CHAPTER 4

Discussion

4.1 Concentration of trace metals in the study area.

Trace metals of interested, cadmium, copper, iron and nickel in the Gulf of Thailand and East Coast of Malay Peninsula were mostly presented as dissolved form (Fig.3-1, Fig.3-6, Fig.3-16), except for iron (Fig.3-11) in which about 33 to 99% were in suspended particulate form. For lead, the concentration of dissolved and suspended particulate form depend on loading (Fig.3-21). Higher dissolved lead was observed at stations off Malay Peninsula. The percentage of dissolved cadmium, copper, nickel and lead in the study area were 40-99 %, 32-94 %, 49-97 % and 17-98 %, respectively. A higher percentage of dissolved Cd, Cu, Ni and Pb found at surface layer (Fig.4-1, Fig.4-2, Fig.4-4 and Fig.4-5), suggest that there were some fresh water input of dissolved metal from rivers. Cadmium, copper and nickel in river water draining into the Gulf of Thailand at surface layer were dominated in dissolved form but iron and lead were in suspended particulate form (Hungspreugs *et al.*, 1990, Chembumroong, 1987, Hungspreugs *et al.*, 1997 and Hungspreugs *et al*, 1998). This also explains the high percentage of suspended particulate iron near the coastal area (Fig.4-3).

Average concentrations of these dissolved trace metals were within the range found else-where, concentration range of dissolved cadmium, copper, iron, nickel and lead were 0.01-0.17, 1.50-9.00, 1.96-54.31, 0.50-9.00 and 0.03-1.00 nM, respectively (Table 4-1).

Table 4-1 Average concentrations of dissolved Cd, Cu, Fe, Ni and Pb in the Gulf of Thailand and Eastern Malaysian Peninsula and others areas (nM) .

Trace metals	*Cd*	*Cu*	*Fe*	*Ni*	*Pb*
South African Coast[a]	0.80	11.02	19.70	37.47	nd
Sea of Japan[a]	0.98	4.72	16.12	17.03	nd
China Sea[a]	0.71	15.74	19.70	27.25	0.27
Severn Estuary[b]	0.18	3.15	nd	nd	0.14
St. Lawrence Estuary[c]	0.53	17.15	537.18	13.80	nd
Mekong Delta[d]	0.11	7.00	50.00	6.49	0.20
study area (range)	**0.01-0.17**	**1.50-9.00**	**1.96-54.31**	**0.50-9.00**	**0.03-1.00**
study area (average)	**0.07**	**3.04**	**22.65**	**3.62**	**0.39**

nd=no data, data from [a]Chester, 1974. [b]Harper, 1991. [c]Yeats and Loring, 1991. [d] Hungspreugs et al, 1998.

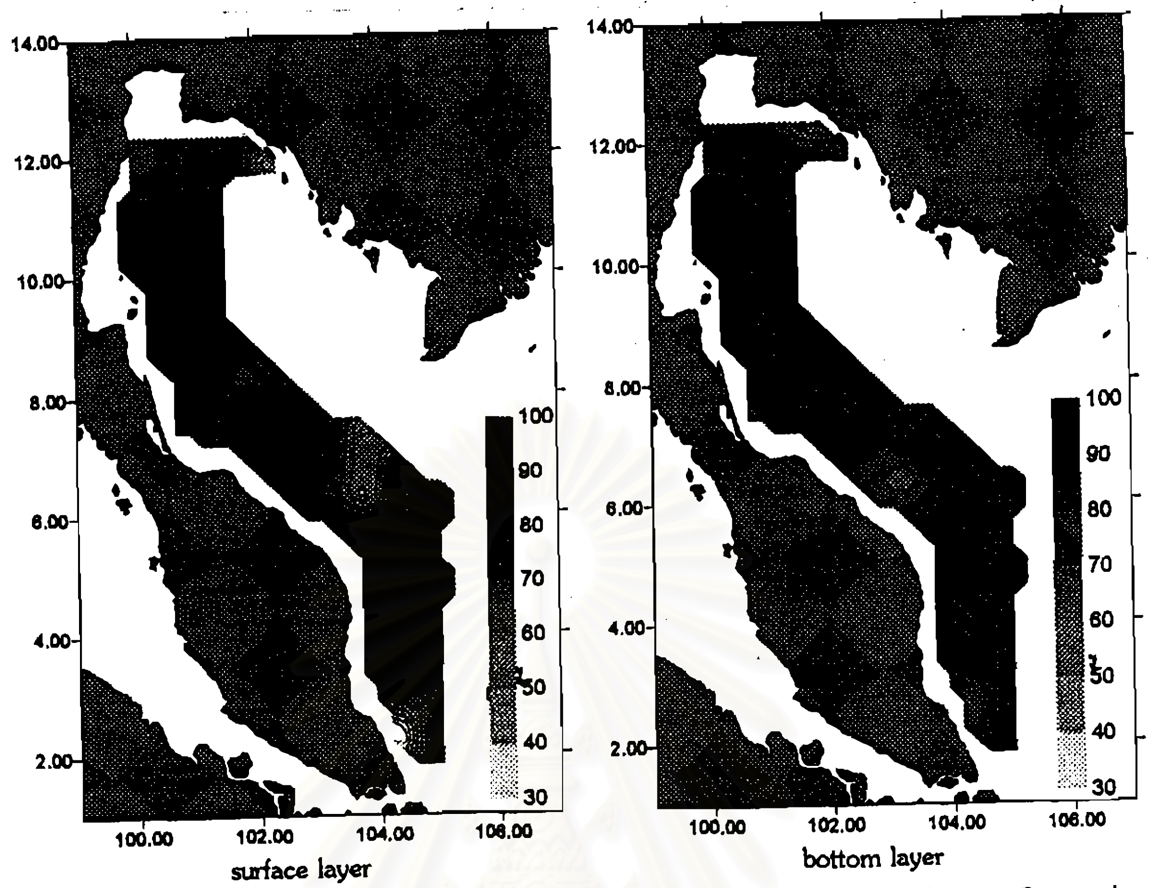

Fig.4-1 Percentage of dissolved Cd in the Gulf of Thailand and East Coast of Malay Peninsula

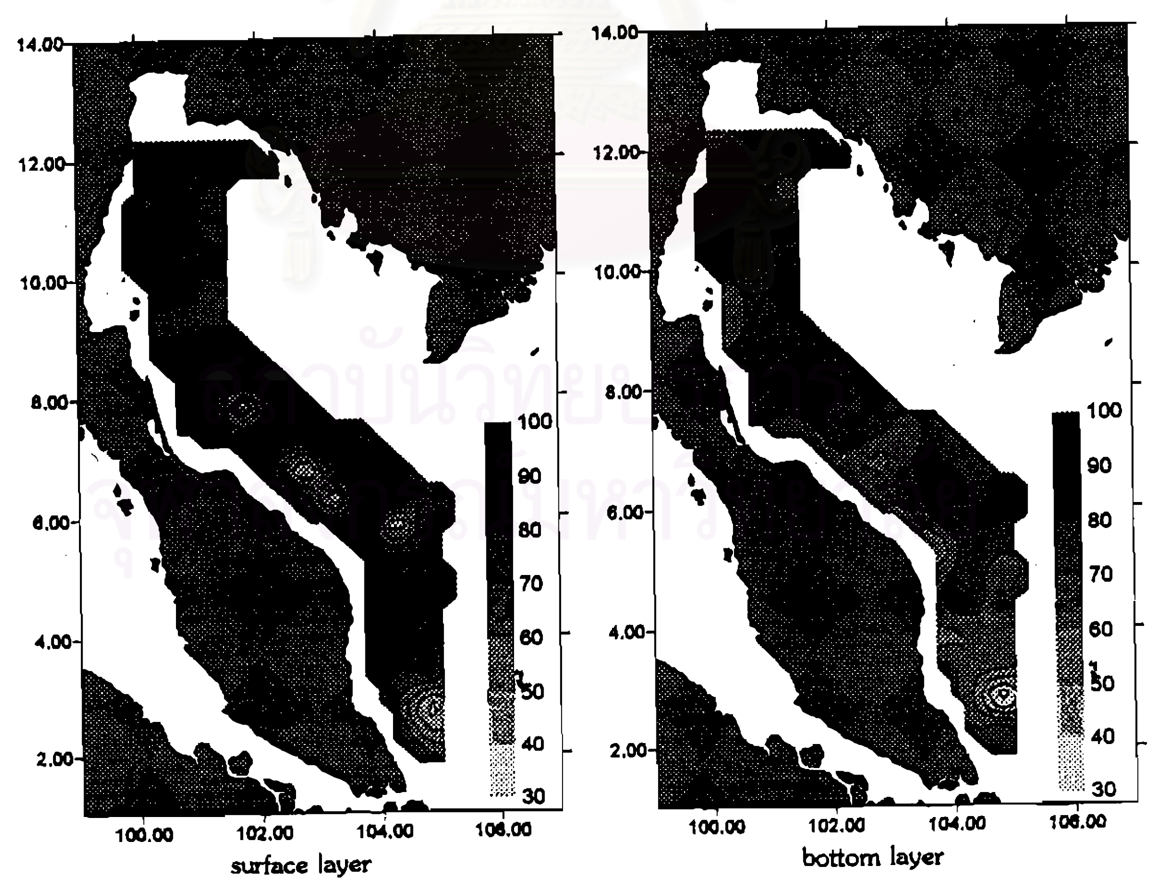

Fig.4-2 Percentage of dissolved Cu in the Gulf of Thailand and East Coast of Malay Peninsula

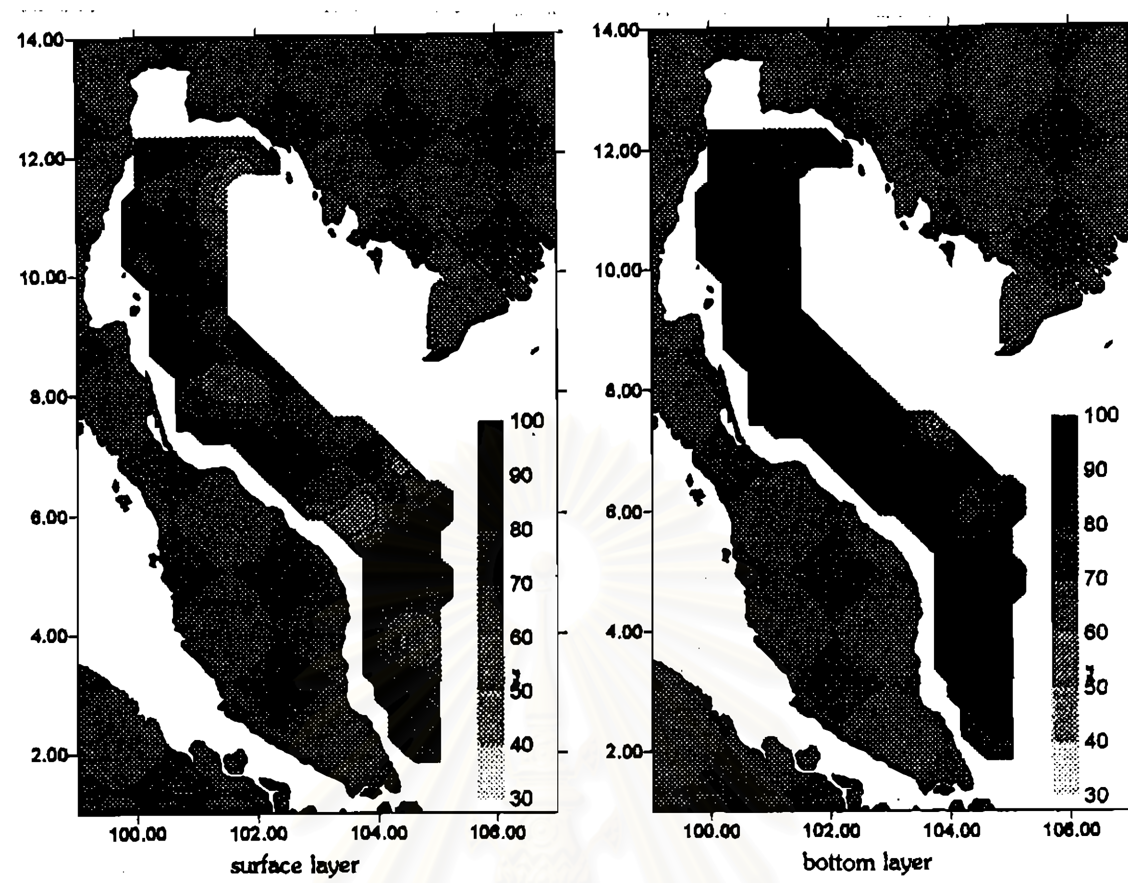

Fig.4-3 Percentage of suspended particulate Fe in the Gulf of Thailand and East Coast of Malay Peninsula

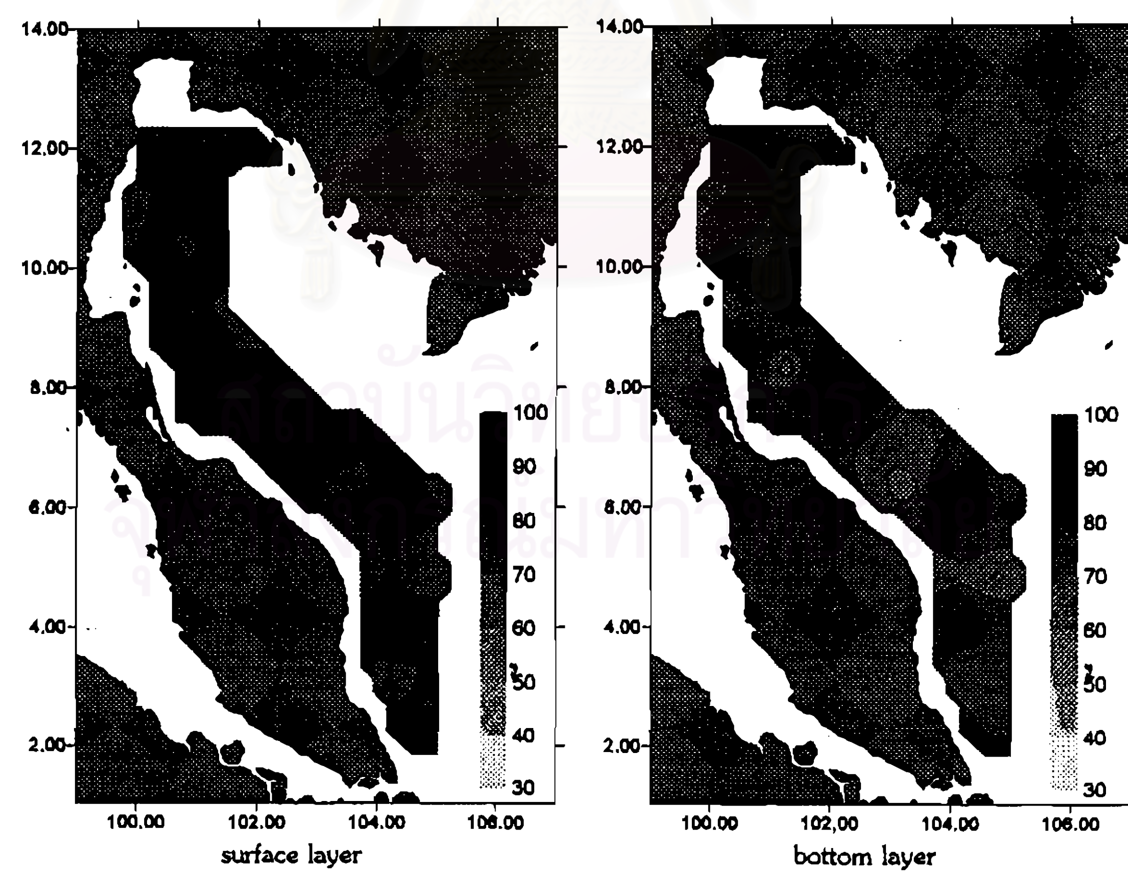

Fig.4-4 Percentage of dissolved Ni in the Gulf of Thailand and East Coast of Malay Peninsula

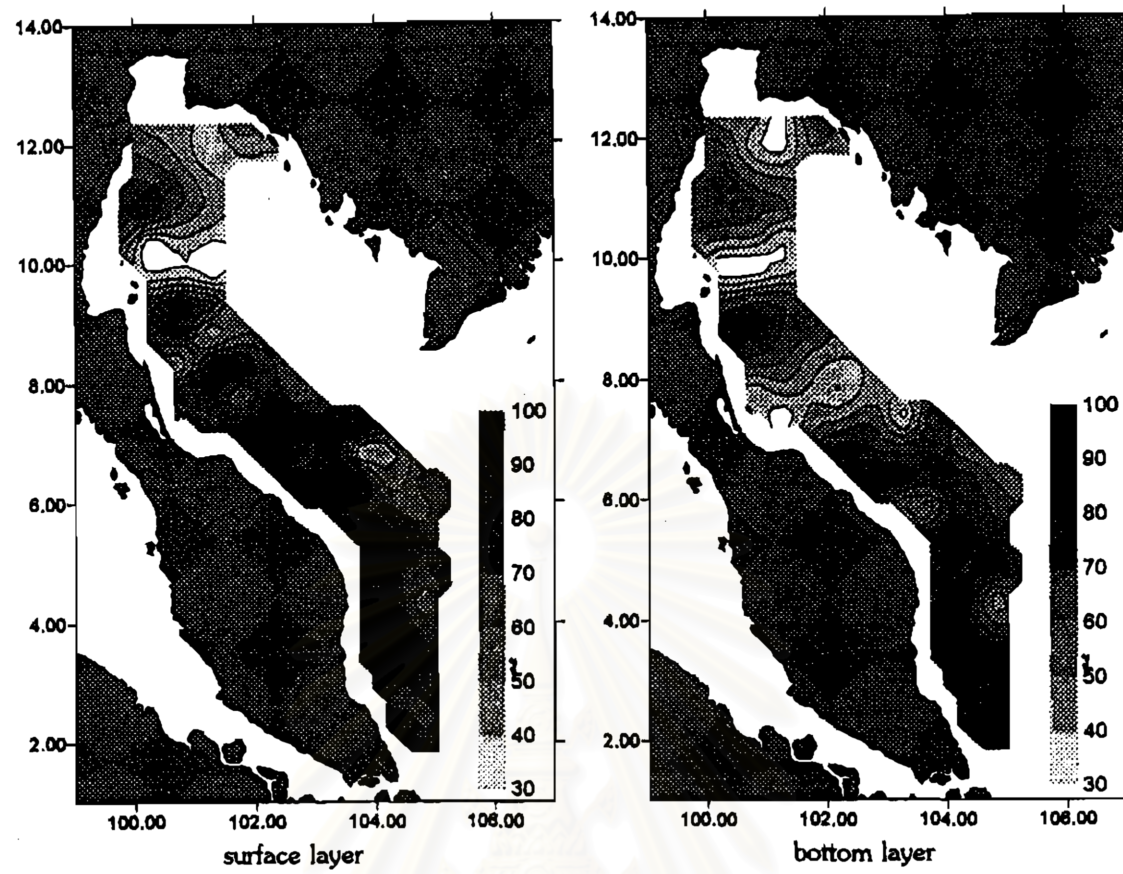

Fig.4-5 Percentage of dissolved Pb in the Gulf of Thailand and East Coast of Malay Peninsula

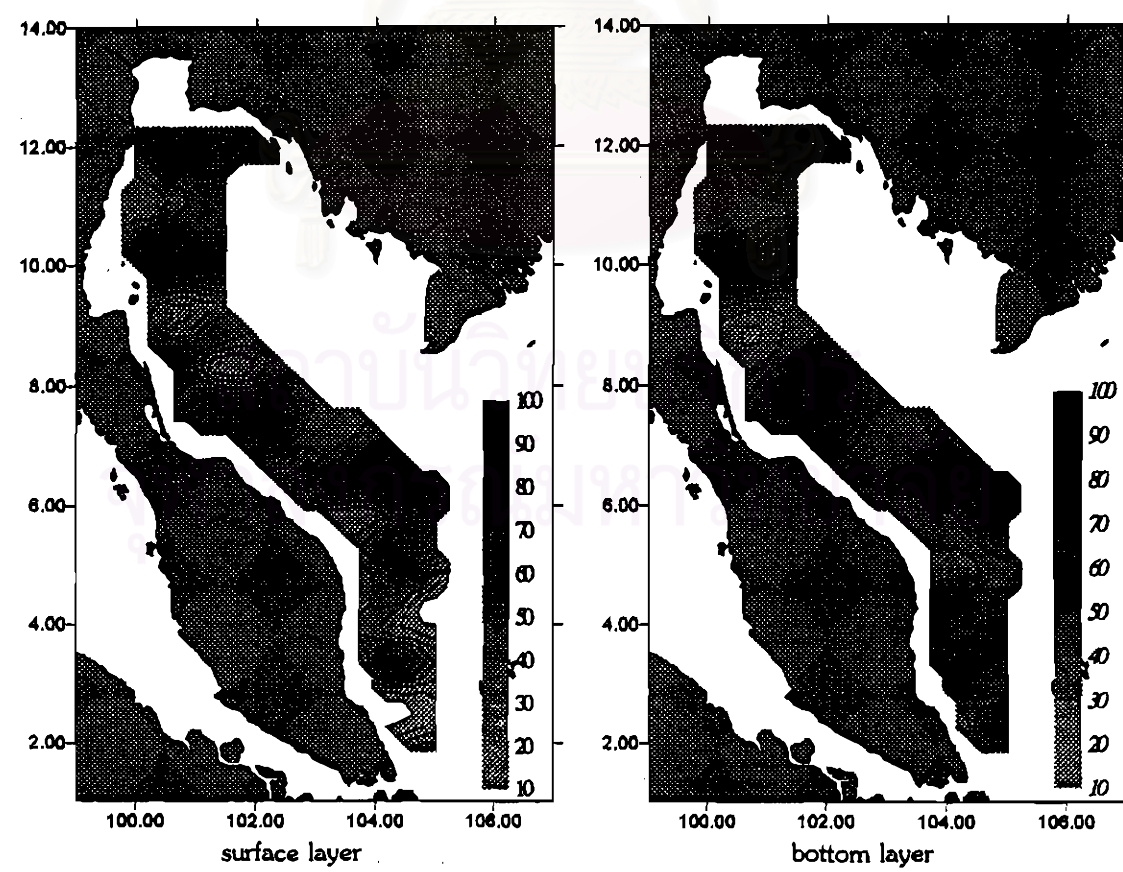

Fig.4-6 Percentage of suspended particulate Pb in the Gulf of Thailand and East Coast of Malay Peninsula

Distributions of cadmium, copper, iron and lead also indicated some land-based sources (Fig. 3-2, Fig. 3-5, Fig. 3-6, Fig. 3-12, Fig. 3-19 and Fig. 3-20). The salinity distribution in Figure 4-7 showed that salinity of the Gulf of Thailand was lower than that in the East Coast of Malay Peninsula, implying freshwater input into the Gulf. Trace metals can be discharged by rivers into the Gulf from various rivers such as the Chao Phraya, the Mae Klong, the Bang Pakong, the Ta Chin in the North of the Gulf of Thailand, and the Tapi River in the Southern-West. These rivers contain higher concentration of the traces metals than in the Gulf. Concentrations of dissolved cadmium, copper and lead in the Bang Pakong were 0.62 nM, 50.36 nM, 9.17 nM, respectively and concentration of suspended particulate form were 0.18 nM, 39.34 nM, 8.21 nM, respectively (Pollution Control Department, 1994/1 and Hungspreugs *et al.*, 1990). The concentrations in the Chao Phraya were 0.89 nM and 14.48 nM for dissolved cadmium and lead and 0.44 nM, 28.96 nM, for the suspended particulate cadmium and lead, respectively (Pollution Control Department, 1994/2).

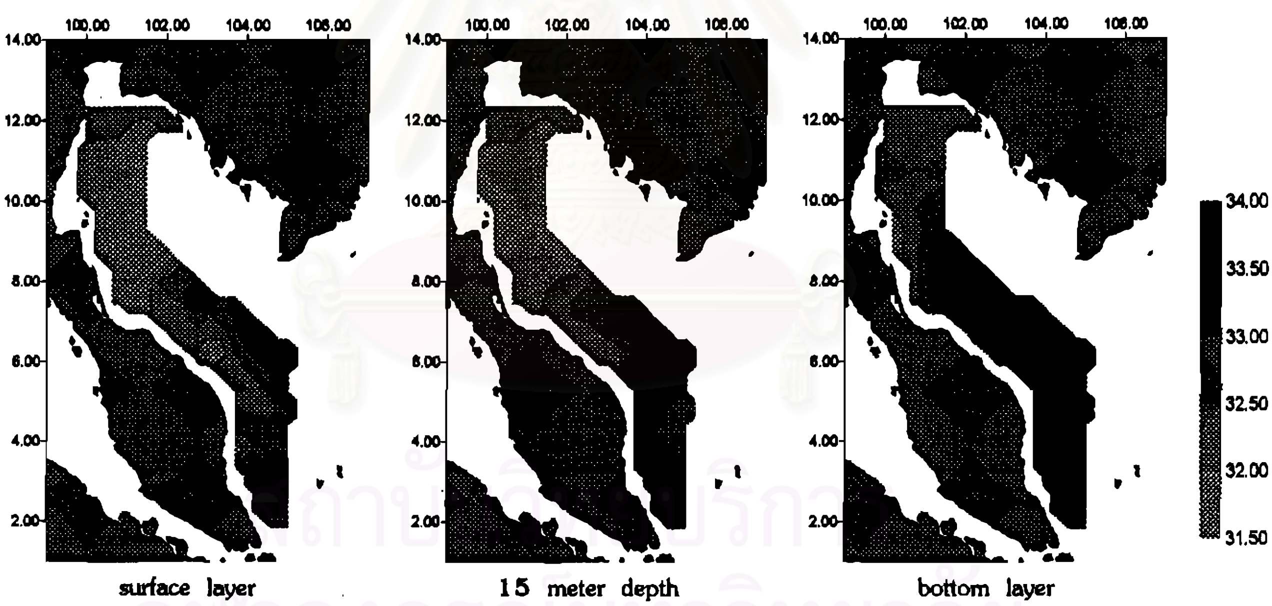

Fig.4-7 Distribution of salinity (psu) at surface layer, at 15 meter depth and at bottom layer.

4.2 Correlation of trace metals with environment variables.

Trace metal distributions in aquatic ecosystem are classified as seven types (Bruland, 1983). Yeat *et al.*, (1995), Nolting *et al.*, (1991) and Knauer and Martin, (1980) found that cadmium has a nutrient-like distribution in which concentration of dissolved cadmium is correlated with phytoplankton and nutrient. Environment variables are shown in Appendix E and F.

The vertical profiles of dissolved cadmium and PO_4 in some off-shore stations, stations 46 and 69 were shown in Figure 4-8.

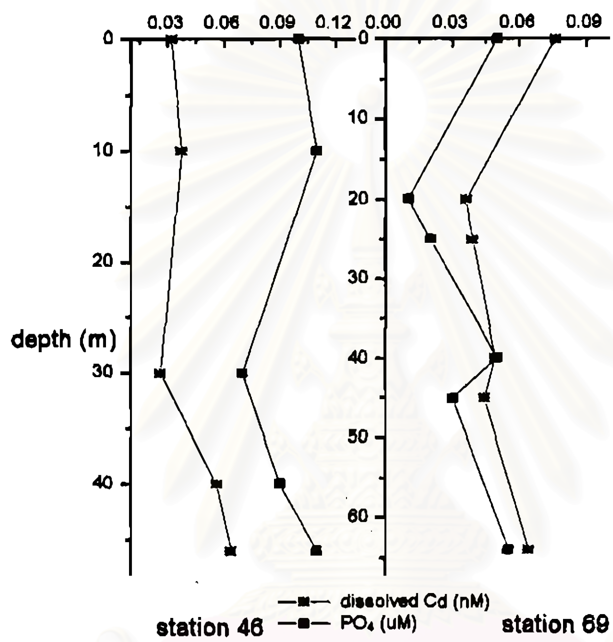

Fig.4-8 Vertical profile of dissolved Cd and PO_4 at stations 46 and 69

Distribution of dissolved cadmium in the Gulf of Thailand and East Coast of Malay Peninsula trend to correlate with PO_4 , but this is not obvious in the coastal stations where there is input from river. A correlation of cadmium and PO_4 of water with salinity greater than 33 psu, which has little effect from fresh water is shown in Figure 4-9.

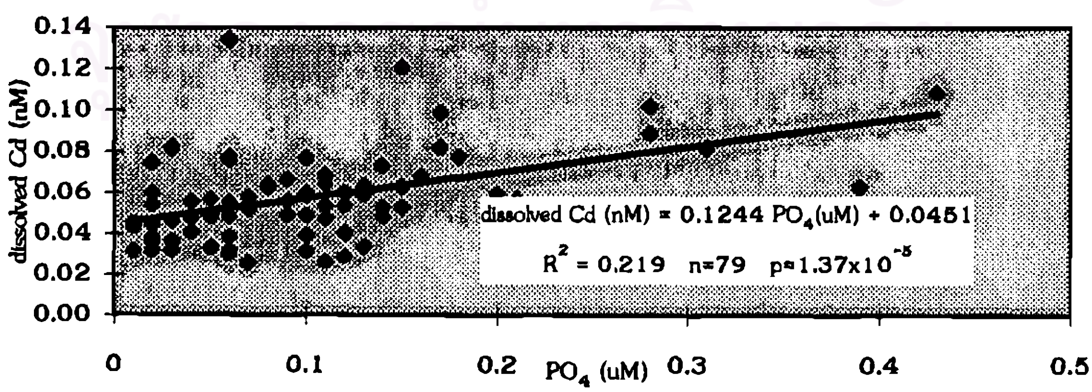

Fig.4-9 Linear relationship between dissolved cadmium and PO_4

pH also exert some affect on the distribution of trace metal. In bottom layer where pH of water was lower than the surface water, high concentration of dissolved cadmium were found (Fig. 3-31), suggesting that cadmium could be released from suspended particulate and sediment when pH decreases. The increases of many trace metals in water result from acid redissolution of sediment (Forstner and wittmann, 1981), low pH in sediments tend to favor the formation of soluble species of many trace metals (Hounslow, 1995). Distribution of dissolved cadmium and pH at bottom layer was shown in Figure 4-10.

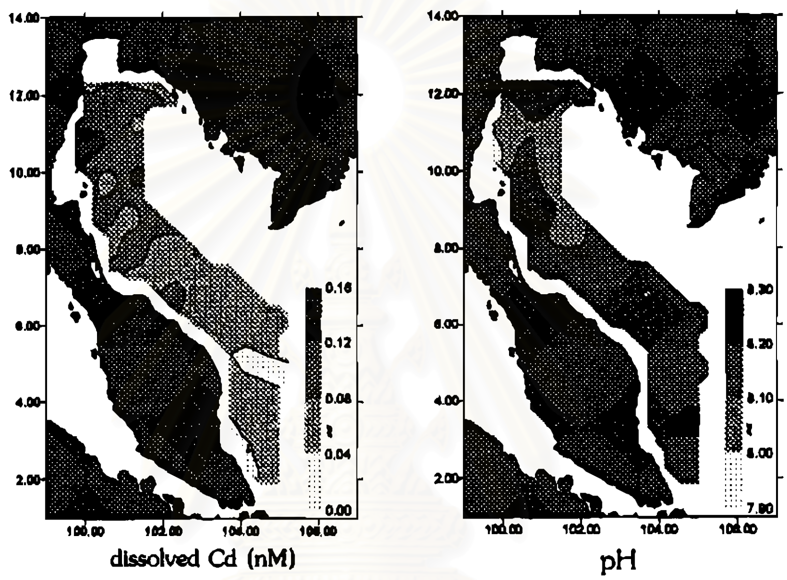

Fig.4-10. Distribution of dissolved Cd and pH at bottom layer

Distribution of dissolved cadmium which was a nutrient type distribution showed a good correlation with pH and dissolved oxygen (Fig. 4-11 and Fig.4-12, respectively). At a water layer of low pH where decomposition of phytoplankton occurs, high concentration of dissolved cadmium was observed while at a layer of photosynthesis dissolved Cd decreased and dissolved oxygen increased.

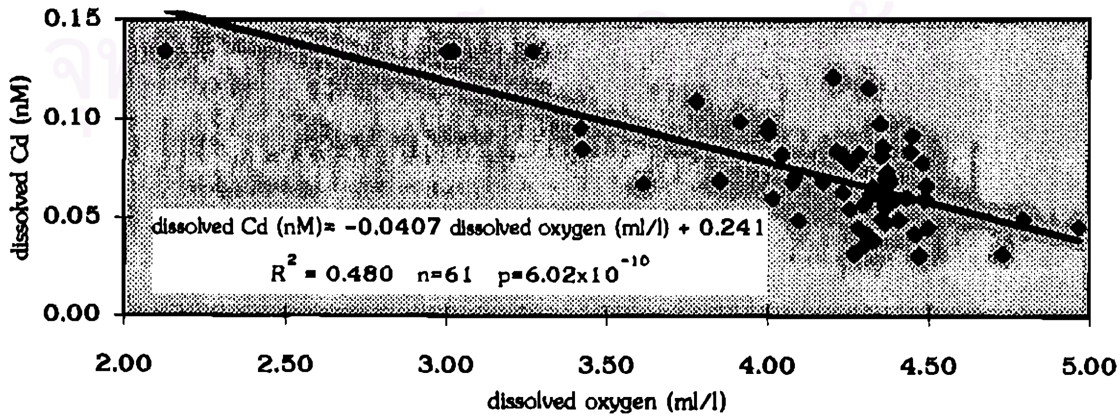

Fig.4-12 Linear relationship between dissolved cadmium and dissolved oxygen at bottom layer

Even though there were report on significant correlation of other trace metals with environment variables such as suspended particulate copper with phytoplankton in Ligurian coastal Italy (depth ≥ 200 m) (Fabiano *et al*, 1985), but this is not obvious in the present study (Fig.4-13).

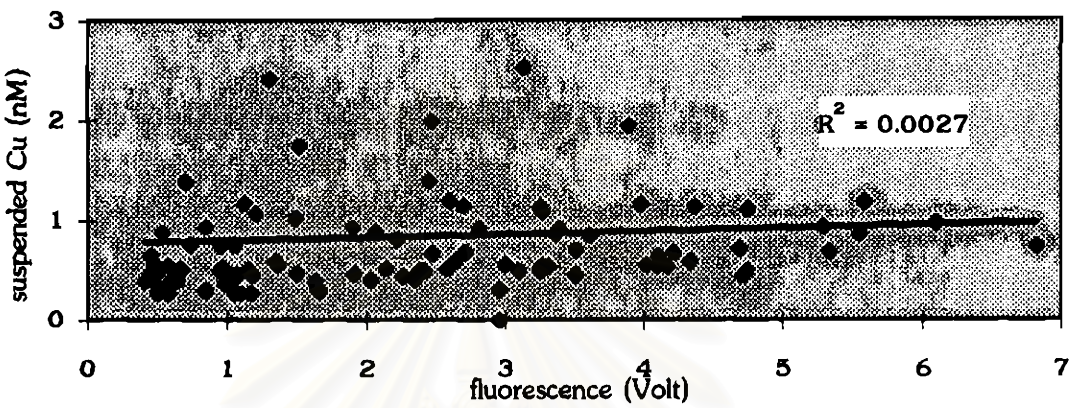

Fig.4-13 Relationship between suspended particulate copper and fluorescence

Comparison of trace metals in the Gulf of Thailand between dry season and wet season are shown in Figure 4-14 to Figure 4-18. It is obvious that concentration of cadmium and lead were higher in dry season than in wet season (Fig.4-14 and Fig.4-18). Study of abundance of phytoplankton in wet season and dry season in The Gulf of Thailand and East Coast of Malay Peninsula showed that a higher density of phytoplankton was observed in wet season than dry season (Shamsudin, 1997). Phytoplankton can store trace metals over long periods even when the metal content in the water is low (Forstner and Wittmann, 1981). The distribution of cadmium was nutrient type i.e. influenced by biological activity. Dissolved cadmium possibly betaken up by phytoplankton during a blooming period in wet season, causing a decreasing in dissolved cadmium concentration. For lead in dry season there are more human activities in the sea than wet season and in dry season there are higher concentration of atmospheric particle than wet season, these may be an important source of lead.

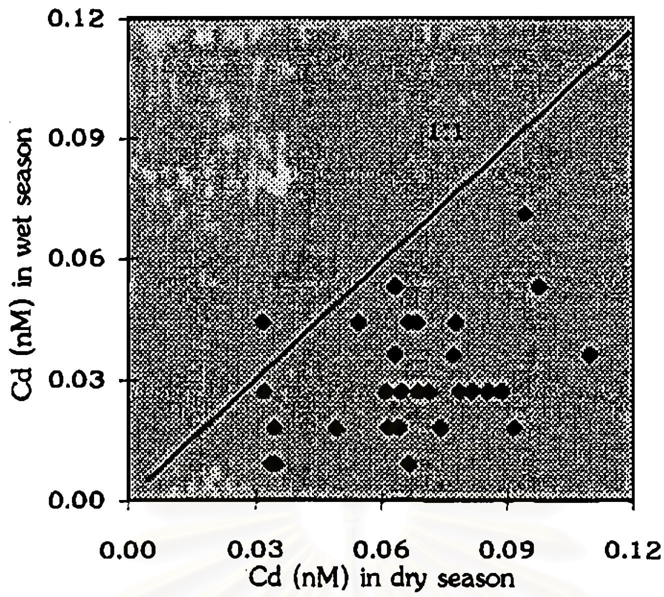

Fig.4-14 Concentration of dissolved Cd(nM) between dry season and wet season.

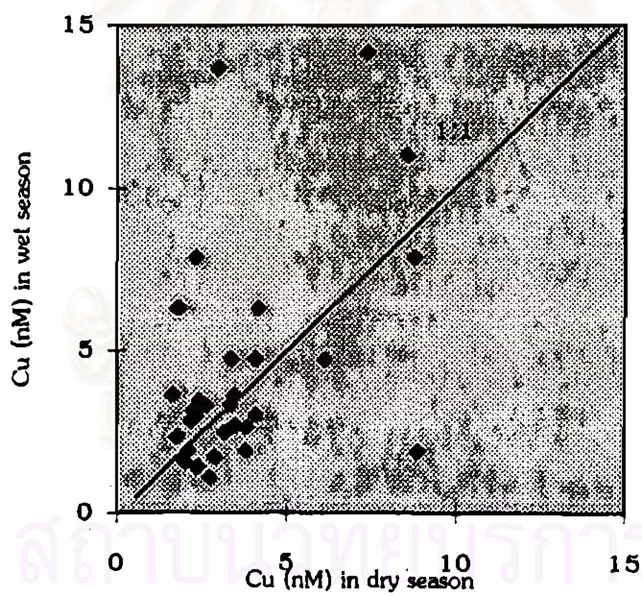

Fig.4-15 Concentration of dissolved Cu(nM) between dry season and wet season.

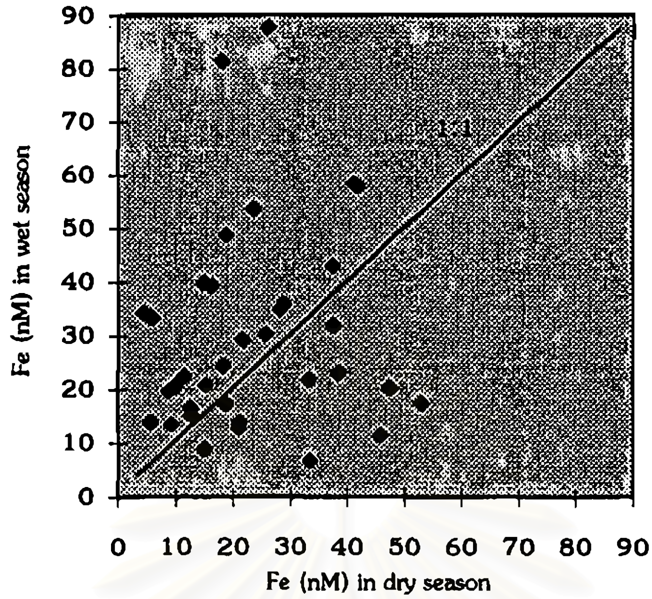

Fig.4-16 Concentration of dissolved Fe(nM) between dry season and wet season.

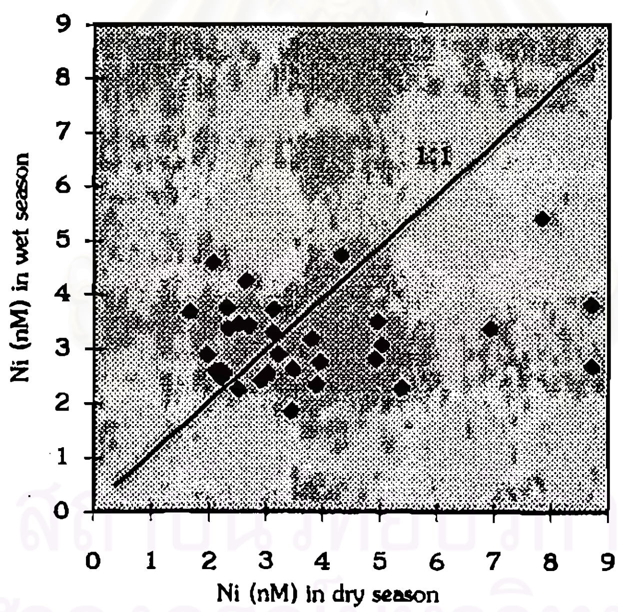

Fig.4-17 Concentration of dissolved Ni(nM) between dry season and wet season.

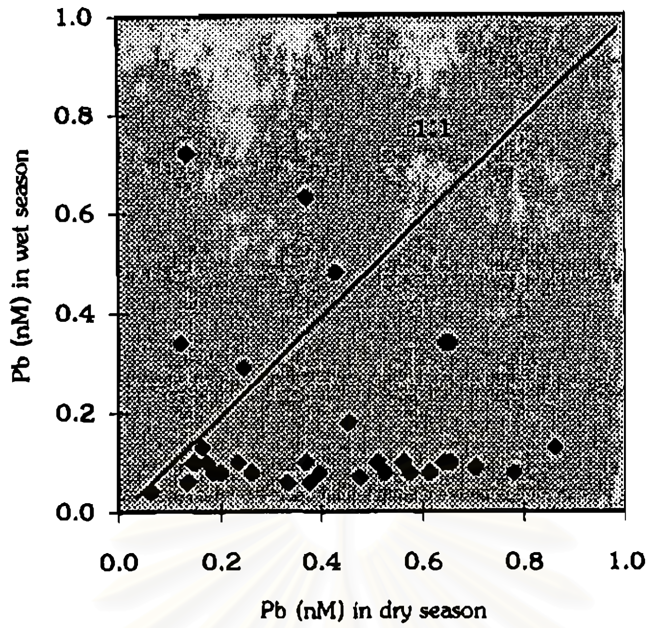

Fig.4-18 Concentration of dissolved Pb(nM) between dry season and wet season.

4.3 The cycling of trace metals in the Gulf of Thailand.

Source of trace metals in the Gulf of Thailand were mainly from the river input of major rivers draining into the Gulf. In the north, there are the Bang Pakong, Chao Praya, Mae Klong and Ta Chin, and the Tapi River is in the Southern-West. From the salt and heat budgets (Stansfield and Garrett, 1997) showed that Mekong River in Vietnam appears to be a vital source of fresh water to the Gulf of Thailand. There is also some evidence that high salinity water from the South China Sea enters the Gulf in the bottom layer (Piyakarnchana *et al.*, 1989). In this study, the amount of water entry the Gulf from South China Sea was calculated from the salt budget. Fresh water input to the Gulf are local rivers ($224 \times 10^9\ m^3\ y^{-1}$), Mekong River ($260 \times 10^9\ m^3\ y^{-1}$) and net fresh water input from the atmospheric (net balance between rainfall and evaporation) about ($100 \times 10^9\ m^3\ y^{-1}$) (Snidvongs, 1998). The out flow is the surface water of salinity 32.5 psu to the South China Sea (Fig.4-19). For balancing the salt budget, the inflow of bottom water from the South China Sea (salinity 34.0 psu) of $10{,}500 \times 10^9\ m^3 y^{-1}$ is required.

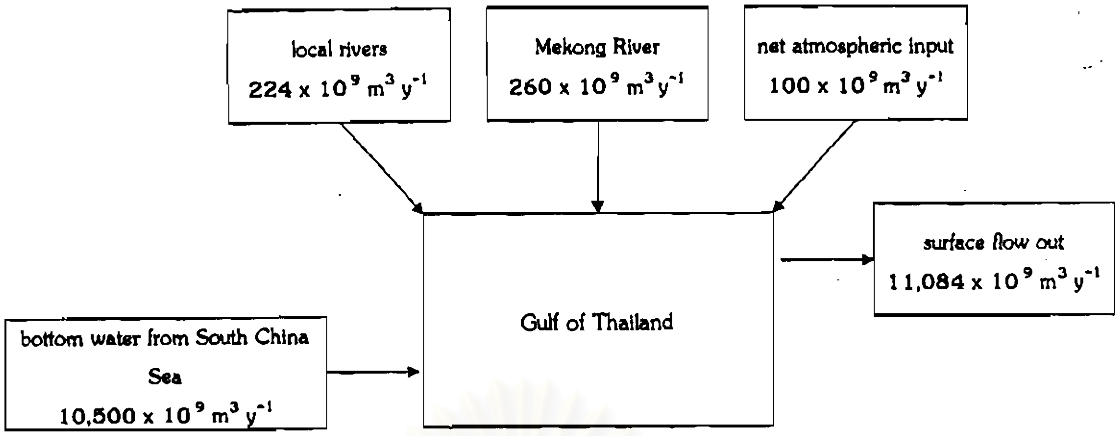

Fig.4-19 Budget of water in the Gulf of Thailand

4.3.1 The river sources of Cd, Cu, Fe, Ni and Pb

The Chao Phraya River is 396 km long. The area along this river is the most developed river bank in Thailand. There are many population and industries along this river especially in Bangkok and adjacent areas. The average yearly flow of the Chao Phraya River is 15×10^9 m^3 (Pollution Control Department, 1997). The annual load of cadmium, copper, iron, nickel and lead of Chao Phraya River is show in Table 4-2.

Table 4-2 Concentration and discharge of Cd, Cu, Fe, Ni and Pb in the Chao Phraya River.

	Dissolved					*Suspended particulate*				
Trace metals	Cd	Cu	Fe	Ni	Pb	Cd	Cu	Fe	Ni	Pb
Concentration (µg/l)[a]	0.1	9	100	5[b]	3	0.05	6.0	200[c]	8	6
Discharge (ton/year)	1.50	135	840	75	45	0.75	90	3000	120	90

data from [a] Pollution Control Department, 1994, [b] Umnuay, 1984, [c] Estimate from concentration of dissolved Fe.

The Bang Pakong River also drains into the Upper Gulf of Thailand. The average yearly flow of the Bang Pakong River is 9.9×10^9 m^3 (Hungspreugs et al, 1990). The annual load of cadmium, copper, iron, nickel and lead of Bang Pakong was show in Table 4-3.

Table 4-3 Concentration and discharge of Cd, Cu, Fe, Ni and Pb in the Bang Pakong River.

	Dissolved					Suspended particulate				
Trace metals	Cd	Cu	Fe	Ni	Pb	Cd	Cu	Fe	Ni	Pb
Concentration (μg/l)	0.07[a]	3.2[a]	23.7[b]	6.0[a]	1.9[a]	0.02[c]	2.5[a]	215.6[b]	3.0[a]	1.7[a]
Discharge (ton/year)	0.69	31.68	234.63	59.4	18.81	0.20	24.75	2134.1	29.70	16.83

data from [a] Pollution Control Department, 1994, [b] Hungspreugs *et al*, 1989, [c]Hungspreugs *et al*, 1990.

The Mae Klong River is 140 km long. Serveral sugar mills and some pulp and paper mills are situated on the bank of the river. The last 40 km of the river is under the tidal influence and fairly densely populated. Its brings a flow of around $8x10^9$ m^3/year into the Upper Gulf of Thailand at Samut Songkram province (Hungspreugs *et al*, 1990). The annual load of cadmium, copper, iron, nickel and lead of Mae Klong River are shown in Table 4-4.

Table 4-4 Concentration and discharge of Cd, Cu, Fe, Ni and Pb in the Mae Klong River.

	Dissolved					Suspended particulate				
Trace metals	Cd	Cu	Fe	Ni	Pb	Cd	Cu	Fe	Ni	Pb
Concentration (μg/l)[a]	0.04	1.2	[b]100	5	0.4	0.02	1	1000	5	10
Discharge (ton/year)	0.32	9.6	400	40	3.2	0.16	8	8000	40	80

data from [a] Hungspreugs *et al*, 1990, [b] Estimate from concentration of dissolved Fe.

The Ta Chin River is 331 km long. The water pollution problem of the Ta Chin River mainly due to domestic and agriculture waste water discharge. Agricultural waste water was from pig raising, fish and shimp cultivation, poultry farm as well as plant and vegetable growing (Pollution Control Department, 1995). The average yearly flow of the Ta Chin River is $1.2x10^9$ m^3. The annual load of cadmium, copper, iron, nickel and lead of Ta Chin River are shown in Table 4-5.

Table 4-5 Concentration and discharge of Cd, Cu, Fe, Ni and Pb in the Ta Chin River.

	Dissolved					Suspended particulate				
Trace metals	Cd	Cu	Fe	Ni	Pb	Cd	Cu	Fe	Ni	Pb
Concentration (μg/l)[a]	1	2.5	nd	nd	3	nd	nd	nd	nd	nd
Discharge (ton/year)	1.2	3	-	-	3.6	-	-	-	-	-

nd=no data, data from [a] Chernbumroong, 1997.

Tapi River is 232 km long. This river is draining in to the Western Gulf of Thailand at Bandon Bay Surat-Thani Province. There are many big industry along this river such as fish canning industry. The average yearly flow of the Tapi River is 3.8×10^{9} m^{3} (NESDB, 1994). The annual loads of cadmium, copper, iron, nickel and lead of Tapi River are shown in Table 4-6.

Table 4-6 Concentration and discharge of Cd, Cu, Fe, Ni and Pb in the Tapi River.

	Dissolved					*Suspended particulate*				
Trace metals	Cd	Cu	Fe	Ni	Pb	Cd	Cu	Fe	Ni	Pb
Concentration (μg/l)	0.01[a]	0.8[a]	800[b]	5[a]	0.4[a]	0.03[a]	0.5[a]	1400[b]	5[a]	0.4[a]
Discharge (ton/year)	0.038	3.04	3043	19	1.52	0.114	1.9	5320	19	1.52

data from [a] Hungspreugs *et al.*, 1991. [b]Luengkangwankij, personal communication.

The Mekong River is 4,500 km long, the drainage area is 7.95×10^{5} km^{2}. It is ranked the 10^{th} large river in the world in terms of annual discharge. The Me Kong drains into the South China Sea about 200 km east of the Gulf of Thailand (Cape Camau) at 106.5°E, 9.5°N. The discharge of Mekong River directly into the Gulf of Thailand was estimated to be 260×10^{9} m^{3}/year (Stansfield and Garrett, 1997). The annual load of cadmium, copper, iron, nickel and lead to the Gulf are shown in Table 4-7.

Table 4-7 Concentration and discharge of Cd, Cu, Fe, Ni and Pb in the Mekong River.

	Dissolved					*Suspended particulate*				
Trace metals	Cd	Cu	Fe	Ni	Pb	Cd	Cu	Fe	Ni	Pb
Concentration (μg/l)[a]	0.08	7.00	25.5[c]	6.49	0.20	0.01	1	255[b]	0.6	1.15
Discharge (ton/year)	20.8	1820	6630	1687.4	52	2.6	260	66300	156	299

data from [a] Hungspreugs *et al*, 1998, [b] Cenci *et al*, 1998, [c] Estimated from concentration of suspended particulate Fe.

4.3.2 The South China Sea source

Besides from the river sources, some trace metals in the Gulf of Thailand were received from the bottom water of South China Sea. The annual flux of bottom water from the South China sea was $10{,}500 \times 10^{9}$ m^{3}. The average fluxes of cadmium, copper, iron, nickel and lead to the Gulf are shown in Table 4-8.

Table 4-8 Bottom concentration and flux of Cd, Cu, Fe, Ni and Pb in the South China Sea to the Gulf of Thailand.

Trace metals	*Cd*	*Cu*	*Fe*	*Ni*	*Pb*
Concentration (ug/l)	0.009	0.192	24.69	0.245	0.128
Out flow (ton/year)	95	2016	259,245	2,573	1,344

4.4 Residence time of trace metals in the Gulf of Thailand

Sedimentation was the major cause of removal of trace metals in the Gulf of Thailand. The average sedimentation rate in the Gulf of Thailand was about 0.05 g cm $^{-2}$ year^{-1} (Srisuksawad *et al*, 1997). The bottom area of the Gulf was 800x400 km^2 (Snidvongs, 1998) and the yearly accumulation of sediment in the Gulf was 160x10^6 ton. The yearly sedimentations of cadmium, copper, iron, nickel and lead in the Gulf of Thailand can be estimated (Table 4-9).

Table 4-9 Average concentration of surface sediment and sedimentation of cadmium, copper, iron, nickel and lead in the Gulf of Thailand.

Trace metals	*Cd*	*Cu*	*Fe*	*Ni*	*Pb*
Average concentration (µg/g)	0.26	18.59	1.24x10^4	22.71	18.84
Sedimentation (ton/year)	41.6	2974.4	1536000	3633.6	3014.4

Another output of trace metals from the Gulf of Thailand is the outflow of surface water to the South China sea. The outflow is equal to the amount of water inflow from various sources, the water outflow is $11,084 \times 10^9$ m^3/year. The annual outflow of cadmium, copper, iron, nickel and lead from the Gulf can be estimated and are shown in Table 4-10.

Table 4-10 Average concentration and out flow of cadmium, copper, iron, nickel and lead at surface layer in the Gulf of Thailand.

Trace metals	*Cd*	*Cu*	*Fe*	*Ni*	*Pb*
Concentration (ug/l)	0.008	0.282	5.63	0.247	0.066
Out flow (ton/year)	89	3126	62,403	2,738	732

Trace metals were discharged by river to the Gulf. Some of trace metals, especially in suspended particulate form were precipitated in the estuarine area. The trace metals in dissolved form and some suspended particulate were transported to the off shore area. With the area of the Gulf of Thailand of 320,000 $km.^2$ and average depth of 50 m, the volume of the Gulf water is 160×10^{11} $m.^3$ The total amount of cadmium, copper, iron, nickel and lead in the Gulf water were 160, 4640, 217440, 4640, 2240 tons, respectively. The average concentrations and total amounts of cadmium, copper, iron, nickel and lead in the Gulf are shown in Table 4-11.

Table 4-11 Average concentration and total amount of dissolved and suspended particulate cadmium, copper, iron, nickel, lead in the Gulf of Thailand.

	Dissolved					*Suspended particulate*				
Trace metals	Cd	Cu	Fe	Ni	Pb	Cd	Cu	Fe	Ni	Pb
Average concentration (µg/l)	0.008	0.23	1.37	0.25	0.08	0.002	0.06	12.22	0.04	0.06
Total amount (ton)	128	3680	21920	4000	1280	32	960	195520	640	960

Budget calculation of cadmium, copper, iron, nickel and lead in the Gulf of Thailand (Fig.4-20, Fig.4-21, Fig.4-22, Fig.4-23 and Fig.4-24) showed that major source of these trace metals was river input, except for iron and lead which major source was South China Sea.

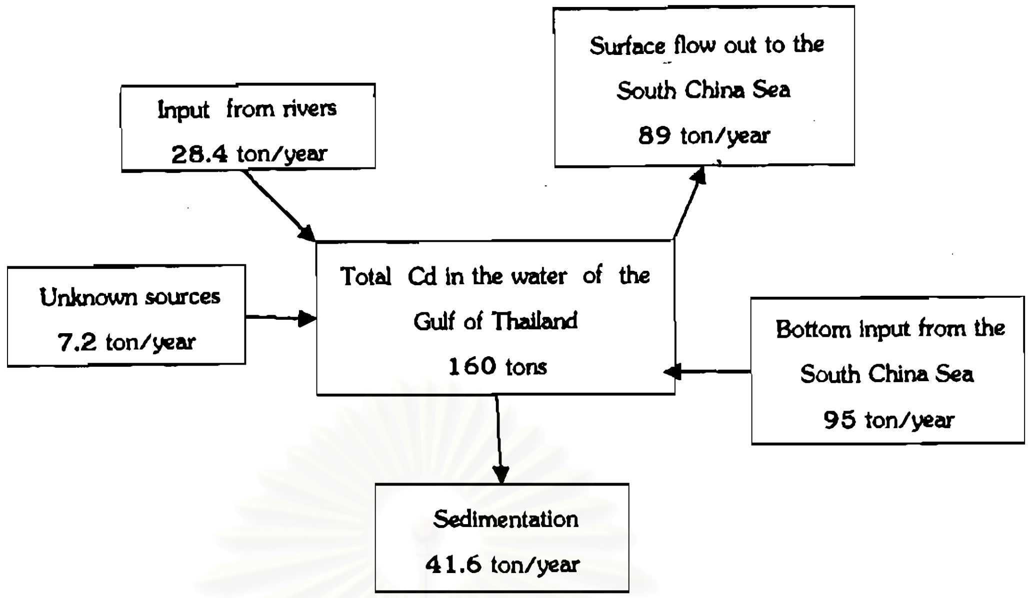

Fig.4-20 Budget of cadmium in the Gulf of Thailand

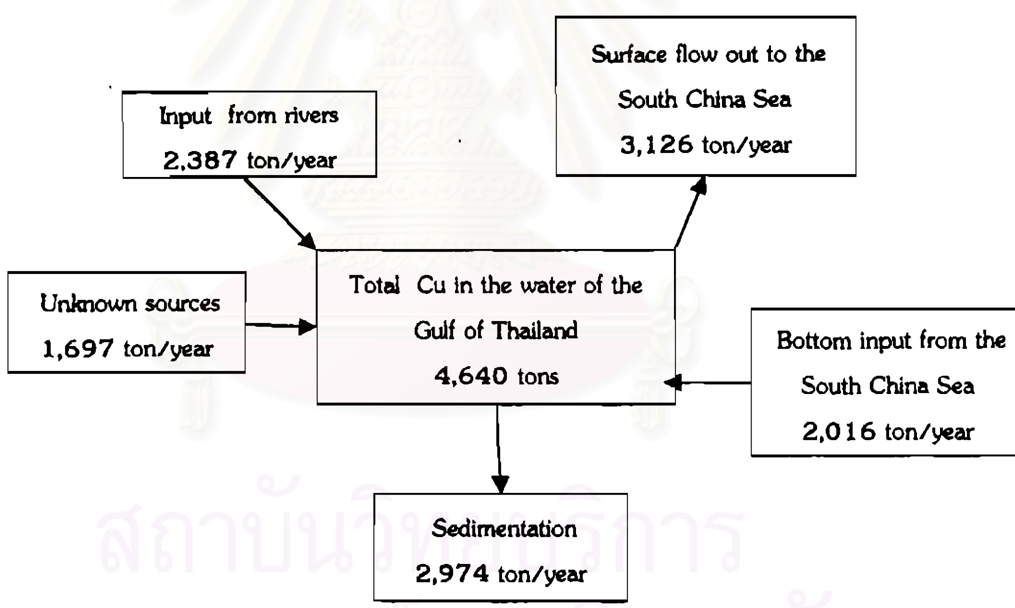

Fig.4-21 Budget of copper in the Gulf of Thailand

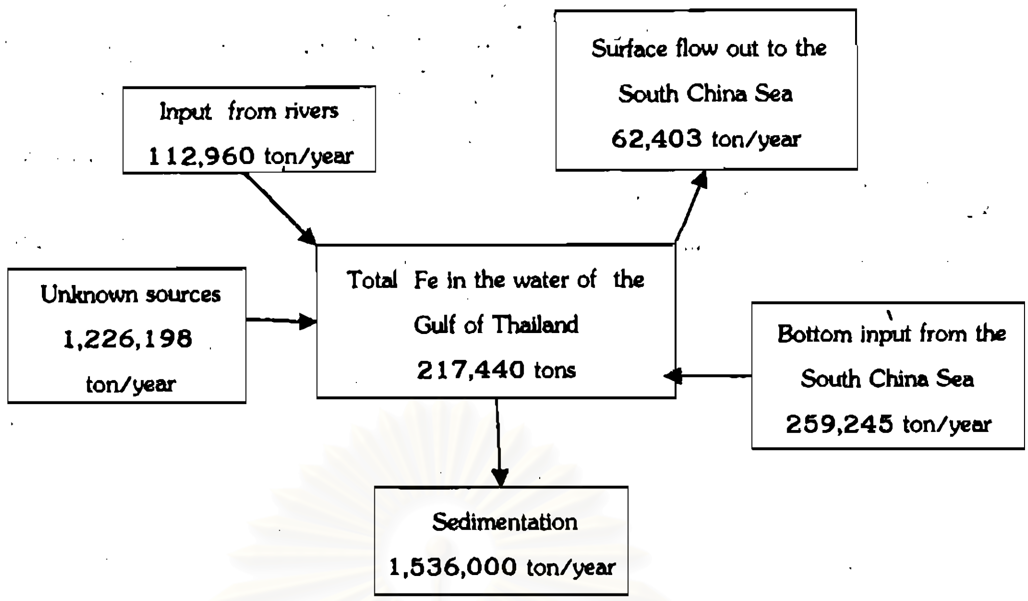

Fig.4-22 Budget of iron in the Gulf of Thailand

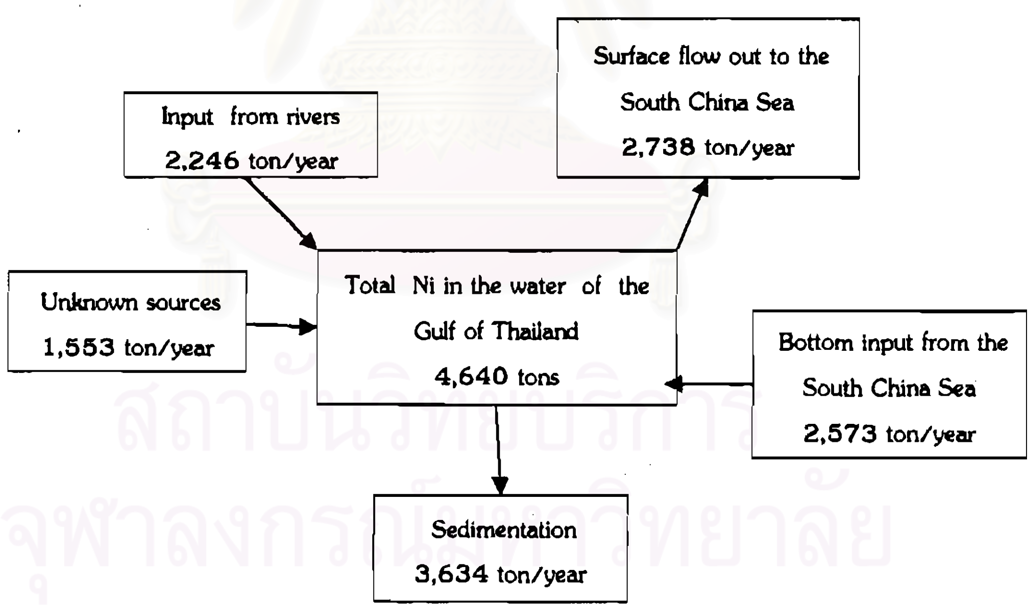

Fig.4-23 Budget of nickel in the Gulf of Thailand

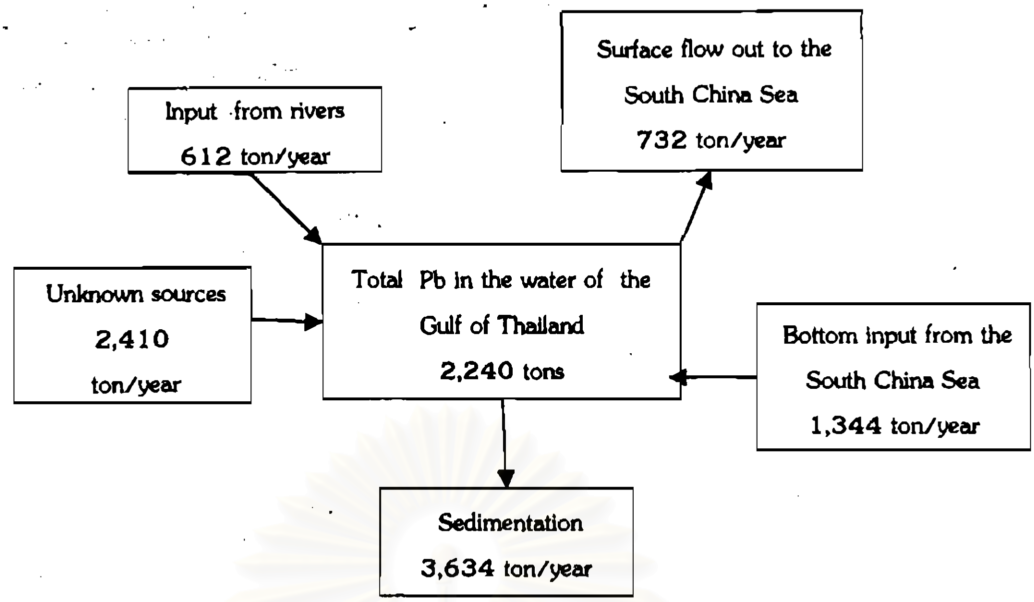

Fig.4-24 Budget of lead in the Gulf of Thailand

The budget calculation of trace metals indicated that there are other unknown sources into the Gulf. The amount of unknown sources of Cd, Cu, Fe, Ni and Pb were 6%, 54%, 77%, 24% and 55%, respectively. These unknown sources may be from other small rivers, streams, canals and also some other point sources which were not taken into account in the calculation. There might also be an under estimating of river input of some trace metals since the concentration of trace metal in river were data from the surface layer only. The unknown sources of iron and lead are higher than cadmium, copper and nickel. The behavior of iron and lead are different from the other three. In river, these two trace metals were mostly present in suspended particulate form. Atmospheric input is another important source, especially for iron and lead. Chester *et al.* (1981) found high concentration of iron and lead in atmospheric particle above Mediterranean, concentration was 400 and 15 ng/m^3 of air, respectively.

From data available, the residence time of Cd, Cu, Fe, Ni and Pb in the Gulf of Thailand can be calculated. The estimate residence time of cadmium, copper, iron, nickel and lead in the Gulf of Thailand, were 1.23, 0.76, 0.14, 0.73 and 0.52 years, respectively. The residence time of iron and lead are low suggesting, that iron and lead were easier adsorbed to suspended matters and settle to the bottom than the other three. Stansfield and Garrett 1997 used a simple model to explain the budget in the Gulf of Thailand. The model suggested that a uniformly distributed tracer would be flushed from the Gulf in 4 to 7 months.

4.5 Aluminium normalization of suspended particulate Cd, Cu, Fe, Ni and Pb

Studying distribution of trace metals has its limitation because we can not separate between natural and anthropogenic sources. If we need to isolate the two sources, we have to define the ratio of those trace metals, Cd, Cu, Fe Ni and Pb against a normalizer, whose concentration is unaffected by human activity. An aluminuim normalization procedure is suggested because aluminium is relatively abundant in terrestrially derived aluminosilicate material and is present in minor amount in biogenic phases and no chemical evidence to suggests that particulate Al is reactive in sea water (Feely *et al.*, 1981).

From a comparison of element/Al ratio, it can be concluded that suspended particulate Cd, Cu, Ni and Pb ratios were high in the surface layer (Fig.4-25, Fig.4-26, Fig.4-28 and Fig.4-29), suggesting that surface water contains more anthropogenic input of those trace metals than bottom layer. The areas of high anthropogenic input are near the Upper Gulf of Thailand where high ratio of Cd/Al, Ni/Al and Pb/Al were found, and off Nakhon Si Thammarat where high ratio of Cd/Al, Cu/Al and Pb/Al were observed.

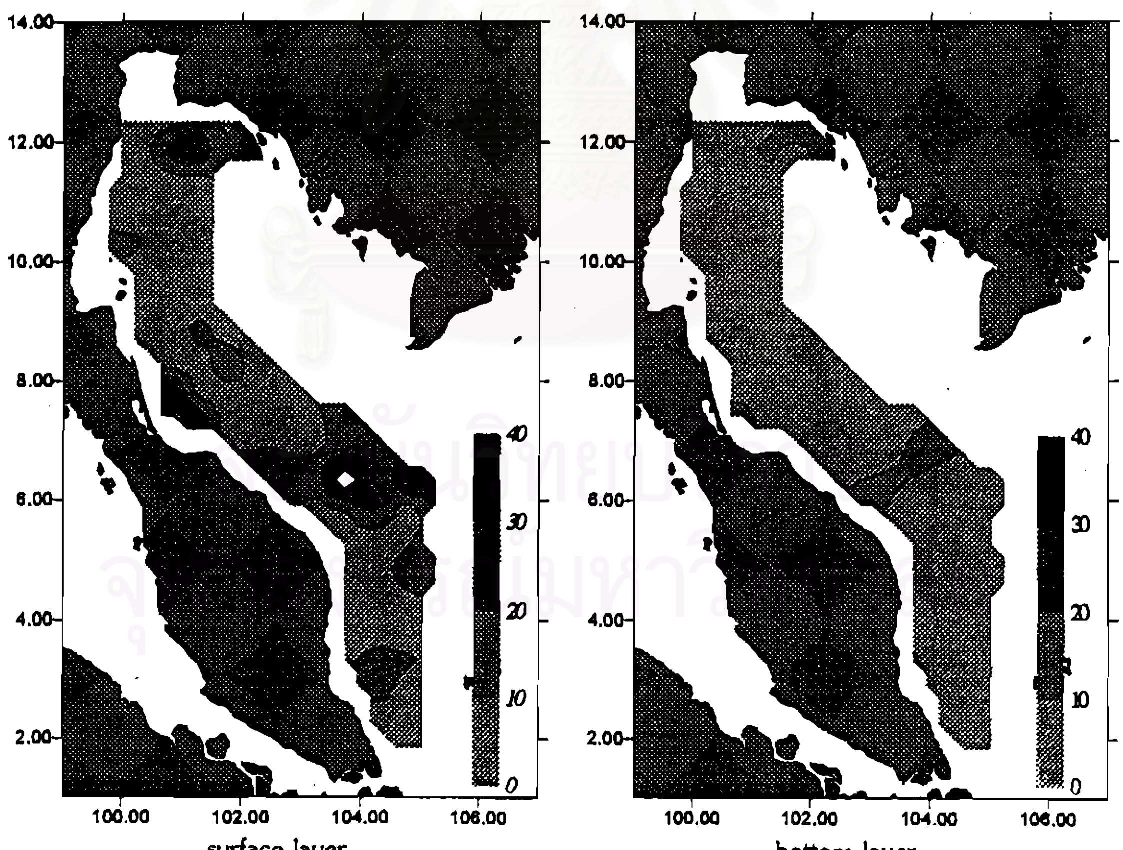

Fig.4- 25 Ratio of suspended particulate Cd/Al in the Gulf of Thailand and East Coast of Malay Peninsula

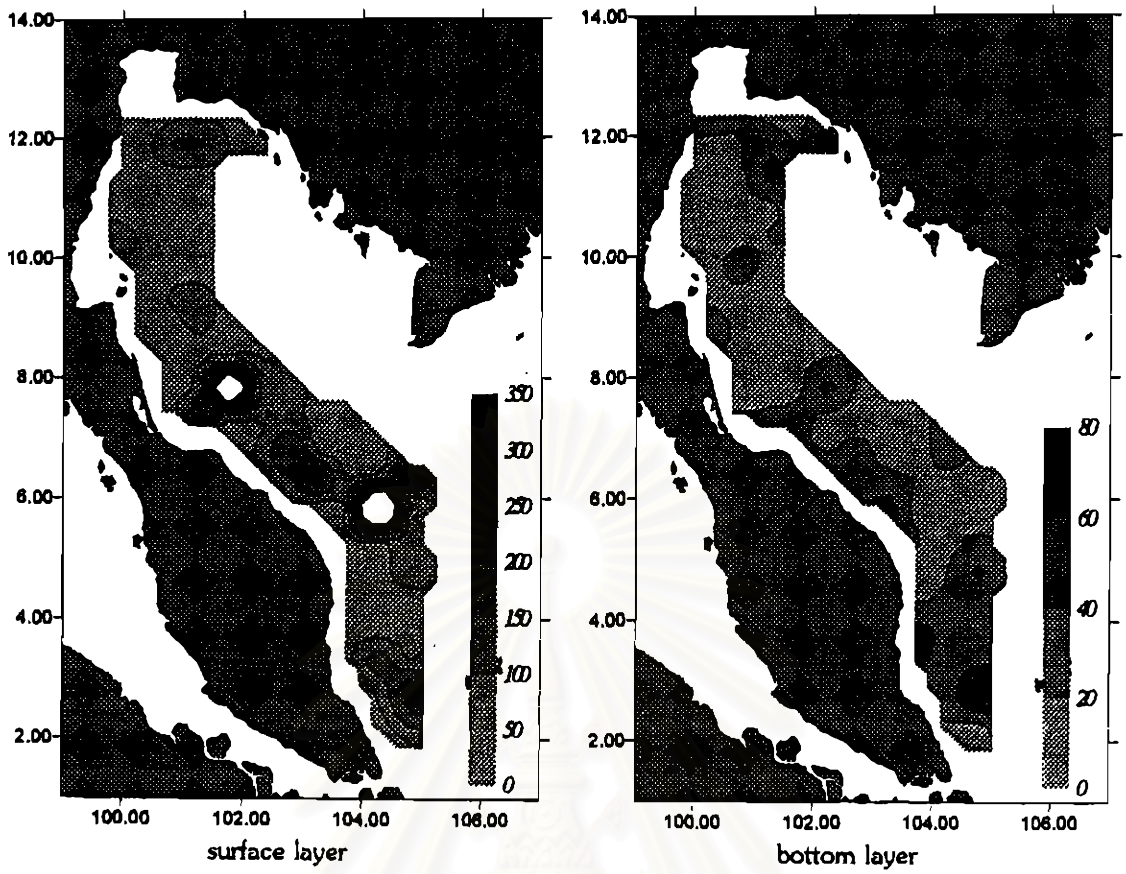

Fig.4- 26 Ratio of suspended particulate Cu/Al in the Gulf of Thailand and East Coast of Malay Peninsula

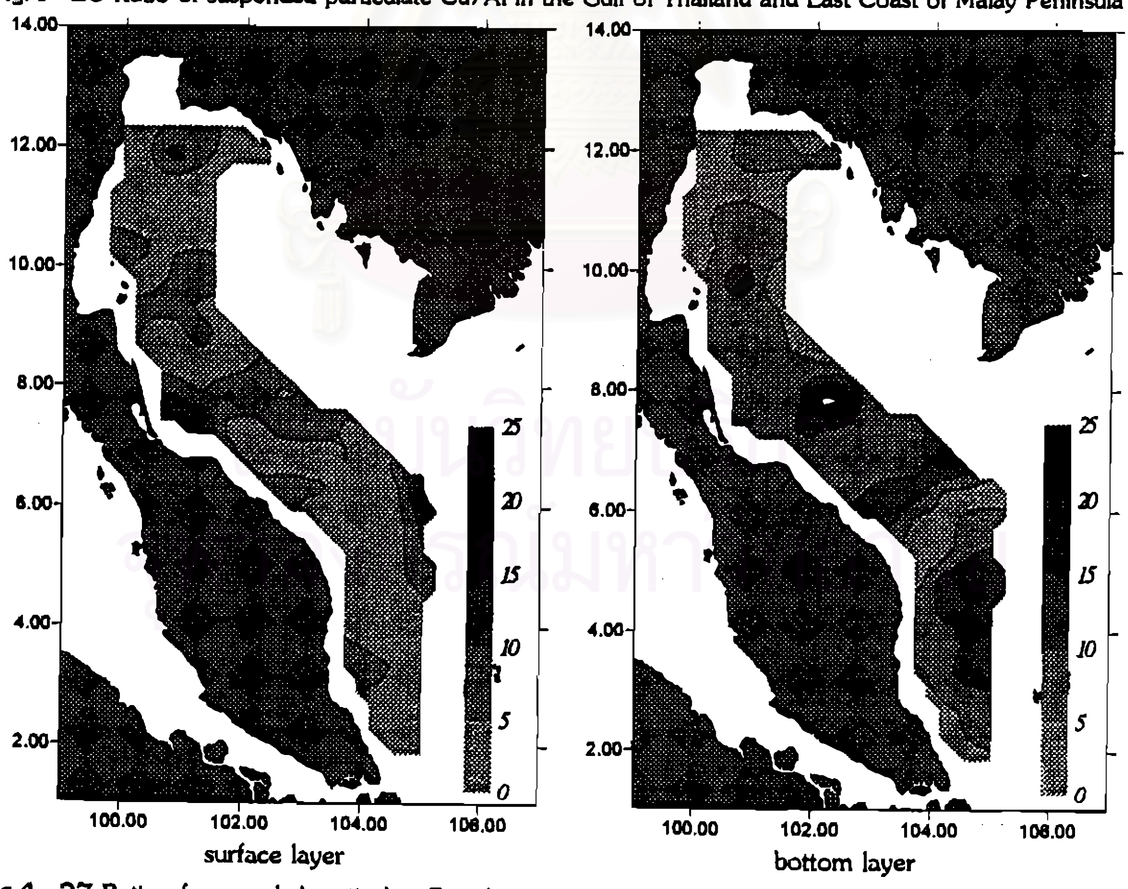

Fig.4- 27 Ratio of suspended particulate Fe/Al in the Gulf of Thailand and East Coast of Malay Peninsula

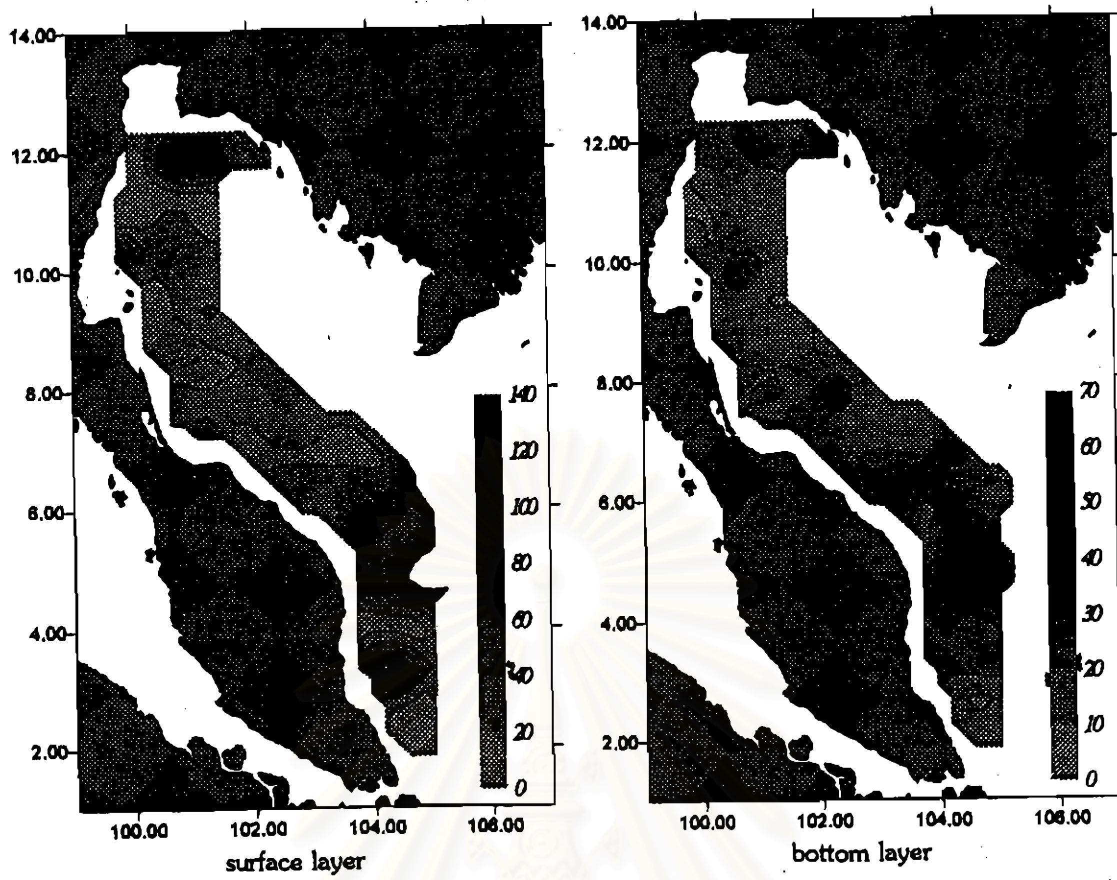

Fig.4- 28 Ratio of suspended particulate Ni/Al in the Gulf of Thailand and East Coast of Malay Peninsula

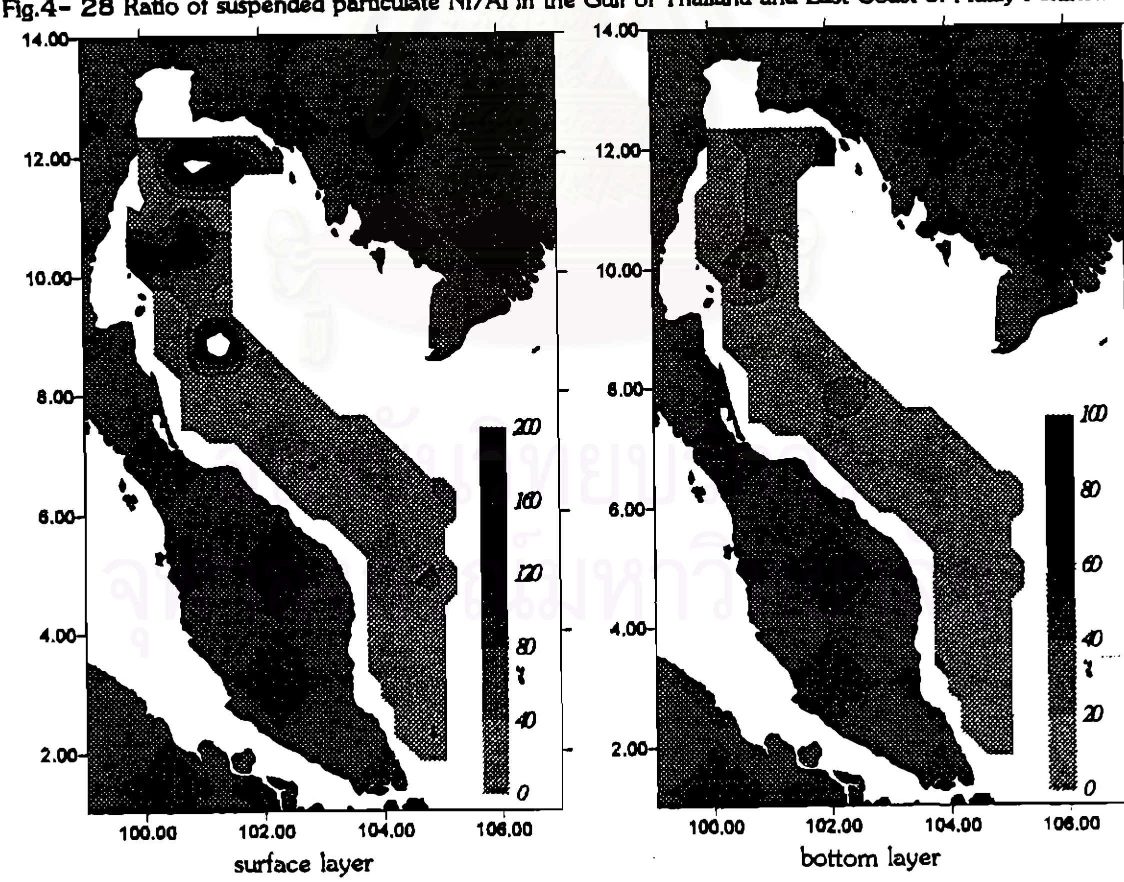

Fig.4- 29 Ratio of suspended particulate Pb/Al in the Gulf of Thailand and East Coast of Malay Peninsula