

CHAPTER 3

RESULTS AND DISCUSSION

3.1 Effect of oxygen and salinity on metals concentration in overlying water under controlled conditions in laboratory

3.1.1 Effect of aerobic and anaerobic condition on metal concentrations

The study of the effect of oxygen on metal concentration in overlying water was investigated in laboratory. The results of the changes in Cd, Cu and Pb concentrations in aerobic and anaerobic conditions are shown in Figure 3-1 and Table C-1 in Appendix C. The concentrations of all metals in the overlying water in both aerobic and anaerobic series were declined through time. In addition, the metals in the aerobic series were removed from the overlying water much faster than the anaerobic series. The interaction of trace elements with the surfaces of solid particles is important in regulating the metal concentration in natural water. The removal of Cd, Cu and Pb from water body may cause by adsorption onto metal-reactive component of sediment (Fe-Mn oxyhydroxide or organic material) or precipitation process. In oxic condition, metals are controlled by adsorption and complexation processes are dominant process in controlling metals while in anoxic condition solubility equilibrium is more important than surface chemical reaction in controlling metals (Luoma, 1990).

In the control bottle (without sediment), metal concentrations in water were quite stable through time in both aerobic and anaerobic conditions. It indicates that surface sediment acts as a sink for these metals from water body. The result is shown in Table C-2 in Appendix C. Figure 3-2 shows the concentration of Cd, Cu and Pb in control bottle under anaerobic condition

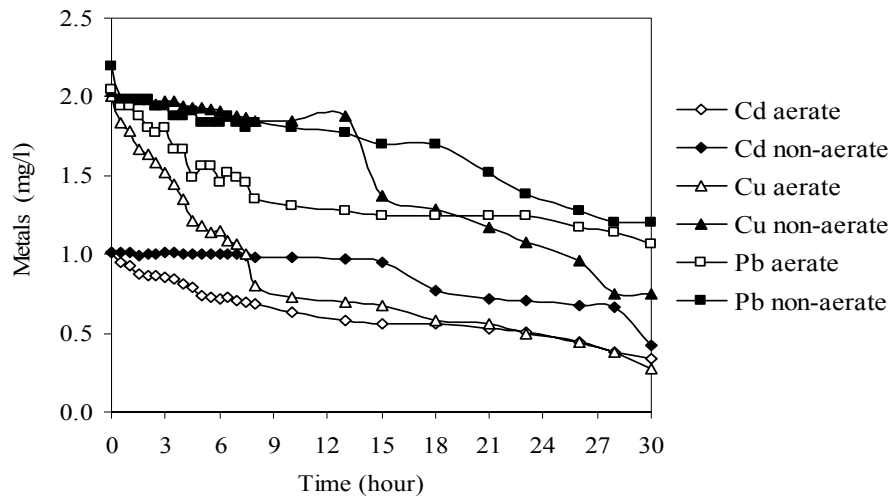


Figure 3-1 The Effect of oxygen on Cd, Cu and Pb concentration in the overlying water

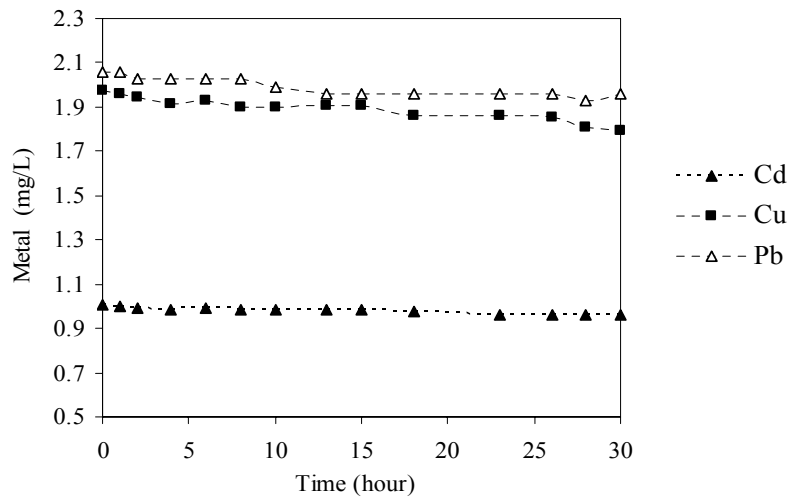


Figure 3-2 Concentration of Cd, Cu and Pb in control experiment under anaerobic condition

3.1.2 Effect of salinity on metal concentrations

The study of salinity effect on metal concentration in overlying water was investigated. Changes of Cd, Cu and Pb concentrations in the overlying water in different salinity are illustrated in Figure 3-3 (Table C-3 to Table C-5 in Appendix C). The concentrations of Cd, in overlying water decreased through time whereas dramatically decreased during the first 6 hours and slightly decreased to reach stable value after 30 hours. Similar patterns were found for Cu and Pb. The depletion of Pb concentration during first 6 hours was faster than Cd and Cu concentration in overlying water. It was found that the declination of Cd and Cu were in the salinity order 30>10>0>20 psu. However, the declination profile of Pb shown different pattern, it was in the salinity order: 30>20>10>0 psu.

The result from this study exemplified a removal of Pb with increasing salinity. In natural water, similar behaviors of Pb were reported by Baeyens *et al.*, 1998 and Wen *et al.*, 1999. The profiles of Cd and Cu concentration versus salinity show a convex shape at 20 psu. The similar profiles of these two metals in Scheldt Estuary, (UK) were reported by Baeyens *et al.*, 1998. This study appears informative for metal behavior in the mixing process of natural water. The increase in salinity marked gradient in ionic strength. Thus the elevated salt concentrations create increased competition between cations and metals for binding sites, resulting increase a tendency to flocculation (Burton and Liss, 1976). This process may result a removal of dissolved metals from water body through precipitation, uptake by particulate phase or exchange with solid phase (Burton and Liss, 1976).

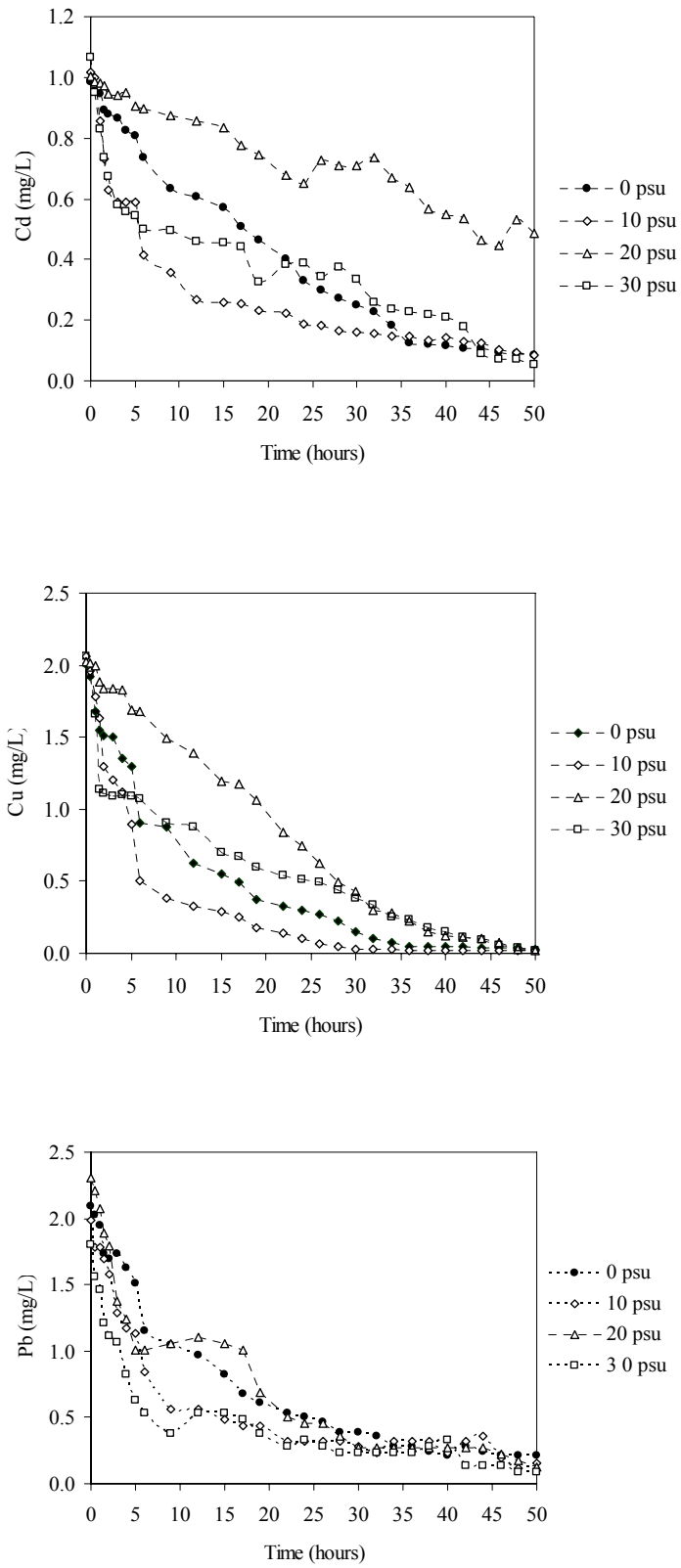


Figure 3-3 Cd, Cu and Pb concentrations changes of the water in different salinity

3.2 Benthic chamber experiment

3.2.1 Physico-chemical characteristics of overlying water

The water quality was performed at site sampling. The physico-chemical characters of overlying water in the chamber at Kor-Yor and Khao-Deang are shown in Table 3-1.

Table 3-1 Physico-chemical characteristics

Parameter	Kor-Yor 22-23 January 2005	Khao-Deang 11-12 April 2005	Khao-Deang 25-27 January 2006
Depth (m)	0.8	1.3 -1.5	1.7-1.9
Total dissolve solid (g L ⁻¹)	-	24.3	15.3-22.4
Temperature (°C)	-	29	26.9-29.4
pH	8.05	7.07-8.51	6.88-7.87
Salinity (psu)	10	30	18.9-29.0
Conductivity (ms cm ⁻¹)	-	47.0-49.6	30.5-44.8
D.O. outside the chamber (mg L ⁻¹)	4.81-7.20	4.00-8.20	6.60-8.50
D.O. in the light chamber (mg L ⁻¹)	2.97-4.13	1.14-6.20	1.50-8.00
D.O. in the dark chamber (mg L ⁻¹)	0.92-2.31	0.95-5.90	1.40-7.90

At Kor-Yor, the benthic chamber experiments were carrier out during 22-23 January 2005. D.O. changes during 30 hours are shown in Figure 3-4 and Table C-6 in Appendix C. The D.O. result shows diurnal variation in the light chamber similar to the water outside the chamber while D.O. in the dark chamber decreased through time. A total production can be calculated from a difference of the regression slopes of photosynthesis and respiration. The total photosynthesis and respiration in the light chamber were 0.2295 and 0.133 mg L⁻¹ h⁻¹, respectively.

At Khao-Deang, the experiments were carrier out during 11-12 April 2005 (dry season) and 25-27 January 2006 (wet season). In dry season, the changes of D.O. during 30 hours are presented in Table C-7 in Appendix C and in Figure 3-5. The diurnal variations of D.O. in the light chamber were similar to the D.O. in the water body of the lake. The D.O is stable during the first 4 hours in light chamber and decreased sharply about 63% in the next 8 hours and small variation in the last 18 hours. Similar profile of D.O in dark chamber was observed but D.O declined about 80% after 9 hours. A total production can be calculated from a difference of the

regression slopes of photosynthesis and respiration. The total photosynthesis and respiration in the light chamber were 0.5938 and $0.4237 \text{ mg L}^{-1} \text{ h}^{-1}$ respectively.

Figure 3-6 and Table C-8 in Appendix C show the variation of D.O. during 56 hours in wet season. The diurnal variations of D.O. in the light chamber were different from the D.O. in the water body of the lake but similar to the D.O. in the dark chamber. This experiment was performed after the flood and heavy rain, thus water in the area contained high total dissolved solid. Light can not penetrate through the light chamber and cause the condition of light chamber similar to dark chamber. The total photosynthesis and respiration in the light chamber were 0.0317 and $0.2173 \text{ mg L}^{-1} \text{ h}^{-1}$ respectively.

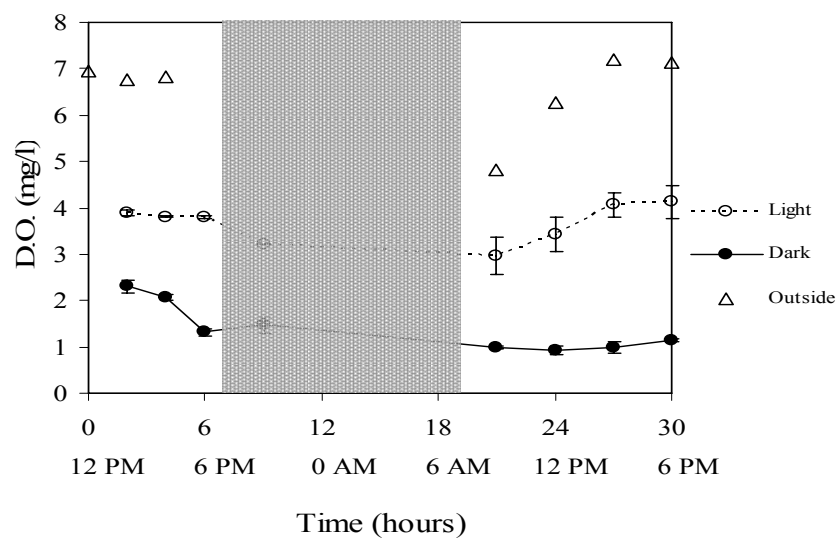


Figure 3-4 D.O. changes of the water inside and outside benthic chambers at Kor-Yor (22-23 January 2005)

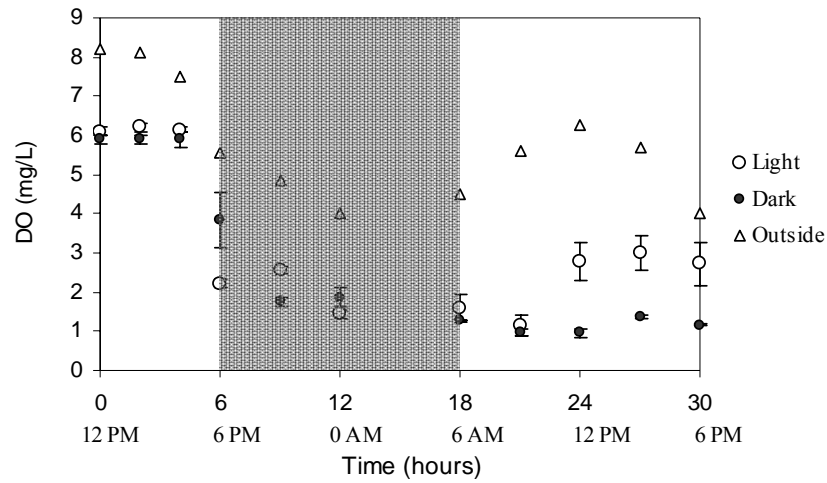


Figure 3-5 D.O. changes of the water inside and outside benthic chambers at Khao-Deang (11-12 April 2005)

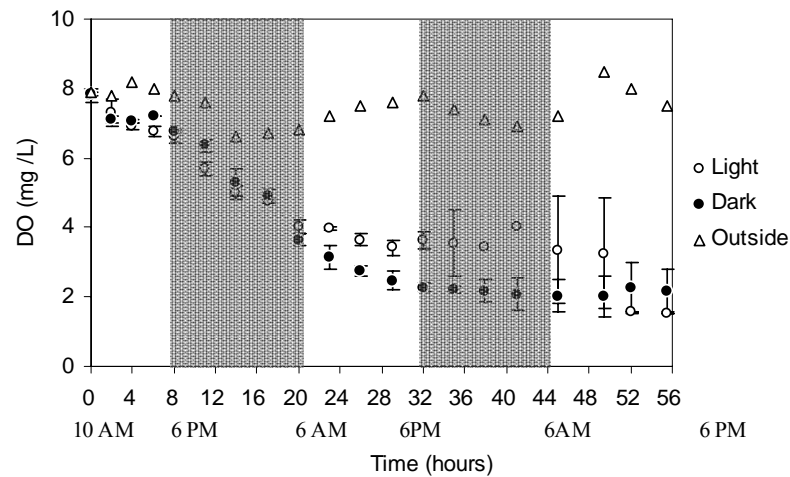


Figure 3-6 D.O. changes of the water inside and outside benthic chambers at Khao-Deang (25-27 January 2006)

The changes of pH of the overlying water in the light and dark chambers were investigated in both dry and wet seasons at Khao-Deang. Figure 3-7 and Table C-9 in Appendix C show the changes of pH during 30 hours in dry season. The Δ pH was approximately 0.8 pH unit in both light and dark chambers. Figure 3-8 and Table C-10 in Appendix C show the changes of pH during 56 hours in wet

season. The Δ pH was in the range of 0.4-0.7 pH unit. Thus there were no obvious changes in pH in overlying water in the light and dark chambers.

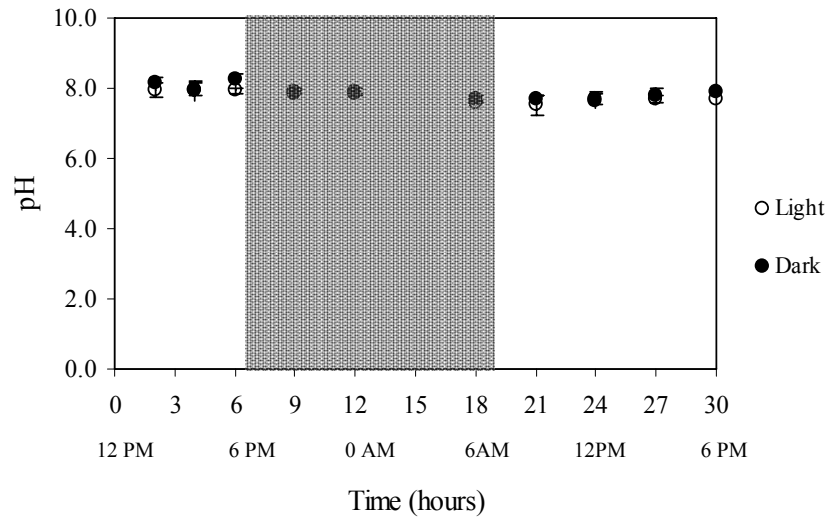


Figure 3- 7 pH changes of overlying water at Khao-Deang in dry season (11-12 April 2005)

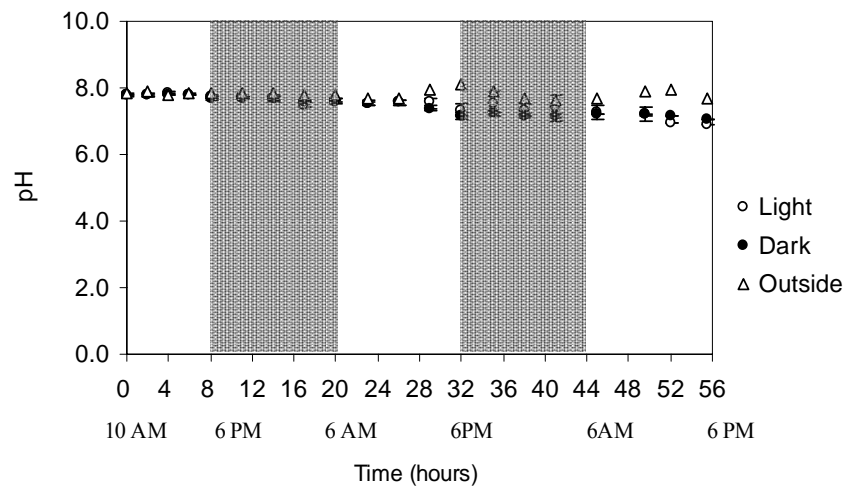


Figure 3- 8 pH changes of overlying water at Khao-Deang in wet season (25-27 January 2006)

Total dissolved solid (TDS), salinity, conductivity and temperature during the experiments collected on 25-27 January 2006 at Khao-Deang station are shown in Figure 3-9 to Figure 3-12 (Table C-11 and Table C-12 in Appendix C). The TDS, salinity, conductivity and temperature results were found in a range of 15.3-22.4 g/L^{-1} , 18.9-29.0 psu, 30.5-44.8 mscm^{-1} and 26.9-29.4°C respectively. Trends of the changes of TDS, salinity, conductivity and temperature show similar patterns. The TDS, salinity and conductivity in water outside the chamber decrease dramatically at 40th hour due to heavy rain.

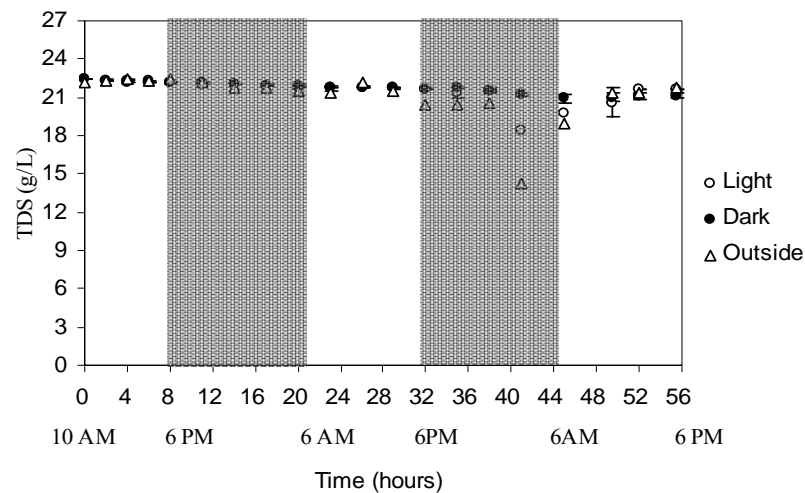


Figure 3-9 Total dissolved solid of water inside and outside benthic chambers at Khao-Deang (25-27 January 2006)

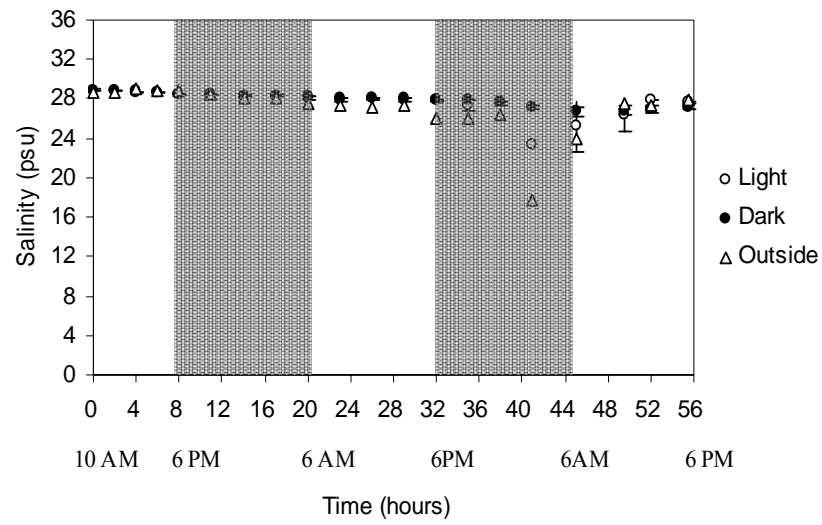


Figure 3- 10 Salinity changes of water inside and outside benthic chambers at Khao-Deang (25-27 January 2006)

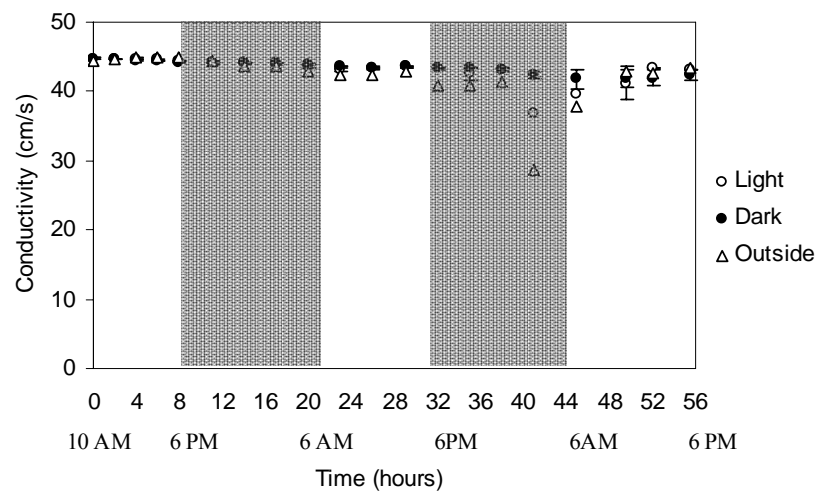


Figure 3- 11 Conductivity changes of water inside and outside benthic chamber at Khao-Deang (25-27 January 2006)

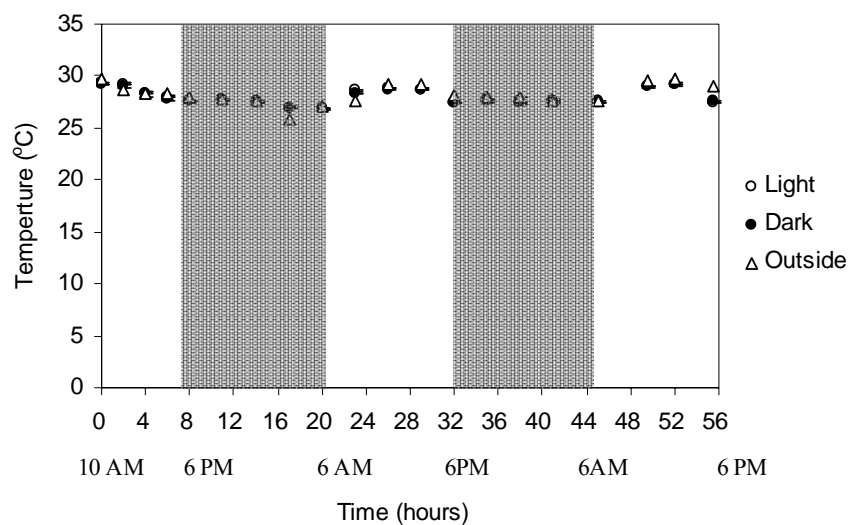


Figure 3- 12 Temperature changes of water inside and outside benthic chambers at Khao-Deang (25-27 January 2006)

3.2.2 Dissolved trace metals

The concentrations of dissolved trace metals in the chambers were performed at two sites; Kor-Yor and Khao-Daeng where show different in salinities.

At Kor-Yor (salinity 10psu), dissolved trace metals in the light chamber ranges (min-max in nmol L^{-1}) were 0.08-0.96 for Cd, 5.6-12.8 for Cu, 0.21-1.4 for Pb, 45-275 for Fe, and 0.09-6.8 for Mn while in the dark chamber were 0.06-0.73 for Cd, 1.36-5.38 for Cu, 0.14-1.16 for Pb, 57-431 for Fe, and 0.19-5.89 for Mn. The results of average concentration of dissolved metals are reported in Table C-13 in Appendix C and the metals profiles are shown in Figure3-13 to Figure3-17.

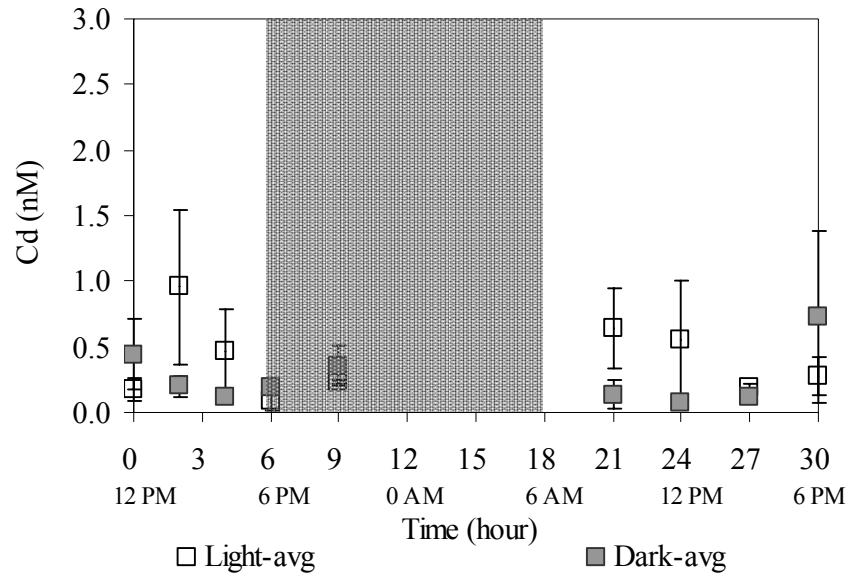


Figure 3- 13 Average dissolved Cd (nM) inside light and dark benthic chambers at Kor-Yor

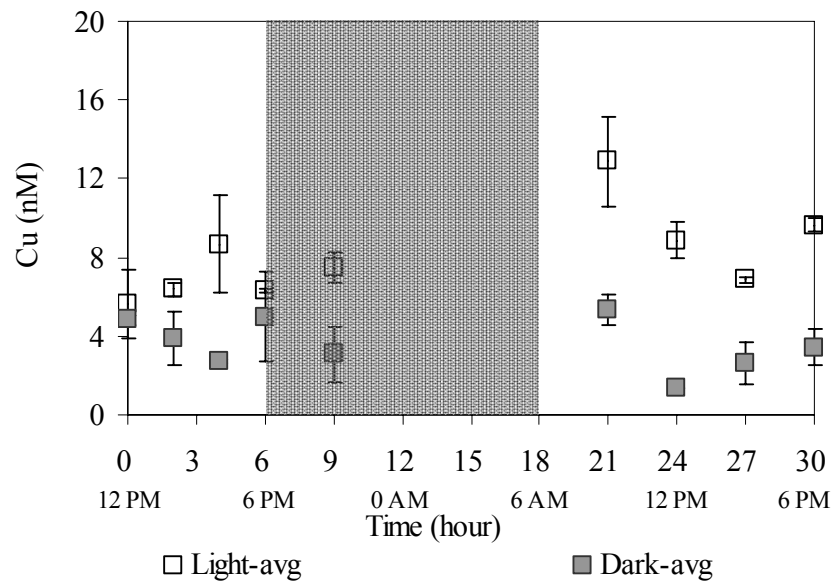


Figure 3- 14 Average dissolved Cu (nM) inside light and dark benthic chambers at Kor-Yor

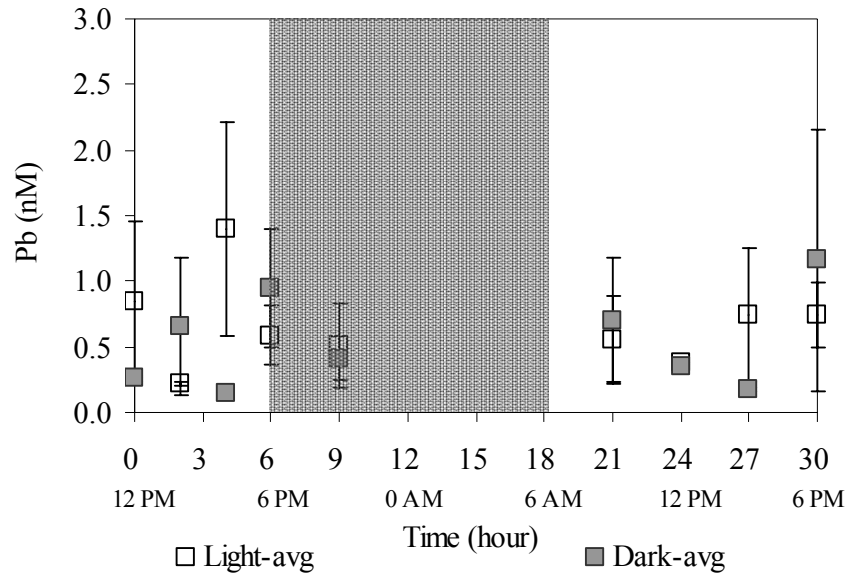


Figure 3-15 Average dissolved Pb (nM) inside light and dark benthic chambers at Kor-Yor

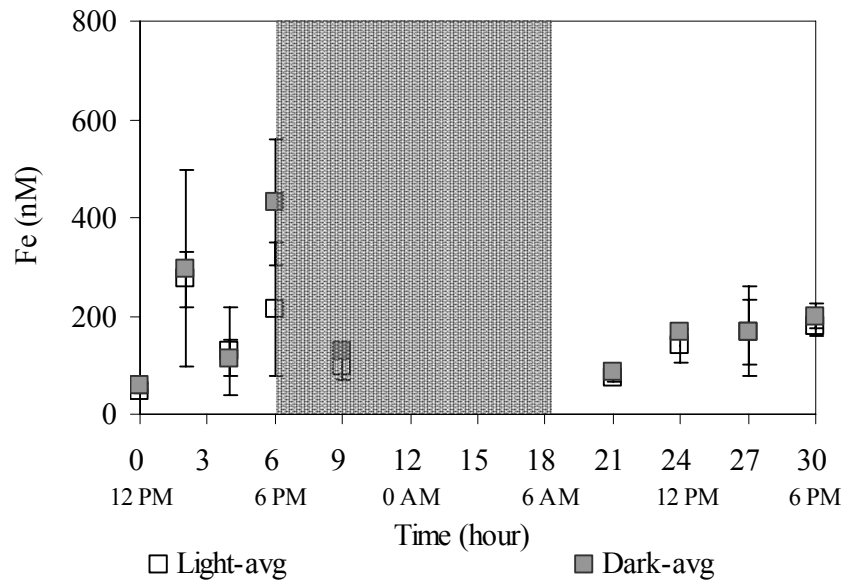


Figure 3-16 Average dissolved Fe (nM) inside light and dark benthic chambers at Kor-Yor

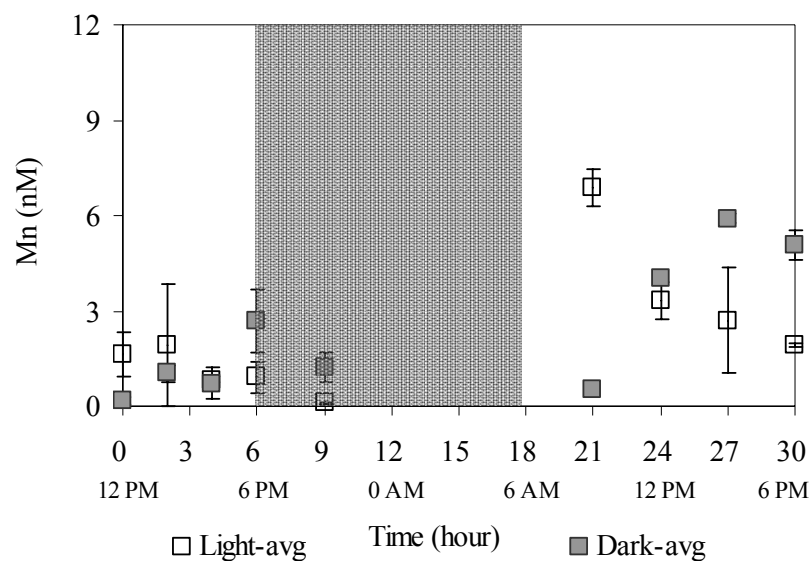


Figure 3- 17 Average dissolved Mn (nM) inside light and dark benthic chambers at Kor-Yor

At Khao-Daeng (salinity ~30psu), the study of dissolved metals concentration in the chambers were performed in dry season (11-12 April 2005) and wet season (25-27 January 2006). The average concentrations of dissolved Cd, Cu, Pb, Fe, and Mn ($\mu\text{g L}^{-1}$) in overlying water were reported in Table C-14 and Table C-15 in Appendix C. In dry season, dissolved trace metals in the light chamber ranges (range in nmol L^{-1}) were 0.09-0.78 for Cd, 2.69-8.44 for Cu, 0.21-2.63 for Pb, 341-947 for Fe, and 1.83-8.22 for Mn while in the dark chamber were 0.302-0.703 for Cd, 2.13-9.03 for Cu, 0.15-0.93 for Pb, 261-938 for Fe, and 9.43-88.98 for Mn. In wet season, dissolved trace metals in the light chamber ranges (range in nmol L^{-1}) were 0.256-6.752 for Cd, 4.94-24.41 for Cu, 0.26-19.51 for Pb, 78-753 for Fe, and 895-56060 for Mn while in the dark chamber were 0.159-3.18 for Cd, 5.75-30.52 for Cu, 0.31-30.63 for Pb, 75-392 for Fe, and 1399-12678 for Mn.

The profiles of Cd, Cu, Pb, Fe and Mn are shown in Figure 3-18 to 3-20. Slightly variations of metal concentrations through time were found. However, visual inspection from these profiles can not reveal the metal behaviors in the chambers. In order to achieve more objective understanding of fate of trace metal at sediment- water interface, a flux calculation was carried out in next section.

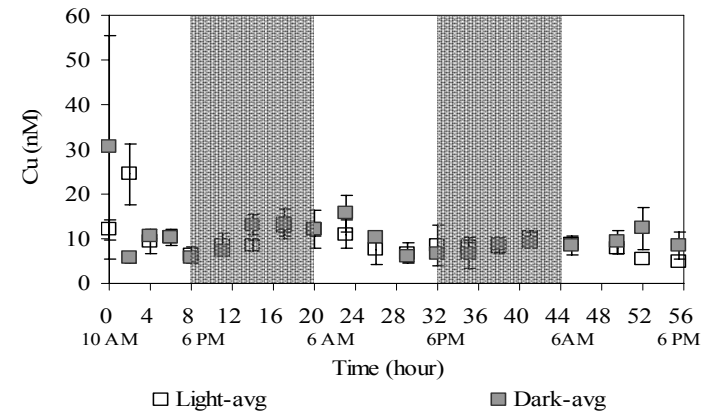
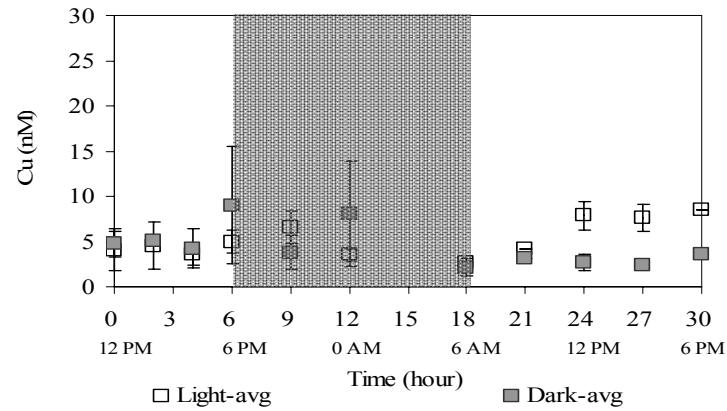
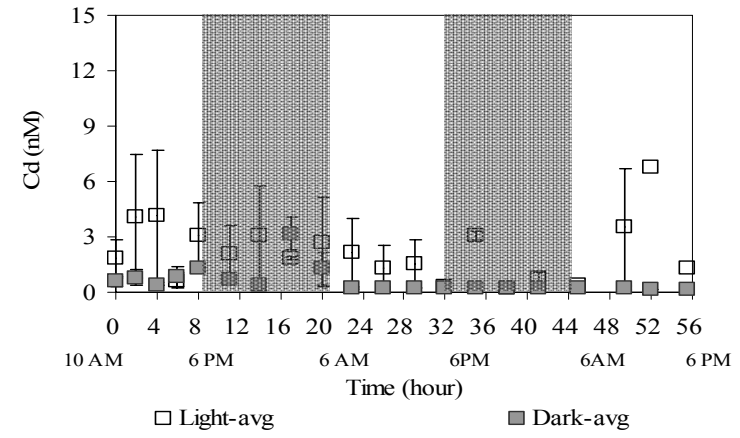
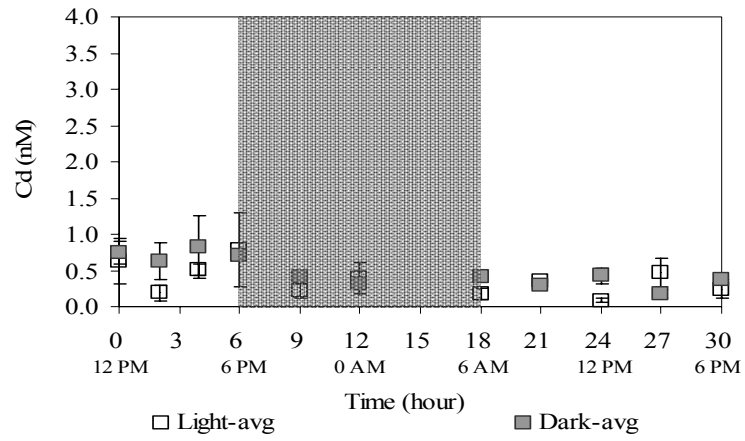


Figure3-18 Average dissolved concentration of Cd and Cu (nM) at Khao-Deang in dry season (Left) and wet season (Right)

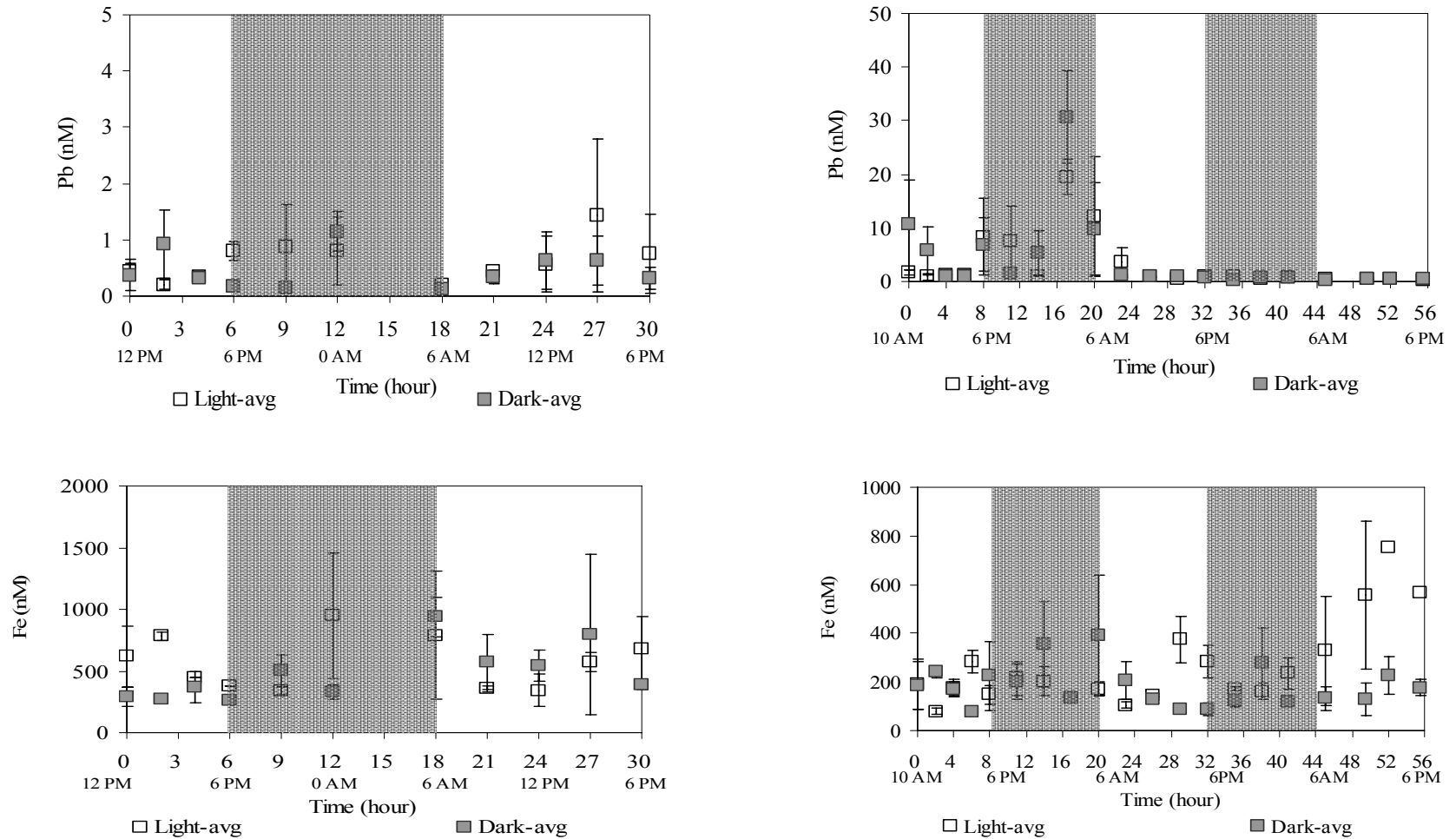


Figure 3-19 Average dissolved concentration of Pb and Fe (nM) at Khao-Deang in dry season (Left) and wet season (Right)

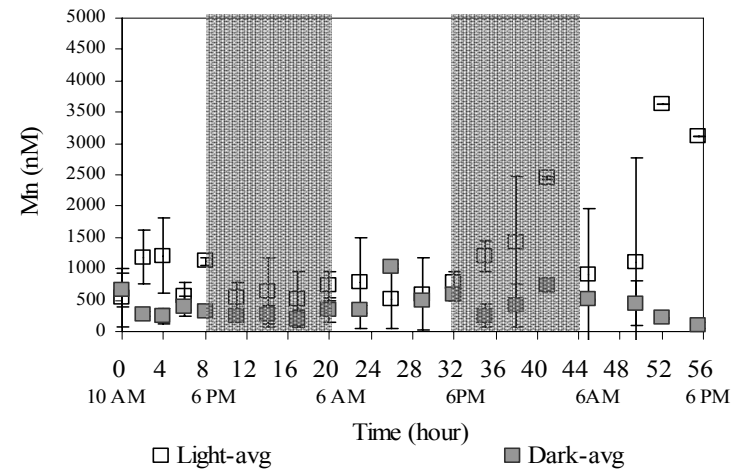
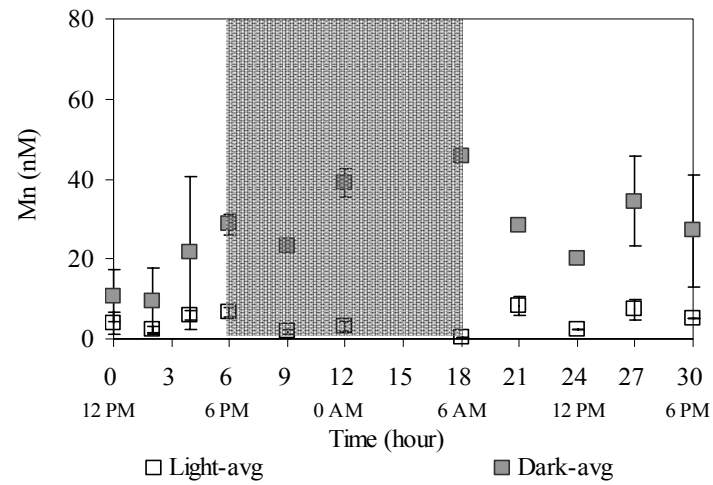


Figure 3-20 Average dissolved concentration of Mn (nM) at Khao-Deang in dry season (Left) and wet season (Right)

3.2.3 Calculation of Metal Flux

3.2.3.1 Benthic Flux

Flux of elements into and out of sediment was calculated by using concentration changes in the enclosed water over time. The parameters used in the calculation were concentration and chamber volume. The volume of the chamber is determined from strontium (as an inert marker) concentration added in the chamber. The data were reported in Table D-1 to Table D-3 in Appendix D. The results show constant chamber volume at Khao-Daeng experiment. However, at Kor-Yor experiment the chamber volume changed about 30% from initial volume. The calculation of fluxes on the basis of point-to point variations contributes to an apparent high variability of the results. Similar changes in chamber volume were also found by Turetta *et al.* (2005). In order to reduce the effect of the uncertainty of the data, the calculation of flux was followed as what suggested by Turetta *et al.* (2005).

$$F_b = R/S$$

Where

F_b	is	the mean benthic flux during the experiment
R	is	the slope of the regression line in pmol/h
S	is	the sediment surface covered by the chamber in cm^2

The slope of the regression line indicated the mean variation of amount of trace elements. Positive fluxes result from an increase in concentration in the water with time; conversely negative fluxes result when concentrations in water decrease with time.

At Kor-Yor experiments, the slopes of regression line and fluxes of Cd, Cu, Pb, Fe and Mn are summarized in Table 3-2. The plots of average Cd, Cu, Pb, Fe and Mn concentrations as a function of time and the fluxes are shown in Figure 3-21 to Figure 3-25. The calculation of sediment surface covered by the chamber is shown in Appendix E.

In the light chambers, the overall fluxes after 30 hours installation was i) 0.026 nmol cm⁻² yr⁻¹ for Cd; ii) 1.156 nmol cm⁻² yr⁻¹ for Cu; iii) -0.044 nmol cm⁻² yr⁻¹ for Pb; iv) 0.061 nmol cm⁻² yr⁻¹ for Fe and v) 0.911 nmol cm⁻² yr⁻¹ for Mn. The results suggested that Cd, Cu, Fe and Mn were removed from sediment into the water column. In the dark chambers, the overall fluxes after 30 hours installation was i) -0.018 nmol cm⁻² yr⁻¹ for Cd; ii) -0.447 nmol cm⁻² yr⁻¹ for Cu; iii) 0.079 nmol cm⁻² yr⁻¹ for Pb; iv) -13.79 nmol cm⁻² yr⁻¹ for Fe and v) 1.568 nmol cm⁻² yr⁻¹ for Mn. The results indicated that Pb and Mn were released from sediment into the overlying water.

Table 3-2 The slopes of the regression line and fluxes of Cd, Cu, Pb, Fe and Mn

Metals	Kor-Yor station (January 2005)			
	Slope of regression line		Fluxes (nmol cm ⁻² yr ⁻¹)	
	Light chamber	Dark chamber	Light chamber	Dark chamber
Cd	2.30	-1.92	0.026	-0.018
Cu	105	-41.0	1.156	-0.447
Pb	-4.1	7.5	-0.044	0.079
Fe	5.69	-1265	0.061	-13.79
Mn	83.5	144	0.911	1.568

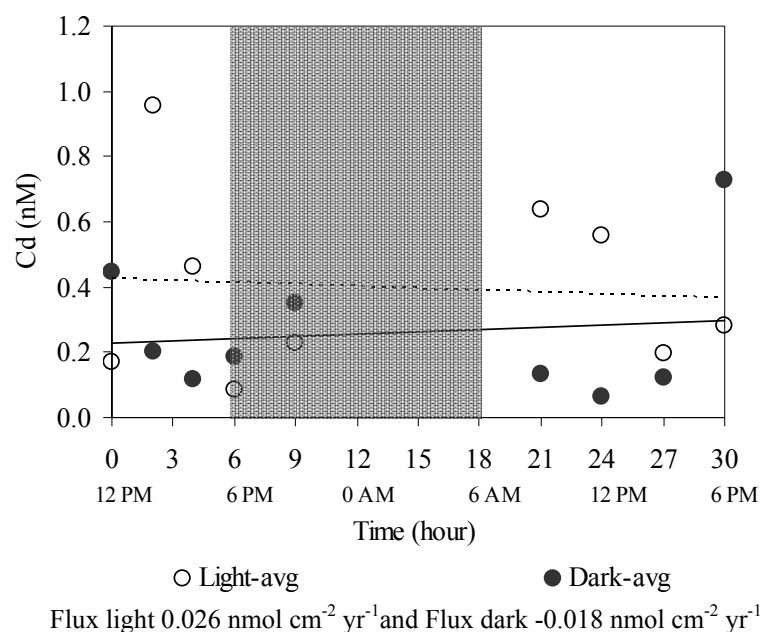


Figure 3-21 Fluxes of Cd (nmol cm⁻² yr⁻¹) at Kor-Yor

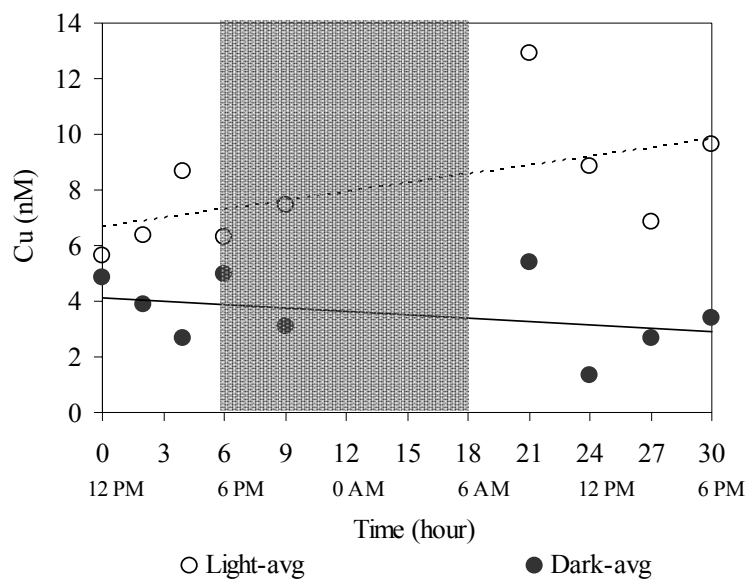


Figure 3-22 Fluxes of Cu ($\text{nmol cm}^{-2} \text{ yr}^{-1}$) at Kor-Yor

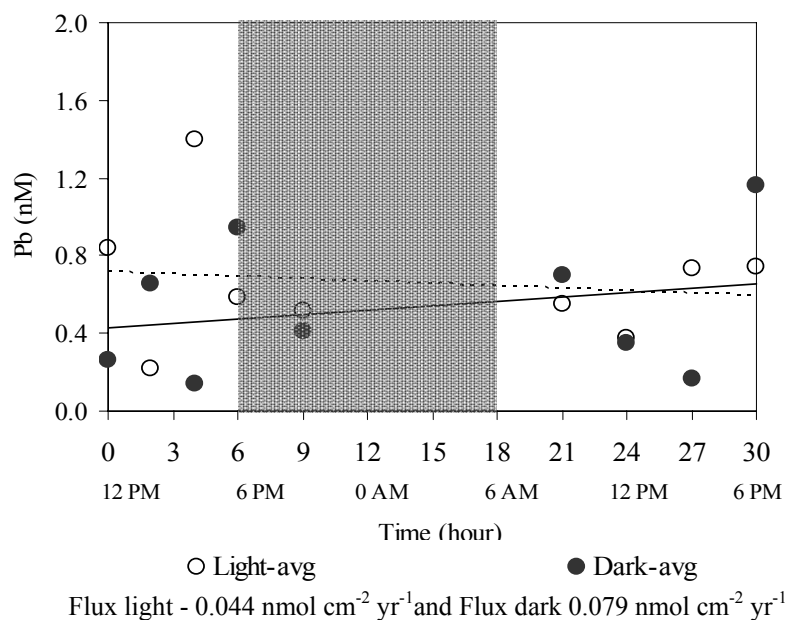


Figure 3-23 Fluxes of Pb ($\text{nmol cm}^{-2} \text{ yr}^{-1}$) at Kor-Yor

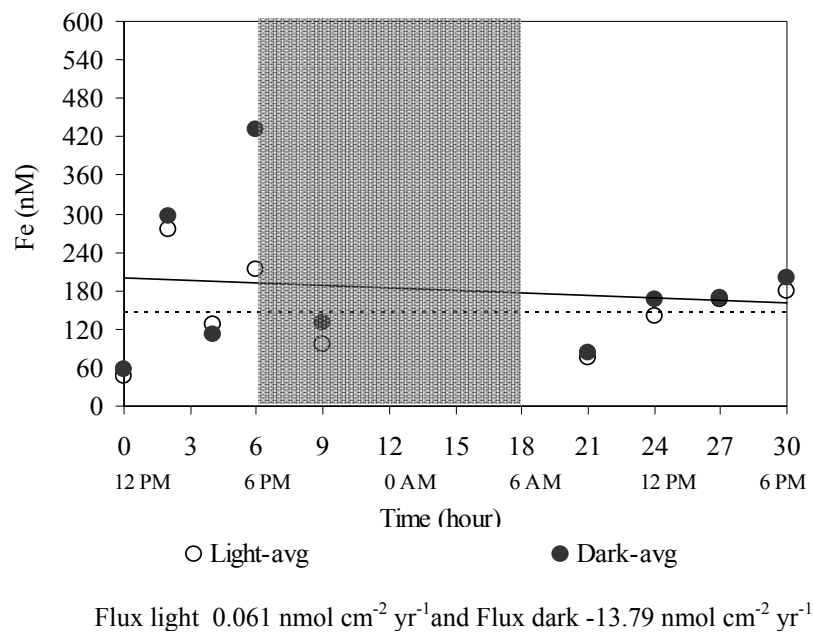


Figure 3-24 Fluxes of Fe ($\text{nmol cm}^{-2} \text{ yr}^{-1}$) at Kor-Yor

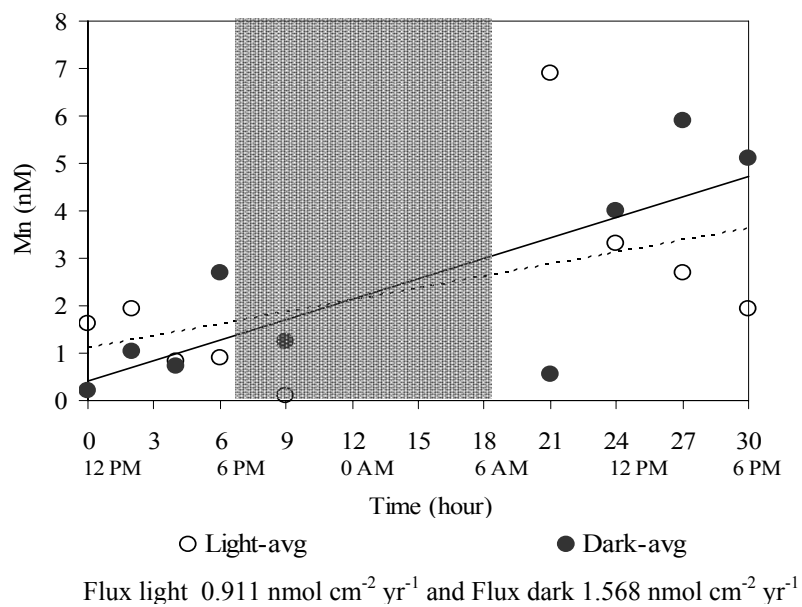


Figure 3-25 Fluxes of Mn ($\text{nmol cm}^{-2} \text{ yr}^{-1}$) at Kor-Yor

At Khao-Daeng experiments, the slopes of regression line and fluxes of Cd, Cu, Pb, Fe and Mn are summarized in Table 3-3. The plots of average Cd, Cu, Pb, Fe and Mn concentrations as a function of time and the fluxes are shown in Figure 3-26 to Figure 3-28.

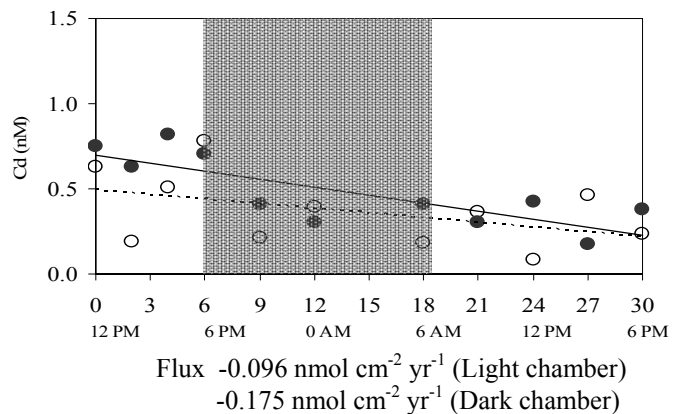
In the light chambers of dry season, the overall benthic fluxes after 30 hours installation were i) $-0.096 \text{ nmol cm}^{-2} \text{ yr}^{-1}$ for Cd; ii) $1.288 \text{ nmol cm}^{-2} \text{ yr}^{-1}$ for Cu; iii) $0.158 \text{ nmol cm}^{-2} \text{ yr}^{-1}$ for Pb; iv) $-11.56 \text{ nmol cm}^{-2} \text{ yr}^{-1}$ for Fe and v) $0.464 \text{ nmol cm}^{-2} \text{ yr}^{-1}$ for Mn. The results suggested that Cd, and Fe were removed from water body into sediment surface. In the dark chambers, the overall benthic fluxes after 30 hours were i) $-0.175 \text{ nmol cm}^{-2} \text{ yr}^{-1}$ for Cd; ii) $-1.253 \text{ nmol cm}^{-2} \text{ yr}^{-1}$ for Cu; iii) $-0.009 \text{ nmol cm}^{-2} \text{ yr}^{-1}$ for Pb; iv) $135.6 \text{ nmol cm}^{-2} \text{ yr}^{-1}$ for Fe; and v) $5.70 \text{ nmol cm}^{-2} \text{ yr}^{-1}$ for Mn. The results show that Fe and Mn in dark chamber were released from sediments and indicated that a removal of Cd, Cu and Pb from water column at high salinity. The mobility of metals in light chambers may exhibit the biogeochemical process in shallow lake where sediment-water interface is usually in aerobic condition while the behavior of metals in the dark chamber represented the hypoxic condition during the period of algae bloom.

In the light chambers of wet season, the overall benthic fluxes after 30 hours installation were i) $-0.061 \text{ nmol cm}^{-2} \text{ yr}^{-1}$ for Cd; ii) $-1.358 \text{ nmol cm}^{-2} \text{ yr}^{-1}$ for Cu; iii) $-1.007 \text{ nmol cm}^{-2} \text{ yr}^{-1}$ for Pb; iv) $219.4 \text{ nmol cm}^{-2} \text{ yr}^{-1} \text{ hr}$ for Fe and v) $367.6 \text{ nmol cm}^{-2} \text{ yr}^{-1}$ for Mn. The results suggested that Fe and Mn were released from sediment surface. In the dark chambers, the overall benthic fluxes after 30 hours were i) $-0.184 \text{ nmol cm}^{-2} \text{ yr}^{-1}$ for Cd; ii) $-0.999 \text{ nmol cm}^{-2} \text{ yr}^{-1}$ for Cu; iii) $-1.621 \text{ nmol cm}^{-2} \text{ yr}^{-1}$ for Pb; iv) $-21.99 \text{ nmol cm}^{-2} \text{ yr}^{-1}$ for Fe; and v) $3.653 \text{ nmol cm}^{-2} \text{ yr}^{-1}$ for Mn. The results show that Cd, Cu and Pb were removed from water body into sediment.

Table 3-3 The slopes of the regression line and fluxes of Cd, Cu, Pb, Fe and Mn

Metals	Khao-Deang station (April 2005)				Khao-Deang station (Jan 2006)			
	Slope of the regression line		Flux (nmol cm ⁻² yr ⁻¹)		Slope of the regression line		Flux (nmol cm ⁻² yr ⁻¹)	
	Light chamber	Dark chamber	Light chamber	Dark chamber	Light chamber	Dark chamber	Light chamber	Dark chamber
Cd	-8.97	-15.7	-0.096	-0.175	-5.45	-16.79	-0.061	-0.184
Cu	118	-115	1.288	-1.253	-124	-91.26	-1.358	-0.999
Pb	14.78	-1.11	0.158	-0.009	-92.1	-148	-1.007	-1.621
Fe	-1063	12440	-11.56	135.61	20135	-2018	219.44	-21.987
Mn	42.4	523	0.464	5.702	35571	335	387.63	3.652

Khao-Deang (11-12 April 2005)



Khao-Deang (25-27 January 2006)

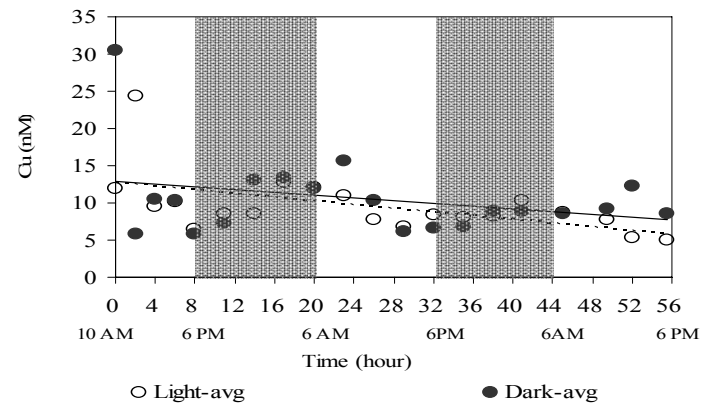
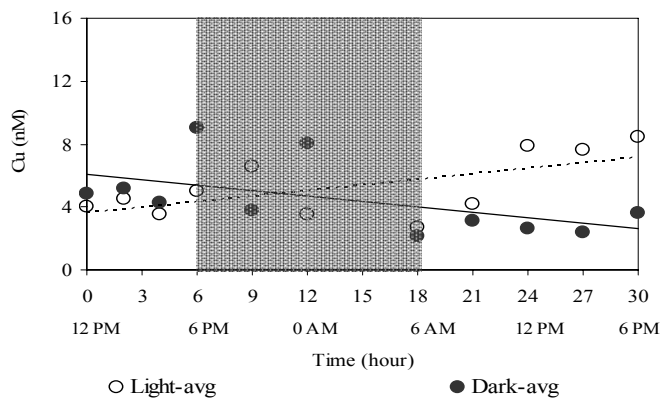
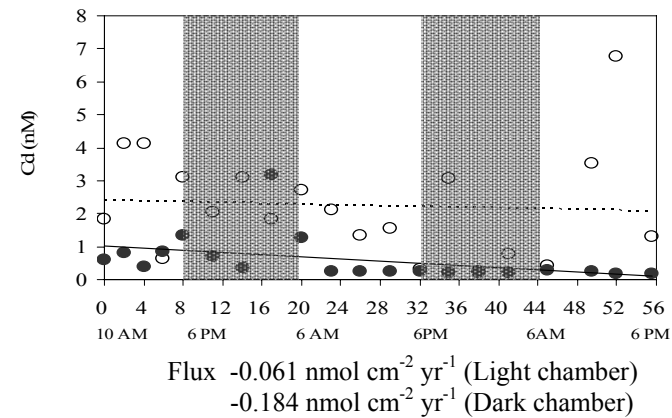
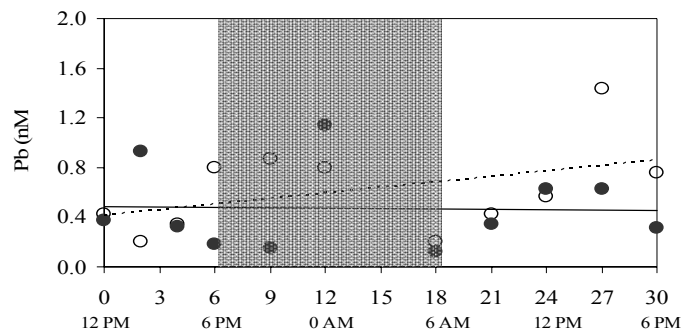
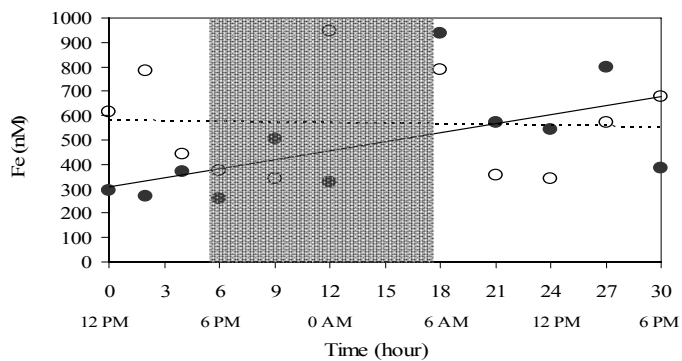


Figure 3-26 Fluxes of Cd and Cu ($\text{nmol cm}^{-2} \text{ yr}^{-1}$) at Khao-Deang

Khao-Deang (11-12 April 2005)

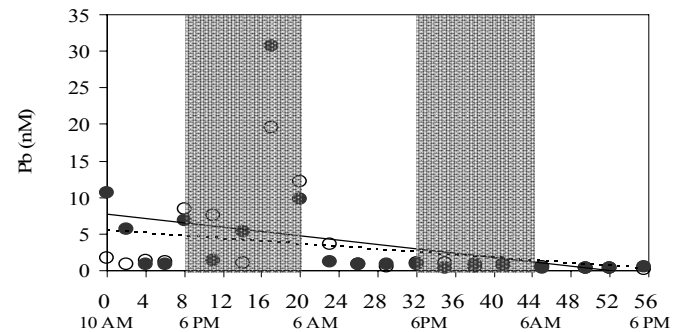


Flux $0.158 \text{ nmol cm}^{-2} \text{ yr}^{-1}$ (Light chamber)
 $-0.009 \text{ nmol cm}^{-2} \text{ yr}^{-1}$ (Dark chamber)

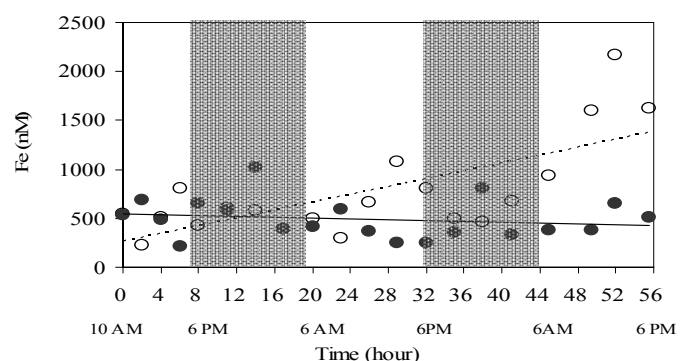


Flux $-11.563 \text{ nmol cm}^{-2} \text{ yr}^{-1}$ (Light chamber)
 $135.61 \text{ nmol cm}^{-2} \text{ yr}^{-1}$ (Dark chamber)

Khao-Deang (25-27 January 2006)



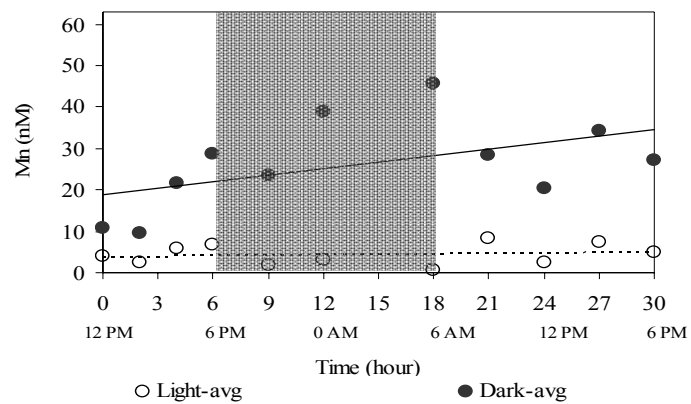
Flux light $-1.007 \text{ nmol cm}^{-2} \text{ yr}^{-1}$ (Light chamber)
 $-1.621 \text{ nmol cm}^{-2} \text{ yr}^{-1}$ (Dark chamber)



Flux $219.44 \text{ nmol cm}^{-2} \text{ yr}^{-1}$ (Light chamber)
 $-21.99 \text{ nmol cm}^{-2} \text{ yr}^{-1}$ (Dark chamber)

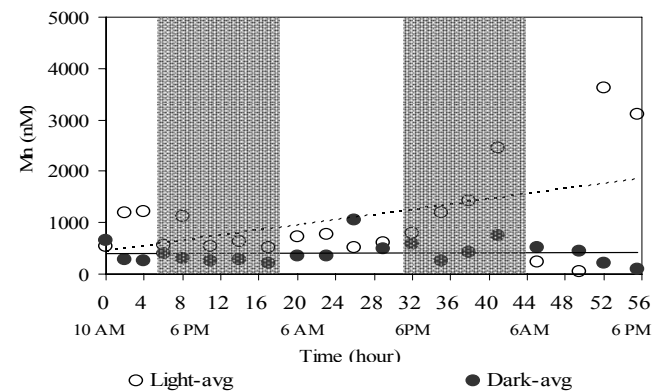
Figure 3-27 Fluxes of Pb and Fe ($\text{nmol cm}^{-2} \text{ yr}^{-1}$) at Khao-Deang

Khao-Deang (11-12 April 2005)



○ Light-avg ● Dark-avg
 Flux 0.464 nmol cm⁻² yr⁻¹ (Light chamber)
 5.703 nmol cm⁻² yr⁻¹ (Dark chamber)

Khao-Deang (25-27 January 2006)



○ Light-avg ● Dark-avg
 Flux light 367.63 nmol cm⁻² yr⁻¹ (Light chamber)
 3.653 nmol cm⁻² yr⁻¹ (Dark chamber)

Figure 3-28 Fluxes of Mn (nmol cm⁻² yr⁻¹) at Khao-Deang

3.2.3.2 Diffusive Fluxes

The diffusive flux is a term to measure the transportation of dissolved metals from pore water in the sediment to the overlying water. The magnitude of diffusive release was estimated using a modification of Fick's first law of diffusion appropriate for sediments (Berner, 1980)

The detail of calculation of diffusive fluxes is shown in Appendix E. Metal concentration in the pore water and overlying water of Cd, Cu, Pb, Fe and Mn are presented in Table 3-4 and Table 3-5. The results indicated that trace metals in the pore water of the sediments show enrichment relative to the overlying water. Similar results had shown by Elderfield *et al.* (1981) and Emerson *et al.* (1984). Diffusive fluxes of all metals (Table 3-6) were positive values indicating that the sediment was a source of these metals to the overlying waters of Lake. Mn has the highest diffusive flux values followed by Fe, Pb, Cu and Cd. In addition, diffusive fluxes in this study are within the same range of the fluxes of metals from the Bang Pakong estuary reported by Chevaporn *et al.* (1995) and Chaichana (1995). It should be noted, the average concentration of metals in pore water from the first 3cm of the sediment was used in this flux calculation in dry season. No significant differences of diffusive fluxes of most metals were found between light and dark chamber in wet season, while small difference of the diffusive fluxes of Fe and Mn was observed in dry season.

Upon comparison of benthic fluxes and diffusive fluxes (Table 3-6), in dry season, the fluxes of Cd and Cu were not differ in light chamber but small different in dark chamber. For Pb, Fe and Mn, the fluxes were significant different in the order of one to two order of magnitude. In wet season, both fluxes of most metals were not significant different in light and dark chamber except Fe in dark chamber was higher than in light chamber in the two order of magnitude. The benthic flux and diffusive flux were derived from samples collected in different time, this could be responsible for the differences. The significant difference in the benthic fluxes and diffusive fluxes of Cu, Fe, Ni and Zn were also reported by Ciceri *et al.* (1992) and Turetta *et al.* (2005).

Table 3-4 Concentration of Cd, Cu, Pb, Fe and Mn in pore water (nmol L⁻¹) at Khao-Deang sediments collected on 12 April, 2005

Depth (cm.)	Cd	Cu	Pb	Fe	Mn
Light chamber					
<u>Core 1</u>					
Overlying water	0.393	7.37	0.09	11500	15.6
1.5	1.321	103.53	135.90	11638	19154
5	1.860	72.39	103.64	26211	26645
<u>Core 2</u>					
Overlying water	0.324	5.21	0.14	25092	7.5
1.5	0.391	72.80	88.91	68867	36433
5	1.321	67.54	126.76	30947	31459
Dark chamber					
<u>Core 3</u>					
Overlying water	0.324	9.11	0.21	6924	47.1
1.5	1.267	71.18	146.83	53787	36625
5	0.324	63.50	41.91	36633	37240
<u>Core 4</u>					
Overlying water	0.324	12.26	0.75	14181	4.7
1.5	0.446	69.76	36.83	17306	65940
5	0.566	73.20	28.20	18509	18815

Table 3-5 Concentration of Cd, Cu, Pb, Fe and Mn in pore water (nmol L⁻¹) at Khao-Deang sediments collected on 27 January, 2005

Depth (cm.)	Cd	Cu	Pb	Fe	Mn
Light Chamber					
<u>Core 1</u>					
Overlying water	5.39	7.70	0.96	201	797
1	49.32	35.65	78.89	2531	39188
2	26.45	41.64	44.00	4836	40387
3	29.23	49.21	67.39	4227	31350
<u>Core 2</u>					
Overlying water	1.30	5.07	0.72	373	1183
1	61.68	23.35	105.44	1711	60857
2	41.93	25.87	108.22	4264	57814
3	30.05	28.71	82.24	3841	64453
6	31.32	61.83	120.29	2914	1660
Dark Chamber					
<u>Core 3</u>					
Overlying water	1.30	13.03	0.39	277	246
1	25.31	35.65	195.47	6620	51636
2	25.75	32.49	193.99	6576	63623
3	38.10	11.67	191.57	4745	55048
6	41.23	25.55	320.96	945	36514
<u>Core 4</u>					
lost					

Table 3-6 Benthic Fluxes and Diffusive Fluxes of Cd, Cu, Pb, Fe and Mn at Khao-Deang (unit in nmol cm⁻² yr⁻¹)

Metals	Khao-Deang station (April, 2005)				Khao-Deang station (Jan, 2006)			
	Benthic Fluxes		Diffusive Fluxes*		Benthic Fluxes		Diffusive Fluxes	
	Light chamber	Dark chamber	Light chamber	Dark chamber	Light chamber	Dark chamber	Light chamber	Dark chamber
Cd	-0.096	-0.175	0.0053	0.0061	-0.061	-0.184	-0.6745	-1.40
Cu	1.288	-1.253	0.9364	0.6850	-1.358	-0.999	-0.6062	-1.10
Pb	0.158	-0.009	1.28	1.05	-1.007	-1.621	-2.81	-3.66
Fe	-11.56	135.61	251	285	219.44	-21.987	169	49
Mn	0.464	5.702	317	317	387.63	3.652	1377	1314

* Diffusive fluxes calculated by using average concentration of metals in pore water at first 3 cm of sediment

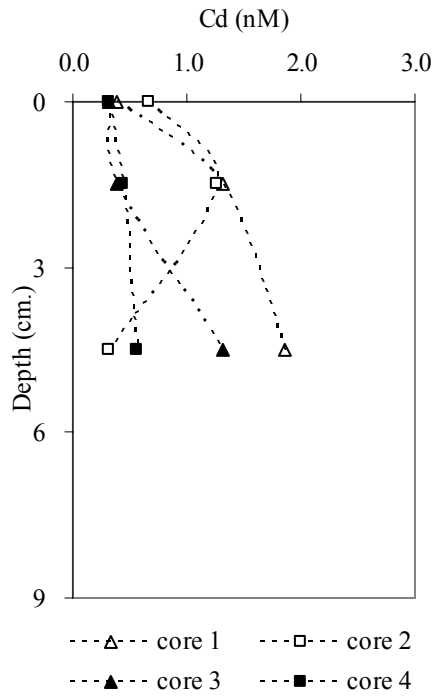
3.3 Metals Profiles in Pore Water and in Sediment

3.3.1 Pore water Profiles

The pore water profiles of Cd, Cu, Pb, Fe and Mn in dry season (April, 2005) and wet season (Jan, 2006) are shown in Figure 3-29 to Figure 3-31. In dry season, the concentration ranges were 0.39-1.86 nmol L⁻¹ for Cd, 63-103 nmol L⁻¹ for Cu, 28.68-147 nmol L⁻¹ for Pb, 11.37-68.87 μmol L⁻¹ for Fe, and 18.82-65.94 μmol L⁻¹ for Mn. In wet season, the concentration ranges were 3.05-61.67 nmol L⁻¹ for Cd, 11.67-61.83 nmol L⁻¹ for Cu, 24.50-320 nmol L⁻¹ for Pb, 0.95-6.62 μmol L⁻¹ for Fe, and 1.66-64.45 μmol L⁻¹ for Mn

In all cores, metal concentrations in surficial pore water were elevated when compared to their respective water column concentrations. Pore water profiles of these metal generally shown concentration maxima at shallow depths (2 cm) which were not found to vary seasonally. This suggests diffusive release from the sediments to the overlying water. The explanation of the elevated value of metals such as Mn and Fe, it may cause by the reduction of Mn(IV) and Fe(III) oxides to dissolved Mn(II) and Fe(II) occurred at the similar depth of approximately 2 cm. The observed pore water enrichments were similar to those determined by Warnken *et al.* (2001) and Turetta *et al.* (2005).

Khao-Deang station (April, 2005)



Khao-Deang station (Jan, 2006)

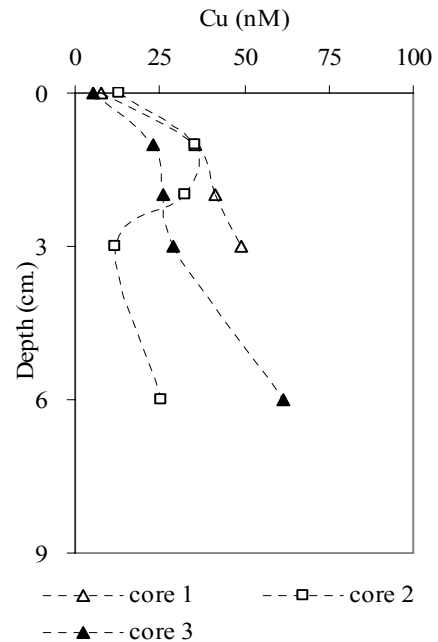
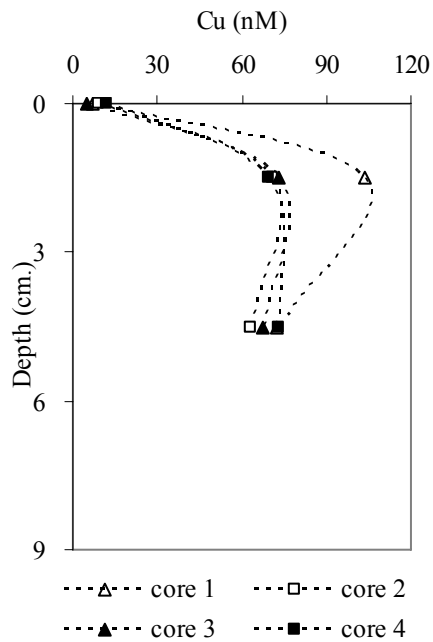
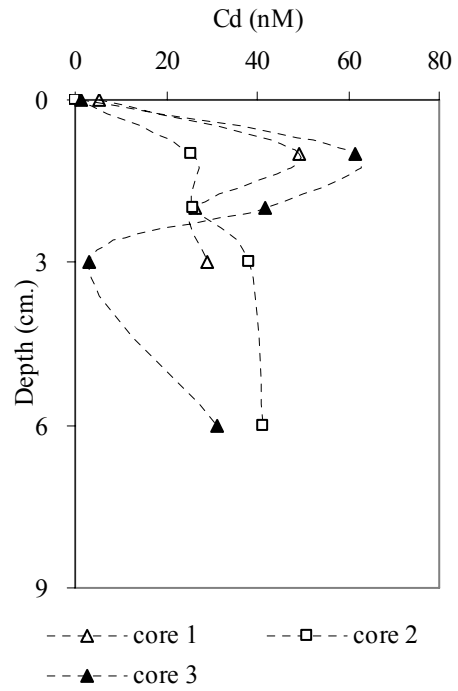
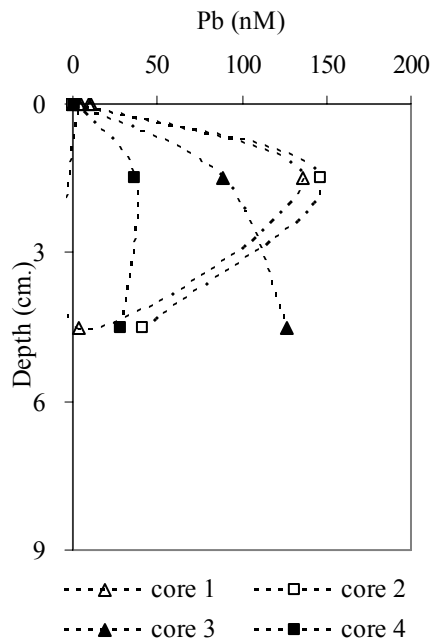


Figure3- 29 Depth profiles of Cd and Cu in pore water at Khao-Deang. Also overlying water column concentration shows at a depth of 0 cm. Open symbols represent the light chambers and dark symbols represent the dark chambers

Khao-Deang station (April, 2005)



Khao-Deang station (Jan, 2006)

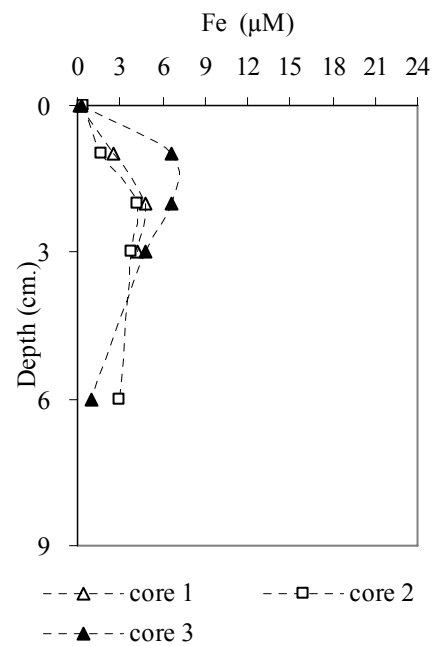
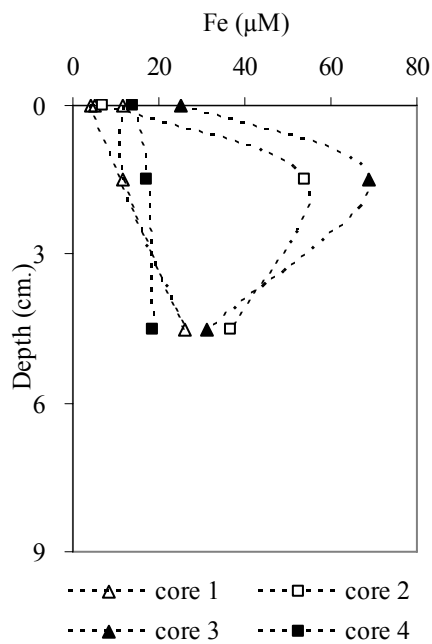
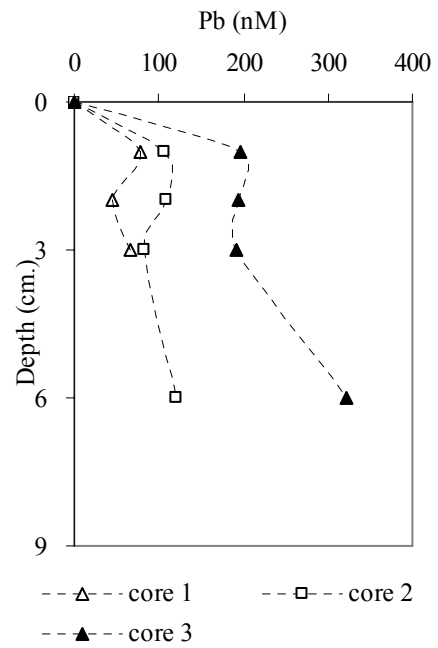


Figure3- 30 Depth profiles of Pb and Fe in pore water at Khao-Deang. Also overlying water column concentration shows at a depth of 0 cm. Open symbols represent the light chambers and dark symbols represent the dark chambers

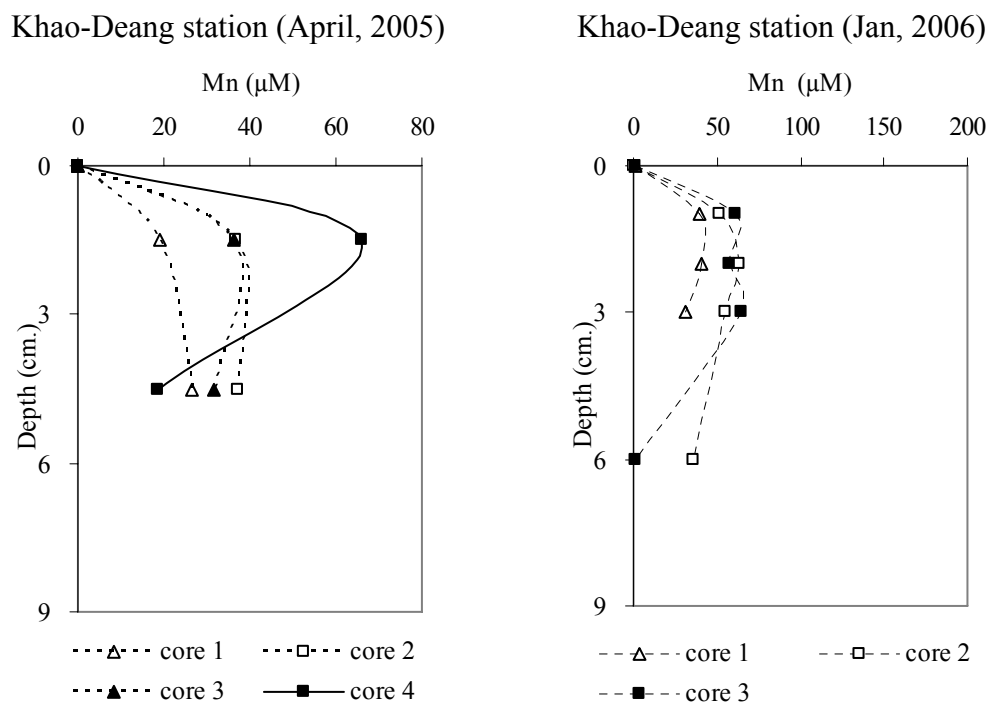


Figure3- 31 Depth profiles of Mn in pore water at Khao-Deang. Also overlying water column concentration shows at a depth of 0 cm. Open symbols represent the light chambers and dark symbols represent the dark chambers

3.3.2 Sediment profiles

The depth profiles of Cd, Cu, Pb, Fe and Mn in dry season (April, 2005) and wet season (Jan, 2006) are shown in Figure 3-32 to Figure 3-34. In dry season, the concentration ranges were 0.007-0.132 mg kg⁻¹ for Cd, 25-52 mg kg⁻¹ for Cu, 39-59 mg kg⁻¹ for Pb, 19-21 g kg⁻¹ for Fe, and 0.18-0.41 g kg⁻¹ for Mn. In wet season, the concentration ranges were 0.026-0.159 mg kg⁻¹ for Cd, 28-52 mg kg⁻¹ for Cu, 38-53 mg kg⁻¹ for Pb, 29-32 g kg⁻¹ for Fe, and 0.386-0.624 g kg⁻¹ for Mn.

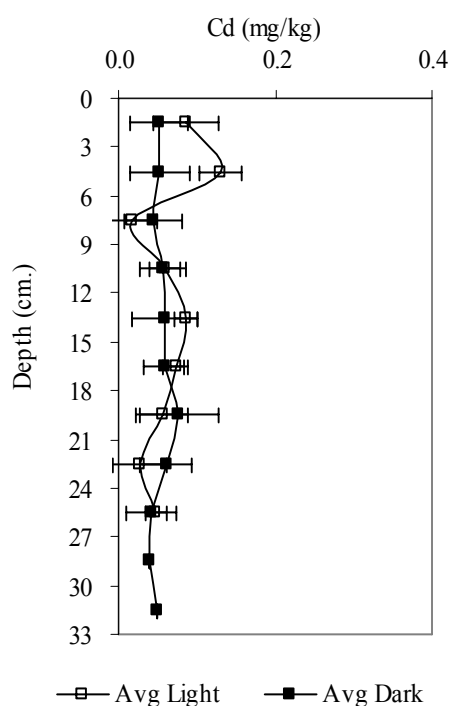
In dry season, the vertical profiles of Cu, Pb and Mn were slightly decreased with depth, except Cd exhibited subsurface maxima and slightly decreases with depth. While Fe concentration exhibited monotonic with sediment depth.

In wet season, the vertical profiles of Cu, Pb, Fe and Mn exhibited similar profiles as shown in dry season except the profile of Cd shown depletion at

subsurface. Since water level is higher than in dry season, pushing the core to the depth infeasible as in dry season. Similar depth profiles of metals in sediments from U-Tapao canal, Songkla (Thailand) and from the Gulf of Papua New Guinea (Papua New Guinea) were reported by Jungsriruntanakun, 2001 and Alongi *et al.*, 1996).

The surficial metal concentrations in sediments from this study were in the same range of those in the Gulf of Thailand (Menasveta, 1981 and Sompongchaiyakul, 1989).

Khao-Deang station (April, 2005)



Khao-Deang station (Jan, 2006)

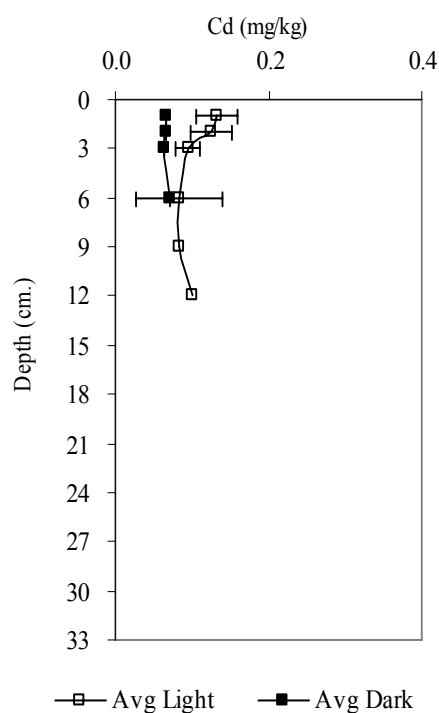
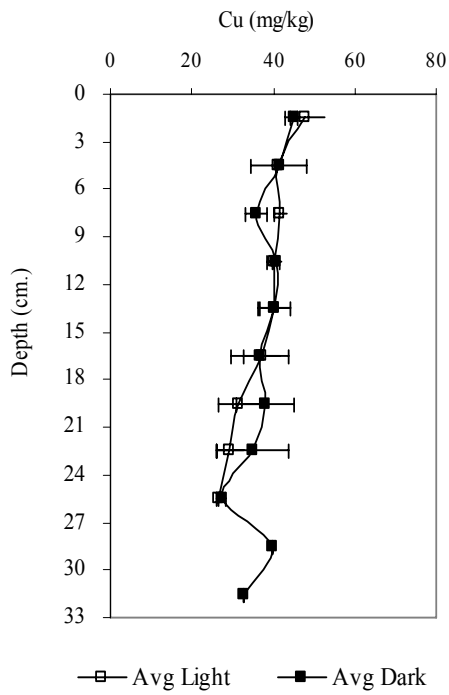


Figure 3- 32 Depth profile of Cd concentration (mg kg^{-1}) in sediment at Khao-Deang. Open symbols represent the light chambers and dark symbols represent the dark chambers.

Khao-Deang station (April, 2005)



Khao-Deang station (Jan, 2006)

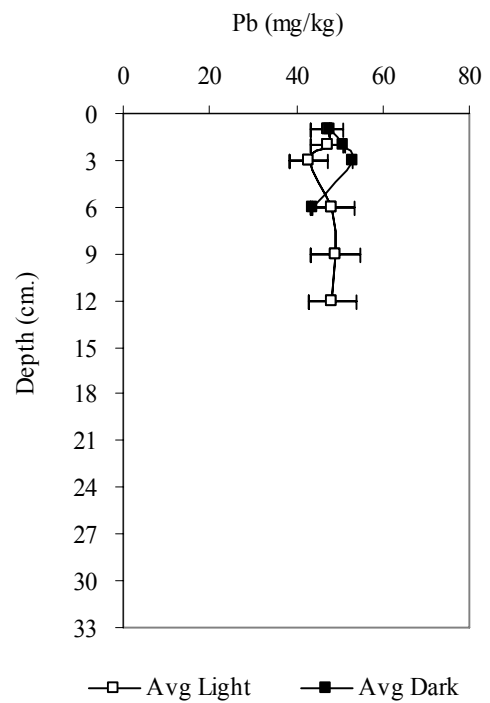
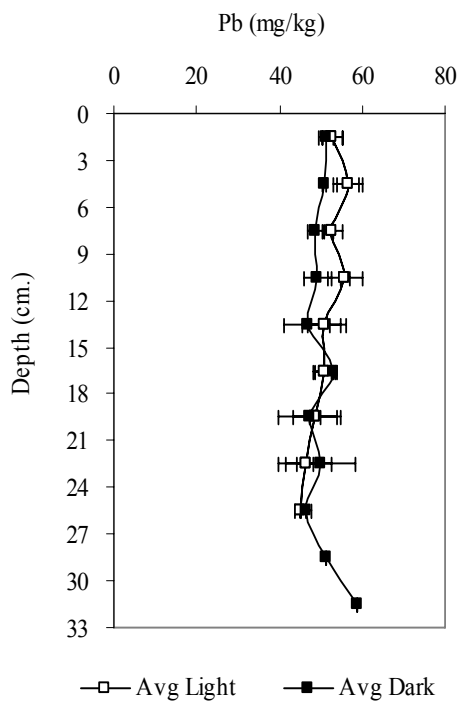
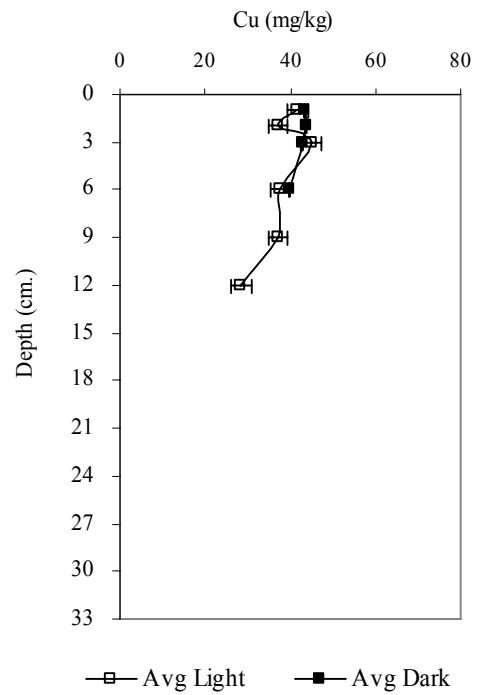
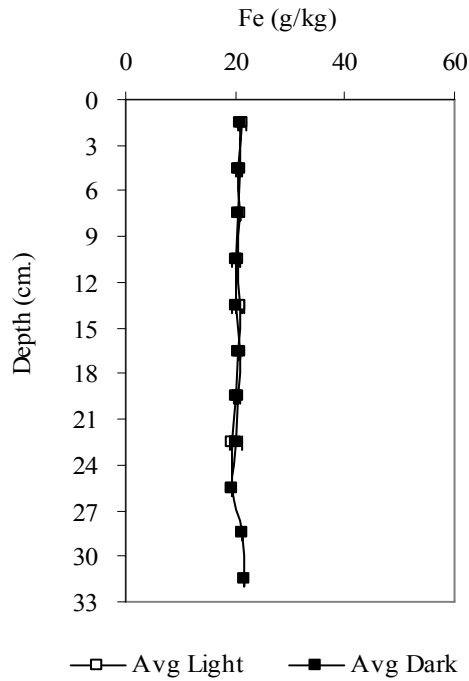


Figure 3- 33 Depth profile of Cu and Pb concentration (nM) in sediment at Khao-Deang. Open symbols represent the light chambers and dark symbols represent the dark chambers.

Khao-Deang station (April, 2005)



Khao-Deang station (Jan, 2006)

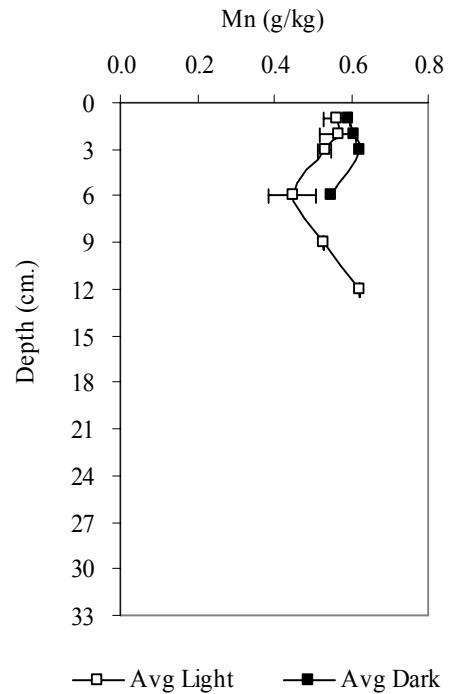
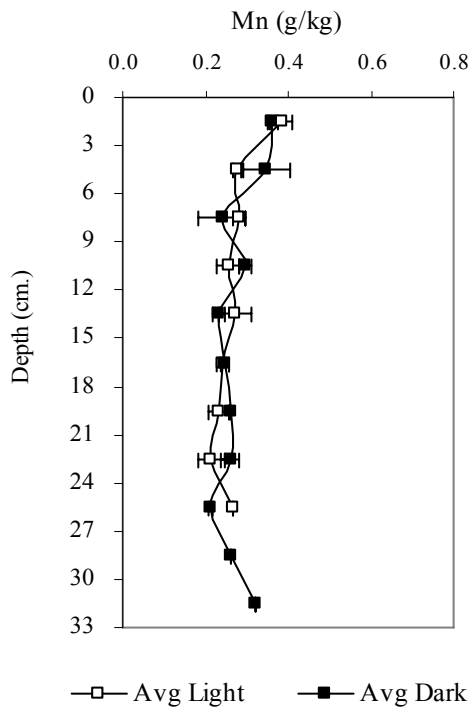
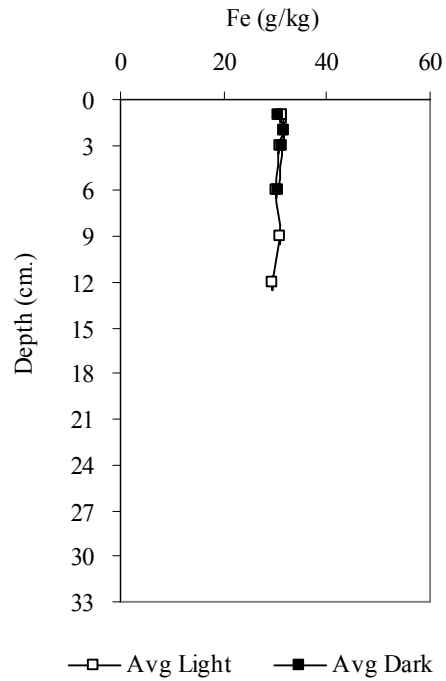


Figure 3-34 Depth profile of Fe and Mn concentration (nM) in sediment at Khao-Deang. Open symbols represent the light chambers and dark symbols represent the dark chambers.

3.4 Optimized the temperature program of GFAAS

In GFAAS technique, the ashing and atomizing temperature for metals should be optimized according to the sample composition. The optimization was performed by changing one parameter and keeping other parameters constant and then the optimum value was selected for all experiments. The optimization tests were carried out by using 4, 25, 50, 25 and 20 $\mu\text{g L}^{-1}$ for Cd, Cu, Pb, Fe and Mn standard solution, respectively. The results are listed in Table C-16 to Table C-20 in Appendix C. The optimal ashing temperature for Cd, Cu, Pb, Fe and Mn were 500, 900, 750, 1100 and 1000 $^{\circ}\text{C}$, respectively. The optimal atomization temperature for Cd, Cu, Pb, Fe and Mn were 1400, 2000, 1500, 1700 and 2100 $^{\circ}\text{C}$, respectively. The operating conditions are listed in Table 3-7.

Table 3-7 The operating conditions

Lamp settings	Cd	Cu	Pb	Fe	Mn
Wavelength (nm)	228.8	324.8	283.3	248.3	279.5
Spectral band width (nm)	0.7	0.7	0.7	0.2	0.7
Furnace temperature ($^{\circ}\text{C}$)					
Drying 1 (ramp 1 s, hold 20 s)	110	110	110	110	110
Drying 2 (ramp 15 s, hold 30 s)	130	130	130	130	130
Ashing (ramp 10 s, hold 20 s)	500	900	750	1000	1100
Atomizing (ramp 0 s, hold 5 s)	1400	2000	1500	2100	1700
Clean-up (ramp 1 s, hold 3 s)	2250	2250	2250	2250	2250

3.5 Quantification of Metals

The calibration curve and standard addition method were used for quantification of the analytes. In order to know whether the matrix would interfere with the measurement of dissolved Cd, Cu, Pb, Fe and Mn by GFAAS technique, the slope of standard calibration curve was compared to a standard addition one. The results show no interference from the sample matrix for Cd and Cu metal as shown in Figure 3-35 and Figure 3-36 (Table C-21 and Table C-22 in Appendix C). The slopes of these two methods were different for Pb, Mn and Fe metal as shown in Figure 3-37 to Figure 3-39 (Table C-23 to Table C-25 in Appendix C). Thus, the standard addition method was used to quantify the amount of Pb, Fe and Mn in extracted samples.

In sediment samples, a calibration curve was used to quantify the metal by using digestion blank as a media in standard preparation in order to gain a same matrix as a sample.

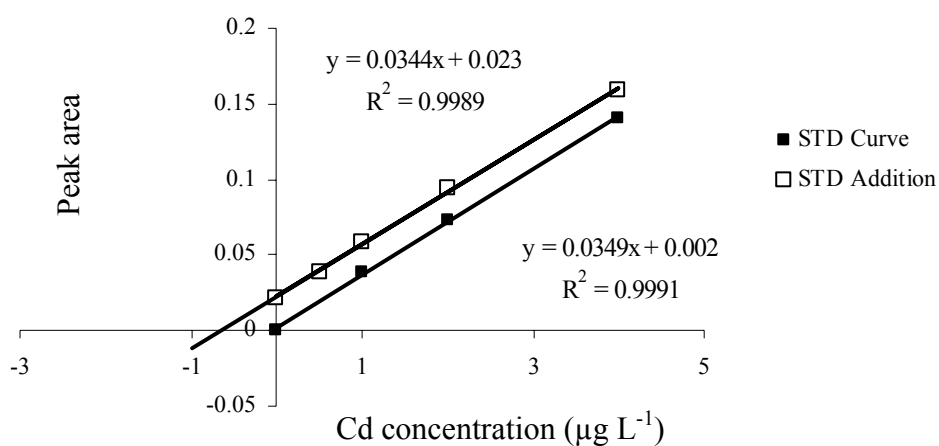


Figure 3- 35 Comparison Cd standard calibration curve and standard addition curve method of extracted sample

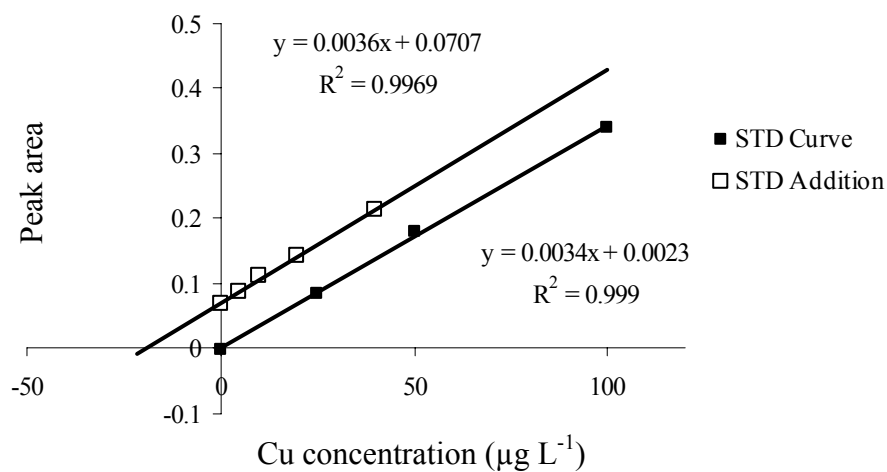


Figure 3- 36 Comparison Cu standard calibration curve and standard addition curve method of extracted sample

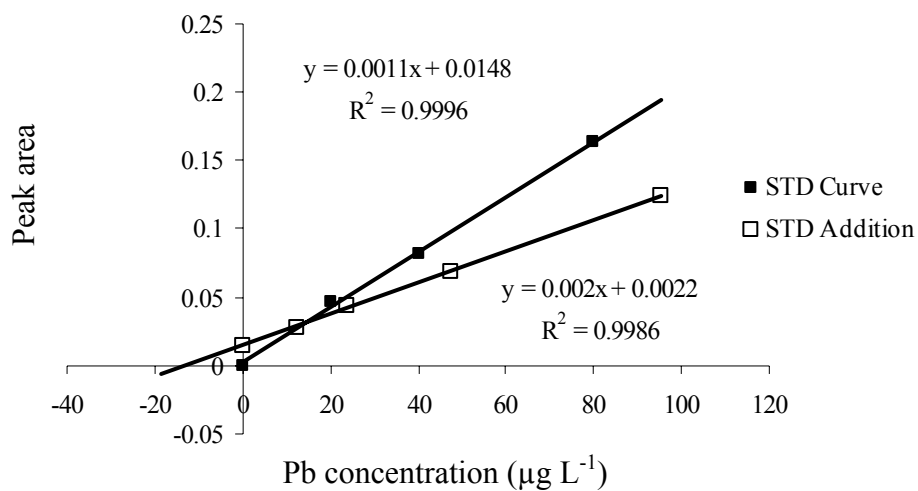


Figure 3- 37 Comparison Pb standard calibration curve and standard addition curve method of extracted sample

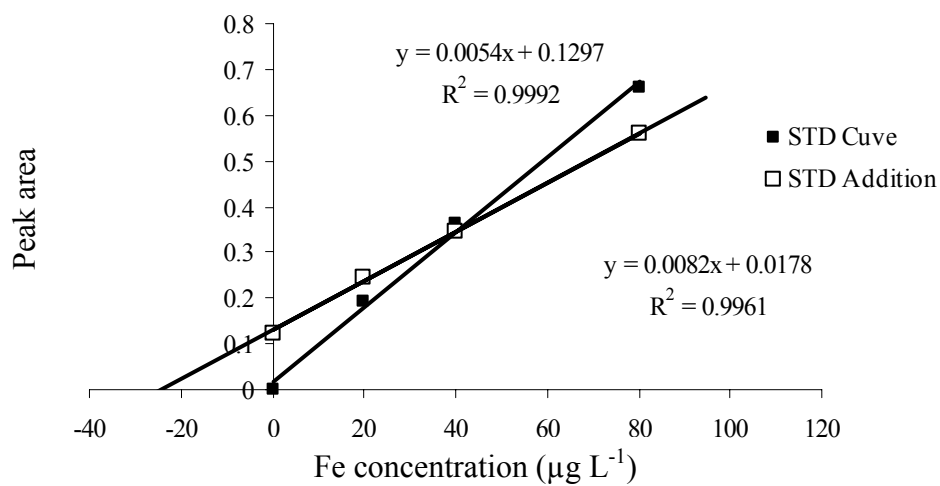


Figure 3- 38 Comparison Fe standard calibration curve and standard addition curve method of extracted sample

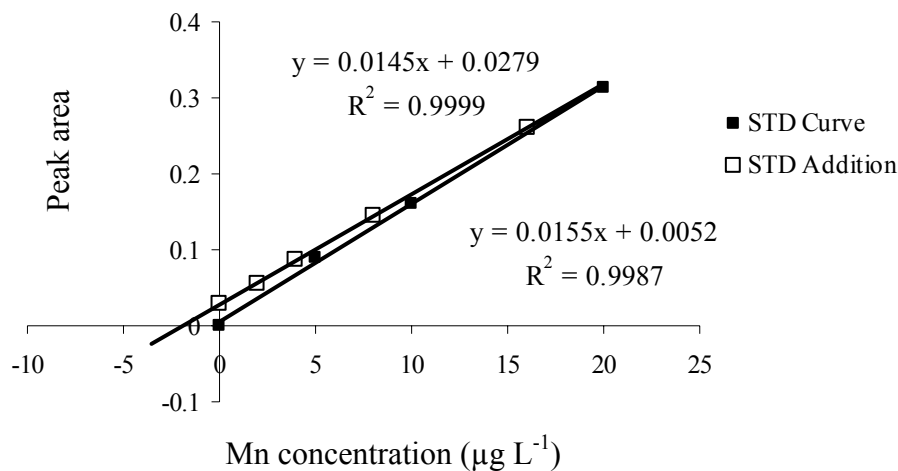


Figure 3- 39 Comparison Mn standard calibration curve and standard addition curve method of extracted sample

3.6 Method of validation

The analytical performance characteristics were evaluated including detection limit, percent recovery, accuracy and precision of the measurements.

3.6.1 Detection Limit (DL)

The detection limits, defined as the concentration equivalent to three times the standard deviation ($n = 10$) of the reagent blank, for GFAAS measurements, were found to be 0.0014, 0.0133, 0.0094, 0.0067 and 0.0048 for Cd, Cu, Pb, Mn and Fe $\mu\text{g L}^{-1}$ respectively (Table C-26 in Appendix C).

3.6.2 Precision

The precision was presented in the term of %RSD of 10 replicated measurements of one sediment sample by GFAAS for Cd, Cu and Pb and FAAS for Fe and Mn. The percentage of relative deviation (%RSD) was 4.2%, 1.6%, 4.6%, for Cd, Cu, Pb, respectively and 2.3% and 2.2% Fe and Mn, respectively (Table C-27 in Appendix C).

3.6.3 Recovery

The recovery tested was performed by using estuarine water from Kor Yor spiked with the studied elements and treated as the same manure as samples. Three replicate analyses were carried out. The recoveries were found in the range of 92-109 % for Cd, Cu, Pb, Fe and Mn. The results are given in Table 3-8.

Table 3-8 Percent recovery of Cd, Cu, Pb, Fe and Mn ($n=3$)

Cd			Cu		
Added ($\mu\text{g/L}$)	Analyzed ($\mu\text{g/L}$)	%Recovery	Added ($\mu\text{g/L}$)	Analyzed ($\mu\text{g/L}$)	%Recovery
0	1.49 \pm 0.02	-	0	20.95 \pm 0.86	-
1	2.56 \pm 0.12	103	20	43.54 \pm 1.02	100.0
2	3.73 \pm 0.06	107	40	64.51 \pm 2.47	101.3
3	4.61 \pm 0.30	102	60	91.39 \pm 1.49	108.4

Pb			Fe		
Added ($\mu\text{g/L}$)	Analyzed ($\mu\text{g/L}$)	%Recovery	Added ($\mu\text{g/L}$)	Analyzed ($\mu\text{g/L}$)	%Recovery
0	2.25 \pm 0.07	-	0	4.17 \pm 0.27	-
10	11.23 \pm 0.06	91.8	10	14.43 \pm 0.30	101.7
20	23.30 \pm 1.35	104.0	20	23.89 \pm 0.93	98.8
30	35.16 \pm 1.00	109.0	30	33.77 \pm 0.16	97.4

Mn		
Added ($\mu\text{g/L}$)	Analyzed ($\mu\text{g/L}$)	%Recovery
0	14.68 \pm 0.72	-
5	19.09 \pm 0.04	97.0
10	24.88 \pm 0.03	100.0
15	29.46 \pm 0.05	99.2

3.6.4 Analytical accuracy

The accuracy of the proposed method was verified with certified reference material (MESS-1) sediment obtained from Institute for National Research Council of Canada (NRCC). The concentration of total Cd, Cu, Pb and Mn obtained by this method were 0.59 \pm 0.05, 25.1 \pm 3.8, 34.0 \pm 6.1 and 513 \pm 25 mg kg⁻¹ while the certified value were 0.59 \pm 0.003, 22.3 \pm 0.47, 32.4 \pm 2.1 and 500 \pm 8.6 mg kg⁻¹ as presented in Table 3-7. This value shows no significant different by using *t*-test at 90% confident limit. The percent relative errors are 11, 4.7 and 2.5 % for Cu, Pb and Mn, respectively.

Table 3-9 Analysis of reference material (MESS-1)

Metals	Certified Value (mg kg ⁻¹)	Present study (n=3)	%accuracy
Cd	0.59±0.05	0.59±0.003	100.0
Cu	25.1±3.8	22.3±0.47	88.8
Pb	34.0±6.1	32.4±2.1	95.3
Mn	513±25	500±8.6	97.5

3 replications of each concentration, % RSD < 7