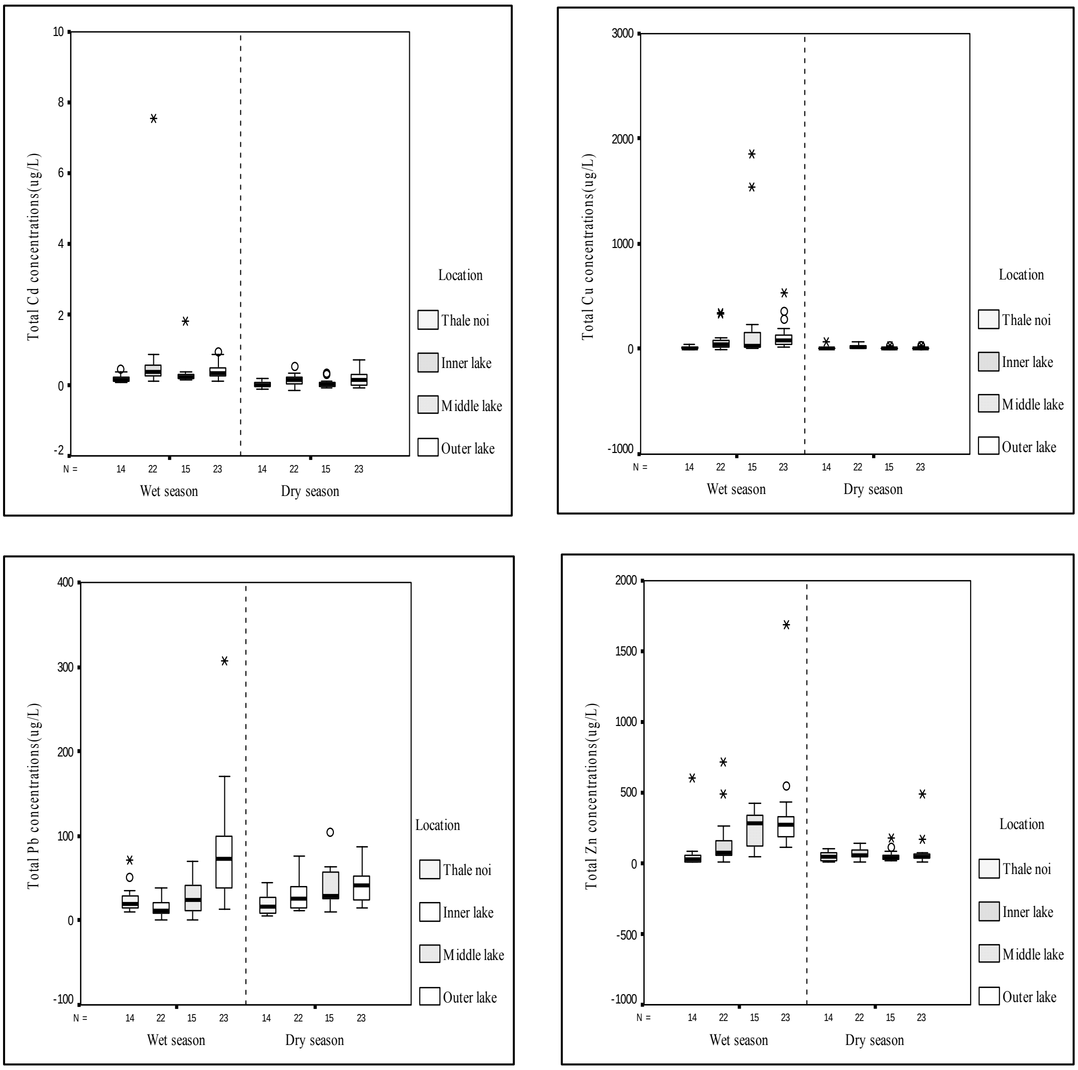


Figure 3-1 Box and outlier plot of total Cd, Cu, Pb and Zn in each area of Songkhla Lake System

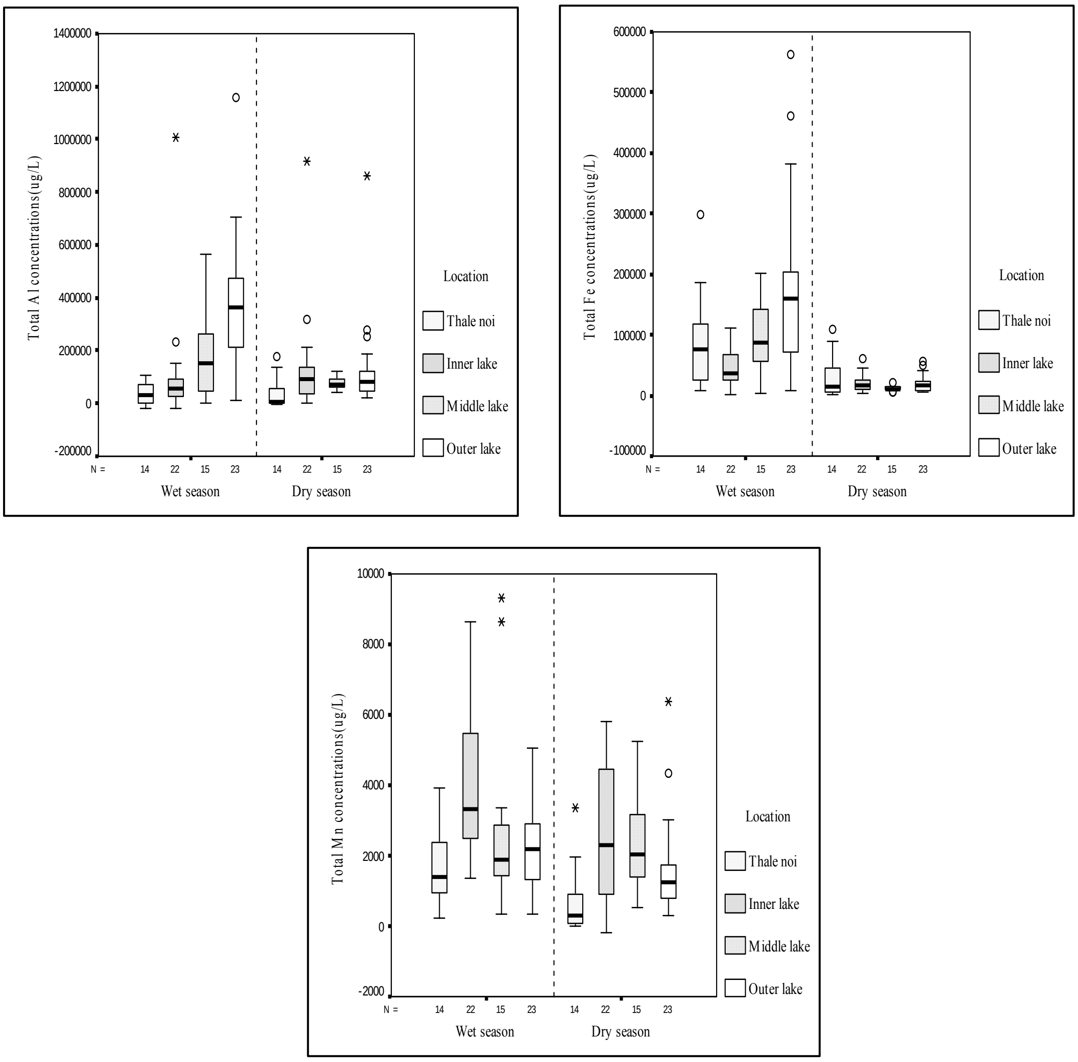


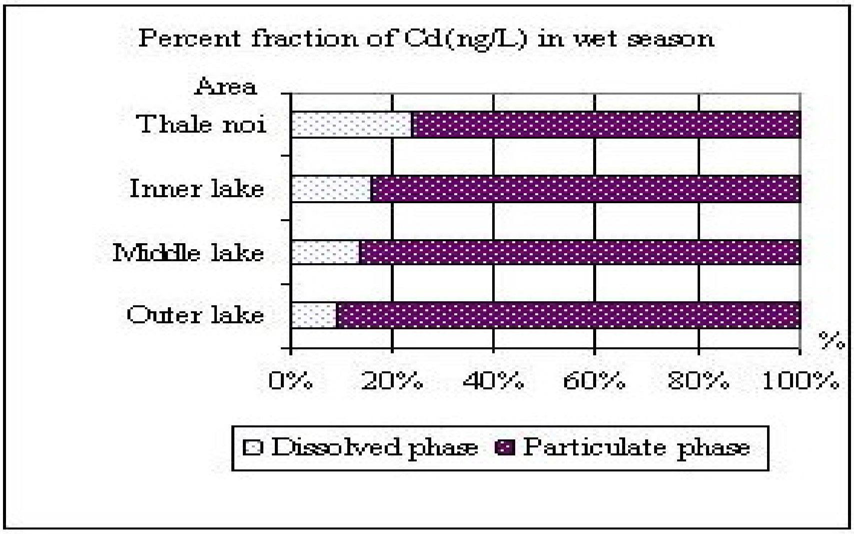
Figure 3-2 Box and outlier plot of total Al, Fe and Mn in each area of Songkhla Lake System

3.4.4 Percent fraction of dissolved and particulate metals.

In natural water, metals can be obtained in dissolved and particulate forms. The concentrations of metals in each form were presented in the previous sections. In order to illustrate visually, the percent fraction of dissolved and particulate in wet and dry seasons at different locations were depicted in Figure 3-3 to Figure 3-6. It can be seen that in wet season Cd, Cu, Pb and Zn were found mainly in particulate fraction (<60%) in most areas. For Al, Fe and Mn (Figure 3-7 to Figure 3-9), the dominant fractions were particulate fractions (>80%). Similar behaviors were reported by Shafer *et al.* (1997); Cenci and Martin (2004); Nguyen *et al*. (2005). This is not surprising as Cd, Cu, Pb and Zn may adsorb or associate onto the scavenging elements such as Al, Fe and Mn (Burton and Liss; 1976).

Considering Cu, Pb and Zn which were classified as a borderline A type (Turner, 1981), they behaved differently in Thale Noi. Zinc was dominated in dissolved fraction (>60%) while Cu and Pb were found in particulate fractions. The explanation of this is probably due to the speciation of these metals which was in different form. Suitcharit (2006) investigated the speciation of metals in the Songkhla Lake System (same sampling cruise with this study). It was found that Cu and Pb were present as inert organic and inorganic bound fraction which tended to adsorbed onto the iron, manganese oxide particles, while Zn was found in free ion form (Suitcharit, 2006). Similar behaviors for Zn were found in Mekong Delta (Hungspreugs *et al.,* 1998) and in Trinity River (USA) (Tang *et al*., 2002).

In dry season, Cd, Cu, Pb, Al, Fe and Mn were found mainly in particulate fraction (>50%) and showed similar pattern as in wet season except Zn was found mainly in dissolved fraction in the whole lake system (>60%).



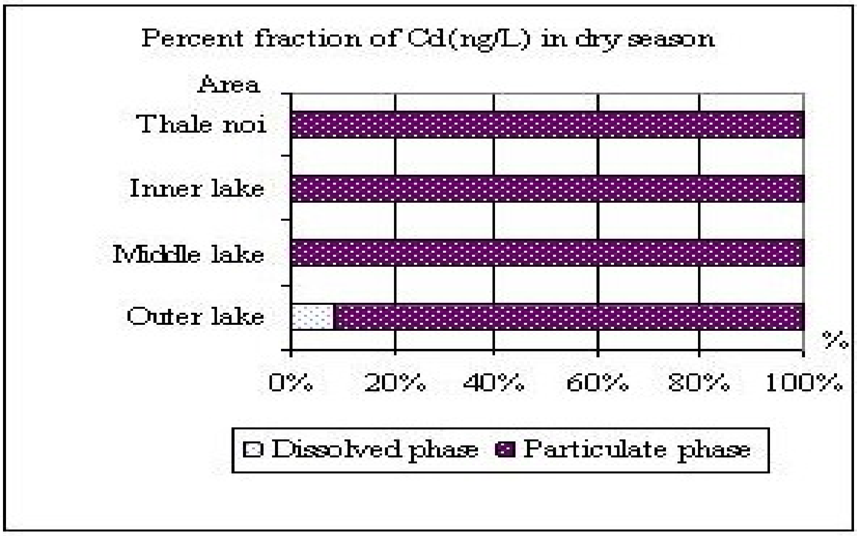
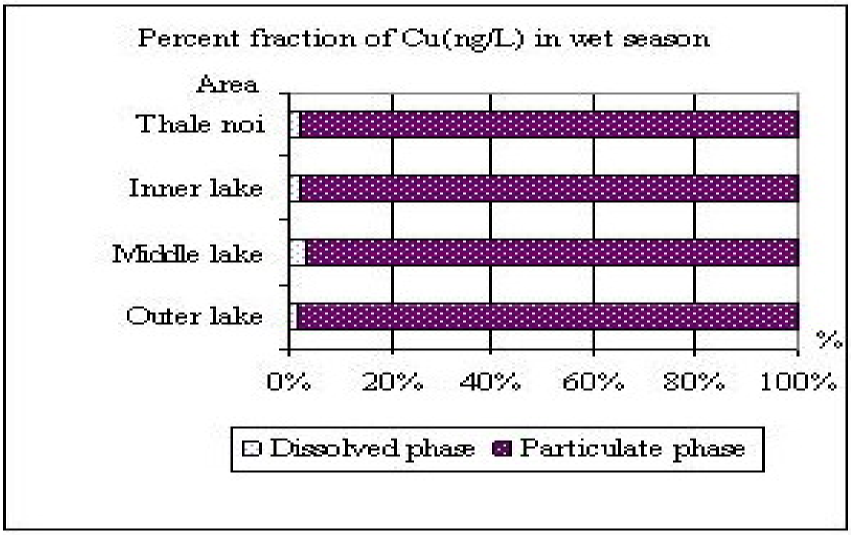


Figure 3-3 The percent fraction of dissolved and particulate Cd (ng/L) in wet and dry season..



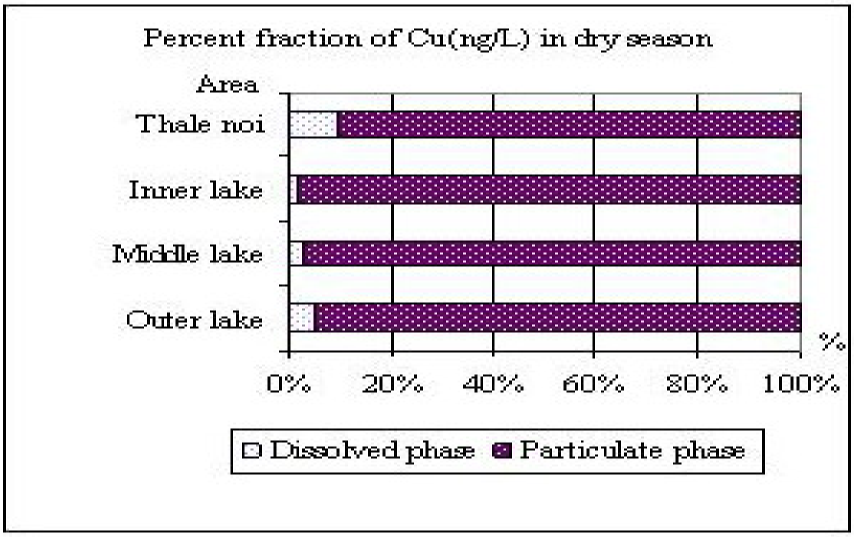
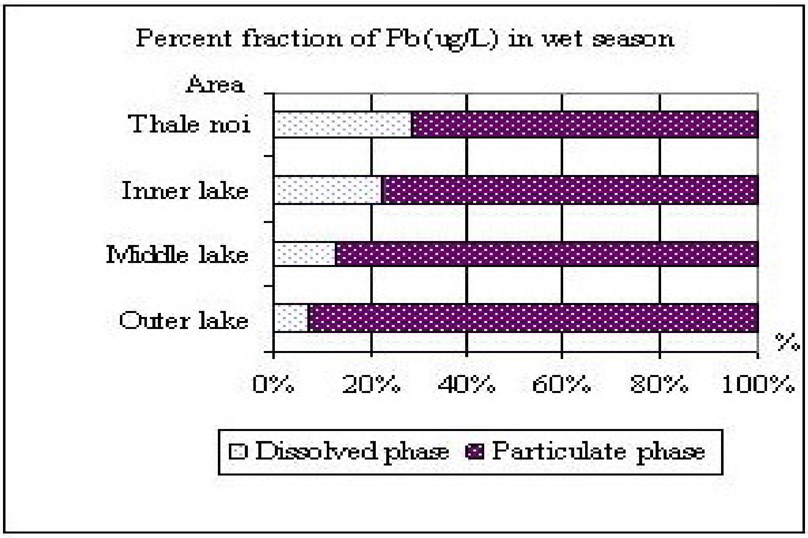


Figure 3-4 The percent fraction of dissolved and particulate Cu (ng/L) in wet and dry season..



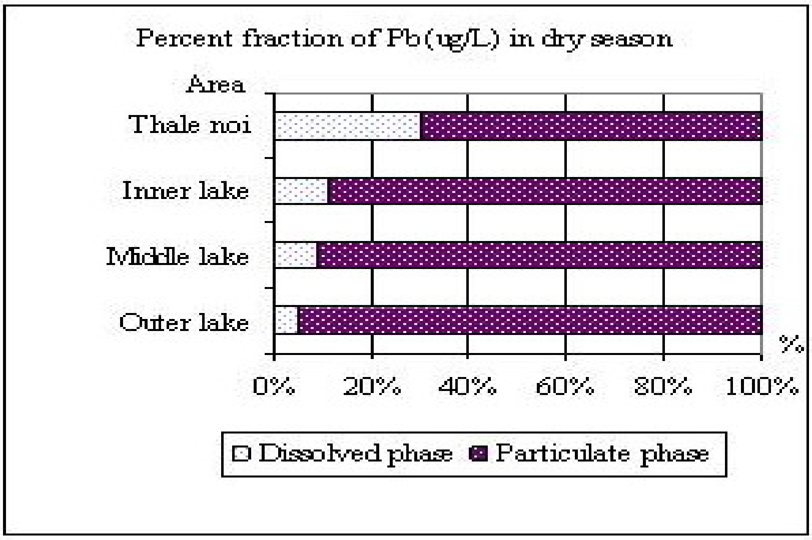
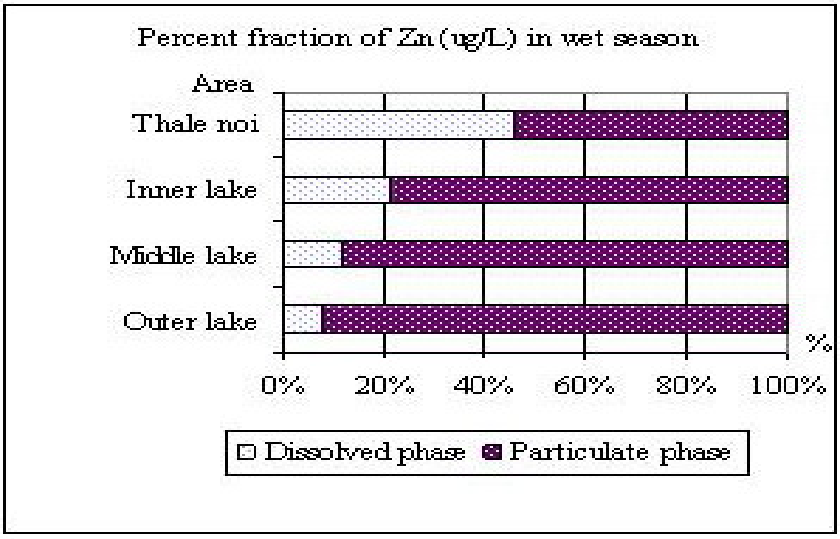


Figure 3-5 The percent fraction of dissolved and particulate Pb (µg/L) in wet and dry season.



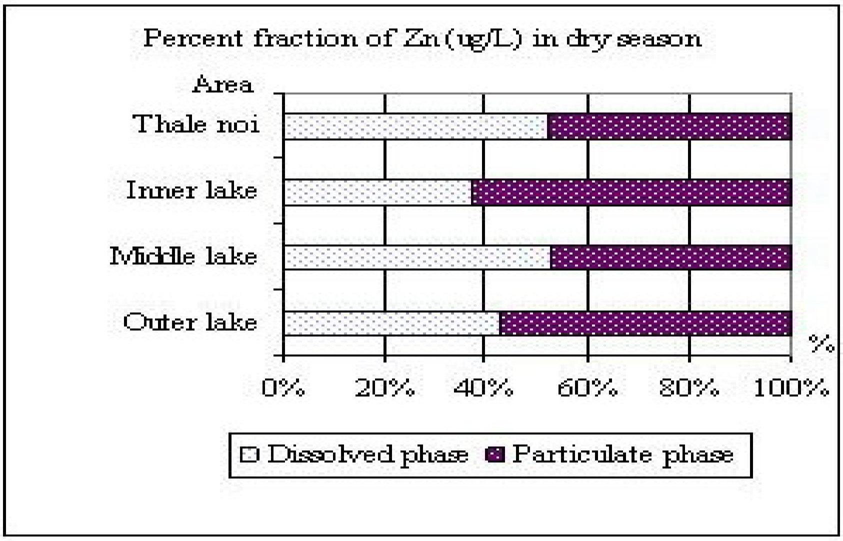
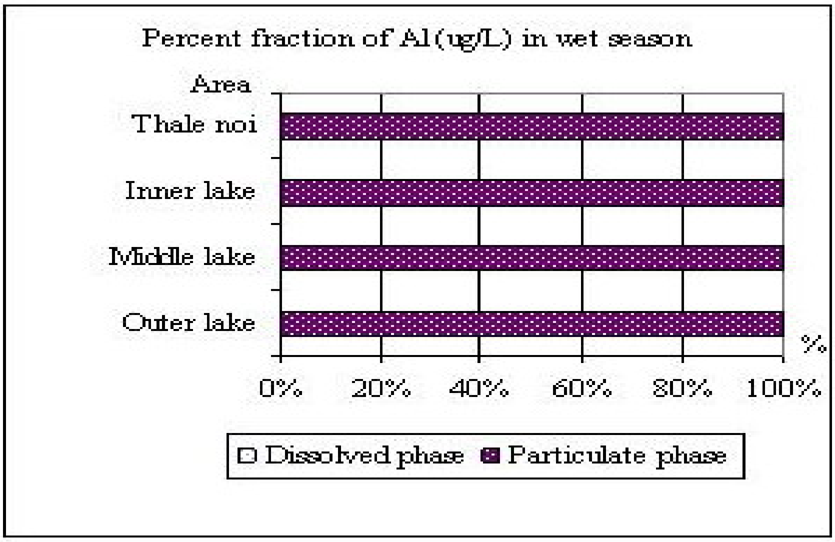


Figure 3-6 The percent fraction of dissolved and particulate Zn (µg/L) in wet and dry season.



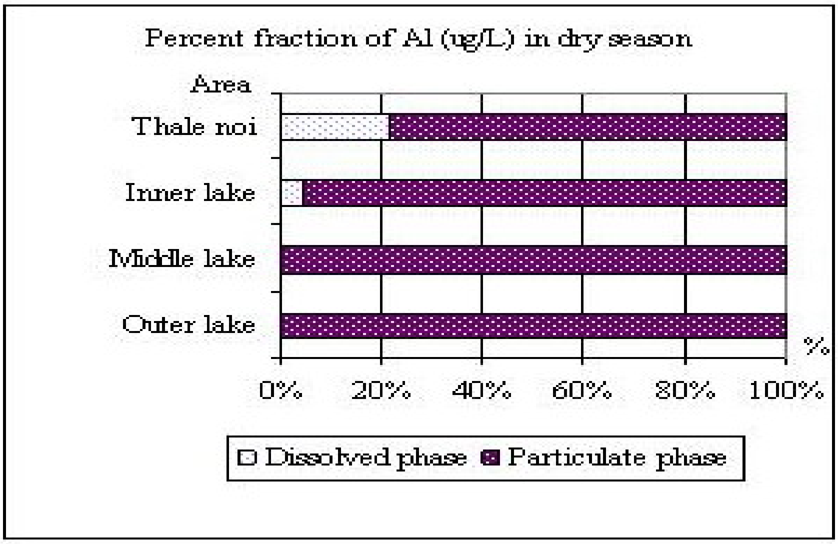
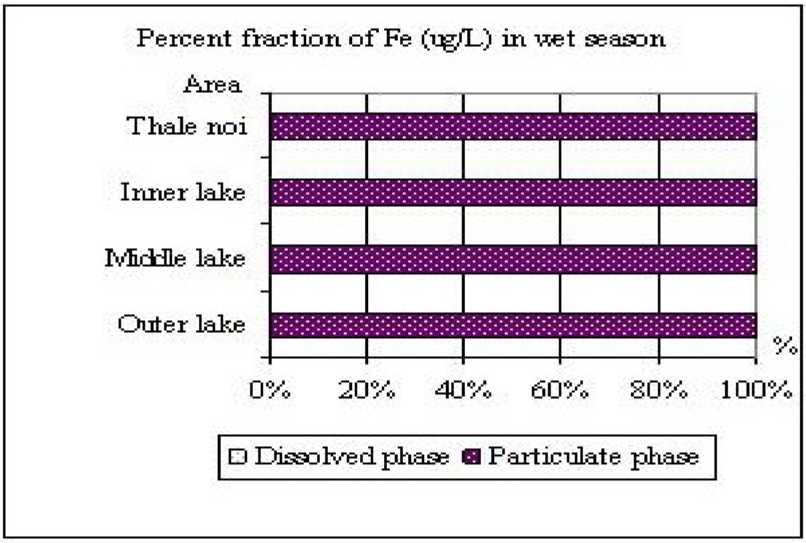


Figure 3-7 The percent fraction of dissolved and particulate Al (µg/L) in wet and dry season.



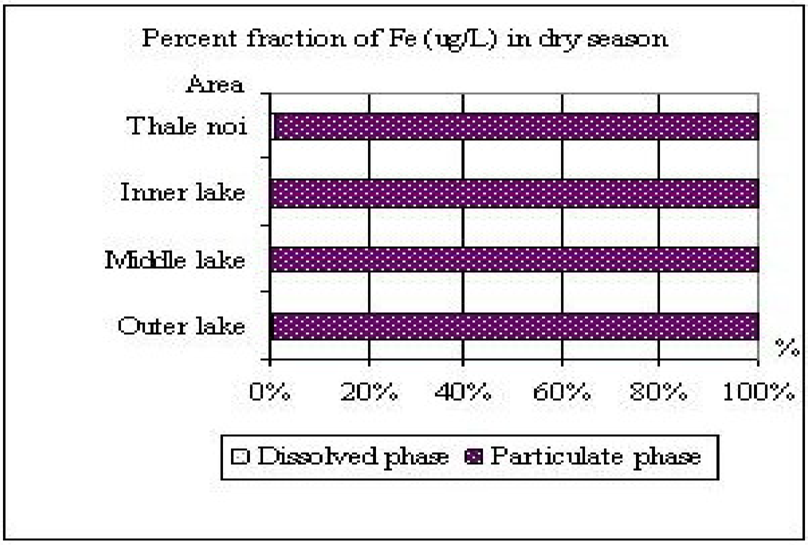
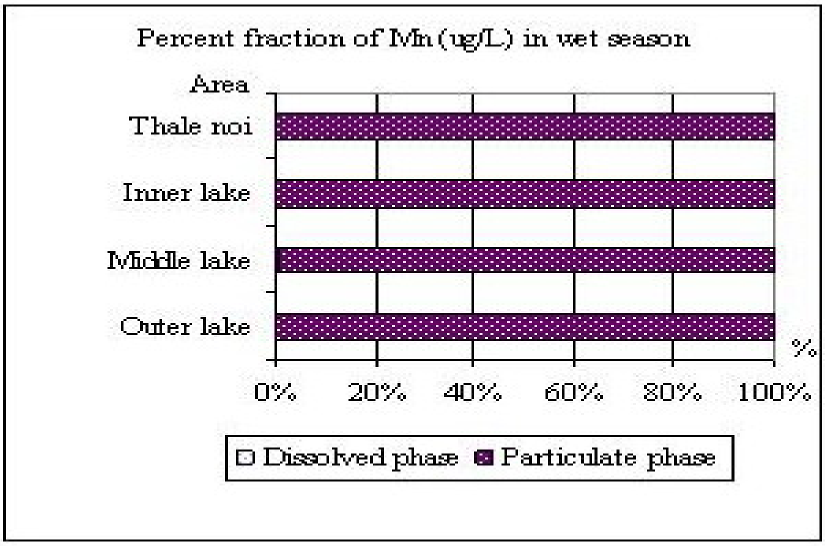


Figure 3-8 The percent fraction of dissolved and particulate Fe (µg/L) in wet and dry season..



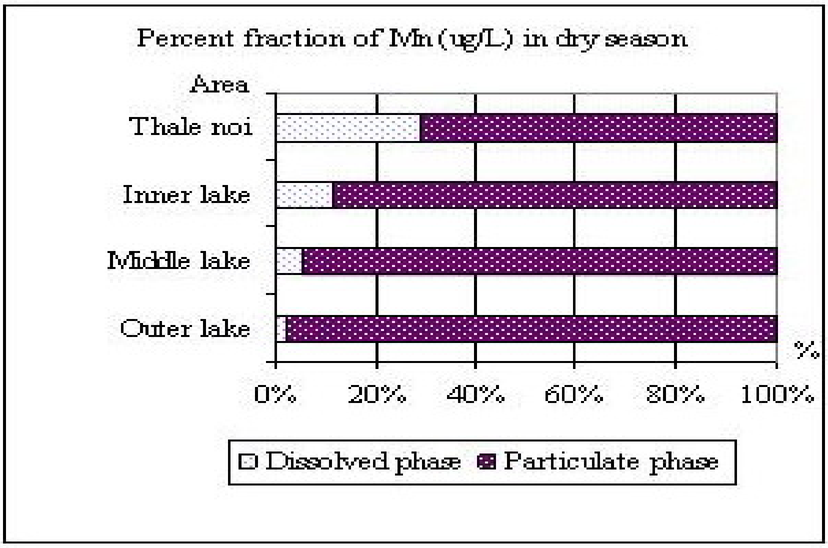


Figure 3-9 The percent fraction of dissolved and particulate Mn (µg/L) in wet and dry season.

3.5 Trace metals -Salinity Profiles

The fate of metals in natural waters depends on physico-chemical properties of aquatic system. The changes of ionic strength (1-4x10^{-3} mol L^{-1} for river water and 0.6 mol L^{-1} for sea water) together with the changes of composition of natural waters cause the removal of some constituents by flocculation, precipitation, sorption, complexation, redox reaction as well as the changes of dissolved chemical forms of metals (Dyrssen and Wedborg, 1980; Millward, 1995). The variation of salinity in the Songkhla Lake System (0-33 psu) depends on the tide and the strength of the inflowing river. The effect of salinity to the fate of metal was discussed.

3.5.1 Dissolved metal-Salinity

The profiles of Cd, Cu, Pb, Zn, Al, Fe and Mn vs salinity in Inner Lake, Middle Lake and Outer Lake were illustrated in Figure 3-10 to Figure 3-30.

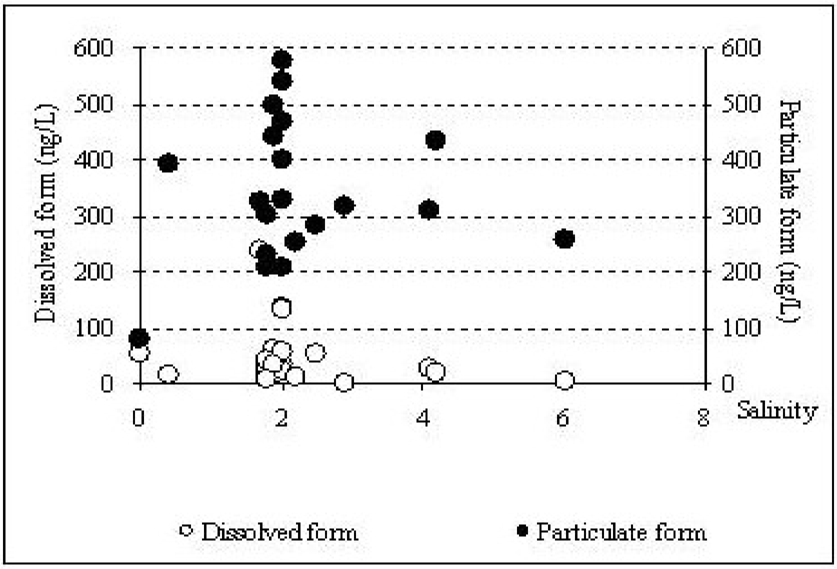
In Inner Lake (Figure 3-10 to Figure 3-16), the removal of all metals occurred when salinity increased in both wet and dry seasons. This may due to salt induce coagulation of colloidal particles in this area. Similar behavior was found in low salinity area in Changjing Estuary (Wang and Lui, 2003). In Middle Lake (Figure 3-17 to Figure 3-23), the dissolved Cd, Pb, Zn, Al, Fe and Mn tend to decrease with salinity in both seasons. Similar behaviors were reported in the Tamar Estuary (Liu *et al*., 1998), Beaulier Estuary (Turner *et al.*, 1998) and Conwy Estuary (Zhou *et al*., 2003). The dissolved Cu in wet season behaved differently, it tends to increase with salinity. In Outer Lake (Figure 3-24 to Figure 3-30), dissolved Cd, Cu, Pb, Al, Fe and Mn in wet season tend to decrease seaward. These metals were removed in the estuary and exhibited non-conservative behaviors. Zinc did not show a removal in the estuary since it remained relatively constant with salinity increases. This may be attributed to the formation of chloride-complexes, occurring during the mixing of fresh water with seawater and/or to desorption of exchangeable metals due to the increasing concentration of major cations (Paucot and Wallast, 1997). The metal behaviors from this study differed from what reported by Sirinawin *et al.* (1998) of which Cu, Pb and Zn exhibit “U“ shape distribution in the Outer Lake and Cd showed conservative character. In dry season, dissolved Cd, Pb, Fe and Mn tend to increase slightly with salinity. The resuspension of sediments and defloculation of particles may affect the behavior of these metals (Wang and Liu, 2003). The dissolved Cu was quite constant at salinity <20 psu and slightly decrease at salinity > 20 psu.

3.5.2 Particulate metal-Salinity

In Inner Lake, the salinities at most sampling sites were found approximately 2 psu in wet season and salinity of <1 psu in dry season. The high variations of particulate Cd, Cu, Pb, Zn, Al, Fe and Mn were found in most part of the lake. This may reflect the characteristic of suspended matter of continental origin distributed in the lake.

In Middle Lake, the particulate Cd showed slightly increase with salinity while the particulate Cu, Pb, Zn, Al, Fe and Mn decrease with salinity in wet season. The removal of particulate phase was pronounced in the east part of the Middle Lake where Al, Fe and Mn distributed more condense. This may result the coagulation or flocculation of clay minerals and allochthonous materials. In dry season, the particulate Cu, Al and Mn showed slightly positive deviation with salinity while the particulate Pb, Zn and Fe showed slightly negative deviation with salinity.

In Outer Lake, the particulate metal of Cd, Cu, Pb, Zn, Al, Fe and Mn tend to decrease with salinity in wet season. The similar behavior of some metals such as Zn and Fe in suspended particles has been reported in the Conwy estuary (Zhou *et al*., 2003), Tamar estuary (Liu, 1996), Beaulier estuary (Turner *et al*., 1998) and Scheldt estuary (Zwolsman and Van Eck, 1999). However, the behaviors of these metals were different from what was reported by Sirinawin (1998) of which most metals exhibited “U “distribution. The particulate Cu, Pb, Al and Fe in dry season tend to increase with salinity while Cd, Zn and Mn showed scattered distribution.



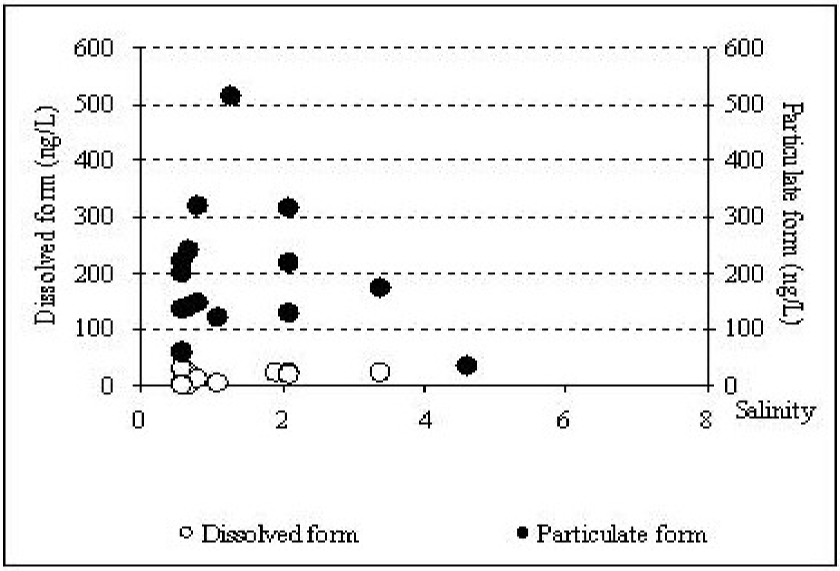
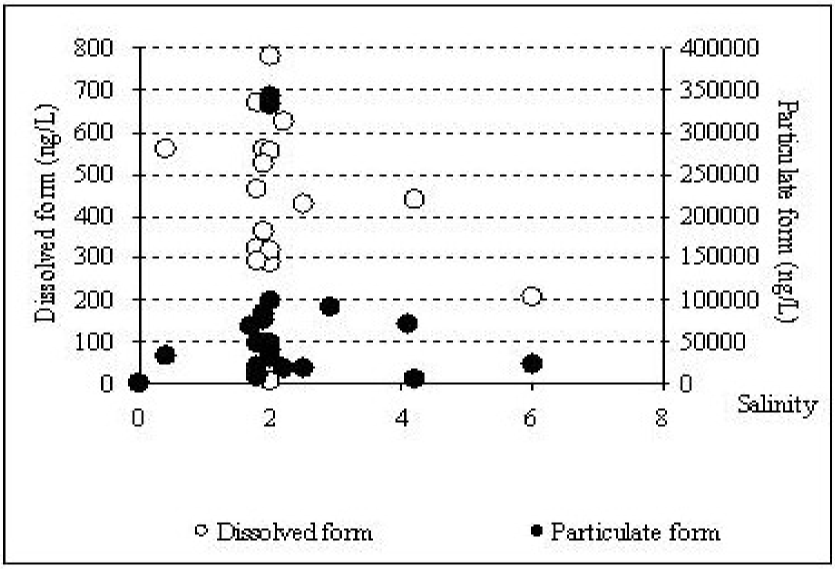


Figure 3-10 Concentrations and distributions of dissolved and particulate Cd in Inner Lake



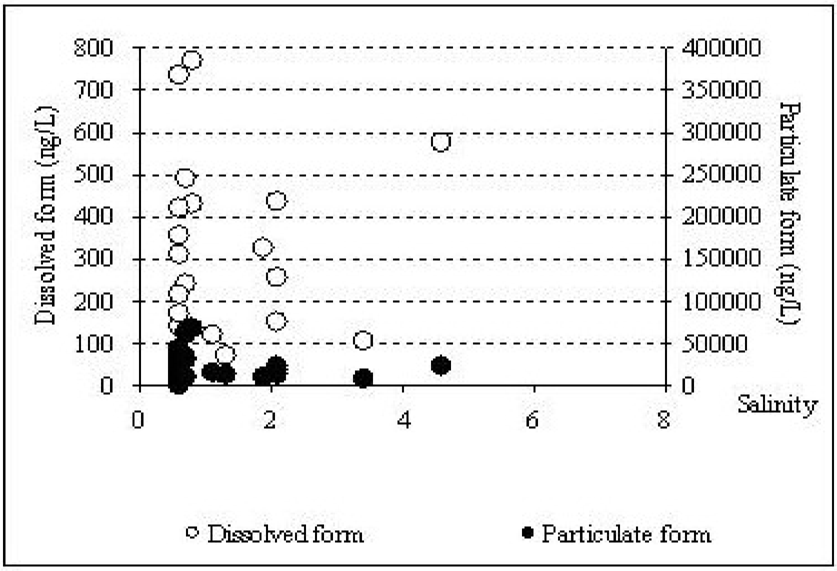
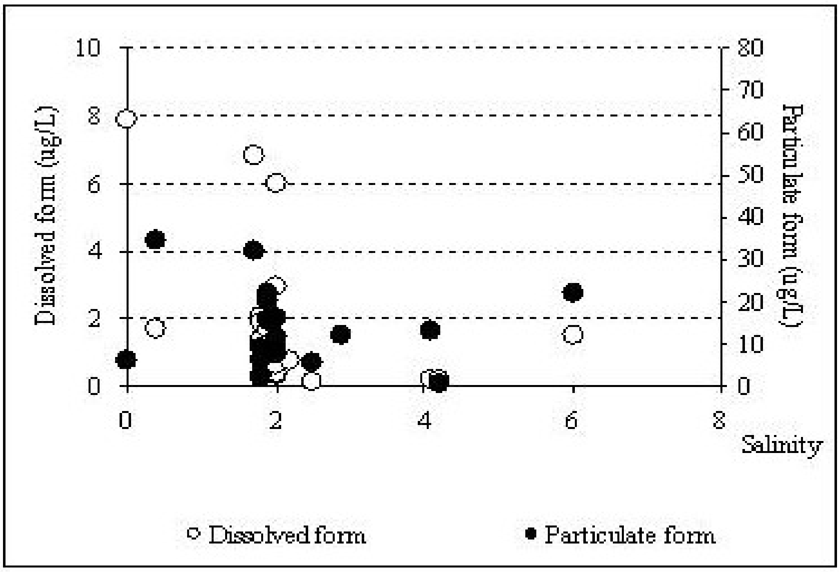


Figure 3-11 Concentrations and distributions of dissolved and particulate Cu in Inner Lake



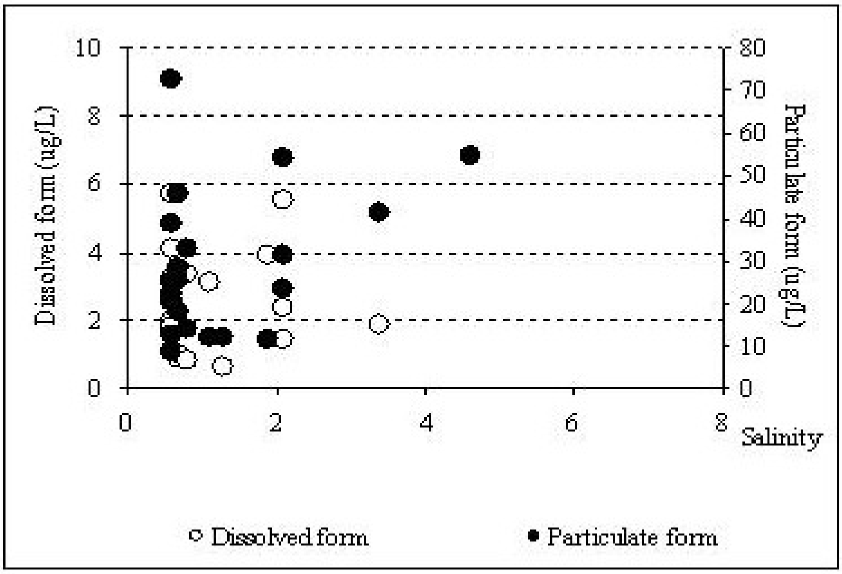
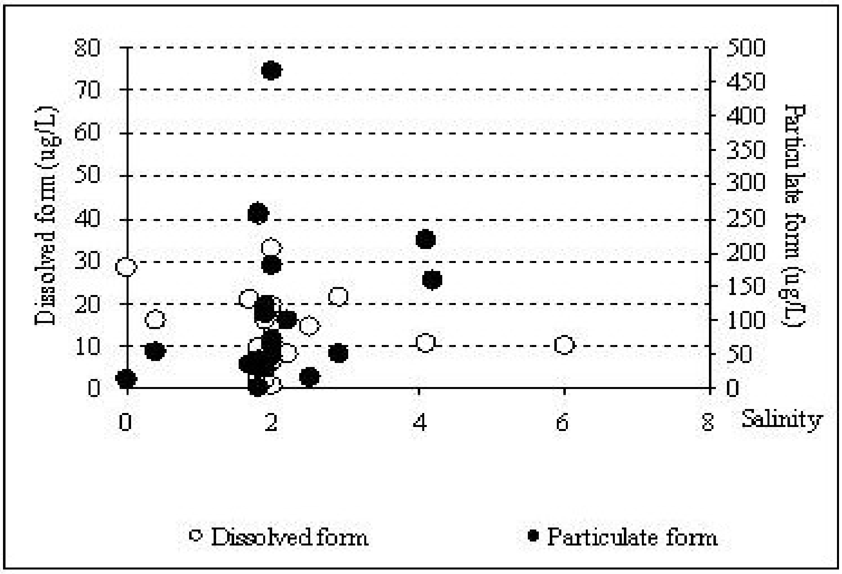


Figure 3-12 Concentrations and distributions of dissolved and particulate Pb in Inner Lake



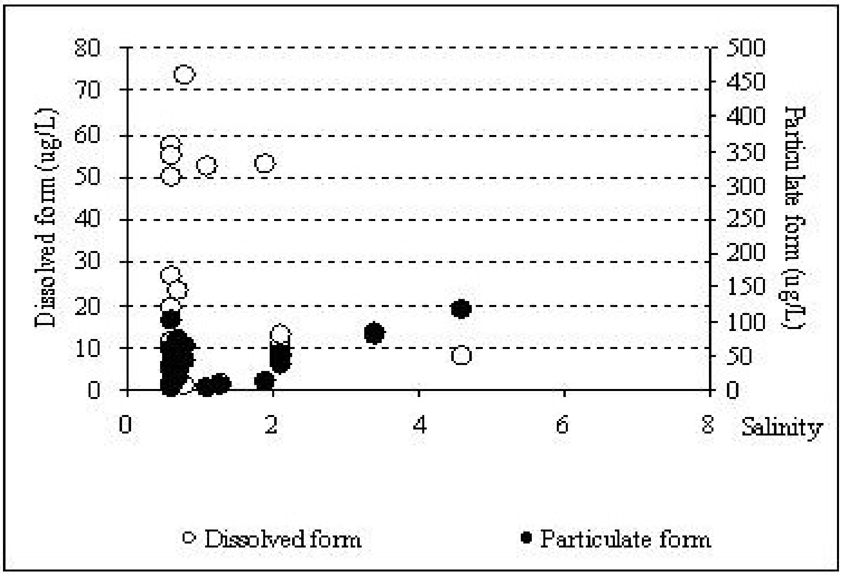
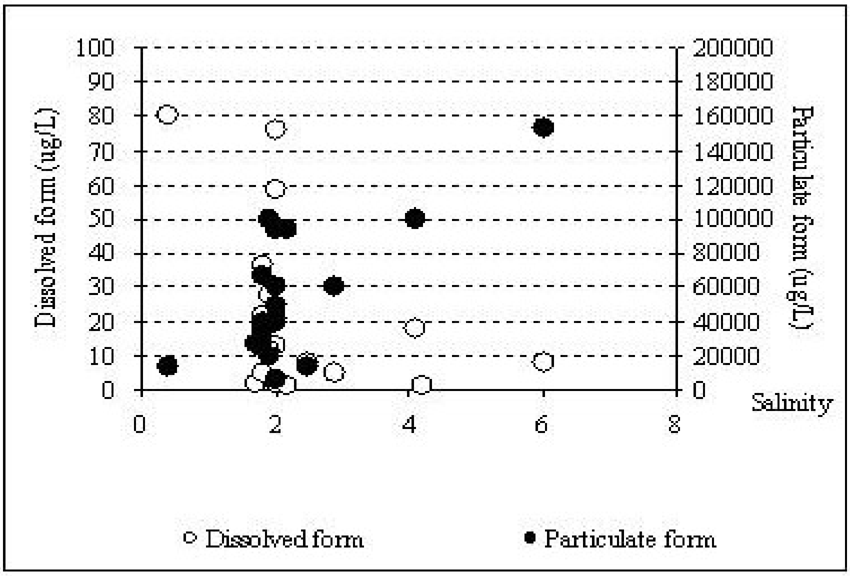


Figure 3-13 Concentrations and distributions of dissolved and particulate Zn in Inner Lake



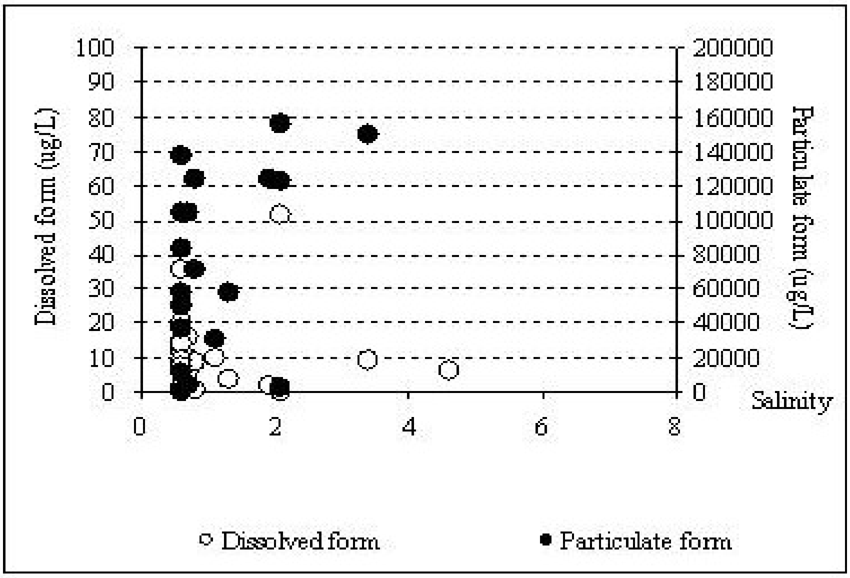
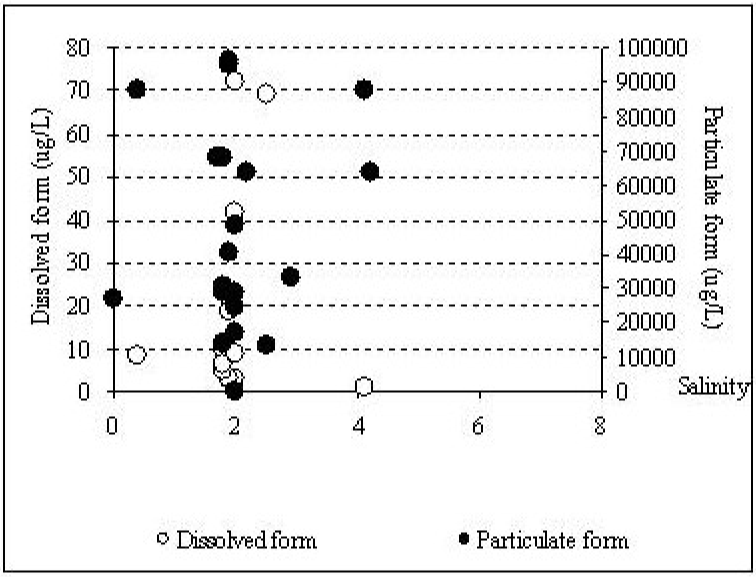


Figure 3-14 Concentrations and distributions of dissolved and particulate Al in Inner Lake



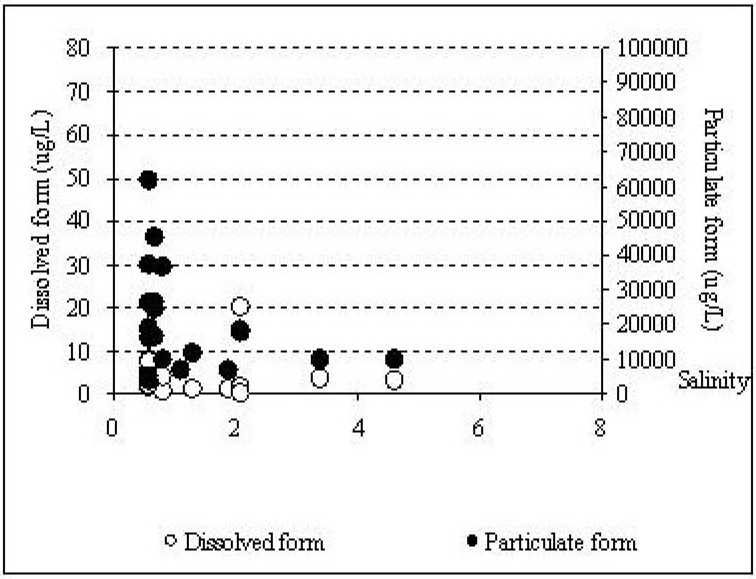
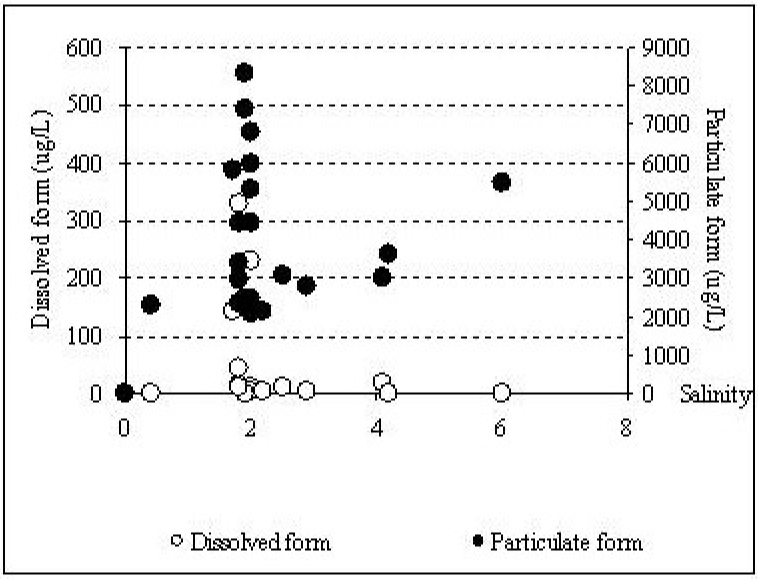


Figure 3-15 Concentrations and distributions of dissolved and particulate Fe in Inner Lake



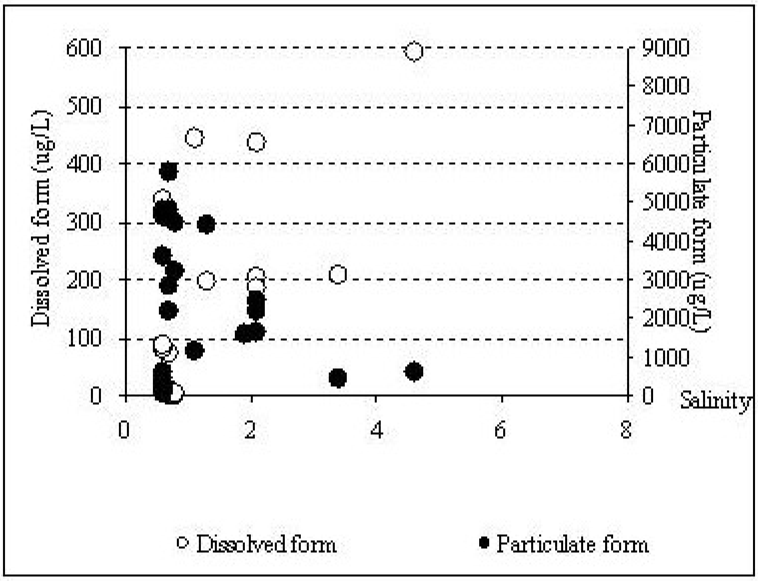
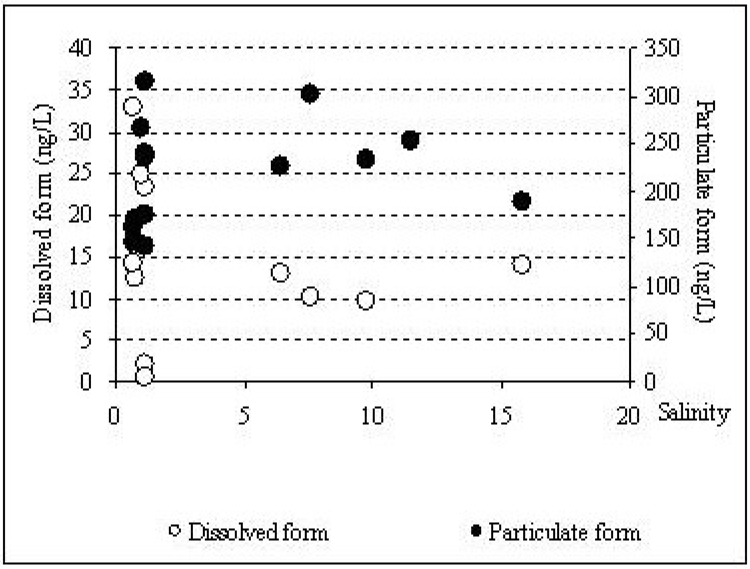


Figure 3-16 Concentrations and distributions of dissolved and particulate Mn in Inner Lake



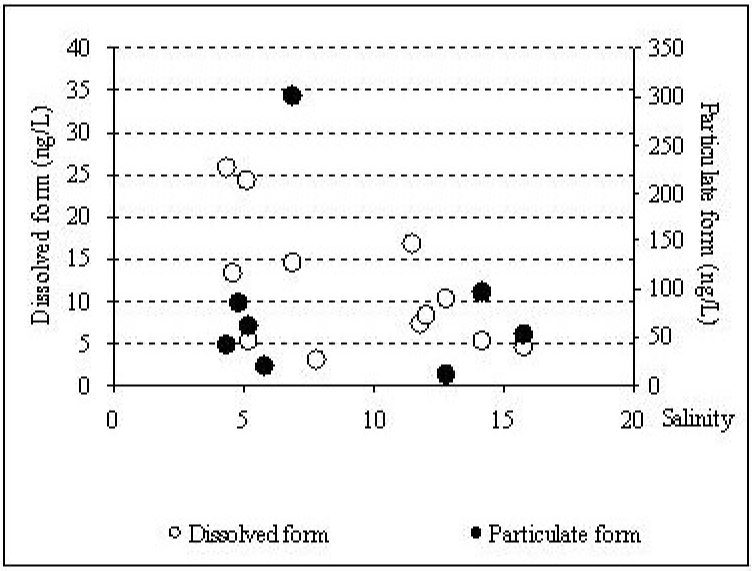
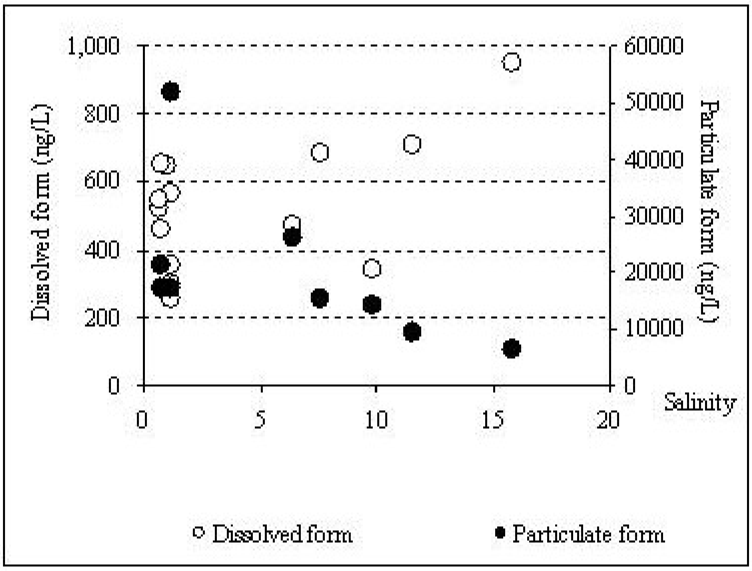


Figure 3-17 Concentrations and distributions of dissolved and particulate Cd in Middle Lake



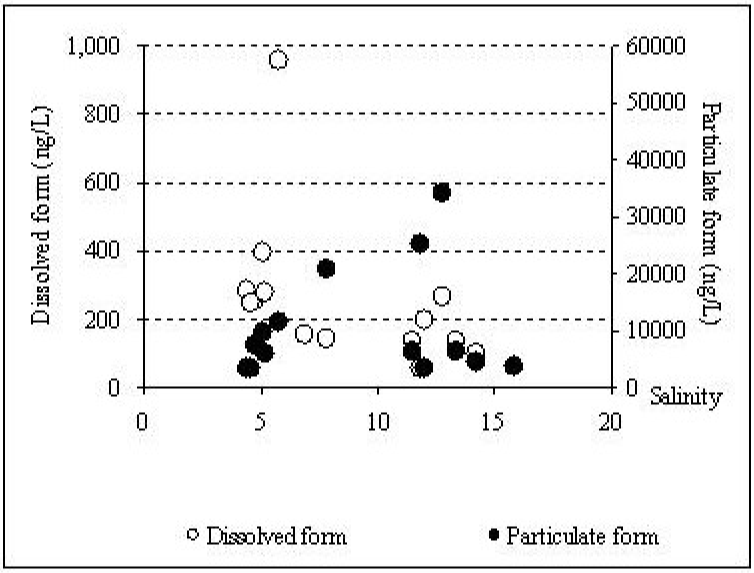
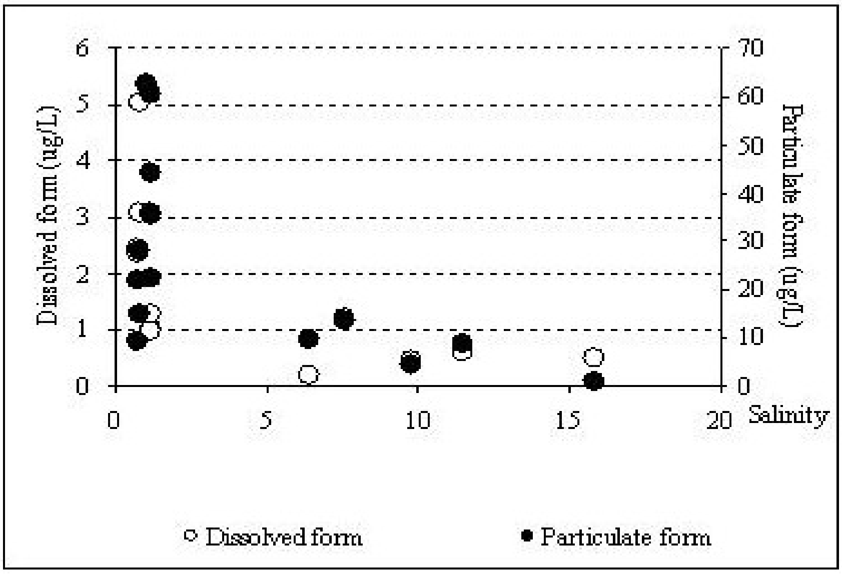


Figure 3-18 Concentrations and distributions of dissolved and particulate Cu in Middle Lake



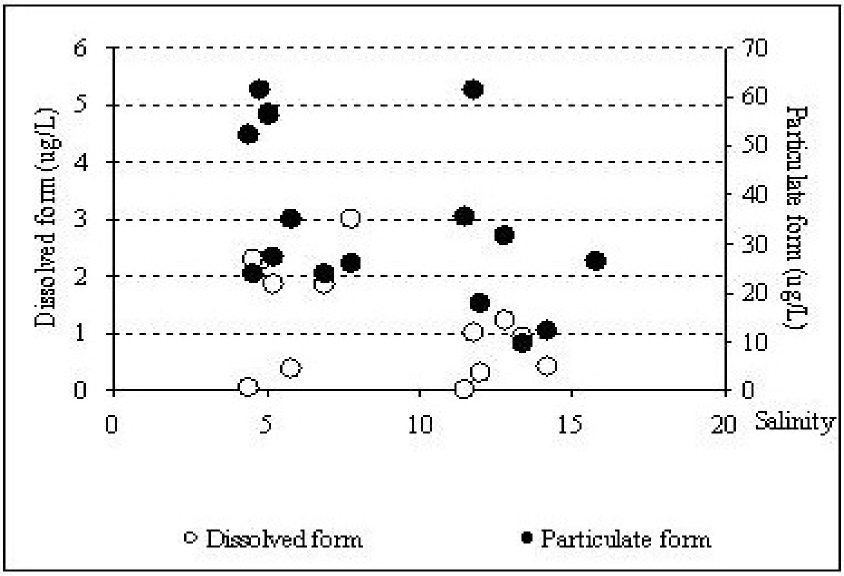
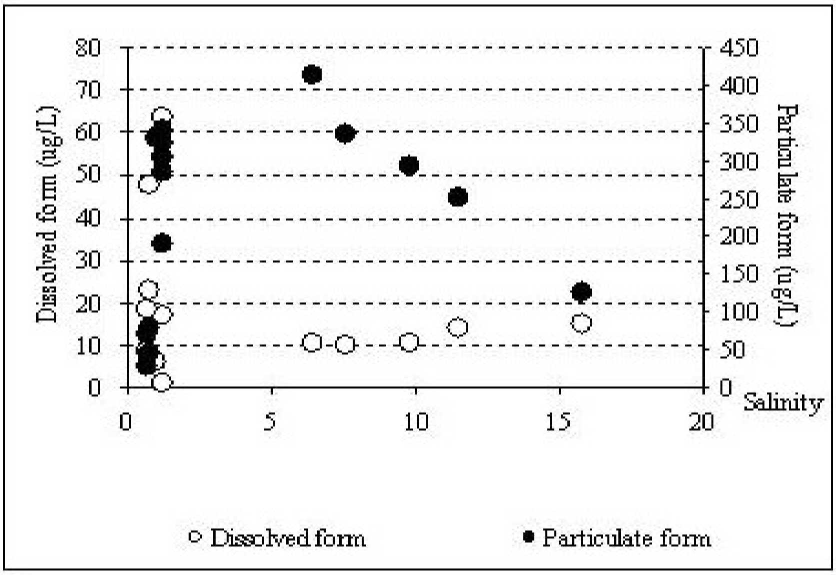


Figure 3-19 Concentrations and distributions of dissolved and particulate Pb in Middle Lake



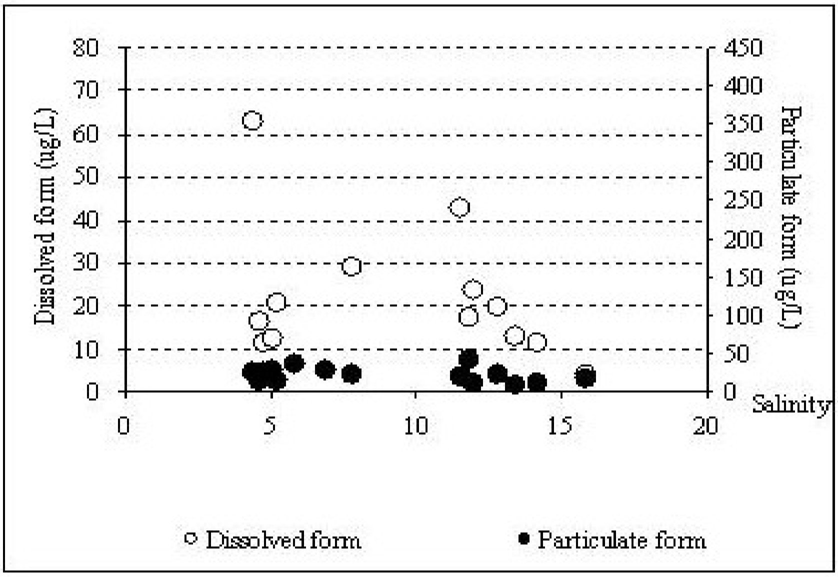
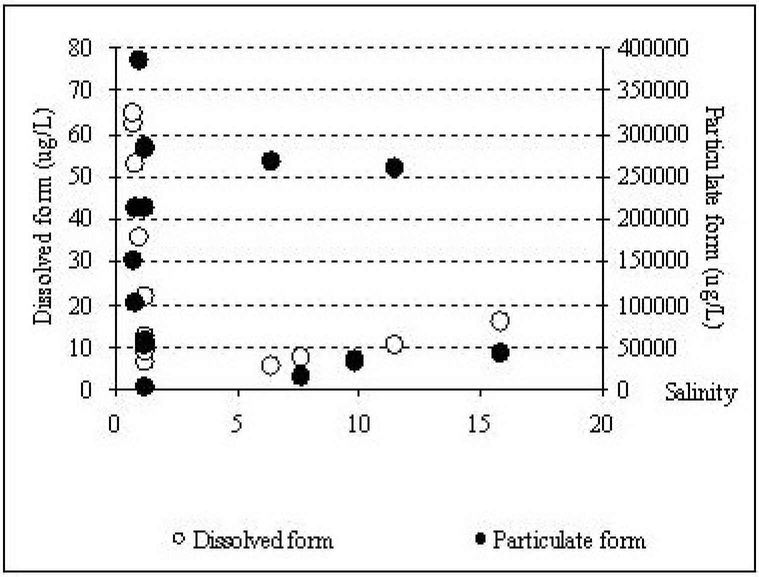


Figure 3-20 Concentrations and distributions of dissolved and particulate Zn in Middle Lake



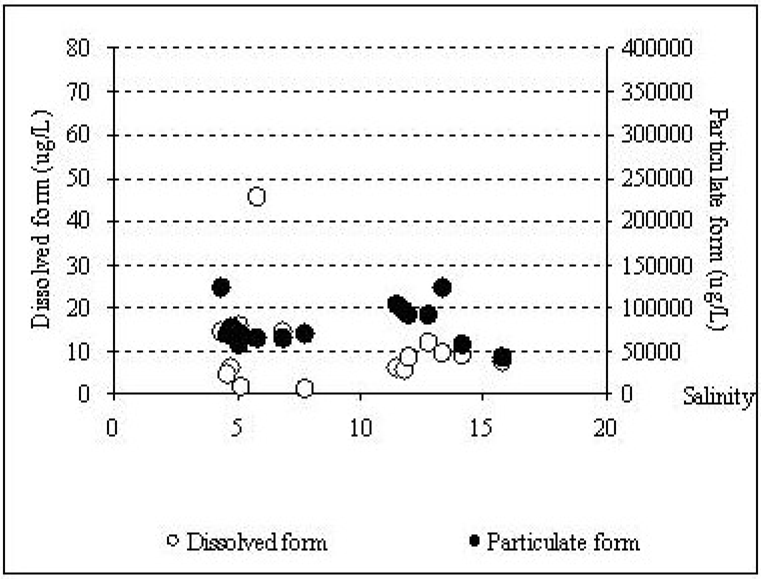
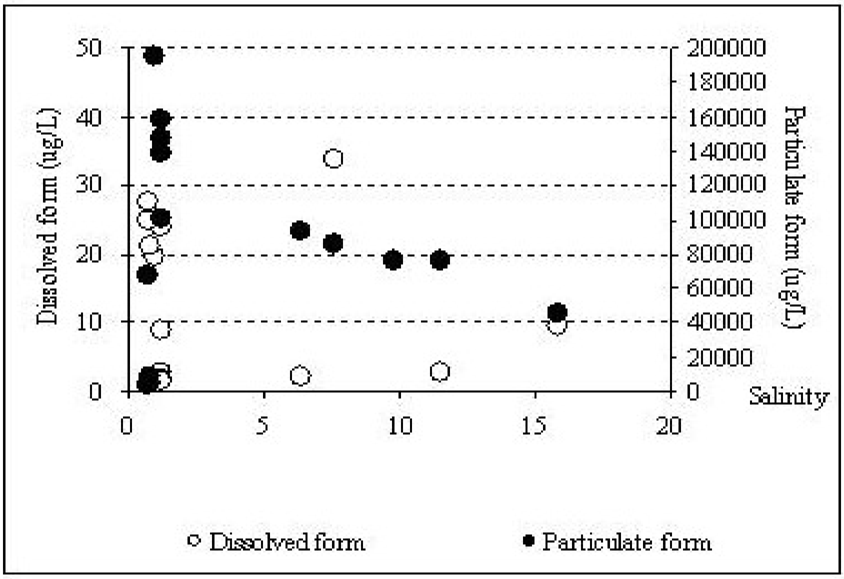


Figure 3-21 Concentrations and distributions of dissolved and particulate Al in Middle Lake



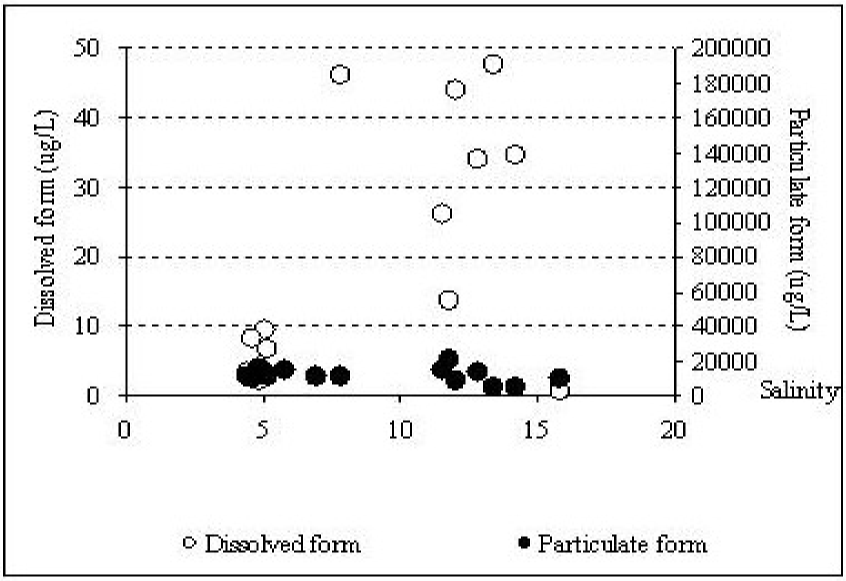
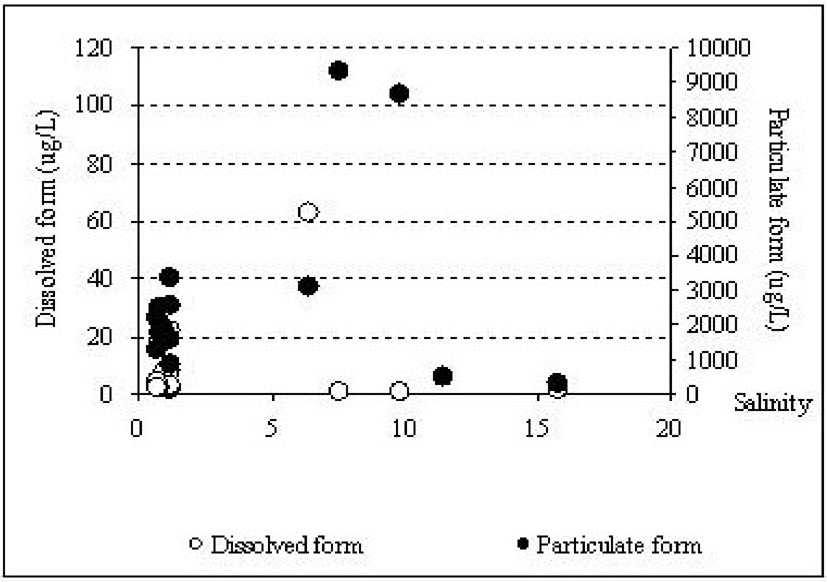


Figure 3-22 Concentrations and distributions of dissolved and particulate Fe in Middle Lake



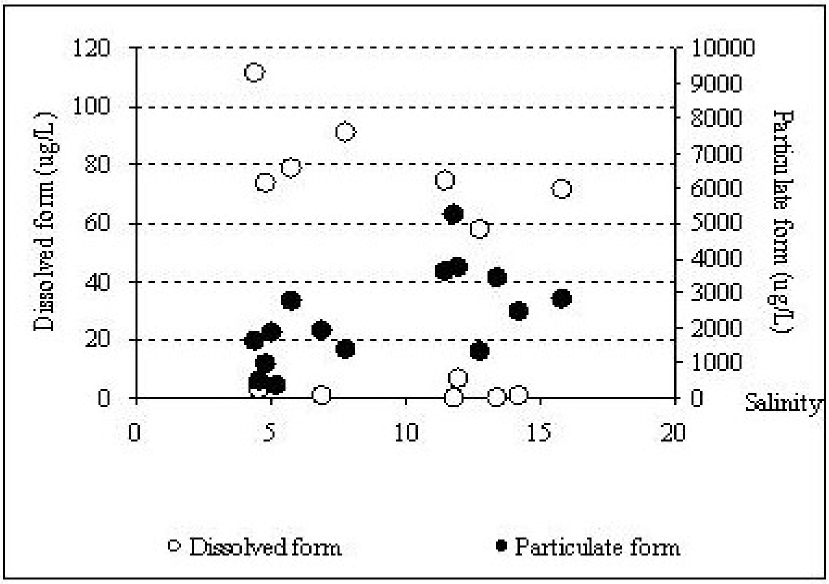
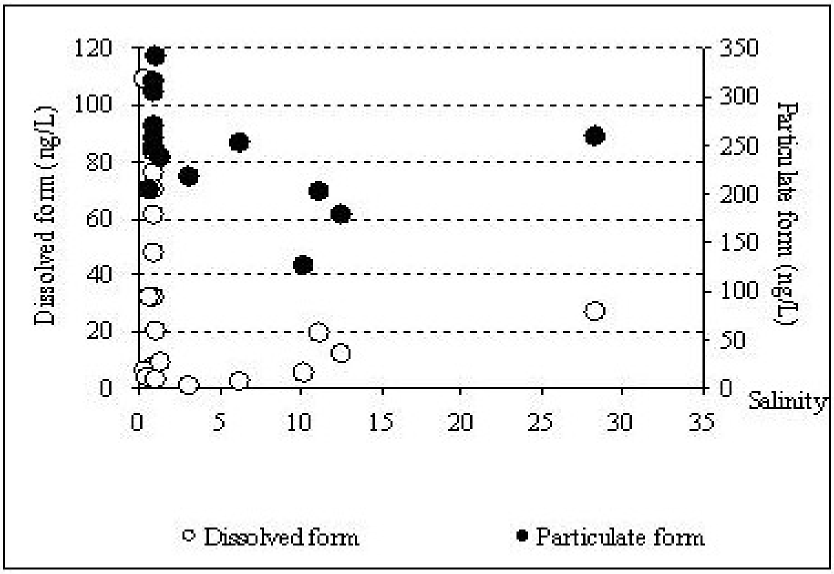


Figure 3-23 Concentrations and distributions of dissolved and particulate Mn in Middle Lake



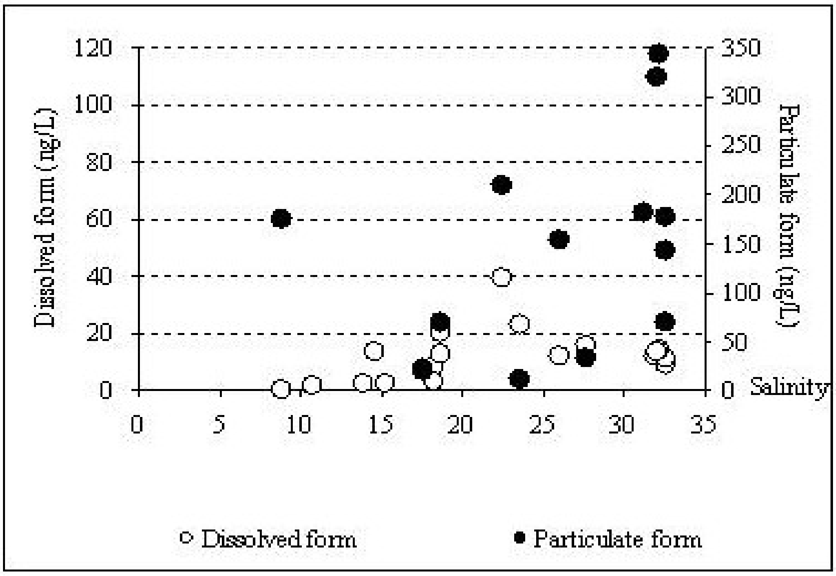
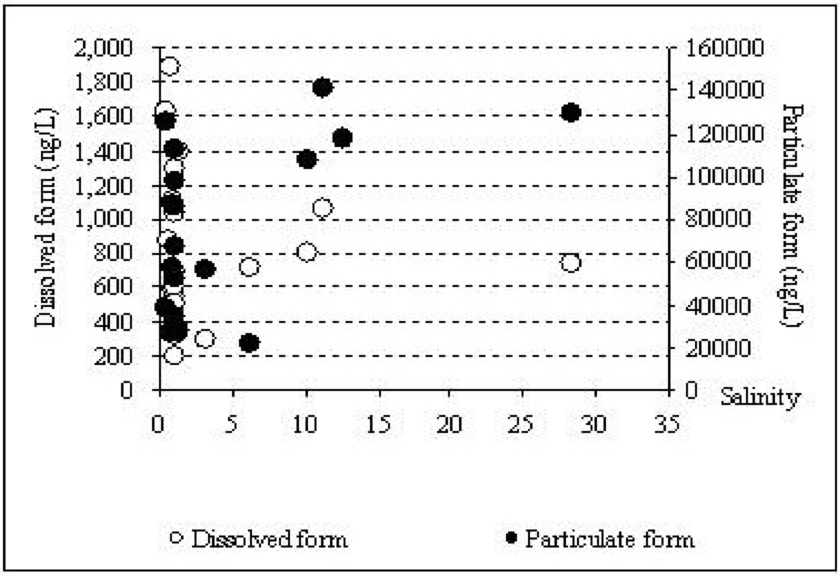


Figure 3-24 Concentrations and distributions of dissolved and particulate Cd in Outer Lake



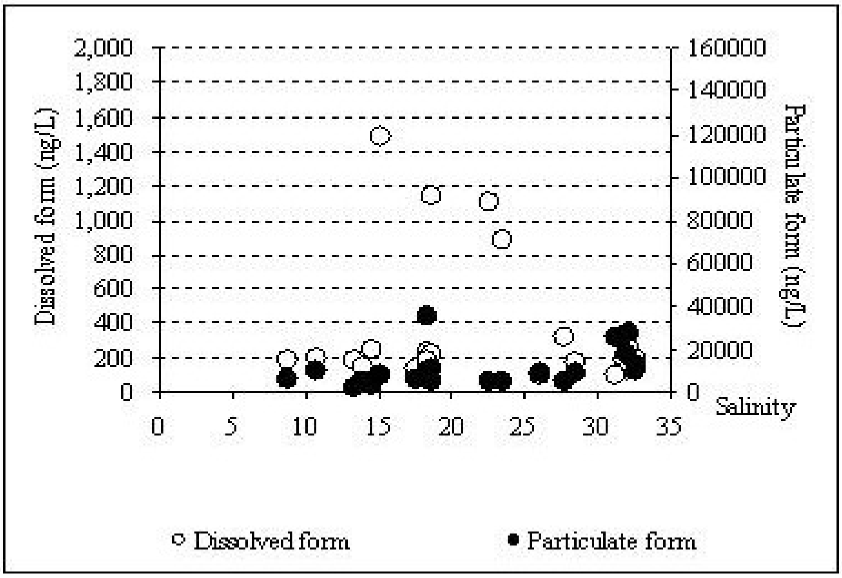
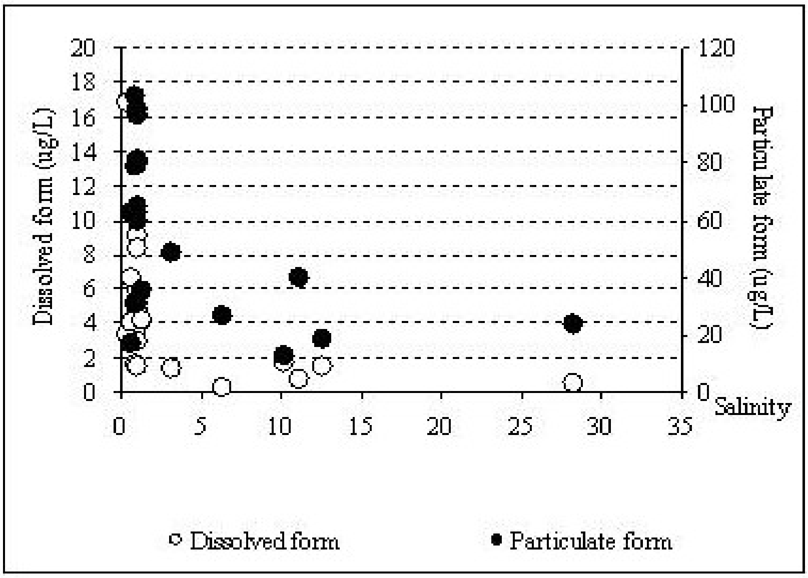


Figure 3-25 Concentrations and distributions of dissolved and particulate Cu in Outer Lake



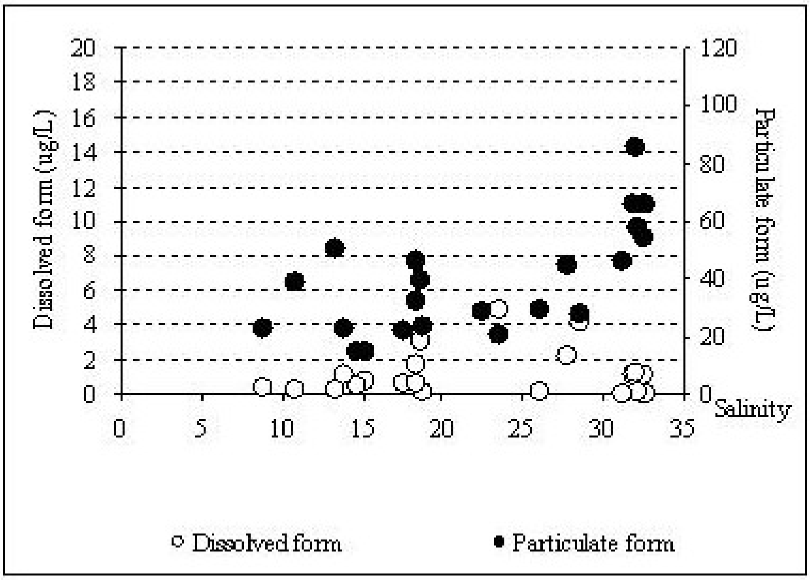
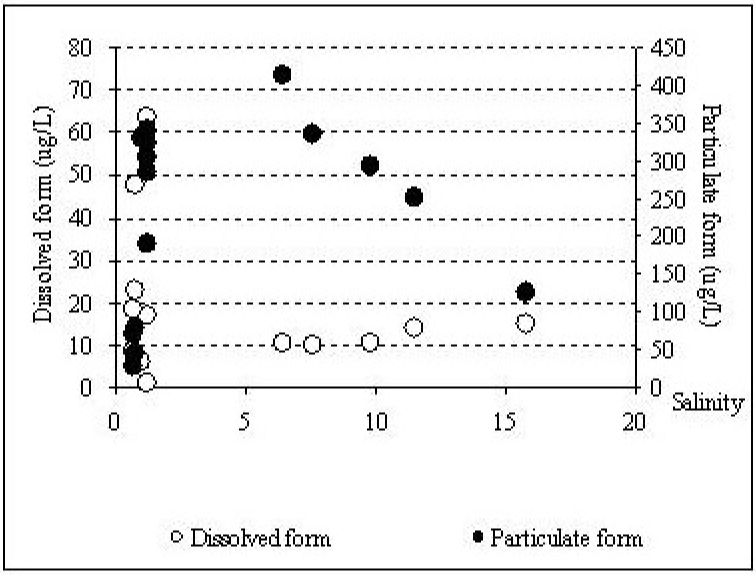


Figure 3-26 Concentrations and distributions of dissolved and particulate Pb in Outer Lake



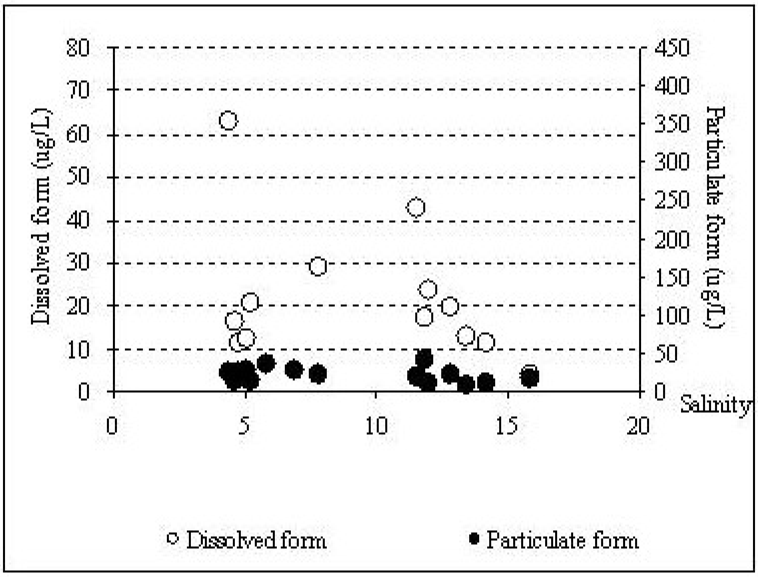
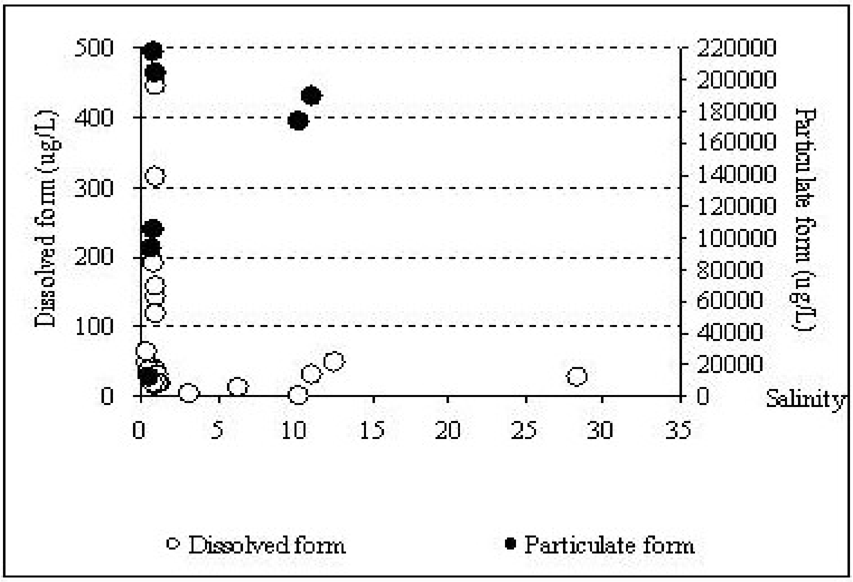


Figure 3-27 Concentrations and distributions of dissolved and particulate Zn in Outer Lake



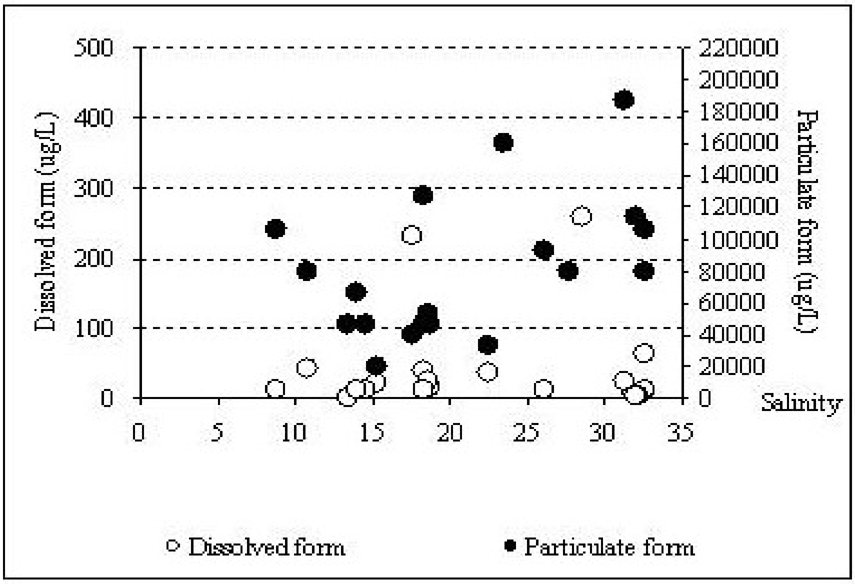
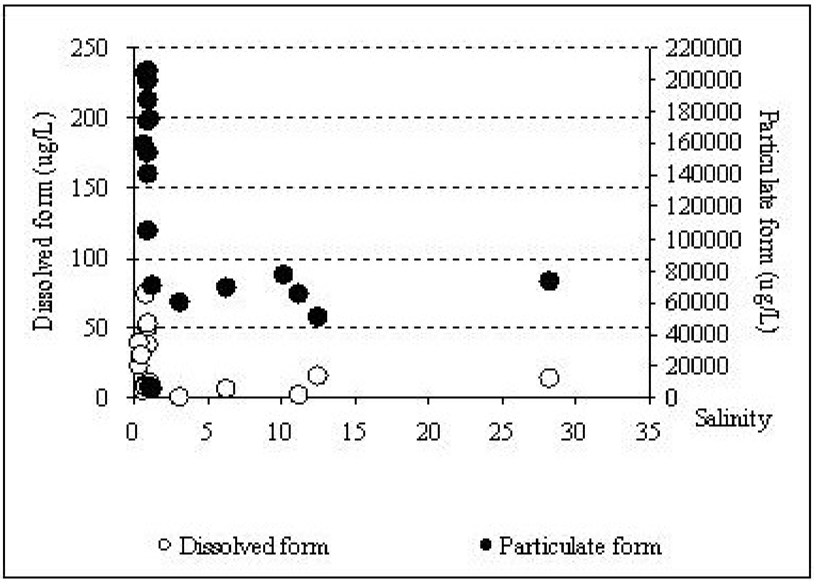


Figure 3-28 Concentrations and distributions of dissolved and particulate Al in Outer Lake



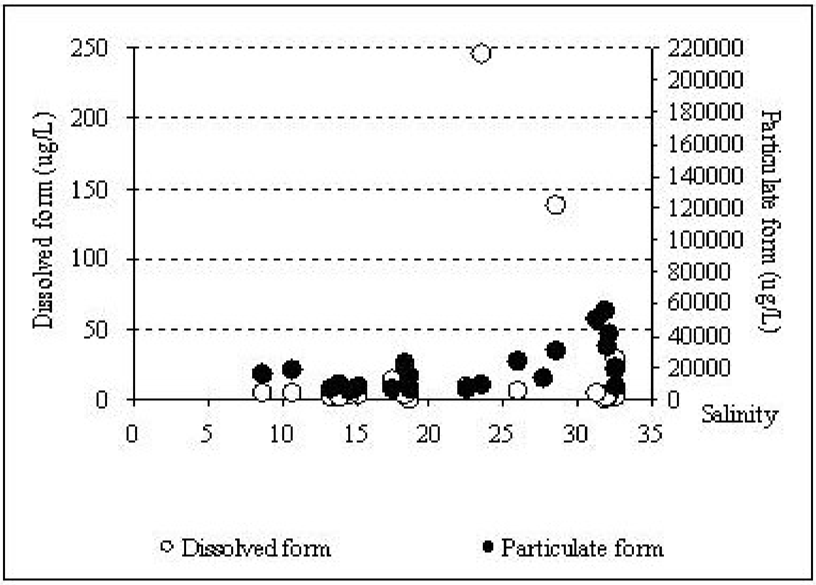
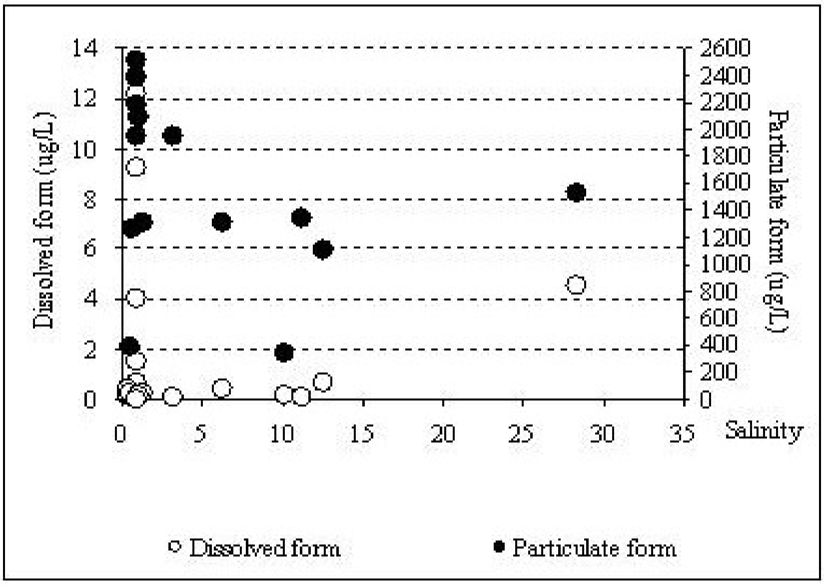


Figure 3-29 Concentrations and distributions of dissolved and particulate Fe in Outer Lake



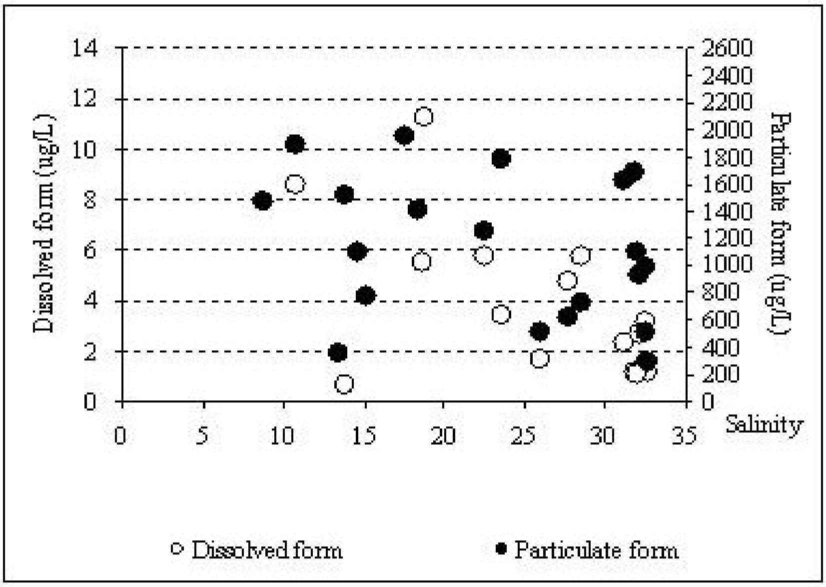


Figure 3-30 Concentrations and distributions of dissolved and particulate Mn in Outer Lake

3.6 The partitioning of trace metals between particulate and dissolved phases

The distribution of metals between the dissolved and the particulate phase was characterized by the distribution coefficient (K_d). It is an essential factor in the description of the geochemical properties of element and give better picture than the fraction of metal ions in solution (Martin and Whitfield, 1983). The seasonal K_d values of Cd, Cu, Pb, Zn, Al, Fe and Mn in Songkhla Lake Systems were presented in Table 3.10. In general, the K_d values of most metals in all areas were similar in both wet and dry season. However, the K_d of Cd and Cu in Thale Noi in dry season were slightly higher than other bodies of the lake. This indicated that in dry season Cd and Cu showed the affinity to solid phase and its tendency to be transported as particulate forms. The interactions with biogenic and detrital particulate phases in Thale Noi are important in controlling dissolved Cd and Cu concentration. A sequence of logK_d values (Al~Fe>Mn>Cu>Cd≥ Pb>Zn) was found in most of areas studied. It is seen that high particle reactivity for a metal would tend to increase that K_d value of metal. Similar sequence of K_d of metals was reported by Munksgaard and Parry (2001). Consideration of the K_d value of metals only in the Outer Songkhla Lake, most of metals showed higher K_d values compared with the results from Sirinawin *et al.* (1998). The lower value of K_d from previous study may due to the weak acid digestion of suspended matter compare to the digestion of this study.

Table 3- 10 The average log K_d value (L/g) in wet and dry season of Songkhla Lake System

	Thale Noi		Inner Lake		Middle Lake		Outer Lake	
	wet	dry	wet	dry	wet	dry	wet	dry
Cd	4.0	4.9	3.8	4.2	3.7	3.5	3.5	4.3
Cu	4.5	5.3	4.8	4.8	4.6	4.6	4.2	4.8
Pb	3.9	4.2	3.7	4.0	3.6	4.4	3.5	5.0
Zn	3.6	3.3	3.6	3.3	3.8	3.0	3.5	3.4
Al	6.0	7.1	6.6	6.9	6.2	7.1	6.1	6.7
Fe	6.1	5.9	6.4	6.7	6.3	6.0	6.1	6.6
Mn	4.8	4.5	5.3	4.5	5.2	5.2	5.8	5.5

3.6.1 K_d and salinity Plot

The interaction of trace metals with settling particles is important in regulating the metal concentrations in aquatic system. The distribution coefficients of metals in natural water are based on ionic strength of solution and adsorption equilibria. Thus it is mainly influenced by salinity and particle concentration. In this study the K_d-salinity plots of Cd, Cu, Pb, Zn, Al, Fe and Mn were illustrated in Figure 3-31 to Figure 3-36 in order to reveal the geochemistry of metals in the system.

The K_d valued of Cd and Cu in Inner Lake, Middle Lake and Outer Lake decrease with salinity in wet season. The decreasing of K_d revealed the desorption of exchangeable metals due to the increasing concentration of major cations. This may be true for some estuaries such as Sanfrancisco Bay and Savannah Estuary where the decreasing of K_d with salinity has been attributed to the formation of chloride-complexes occurring during the mixing (Turner, 1996). However, this mechanism can not explain for the K_d in Songkhla Lake System as both dissolved Cd and particulate decrease with salinity. The K_d valued of Cu in dry season of Middle Lake show an increase with increasing salinity. The similar result was found in Humber Estuary (Comber, 1995) where Cu is bound strongly to natural organic ligands and the concentration of such ligands in the dissolved phase had been shown to generally decrease with increasing salinity (Apte *et al.,* 1990).

The K_d valued of Zn in both seasons in Outer Lake decrease with salinity, similar result was found in Scheldt Estuary and Weser Estuary (Paucot and Wallast, 1997). The K_d valued of Mn in both seasons in Inner Lake, Middle Lake and Outer Lake increase with salinity. The similar trend was showed in Scheldt Estuary (Paucot and Wallast, 1997) which suggests that the additional input of this element due to the resuspension of sediment and its subsequent release to the water column from interstitial water enriched in dissolved metals.

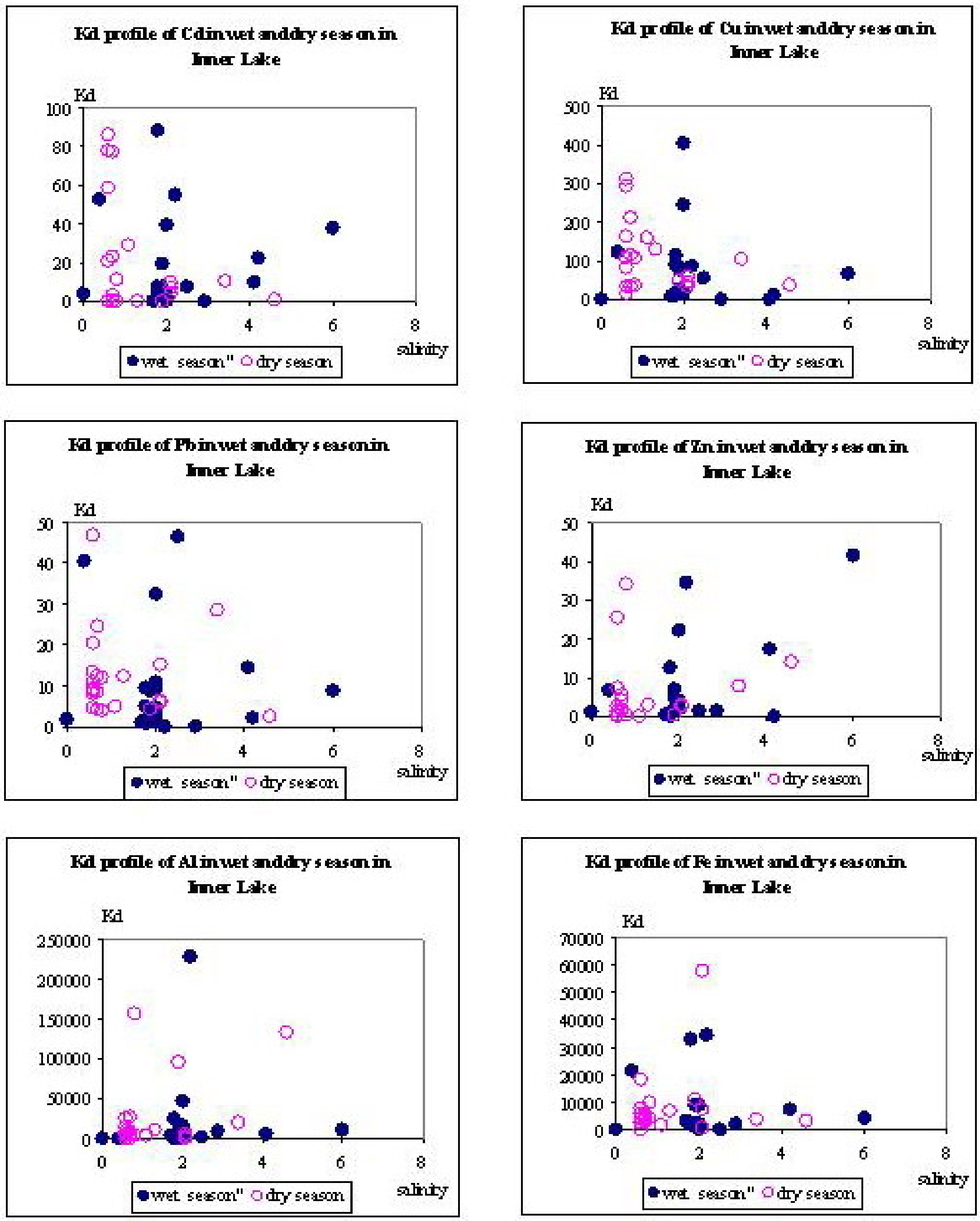


Figure 3-31 The K_d profile of Cd, Cu, Pb, Zn, Al and Fe in wet and dry season in Inner Lake

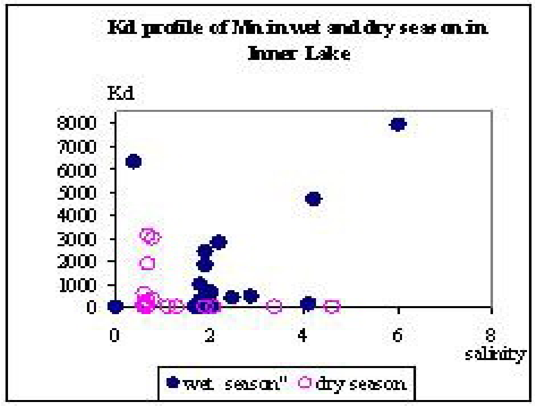


Figure 3-32 The K_d profile of Mn in wet and dry season in Inner Lake

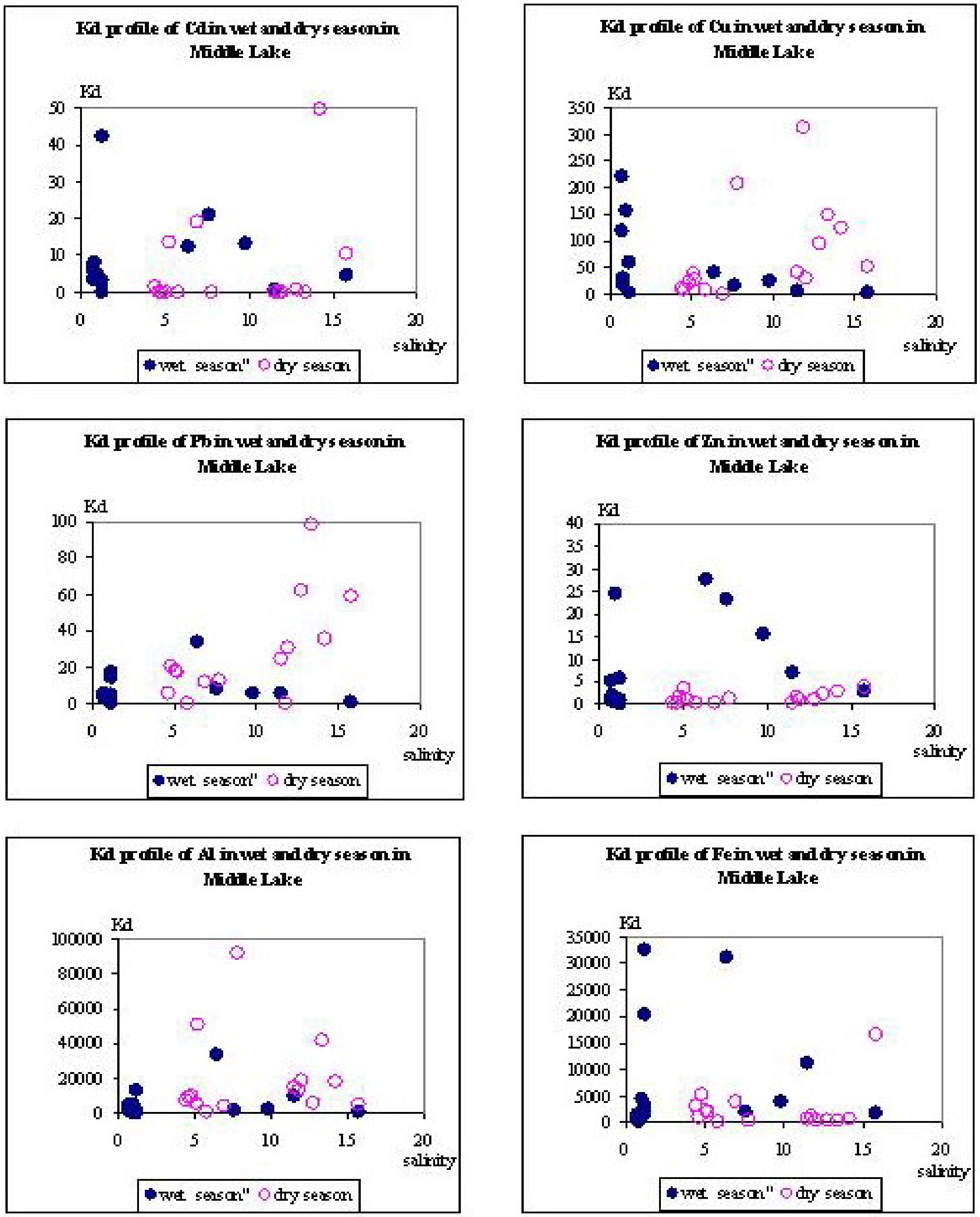


Figure 3-33 The K_d profile of Cd, Cu, Pb, Zn, Al and Fe in wet and dry season in Middle Lake

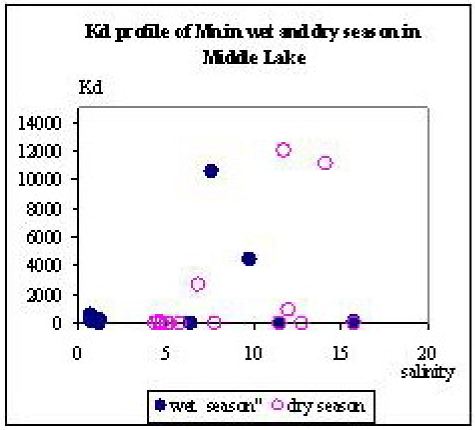


Figure 3-34 The K_d profile of Mn in wet and dry season in Middle Lake

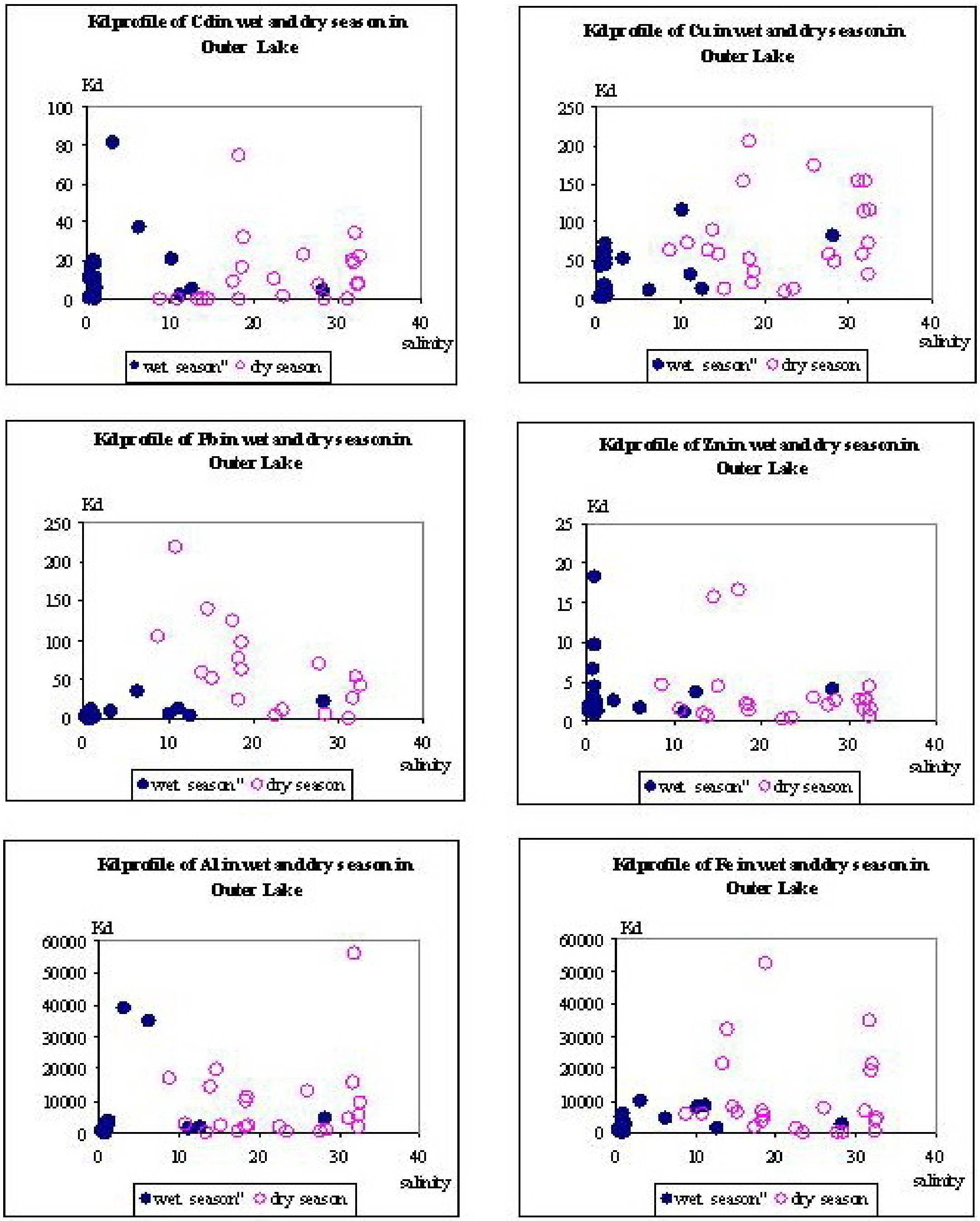


Figure 3-35 The K_d profile of Cd, Cu, Pb, Zn, Al and Fe in wet and dry season in Outer Lake

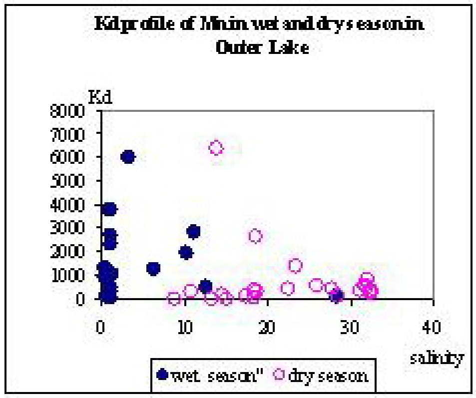


Figure 3-36 The K_d profile of Mn in wet and dry season in Outer Lake

3.6.2 K_d-PCA Plot

The K_d profiles of metals in Songkhla Lake System exhibited in different patterns as mentioned in previous section. In order to achieve more objective classification of the K_d profiles, the principal component analysis was applied to reveal the categories of metals.

Principal component analysis (PCA) has been used to extract information from the chemical analysis in order to find the relationships among these heavy metals. The PCA loading plot for K_d profiles allowed to recognize groups of samples with similar behavior and the existing correlation among the original variables usually the PCA are obtained by their eigenvalues >1 (Wang *et al.*,2005). The loading plots of correlated elements in Songkhla Lake System were showed in Figure 3-37 to Figure 3-38 and the categories of metals were summarized in Table 3-11.

Table 3-11 The categories of metals in Songkhla Lake System in wet and dry season

Location	season	Group I	Group II	Group III
Thale Noi	wet	Cd, Cu, Pb, Zn	Al, Fe, Mn	
	dry	Cd, Mn	Cu, Pb, Zn, Al, Fe.	
Inner Lake	wet	Cd, Pb, Zn;	Cu	Al, Fe, Mn
	dry	Cd, Cu, Pb	Zn, Al, Mn	Fe
Middle Lake	wet	Cd, Cu, Pb	Zn, Mn	Fe, Al
	dry	Cd, Zn, Fe	Pb	Cu, Al, Mn
Outer Lake	wet	Cd, Cu, Pb, Zn, Al, Fe	Mn	
	dry	Cd, Zn	Cu, Pb, Al	Fe, Mn

It can be seen that the PCA plot was a useful tool to provide a clear classification of metals in natural waters. The geochemistry of metals changed seasonally due to the changes of physico-chemical properties of natural water. In wet season of Thale Noi, Cd, Cu, Pb and Zn are not associated to suspended particles Al, Fe and Mn. This behavior was also found in Inner Lake and Middle Lake in wet season. However, in wet season of the Outer Lake, Cd, Cu, Pb and Zn are associated to suspended Al and Fe oxide. During dry season of Inner Lake, Middle Lake and Outer Lake, Cd, Cu Pb and Zn tend to closely bound to settling particles; either allochthonous aluminum silicates or Fe/Mn oxide. The behaviors of Cd, Cu, Pb, Zn, Al, Fe and Mn from this study were different from previously reported by Sirinawin *et al*. (1998).

It is of interest to mention about the behavior of Cd in Songkhla Lake waters. Cadmium is classified as a borderline B type (Turner *et al.,* 1981). However, the result from this study exhibited that Cd was closely related to Cu, Pb, Zn, Fe, and Mn which classified as borderline A type. The speciation study by Suitcharit (2006) reported that 54-83% of Cd was in cationic form as well as Pb and Zn. This may responsible for the geochemistry behavior of Cd in this lake system.

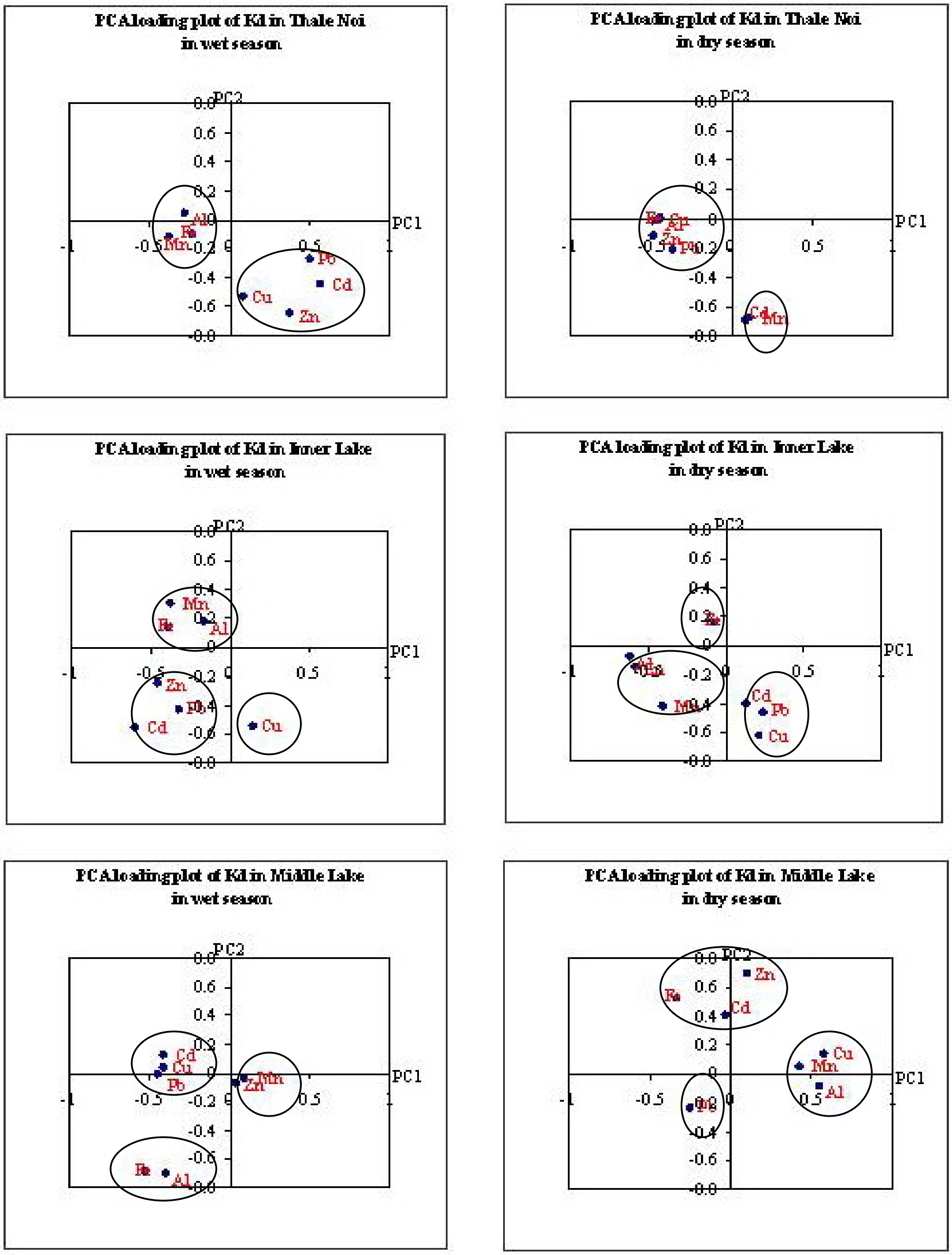


Figure 3-37 The PCA loaing plot of K_d in wet and dry season

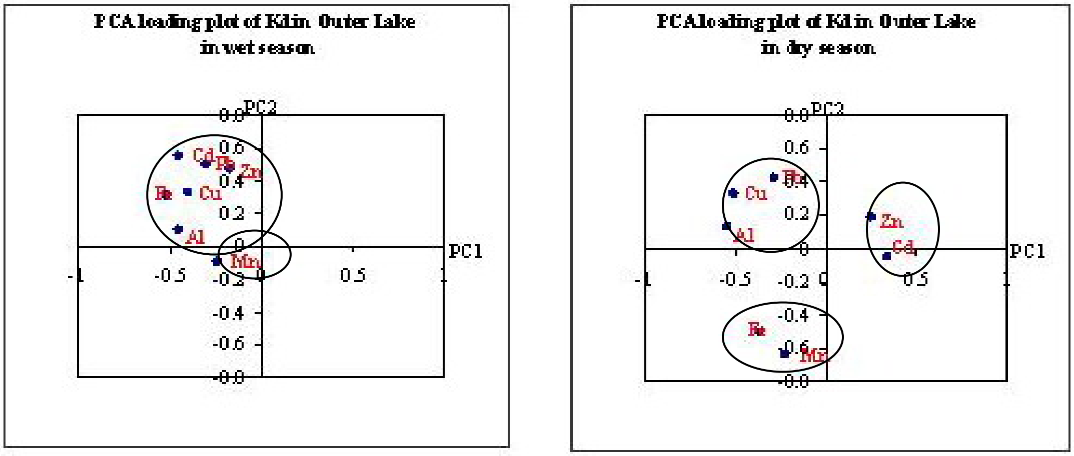


Figure 3-37(Cont.) The PCA loaing plot of K_d in wet and dry season