CHAPTER VI

DISCUSSION

This chapter focuses mainly on four essential topics. The first part deals with analytical results in relation to those of the previous workers. The second part concern about statistical procedure applied for testing assumption of constant variance and normal distribution of elemental data in this study. The third part focuses on the relationship between trace metals and reference elements. The last part is the analytical results of sediments in Mae Klong estuary with discussion on metal pollution in Mae Klong river based on enrichment factor values.

6.1 ANALYTICAL RESULTS

Igneous Rocks

Two samples were collected to represent the igneous rocks. These include one sample of granite and one for basalt. Analytical results of elemental composition of these two igneous rocks are presented in Table 6.1 which show average, standard deviation and range of Al, Fe, Mn, Zn, Cu, and Pb.

Table 6.1 Elemental concentration of igneous rocks in Mae Klong watershed area (ppm).

type	Al	Fe	Mn	Zn	Cu	Pb
granite	82066	31575.76	544.06	62.97	31.94	19.84
basalt	73266	66962.62	1049.5	64.15	42.52	16.24

The average values of each metal in this study are consistent with the previous study of Turekian and Wedepohl (1961) (see also table 2.1).

The result of the granite in this study (in Table 5.5) shows the similar trend as found in the report of high-calcium granitic rocks by Mielk (1976). The result of the basaltic rock is also compared with the report of Mielk, (1976). It is found that there are differences in some elements such as Pb and Fe.

In Mae Klong watershed area, Charusiri (1989) analysed elemental composition of a granitic rock in Pilok, Thong Pha Phum district, Kanchanaburi province situated in the western part of this area. The analytical result is shown in Table 6.2.

Table 6.2 Analytical result of some elemental compositions in a granitic rock at Pilok, Kanchanaburi province (Charusiri, 1989)(ppm).

Rocks	Al	Fe	Mn	Zn	Cu
Granite	75735	14332	380	8.25	3.4

Analytical results of Charusiri (1989) is very similar to those of Mielk (1979) for the low calcium granitic rocks (see also Table 2.1). However, when compared with the results of this study, there is a difference between these two results. This perhaps due to the different in the origin of these two granitic rocks, in geological time and the area of sampling. Granitic rock in this study was collected at Kha Chon Kai, Muang district, Kanchanaburi province. Generally, the elemental composition of a rock depend on the sequence of crystallization (Krauskopf and Bird, 1995). Since conditions of crystallization has been changing all the time, the elemental compositions of the two granitic rocks are different.

For basaltic rocks in Mae Klong watershed area, Yamniyom (1982) analysed elemental composition of basaltic rock in Bo Ploi district, Kanchanaburi province in northern part of this study area. The analytical result is presented in Table 6.3.

Table 6.3 Analytical result of some elemental compositions in a basaltic rock at Bo Ploi district, Kanchanaburi province (Yamniyom, 1982)(ppm).

Rocks	Al	Fe	Mn	Zn	Cu
basalt	72154	23087	309	46.3	10.76

The basaltic rock analysed in this study shows values different from the value of Yamniyom, (1982). It is possible that the basalt collected in this study and Yamniyom's area, though come from the same locality, but may have been collected from different flow layers (i.e., different age of crystalization). Therefore, analytical results obtained from these two show dissimilar values.

Sedimentary Rocks.

Generally, the formation of sedimentary rocks depends on several factors, viz. chemical precipitation, solubility, resistance to weathering,, biological concentration, reactivity with organic compound, ionic substitution in clays or sedimentary minerals and absorption (Rankama and Sahama, 1960 and Mielk, 1979). These factors, in turn, have affected elemental contents in sedimentary rocks.

Sedimentary rocks in Mae Klong watershed area are composed of three main types such as limestone, sandstone and shale. A total of fifty sedimentary rock samples were collected in this area.

Limestones

Twenty-six limestone samples were collected from both Kanchanaburi and Rachaburi provinces.

Analytical results of Al, Fe, Mn, Zn, Cu, and Pb contents in limestones are shown in Table 6.4.

Table 6.4 Average, standard deviation and range of elemental composition of limestones in Mae Klong watershed area (ppm).

Elements	Average	standard deviation	Range Min - Max
Al	5729.15	3954.21	1756 - 17533
Fe	2549.58	2461.30	117.21 - 11771
Mn	388.10	254.13	15.72 - 1008.16
Zn	19.12	8.48	7.03 - 33.19
Cu	6.51	3.68	2.5 - 15.02
Pb	6.59	6.51	2.04 - 19.73

When the average values of this study are compared with results of previous works in Table 2.2, the following are observed :

-Al and Fe values of Clarks (1924), of Turekian and Wedepohl (1961), and of Mielk (1979) show similar trend as those found in this study,

-Mn contents in previous works varies considerably from 385 to 1100 ppm, however, Mn contents in this study have the same level as those found by Clarks (1924),

-Trace elements viz. Zn, Cu, and Pb, are nearly equal with the corresponding average values reported by Bowen, 1979.

Department of Mineral Resources (1986) studied major elemental constituent of limestines in Mae Klong watershed area covering Kanchanaburi and Rachaburi provinces. The results are shown in Table 6.5. Whereby, limestones of Permo-Carboniferous and Quaternary (?) were analyzed. Elemental contents from those periods are clearly different especially in Al and Fe.

The concentration of Al and Fe in Permo-Carboniferous are lower than those in Quaternary. This, perhaps is the result of difference in geologic times, hence giving rise to different composition.

Table 5.5 Major element in limestones of Mae Klong watershed area

Geological Time	Al_2O_3 ppm	FeO ppm	MnO ppm
Permo- Carboniferous			
Rachaburi province			
- Muang district	318	2098	77
- Chom Bung district	-	2176	155
Samut Songkhram province			
- Pak Tho district	688	1632	-
Quaternary (?)			
Kanchanaburi province	11276	8237.8	-
- Tha Muang district	8629	622	-
Rachaburi province			
- Muang district	17418	10491	-
- Chom Bung district	5770	14067	-

source :Department of Mineral Resources, 1986.

Sandstones

Six samples of sandstone were collected from Mae Klong watershed area. Analytical results of elemental concentration of sandstone are grouped in Table 6.6 showing average, standard deviation and range of Al, Fe, Mn, Zn, Cu, and Pb.

Table 6.6 Average, standard deviation and range of elemental composition of sandstones in Mae Klong watershed area (ppm).

Elements	Average	Standard Deviation	Range
Al	17955.3	5611.31	11366 - 25750
Fe	5649.37	4104.65	924.54 - 11518.3
Mn	476.43	418.95	71.18 - 933.19
Zn	23.89	10.30	12.5 - 39.35
Cu	12.35	2.25	10.22 - 15.53
Pb	9.28	3.55	5.55 - 14.83

As illustrated in Table 6.6, when these average values are compared with previous works in Table 2.3. It is found that Al and Fe contents in sandstones of this study are lower than those of the previous works.

Sand-sized particle are enriched in quartz and feldspars which account for the high silica contents of sandstone (Ernst, 1969). Since most sandstones are largely quartzitic and arkosic in composition. It is possible that sandstones in Mae Klong watershed area compose mainly of quartz mineral, Si (Silica) in quartz mineral is capable of diluting Al and Fe content in sandstone (Rankama and Sahama, 1960). The extremely low elemental concentration encountered in quartz and feldspar component is chiefly the result of dilution (Salomons and Forstner, 1984).

Mn contents in this study shows similar value to those of Vinogradov and Ranov (1956) and Bowen (1979).

Trace elements, Zn and Pb, of this study also shows similar level to those of by Bowen (1979) and Horn and Adam (1966) while Cu is lower.

In Mae Klong watershed area, elemental composition of sanstones have not been studied. Thus data in this study cannot be compared to any others.

Shales

Twelve shale samples were collected from Kanchanaburi province and 6 samples from Rachaburi province. Analytical results of Al, Fe, Mn, Zn, Cu, and Pb in shale are shown in Table 6.7.

Table 6.7 Average, standard deviation and range of elemental compositions of shale in Mae Klong watershed area (ppm)

Elements	Average	Standard Deviation	Range Min - Max
Al	67616.8	17056.7	38866 - 89433
Fe	29770.8	14948.4	11269.2 - 45248.8
Mn	682.02	177.92	410.6 -988.09
Zn	43.95	13.62	30.77 - 66.44
Cu	27.25	6.31	15.53 - 39.86
Pb	21.31	5.97	9.12 - 29.07

Average elemental composition in Table 6.7 as compared with those of previous studies in Table 2.4 indicates that concentrations of each element in this study are lower than those of Table 2.4.

Generally, the origin of shale depends on depositional processes of weathered products of igneous and metamorphic rocks (Rankama and Sahama (1960) and Rose (1979)) especially clay minerals. Compared to the average shale values, elemental contents in average igneous rocks (see also Table 5.1) show wider range. The elemental contents of shale in this study (except Pb) are generally lower than those of the igneous rocks. It may be possible that in Mae Klong watershed area, igneous rocks may have been subjected to incomplete weathering, so it have low concentration especially in major elements.

Pb concentration has relatively high values in shale. Therefore, it may be assumed that during the formation of shale, Pb may mainly adsorb in structure of shale (Mielk, 1979).

In Mae Klong watershed area, again no body has ever systematically studied elemental compositions of shale. Therefore, comparisoncan not be made.

Metamorphic Rocks

Four metamorphic rock samples were collected from this study area. Analytical results of elemental composition of metamorphic rocks are summarized in Table 6.8.

Table 6.8 Average, standard deviation and range of elemental composition of metamorphic rocks in Mae Klong watershed area (ppm).

Elements	Mean	standard deviation	Range
Al	58973	24711.8	31053 - 81333
Fe	24880	12068.9	12332.4 - 40487.3
Mn	494.01	137.21	358.65 - 683.85
Zn	40.40	15.00	24.73 - 54.88
Cu	24.51	4.76	20.5 - 30.02
Pb	16.72	6.61	8.95 - 23.87

Again comparison with previous works cannot be made. Since elemental compositions of metamorphic rocks from Table 6.8 are those granitic shale. While metamorphic rocks in this study are regarded to be originated from quartz-rich sandstones and pelitic sediments. Metamorphic of the latter type is distinguished by having banded quartzite and quartz-feldspargneiss, respectively. And their compositions may be silica-enriched.

Thus, it is possible that elemental contents in metamorphic rocks in Mae Klong watershed area may be diluted by Si.

In Mae Klong watershed area, elemental composition of metamorphic rocks has never been done prior to this study.

Soils

Six soil samples were collected from Mae Klong watershed area. Analytical results of Al, Fe, Mn, Zn, Cu, and Pb in soils are summarized in Table 6.9.

Table 6.9 Average, standard deviation and range of elemental composition of soils in Mae Klong watershed area (ppm)

Elements	Average	Standard Deviation	Range
Al	74735.33	12283.55	58413 - 88536
Fe	34177.98	8899.28	19866.96 - 44525.52
Mn	1089.79	43.68	1027.18 - 1145.04
Zn	54.94	4.86	50.10 - 63.62
Cu	29.99	8.16	20.21 - 40.81
Pb	23.05	2.33	20.49 - 26.30

When average elemental composition of soils in Table 6.7 are compared with those of previous studies in Table 2.6. It is found that average values of major elements have the similar level to those reported by Martin and Whitefield (1983). However, the average values of Cu and Pb are lower than those of Martin and Whitefield (1983) while it showing the similar level as found by Ure and Berrow (1982), instead.

Average value of Zn of this study is lower than those reported in table 2.6.

In general, parent materials contribute the raw materials to soil and is, therefore, controlling the nature of the resultant soil (Rose, 1979). Thus, elemental composition of soil in this study should depend largely on parent material in Mae klong watershed area as well. However, it is interesting to note that elemental concentration of rocks in Mae Klong watershed are lower than of soils.

Department of Land Development, (1977) studied the soil series in Mae Klong watershed area and found that Kanchanaburi has 171 soil series, Rachaburi has 79 soil series, and Samutsongkhram has 9 soil series. However, the study on elemental composition has not been carried out so far for all soil series. In addition, Department of Land Development focused their effort mainly on elements which help fertilizing plants such as Ca and Mg. Thus, it can not be of any use in this study.

Average Crust

Elemental composition of crust (average for rocks and soils) in Mae Klong watershed area are compared with Average world elemental composition of crust (see also in table 6.10). It seems that average elemental composition of each elements in this study are lower than in the works of Taylor (1964) and Bowen (1979). Since limestone is the dominant rock exposed in Mae Klong watershed area and limestone is always low in the metal selected for this study. Therefore, when comparing the result of this study with those of other rocks, the average concentrations of this study is lower for every elements.

Table 6.10 Average world elemental composition of crust comparing with average crust in Mae Klong watershed area (ppm).

Average crust	Al	Fe	Mn	Zn	Cu	Pb
Taylor (1964)	82300	56300	950	70	55	12.5
Bowen (1979)	82000	41000	950	75	50	14
Average crust in Mae Klong watershed area.	37313	16761	569	33	17	13

6.2 STATISTICAL PROCEDURE FOR TESTING ASSUMPTION.

Schropp and Windom (1988) suggest that the data under scrutiny for this type of study should have constant variance and be normally distributed. These two assumptions are tested by parametric statistical analyses.

1. The assumption of constant variance.

To examine this assumption, plots of mean values versus standard deviations are generated for each metal. Examples of these plots which use the data of zinc and iron are shown in Figure 6.1. Plot in figure 6.1,shows that standard deviations are not proportional to mean values, indicating that the assumption of constant variance is satisfied. Many geological data very obviously do not follow a normal distribution. But if the data are converted to logarithmic form, it is found that their distributions become nearly normal distributed, such data are said to be "log-normal distribution" (Davis,1986). Therefore, data, mean values, and standard deviations, are transformed to log 10 values. After log 10 transformation, the proportion between mean values and standard deviations is aggregated (in Figure 6.2). On the whole, the testing apparently indicates that the untransformation confirms the assumption of constant variance more satisfying than log 10 transformation.

2. The assumption of normal distribution.

A more effective way to check the assumption of normality is to construct a special graph called a normal-scores plot of sample data. In general, normal-score refers to an idealized sample from standard normal distribution-namely, the Z-values that divide the standard normal distribution in to equal-probability intervals (Johnson and Bhattacharryya,

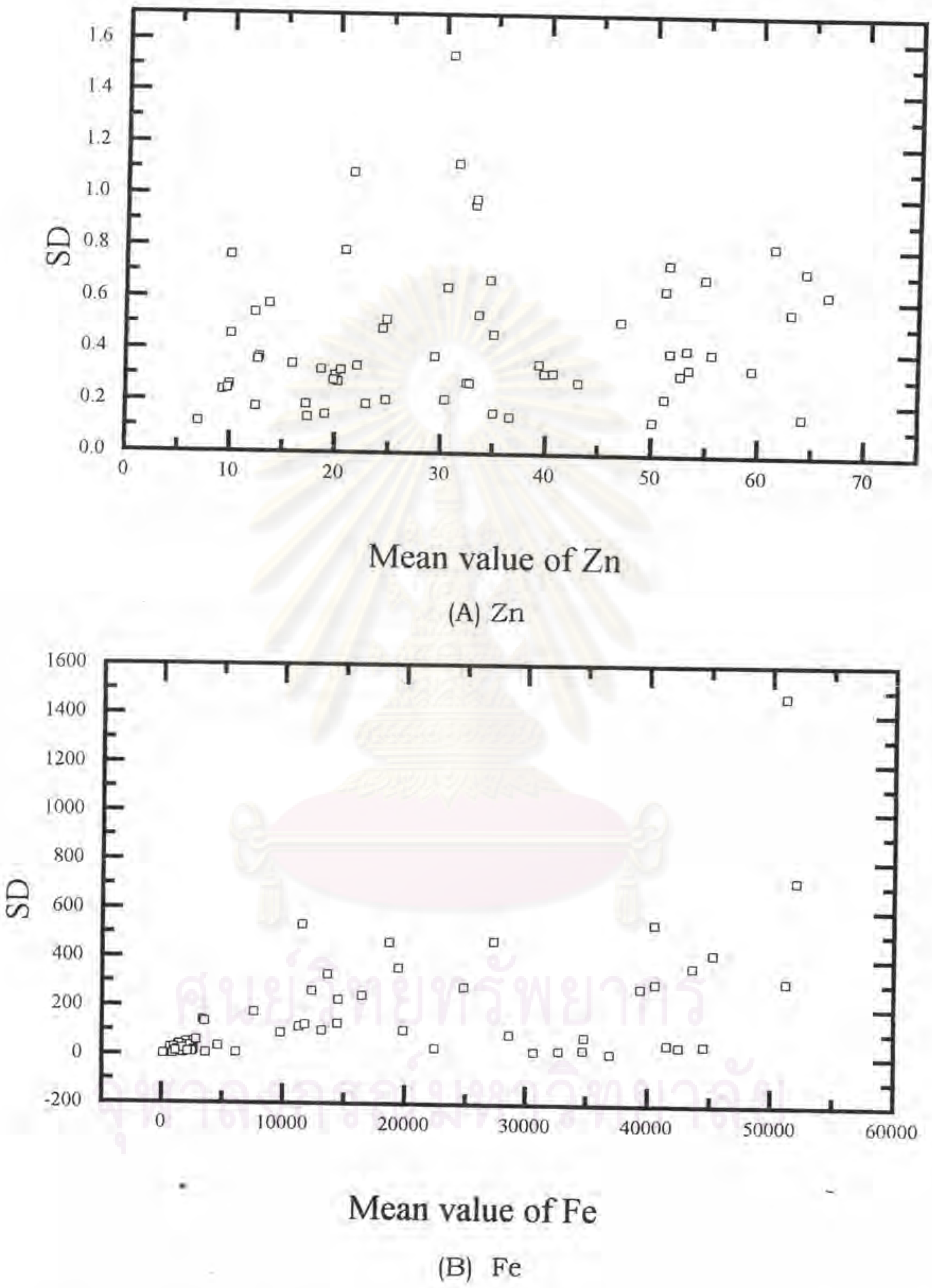
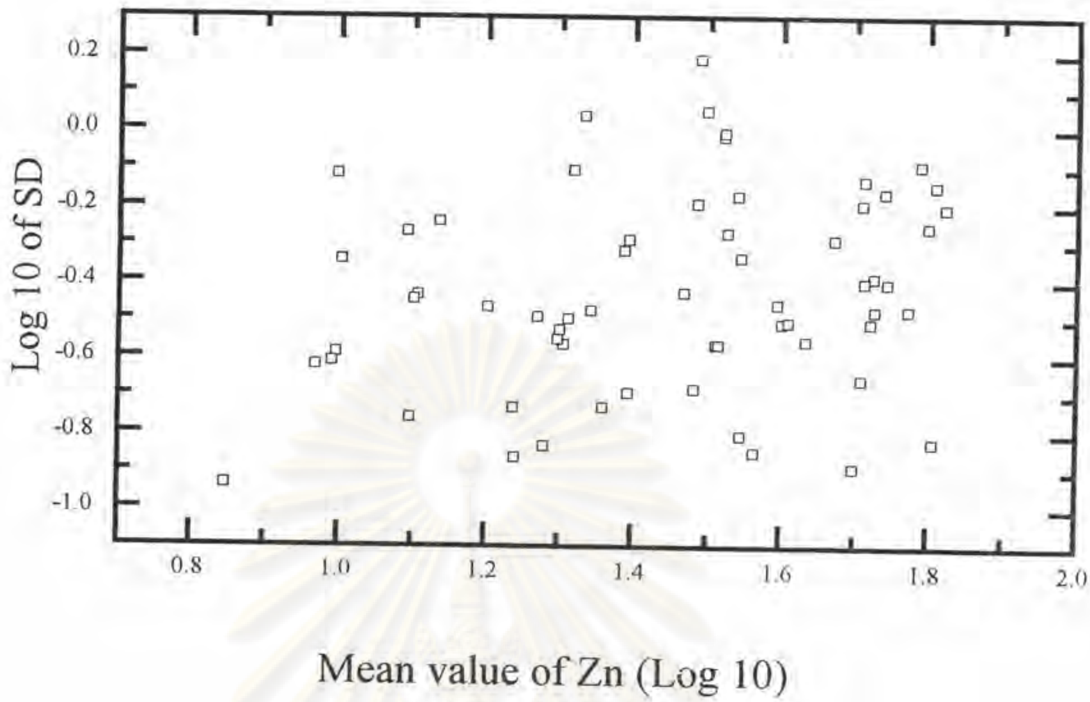
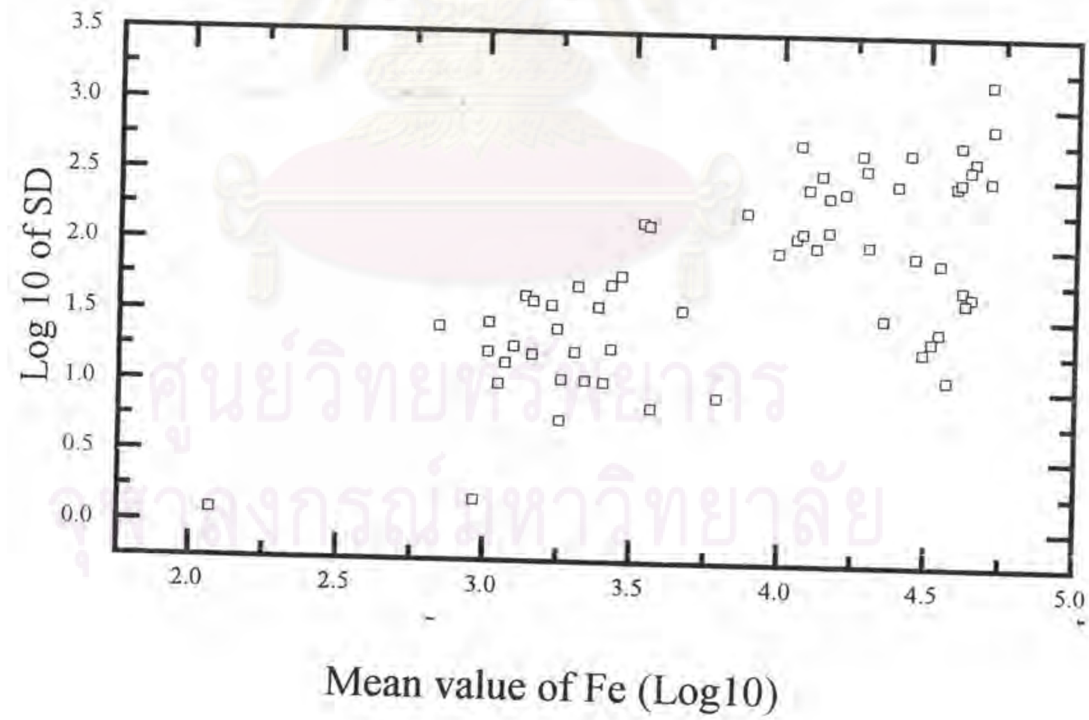


Figure 6.1 Mean values versus standard deviations for untransformed data .



(A) Zn



(B) Fe

Figure 6.2 Mean values versus standard deviations for log 10-transformed data.

1985). To examine this assumption, normal-scores plots are created by calculating normal scores and ploting them against original data.
The normal-scores plot of original data and log 10 transformation are shown in Figures 6.3 and 6.4. Figure 6.3, as an example, illustrates scatter plots of normal scale against original data of Zn (A) and compares with scatter plots with transformed data of zinc (B). Figure 6.4 illustrates scatter plots of Fe.

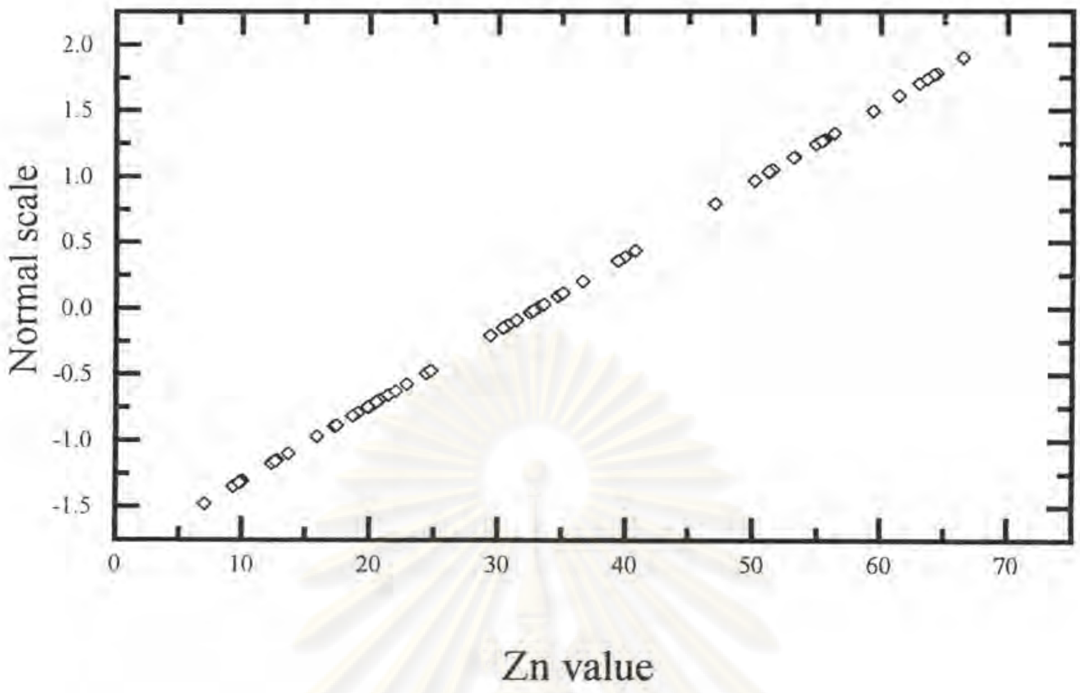
The relative linear plots for original data of Zn and Fe concentrations (Figure 6.3 and 6.4) indicate that the data are normally distributed, likewise for the relatively linear in plot for log 10 transformation of Zn and Fe . Thus, it can be said that our data are normal distributed (Wilkinson, 1986). Hence, it is not necessary to transform data by log 10.

The normal distributions of transformed data are confirmed using the probability plot correlation coefficient test (Filliben , 1975). This test viz. the null hypothesis (H_0) of normality is examined relative to the alternative hypothesis (H_A) of non-normality. A significant high correlation coefficient between normal scores and original data of zinc and iron results into rejection of H_0 (accept that the data are normally distributed). Results of this testing are shown in Table 6.11.

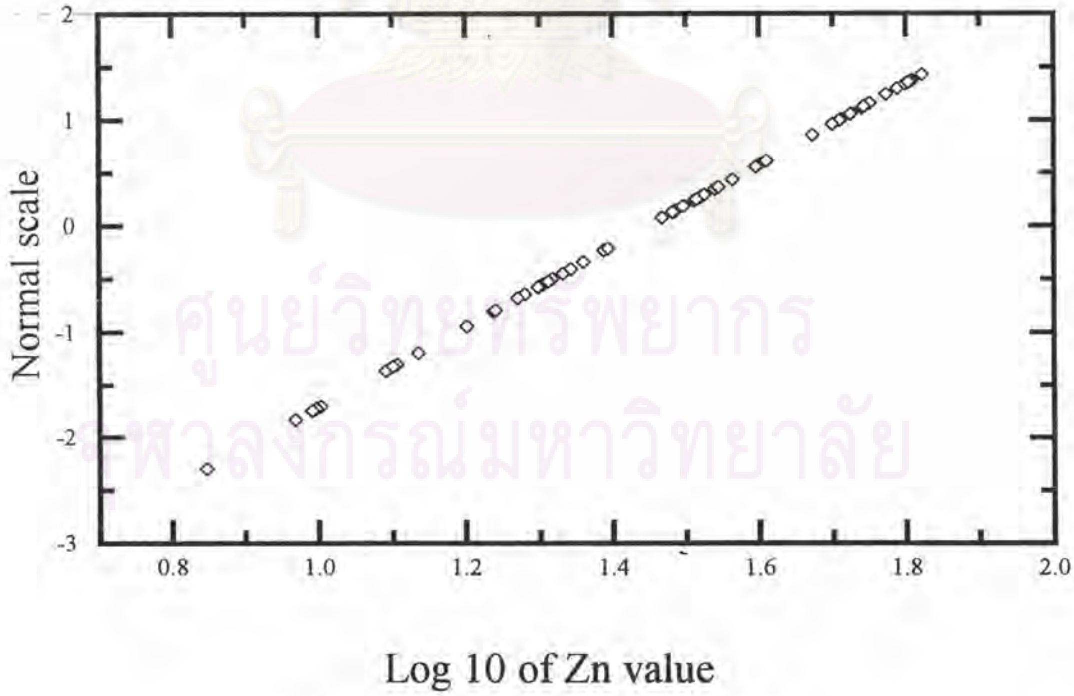
Table 6.11 Results of probability plot correlation coefficient tests for normality data of zinc and iron.

Mean vs standard deviation	correlation coefficient of untransformation	correlation coefficient of log 10 transformation
Fe	1	1
Zn	1	1

In Table 6.11, correlation coefficients of untransformed data and log 10 transformed data are both fitted to normal distribution.

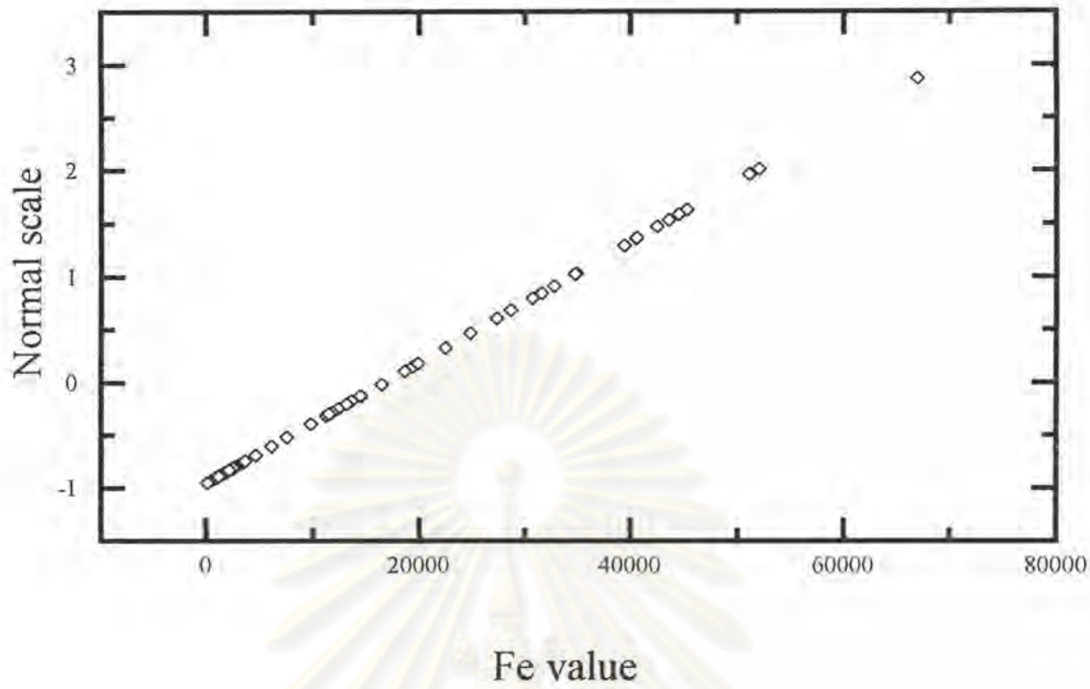


(A) Original data.

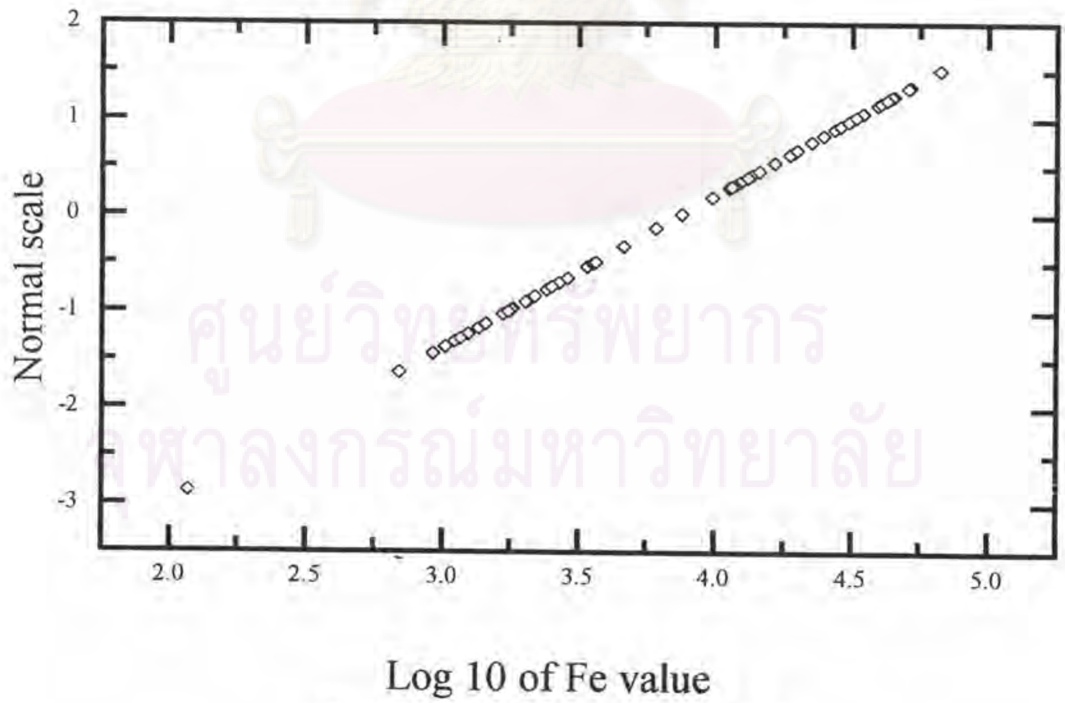


(B) log 10 - transformed data.

Figure 6.3 Normal score vs. values of Zn



(A) Original data.



(B) log 10 - transformed data.

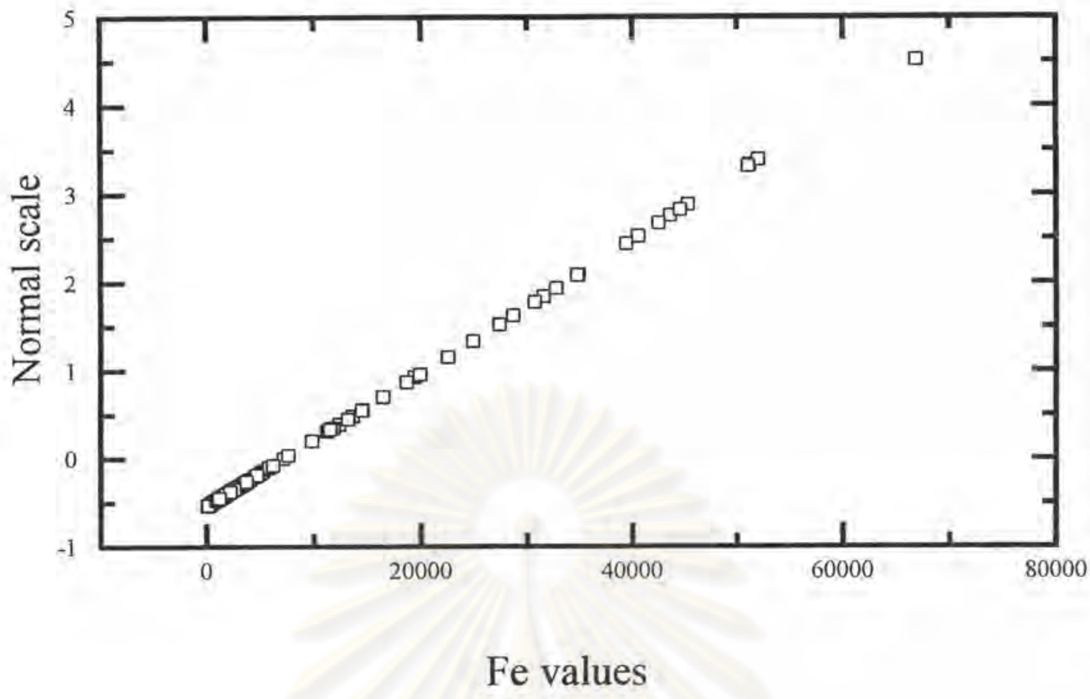
Figure 6.4 Normal score vs. values of Fe

Confirmation of normal distribution

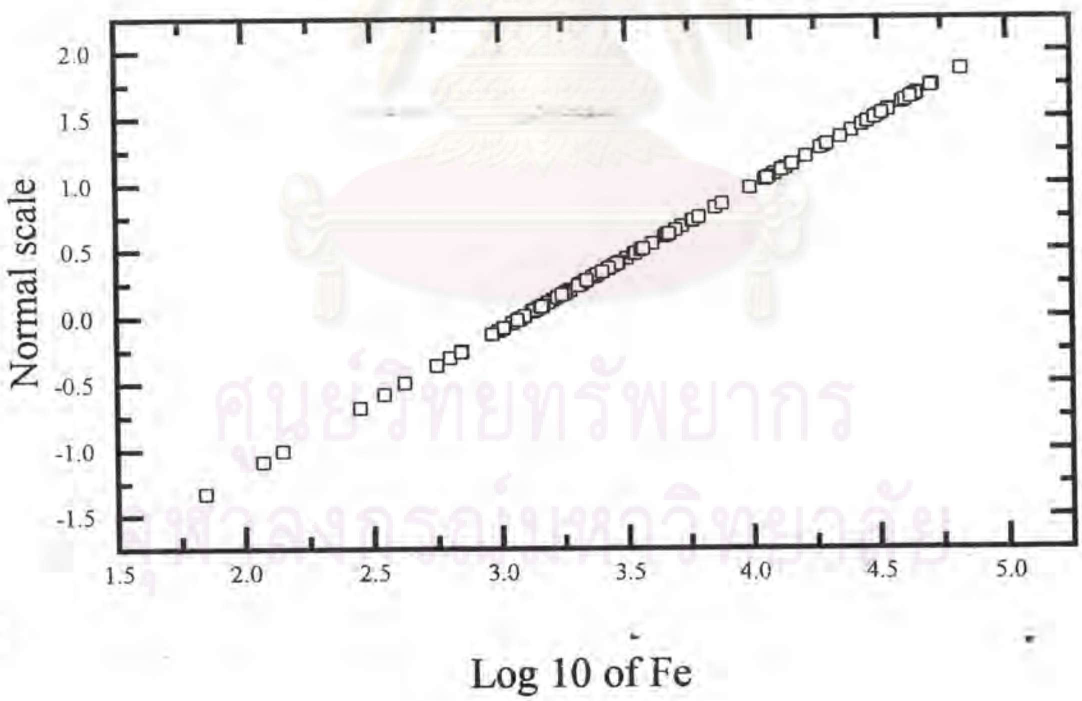
To ensure that the data of geological materials in Mae Klong watershed area is normally distributed. It has to be confirmed by making normal-score plots of Fe original data which add data of limestone in Rachaburi province studied by Department of Mineral Resources in 1993 (Data are shown in appendix B and plots are shown in Figure 6.5).

The relatively linear plot for original data of Fe concentration (Figure 6.5) indicates that the data are normally distributed, likewise the relatively linearity in plot for log 10 transformation of Fe .

From several statistical testing it can be concluded that the original data have constant variance and are normally distributed. In the following section, relationship of metals/reference elements is discussed.



(A)



(B)

Figure 6.5 Normal score vs. values of Fe together with the data of limestone in Ratchaburi province

(A) Original data

(B) Log 10-transformed data

6.3 METALS/REFERENCE ELEMENTS RELATIONSHIP

Aluminium, iron, and manganese are selected as reference elements which have been used to normalize metal data as an aid to interpret analytical results of sediments in this research.

After testing that the data meet fairly well with the assumption of normality and constant variance, metal/reference element ratio is examined. The data are then analyzed using the regression results and 95 % confidence limits which are calculated according to Sakal and Rohlf (1969). Least square regression is applied using reference elements as the independent variable and some trace metals as dependent variables. Results of the regressions are pressent in Figure C.1-Figure C.24.

The strength of the relationships varies considerably among metals which is indicated by the magnitude of the correlation coefficient (r) and coefficient of determination (r^2) (see also Table 6.12-6.13).

So far, it has been demonstrated that statistically significant relationships exist between three of reference elements and three of trace metals examined in geological materials of Mae Klong watershed area.

Table 6.12 and 6.13 depicts the correlation coefficient computed between the ranks of the original values of regression model residuals and the ranks of the reference elements concentrations. Seven groups of relationship are as follows.

Table 6.12 Matrix correlation among elements for the Mae Klong watershed area.

	Al	Fe	Mn	Zn	Cu	Pb
Al	1	0.8486	0.3883	0.8047	0.8796	0.8135
Fe	-	1	0.3762	0.8118	0.8022	0.6939
Mn	-	-	1	0.3683	0.4295	0.3776
Zn	-	-	-	1	0.7269	0.7736
Cu	-	-	-	-	1	0.7579
Pb	-	-	-	-	-	1

Table 6.13 Results of regression analyses using reference elements (Al, Fe, and Mn) as independent variables and other metals as dependent variables in Mae Klong watershed area.

Relationship	r	r^2	β_0	β_1
Fe/Al	0.9212	0.8486	8247.50	1.73
Mn/Al	0.6231	0.3883	301.47	64.94
Zn/Al	0.8971	0.8047	-18233	1680
Cu/Al	0.9379	0.8796	-8828.3	2632.57
Pb/Al	0.9020	0.8135	-10866	3505.37
Mn/Fe	0.6134	0.3762	-2593.6	33.96
Zn/Fe	0.9010	0.8118	-12876	896.37
Cu/Fe	0.8957	0.8022	-6647.3	1335.54
Pb/Fe	0.8330	0.6939	-6876.7	1719.81
Zn/Mn	0.6553	0.4295	180.55	11.77
Cu/Mn	0.6145	0.3776	279.83	16.55
Pb/Mn	0.6069	0.3683	258.85	22.63
Zn/Al+Fe	0.9149	0.8371	-31109	2576.37
Cu/Al+Fe	0.9402	0.8829	-15476	3968.11
Pb/Al+Fe	0.8941	0.7995	-17742	5225.18
Zn/Al+Mn	0.8980	0.8063	-180.53	1691.78
Cu/Al+Mn	0.9381	0.8801	-8548.50	2649.12
Pb/Al+Mn	0.9024	0.8143	-10607	3528
Zn/Fe+Mn	0.9027	0.8149	-12695	908.146
Cu/Fe+Mn	0.8968	0.8042	-6367.50	1352.09
Pb/Fe+Mn	0.8347	0.6966	-6617.80	1742.45
Zn/Al+Fe+Mn	0.9154	0.8379	-30929	2588.15
Cu/Al+Fe+Mn	0.9403	0.8842	-15196	3984.66
Pb/Al+Fe+Mn	0.8944	0.8000	-17483	5247.81

r : correlation coefficient. r^2 : coefficient of determination.

β_0 : Y-intercept of regression line. β_1 : Slope of regression line.

Table 6.14 Ratio of some metals/Al of geological materials in Mae Klong watershed area in comparison with those calculated from average elemental composition of earth's crust (Turekian and Wedepohl, 1961).(Ratio * 1000)

Rock types	Fe/Al	Mn/Al	Zn/Al	Cu/Al	Pb/Al
Igneous					
A	615	11.69	0.86	0.68	0.16
B	634.37	10.25	0.81	0.47	0.23
Limestone					
A	904.76	261.90	4.76	0.95	2.14
B	445.01	67.74	3.33	1.13	1.15
Sandstone					
A	392	4	0.64	0.4	0.28
B	314.63	26.54	1.33	0.68	0.51
Shale					
A	590	10.62	1.18	0.56	0.25
B	440.28	10.08	0.65	0.4	0.31
Metamorphic					
A	360.97	6.58	0.73	0.36	0.18
B	421.88	8.37	0.68	0.41	0.28
Average crust					
A	515.22	12.99	0.95	0.52	0.23
C	500	11.58	0.91	0.61	0.17
B	449.5	15.27	0.89	0.47	0.36

A : Turekian and Wedepohl (1961).

B : Analytical results of elemental composition in Mae Klong watershed area.

C : Bowen (1979).

Table 6.15 Ratio of some metals/Fe of geological materials in Mae Klong watershed area in comparison with those calculated from average elemental composition of earth's crust (Turekian and Wedepohl, 1961).(Ratio * 1000)

Rock types	Mn/Fe	Zn/Fe	Cu/Fe	Pb/Fe
igneous				
A	19	1.4	1.1	0.26
B	16.17	1.27	0.75	0.36
Limestone				
A	289.47	5.26	1.05	2.36
B	152.22	7.49	2.55	2.58
Sandstone				
A	10.20	1.63	1.02	0.71
B	84.83	4.22	2.18	1.64
Shale				
A	18	2.01	0.95	0.42
B	22.9	1.47	0.91	0.71
Metamorphic				
A	18.24	2.02	1.01	0.5
B	19.85	1.62	0.98	0.67
Average crust				
A	25.21	1.85	1.02	0.45
C	23.17	1.82	1.21	0.34
B	34	1.97	1.04	0.81

A : Turekian and Wedepohl (1961).

B : Analytical results of elemental composition in Mae Klong watershed area.

C : Bowen (1979).

Table 6.16 Ratio of some metals/Mn of geological materials in Mae Klong watershed area in comparison with those calculated from average elemental composition of earth's crust (Turekian and Wedepohl, 1961).(Ratio * 1000)

Rock types	Zn/Mn	Cu/Mn	Pb/Mn
igneous			
A	73.68	57.89	13.68
B	79	46.43	23
Limestone			
A	18.18	3.63	8.18
B	49.26	16.77	16.98
Sandstone			
A	160	100	70
B	50.14	25.92	19.47
Shale			
A	111.76	52.94	23.52
B	64.4	39.95	31.24
Metamorphic			
A	111.11	55.55	27.77
B	81.77	49.61	33.84
Average crust			
A	73.72	40.6	18.07
C	78.9	52.63	14.73
B	58.10	30.74	24.10

A : Turekian and Wedepohl (1961).

B : Analytical results elemental composition of Mae Klong watershed area.

C : Bowen (1979).

1. Using Al as reference elements.

Figure C.1-C.5 in appendix C, show the scatter plots of Fe vs. Al, Mn vs. Al, Zn vs. Al, Cu vs. Al, and Pb vs. Al, with the resultant regression line at 95% confidence limits.

Fe is shown herein to have a very strong positive correlation with Al, with an r^2 (coefficient of determination) value of 0.8486. Previously, Hirst (1962) cited by Calvert (1976) studied the relationship between Fe_2O_3 and Al_2O_3 in minerals, such as limonite, glauconite and illite. He assumes that in sedimentary rocks free from these minerals, the Fe_2O_3 / Al_2O_3 ratio is resonably constant which shows that Fe is held in the structural positions within the aluminosilicate.

When the ratio of Fe / Al from this study is compared with those of individual rock types reported by Turekian and Wedepohl (1961) (Table 6.14). Similarity is found with ratios of every rock types except limestones. Among each rock types, limestones have the highest ratio value because Al concentrations in limestones are frequently lower than those in the other rocks (Turekian and Wedepohl, 1961).

However, comparing the value from this study with the average crust of Bowen (1967) and Turekian and Wedepohl (1961), it is found that all values are at the same order of magnitude.

The relationship of Mn and Al indicates that Mn does not covary with Al. Regression analyses herein yield an r^2 value of only 0.3883. Generally, maganese forms a number of independent minerals in igneous rocks, but usually they are geochemical rare and insignificant (Rankama and Sahama, 1960). The scatter plots (Fig. C.2) may indicate association of Mn in independent minerals in our samples, thus making the Mn/Al ratio values to vary widely in various types of rocks.

This trend is most obvious in limestone and sandstone where the ratios are the most different. However, in other types of rock the ratios are at the same level as those averages of Turekian and Wedepohl (1961) and the same level as average crust.

For trace elements, very strong positive covariance is also indicated for Cu and Al, with an r^2 value of 0.8796. Concentration of Zn and Pb seem to correlate well with those of Al, as reflected by r^2 values of 0.8047 and 0.8135 , respectively.

In rocks, trace metals can be associated with mineral structure. For example in sedimentary rock, Cu is incorporated into clay minerals (Mielke, 1979). Zn can be readily adsorbed by clay minerals and also accumulates in sediments containing organic material prior to shale (Rankama and Sahama (1960); Wedephol (1979), Mielke (1979)). Pb is concentrated in resistates as well as clay minerals and can enter sedimentary carbonate rocks, where it may occupy spaces of Ca and Sr (Mielke,1979). For prior passages, it indicates that chemical structures of clay minerals in composition of sedimentary rocks are quite essential.

Sedimentary rocks originate from weathering of igneous and metamorphic rocks and even previous sedimentary rocks. During weathering, new minerals are formed which are more stable under the new condition. It was found that the univalent K^+, Na^+, and bivalent cations as Ca^{2+}, Mg^{2+}, Zn^{2+}, Cu^{2+} and Pb^{2+} readily go into solution, but the behaviour of aluminum and silicon has been less well understood. Older hypothesis assumed hydrolysis of aluminosilicates with the formation of colloidal silicic acid and aluminum hydroxide, which later reacted to give clay minerals (Mason,1952). The clay minerals are abundant in the most weathered materials, and vary widely in chemical composition and ion-exchange capacity. The crystal structures of all common clay mineral are composed of Al^{3+} , Si^{4+}, and Mg^{2+} or Fe^{2+} ion and surrounded by O^{2-} or OH^- (Rose *et al.*, 1981). With this process, some cations may exchange with other cations including trace elements or become associated in structure of alumino-silicates in clay minerals. Its constituents are then transported and redeposited as sediments. In sediments, the correlation of metals and aluminium is readily studied and found that some metals are correlated with Al.

In igneous and metamorphic rocks, the distribution of elements can be explained fairly satisfactorily by assuming the crystallization of an orderly sequence of minerals from melt, usually leading to differentiation (Krauskopf,1967). It is indicated that elemental contents in those rocks types depend primarily on environmental conditions espicially temperature and humidity. Therefore, correlation of metal and Al may be a tedious task because condition of crystallizations needs to be well studied.

For all these reasons, it is obvious that trying to explain why each types of rocks acquired its existing elemental composition is nearly impossible. However, it can be, at least, concluded that these trace elements show the highest ratio in limestones in comparision with other rock types and average crust because of the lowest content of Al in limestones. For other rock types trace metals/Al ratios are all comparable and are at the same level as average crust values.

2. Using Fe as reference elements.

Figure C.6-C.9 in appendix C show the scatter plots of Mn vs. Fe, Zn vs. Fe, Cu vs. Fe, and Pb vs. Fe with the resultant regression line at 95% confidence limits.

The testing of relationship between Mn and Fe indicates that Mn does not covary with Fe. Regression analysis here results in an r^2 value of 0.3762. Eventhough, Mn is related to iron in its chemical properties and is a member of iron family (Goldschmidt, 1929) or the ferrides. Daly (1933) showed that the correlation between Mn and Fe in igneous rocks is the result of a process occurred during the very stable main stage of crystallization.

It is observed in Table 6.15 that ratios of Mn/Fe in each rock types (except limestones and sandstone) show the same trend as found by Turekian and Wedepohl (1961) and are quite comparable with the ratio of those from average crust.

Zn and Cu have very strong positive correlation with Fe, with an r^2 value of 0.8118 and 0.8022, respectively. Pb shows weaker correlation with Fe. Its regression analysis results in an r^2 value of only 0.6939. The scatter plots of Zn, Cu, and Pb against Fe are shown in Figure C.7-C.9.

Calculated values of element/Fe ratio are shown in Table 6.15. These ratios compare quite favorably with those of individual rock types from Turekian and Wedepohl, (1961) and also with those of average crust. However, it should be noted that limestones are also generally low in Fe contents, thus making the element/Fe ratio in limestones the highest.

3. Using Mn as reference elements.

Figure C.10-C12 in appendix C are the scatter plots of Zn vs. Mn, Cu vs. Mn, and Pb vs. Mn. Those plots are delineated with the resultant regression line at 95% confidence limits.

The relationship between trace metals and Mn indicates that these metals do not covary with Mn. Regression analyses here result in an r^2 value of 0.4295, 0.3776, and 0.3683, respectively.

It is likely that Mn does not associate with these metals in any minerals.

4. Using Al + Fe as reference elements.

Figure C.13-C.15 are the scatter plot for Zn vs. Al+Fe, Cu vs. Al+Fe, and Pb vs. Al+Fe, with the resultant regression line at 95% confidence limits.

The result of the regression analyses indicates that all three metals, Zn, Cu and Pb have positive co-variance with Al+Fe. Cu is shown here to have the highest correlation with Al+Fe with an r^2 value of 0.8829, while the r^2 value of Zn znd Pb are 0.8371 and 0.7995, respectively.

Al in aluminosilicate minerals and Fe in ferrous and ferric oxide minerals are major compositions in many rocks. In this relationship study, it is found that after adding Fe to Al, the r^2 value remains fairly constant and is close to that of Al as reference element. It is likely that Fe may be associated in crytal structure of aluminosilicate of rocks.

5. Using Al + Mn as reference elements.

Figure C.16-C.18 show the scatter plots of Zn vs. Al+Mn, Cu vs. Al+Mn, and Pb vs. Al+Mn, with the resultant regression line at 95% confidence limits.

Very strong positive covariance is indicated for Cu and Al+Mn, with an r^2 value of 0.8801. Concentration of Zn and Pb seem to correlate well with those of Al+Mn, as reflected by an r^2 value of 0.8063 and 0.8143 , respectively.

The r^2 values of this relationship have the same trend as those found when using Al singly as reference element. This is probably because Mn appears in crust at a much lower level than Al. Therefore, it will not be able to exert much influence on the relationship of trace elements and Al in rocks.

6. Using Fe + Mn as reference elements.

Figure C.19-C.21 display the scatter plots for Zn vs. Fe+Mn, Cu vs. Fe+Mn, and Pb vs. Fe+Mn, with the resultant regression line at 95% confidence limits.

Zn is shown here to have a very strong positive correlation with Fe+Mn with an r^2 value of 0.8149. The regression analysis show that Cu correlates strongly with Fe+Mn. with in an r^2 value of 0.8042. Pb is shown here to have a weaker positive correlation with Fe+Mn with an r^2 value of 0.6966.

The r^2 values of these relationships have the same trend as those found when using Fe as reference element because Mn appears at in crust a much lower level than Fe. Thus Mn will not be able to strongly affect the change in relationship between trace elements and Fe in rocks.

7. Using Al + Fe + Mn as reference elements

Figure C.22-C.24 show the scatter plots for Zn vs. Al+Fe+Mn, Cu vs. Al+Fe+Mn, and Pb vs. Al+Fe+Mn, with the resultant regression line at 95% confidence limits.

The regression of Zn, Cu and Pb on Al+Fe advocate that all three metals have a positive co-variance with Al+Fe. Cu is shown here to have a very strong positive correlation with Al+Fe with an r^2 value of 0.8842. A positive linear regression line is shown here for the plot of Zn and Pb against Al+Fe, with an r^2 value of 0.8379 and 0.8000, respectively.

The r^2 values of this case have the same trend as these found when using Al as reference element. This may be helpful in supporting the fact that some trace elements mentioned-above may be associated in crytal structure of aluminosilicate of rocks.

Conclusion

For the study of relationship between trace elements and reference elements, it is concluded that in Mae Klong watershed area, Al is the most suitable as reference element.

Schropp and Windom (1988) have described criteria of reference elements suitable to normalize metals concentrations in sediments as follows.

- It should be the most abundant naturally occurring metal.

Results of this study confirm that Al are the most abundant and dominant metal in at Mae Klong watershed area .

- It should be highly refractory.

Results from several studies have indicated that proportions of Al in crustal materials are fairly constant (Rankama and Sahama, 1960

Martin and Whitefield, 1983; Taylor, 1964; Taylor and McLennan, 1981; Turekian and Wedepohl, 1961; Schropp and Windom ,1988)

- Its concentration should not generally be influenced by anthropogenic.

Since the natural level of alluminium in Mae Klong watershed area is quite high so influence of input from anthropogenic sources should be relatively insignificant.

Several researchers (Schropp and Windom ,1988; Windom *et al.*, 1989; Din, 1992; Hanson *et al.*, 1993) studied the relationships between trace metals and reference element (Al) in sediments, found that most trace metals have correlation with Al (see also Table 5.17).

Table 6.17 Correlation of some metals (Zn, Cu and Pb) and Al in sediments.

metal / Al	coefficient of determination (r^2)		
	Windom et al., 1989 log transform	Din, 1992 log transform	Hanson et al., 1993 untransfrom
Fe / Al	0.88	0.93	0.82
Mn / Al	0.50	0.19	0.24
Zn / Al	0.83	0.90	0.72
Cu / Al	0.61	0.89	0.78
Pb / Al	0.69	0.86	0.76

These studies agree that Al can be used as a reference element to normalize granular variability of most trace metals in sediment.

6.4 ANALYTICAL RESULTS OF SEDIMENTS IN MAE KLONG ESTUARY.

Estaurine sediments were collected from three locations in Mae Klong estaury and solubilized by a total digestion method. A certified sediment, IAEA SD-M-2/TM was used to check accuracy of the analytical results.

Table 6.18 Recommended values and confidence intervals for trace elements in IAEA SD-M-2/TM

Metal	Recommended values	confidence interval
Aluminium	32.0 ppt	15.6 - 55.4
Iron	27.1 ppt	25.0 - 28.5
Manganese	1.17 ppt	1.10 - 1.19
Zinc	74.8 ppm	72.0 - 78.3
Copper	32.7 ppm	31.7 - 34.2
Lead	22.8 ppm	20.1 - 25.6

Table 6.19 Analytical results of metals in Mae Klong sediments.

Sample code	Al ppm	Fe ppm	Mn ppm	Zn ppm	Cu ppm	Pb ppm
MK-1	38600	24600	945	37.8	21.15	17.33
MK-2	40575	27000	1120	41.8	26.9	24.77
MK-3	40175	27100	1117	38.3	25.31	20.96

Sediment Enrichment Factor

The analytical results in Table 6.19, are converted to sediment enrichment factor [SEF] values using the equation in Chapter I. Al is used singly as reference element.

Table 6.20 Average elemental compositions in crust.

Al μg/g	Fe μg/g	Mn μg/g	Zn μg/g	Cu μg/g	Pb μg/g	Ref.
82300	56300	950	70	55	12.5	Taylor (1964)
72000	41000	770	95	33	19	Bowen (1979)
37313.37	16761.06	569.9	33.06	17.52	13.74	this study

Ea (The average observed elemental concentration in crust) and Ra (The average Al concentration, reference element, in crust) for calculation from 3 sources (Table 6.20) are used and the results are then compared.

Note

1. SEF becomes positive when ratio of elements/Al in crust is lower than those in sediments in Kae Klong watershed estuary,
2. SEF become negative when ratio of elements/Al in crust is higher than those in sediments in Kae Klong watershed estuary.

Zn,

SEF values calculated from the Ea and Ra values of Taylor (1964) and this study show that Zn is enriched in the sediments. On the contrary, SEF values calculated from the Ea and Ra of Bowen (1979) are negative because Zn/Al in the sediments are higher values.

Table 6.21 Sediment Enrichment Factor in Mae Klong watershed area (using Al as reference element)

	MK-1	MK-2	MK-3	Values used in calculation from
Zn	0.1513 -0.2578 0.105	0.2112 -0.2192 0.1627	0.1208 -0.2774 0.0759	Taylor (1964) Bowen (1979)
Cu	-0.1801 0.1954 0.1669	-0.0079 0.4464 0.4119	-0.0573 0.3745 0.3417	Taylor (1964) Bowen (1979)
Pb	1.9559 0.7013 0.2192	3.0193 1.3133 0.6578	2.4349 0.9770 0.4168	Taylor (1964) Bowen (1979)

Cu

SEF values calculated from the Ea and Ra values of Bowen (1979) and this study show that copper is enriched in the sediments, while these calculated from Taylor (1964)'s values are negative.

Pb

No matter whose Ea and Ra values are employ, the SEF values indicate that Pb is enriched in the sediments.

However, enrichment of these metals here is relatively insignificant since the anomaly that come from anthropogenic input is significant only when the SEF values exceed 15 (Kemp *et al.*, 1976).