

CHAPTER IV

GEOCHEMISTRY OF SEDIMENTS IN THE GULF OF THAILAND

Characterization of Some Geochemical Properties

1. Readily Oxidizable Organic Content

The results of percentage of oxidizable organic matter in silt and clay fraction, and in total sediment of this study are presented in Appendix M. The values of oxidizable organic matter analyzed by the chromic acid method are more reliable and are better estimation for organic matter in sediments. The average values of organic matter in silt and clay fraction are 2.172, 1.597 and 1.760% for the Upper Gulf, the Lower Gulf, and the Whole Gulf respectively, which shows the same trend as found by Umuay (1984). The total organic content in the Gulf sediment reported by Kasemsupaya (1981) is much higher (3.01-13.12%) which may due to the nature of ignition loss technique that tends to overestimate organic content in sediments.

Organic matter is likely to associate with fine-grained sediment, particularly of silt and clay size classes (Calvert, 1976, Salomons and Forstner, 1984), rather than coarse-grained sediment. It is confirmed in this study by which the amount of organic matter increases as the percentage of fine-grained particles, particularly clay, increases (Figure 16).

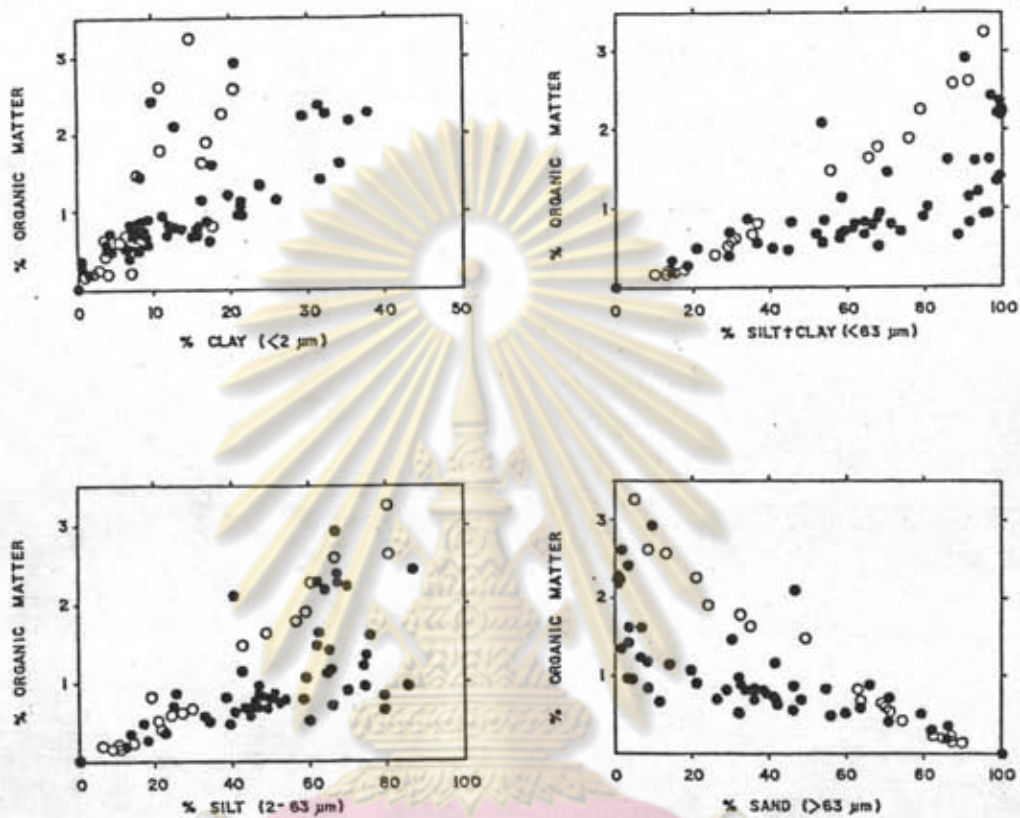


Figure 16 Relationship between percentage of organic matter and percentage of
 (a) clay size particle (b) silt and clay size particle
 (c) silt size particle (d) sand size particle
 (○) Upper Gulf (●) Lower Gulf

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2. Inorganic Carbon Content

The carbonate content is slightly lower in the Lower Gulf than in the Upper Gulf and has the average of 12.8 % for the Whole Gulf. Low concentrations, ca <10%, are found in the samples collected from stations located along the coast on both sides of the Gulf, which is the same trend as Emery and Niino (1963). The analytical data are presented in Appendix N.

The content of inorganic carbon was seldom study in the Gulf of Thailand. However, Emery and Niino (1963) found the content of inorganic carbon (in total portion of sediment) in form of calcium carbonate in the Gulf of Thailand range from 0-33% (Figure 17), and no relationship between the carbonate content and grain size was found. This finding is confirmed in this study.

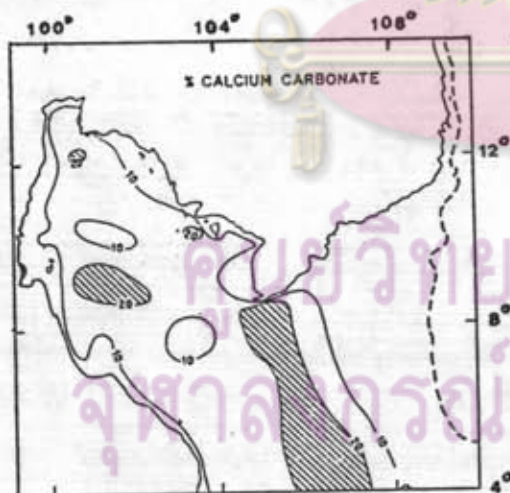


Figure 17 Distribution of contents of calcium carbonate of sediments, Gulf of Thailand and adjacent continental shelf (Emery and Niino, 1963).

3. Non-lattice Held Metal Content

The data of non-lattice held metals analyzed by single leaching method are presented in Appendix O. The concentrations are calculated per unit of dry, <70 μm sediment on the carbonate-free

basis.

Every leachable metal, Cd, Cr, Zn, Fe and Mn, establishes the same trend of having slightly higher concentrations in the Upper Gulf than in the Lower Gulf. The leachable fraction is considered mobile and is bound to the sediment in sorbed, precipitated or co-precipitated (carbonates, and hydrous Fe/Mn-oxides and hydroxides) and in an organically complexed form. Therefore, by plotting the concentration of leachable fraction against organic content, carbonate content, and Fe and Mn contents the partitioning pattern of such metal in sediment might be established (Figure 18-22).

Fe and Mn do not favourably associate with any particular size fraction that is smaller than $<70 \mu\text{m}$. Both Fe and Mn show the same trend of increasing in concentration with the increase in the content of organic carbon. This may indicate that organic matter present as coating on the surface of Fe and Mn solid in the form of oxyhydroxides.

However it can be found from this study that Fe and Mn concentrations related with clay size particle, carbonate content and organic content, but poorly relate with silt size particle as shown in Figure 18 and 19.

Cd is not preferentially sorbed on any fraction and tends to have very low concentration in every fractions.

Cr and Zn show relatively the same partitioning pattern of favourably associated with oxyhydroxides, organic and carbonate fraction.

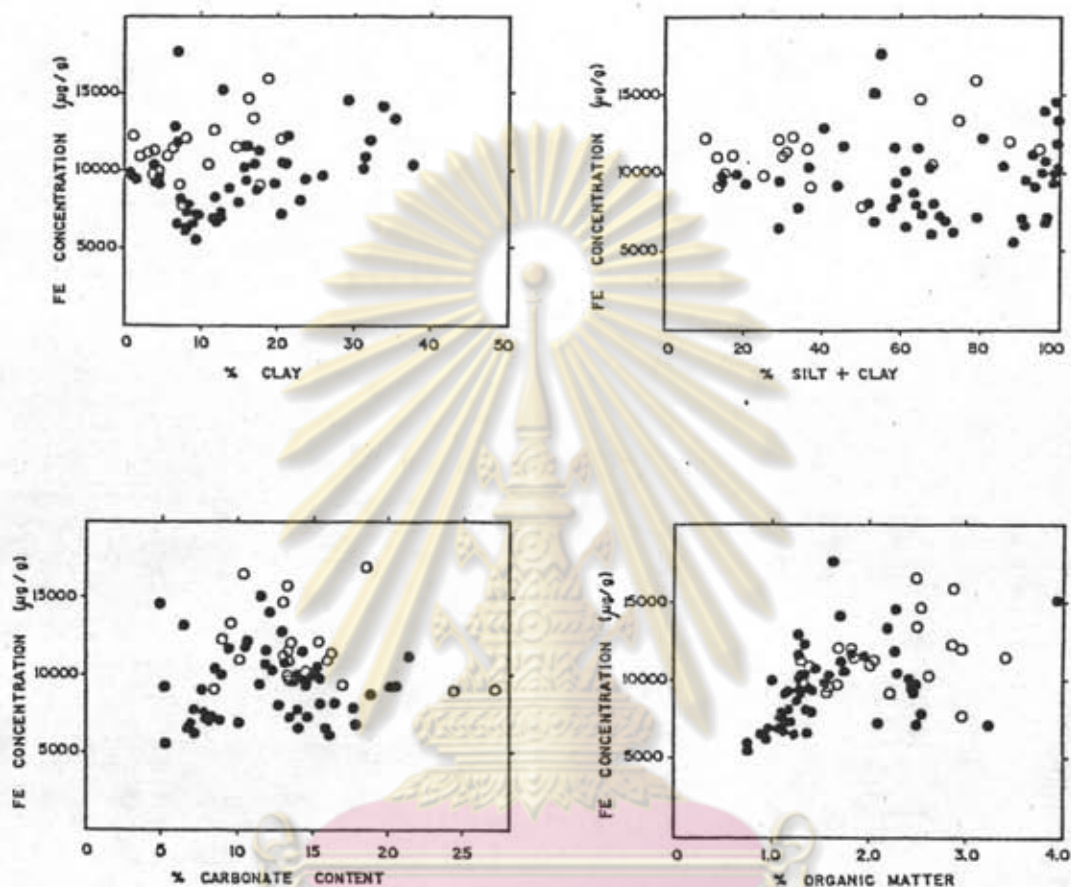


Figure 18 Relationship between leachable iron and
 (a) clay minerals, represented by percentage of clay size fraction
 (b) percentage of fine grained particles, represented by silt and clay fraction
 (c) carbonate content (d) oxidizable organic matter
 (○) Upper Gulf (●) Lower Gulf

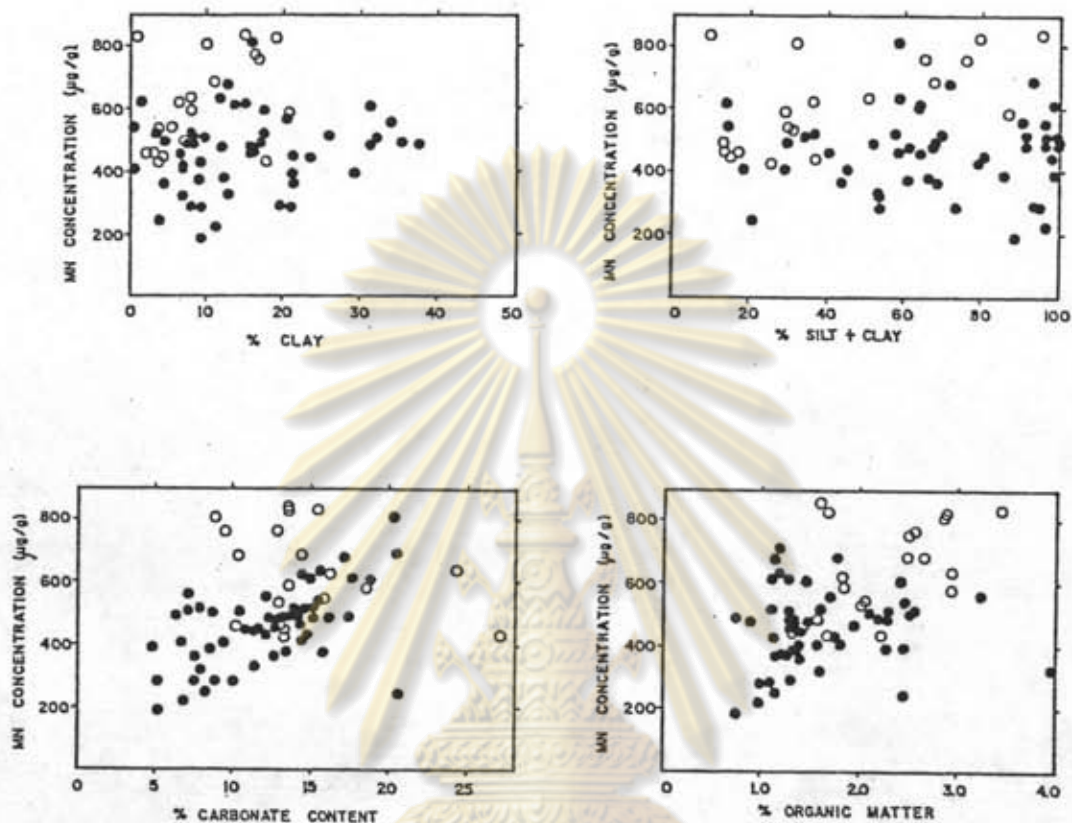


Figure 19 Relationship between leachable manganese and
 (a) clay minerals, represented by percentage of clay size fraction
 (b) percentage of fine grained particles, represented by silt and clay fraction
 (c) carbonate content (d) oxidizable organic matter
 (○) Upper Gulf (●) Lower Gulf

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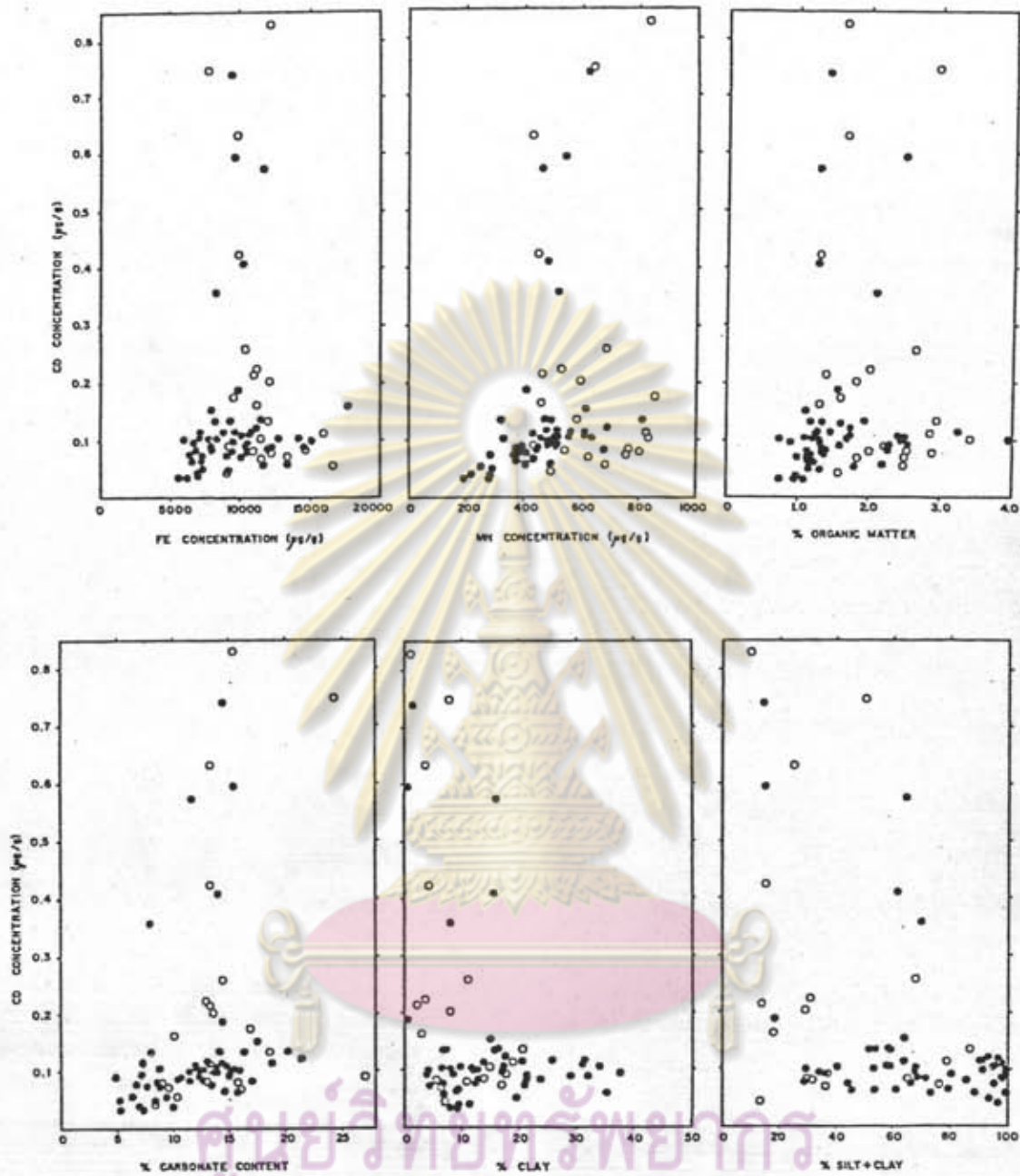


Figure 20 Relationship between leachable cadmium and
 (a) iron oxide (b) manganese oxide
 (c) oxidizable organic matter
 (d) clay minerals, represented by percentage of clay size fraction
 (e) percentage of fine grained particles, represented by silt and clay fraction
 (○) Upper Gulf (●) Lower Gulf

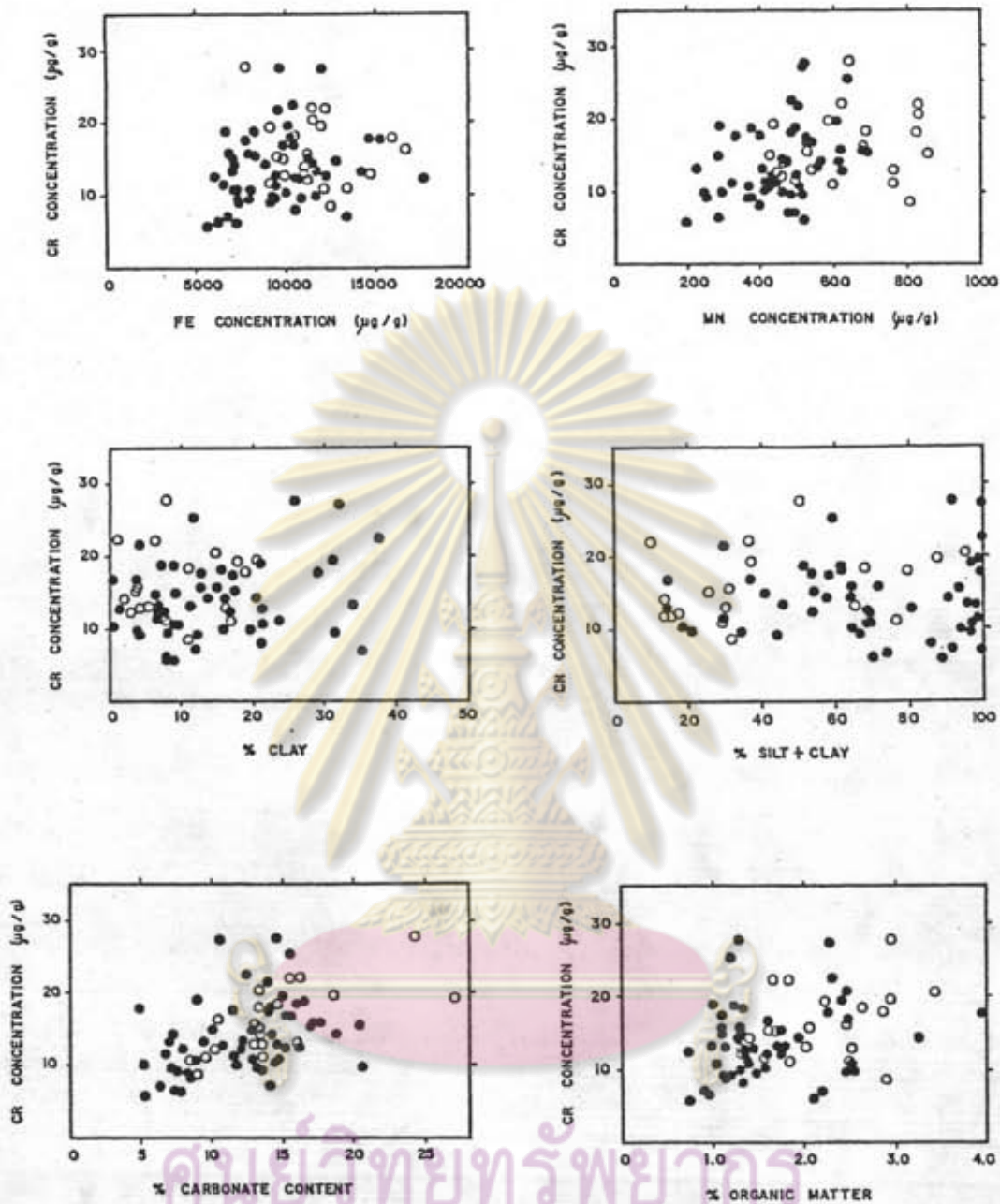


Figure 21 Relationship between leachable chromium and
 (a) iron oxide (b) manganese oxide
 (c) oxidizable organic matter
 (d) clay minerals, represented by percentage of clay size fraction
 (e) percentage of fine grained particles, represented by silt and clay fraction
 (○) Upper Gulf (●) Lower Gulf

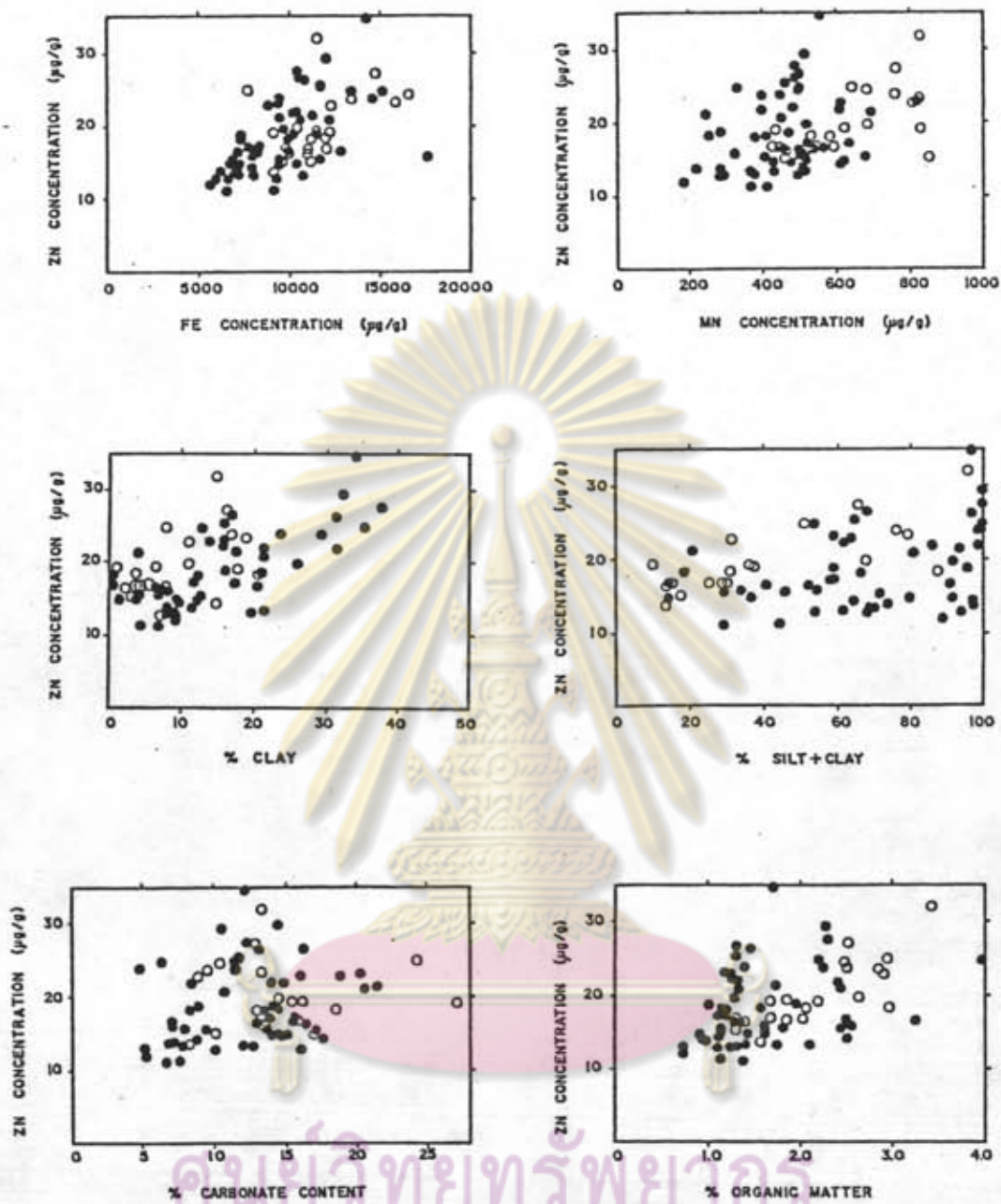


Figure 22 Relationship between leachable zinc and
 (a) iron oxide (b) manganese oxide
 (c) oxidizable organic matter
 (d) clay minerals, represented by percentage of clay size fraction
 (e) percentage of fine grained particles, represented by silt and clay fraction
 (○) Upper Gulf (●) Lower Gulf

According to the HSAB principle (Pearson, 1968a) and stability of complexes (Irving and William, 1948) the 3 metals show the patterns of partitioning which are controlled by their chemical properties.

Cd, Cr and Zn are found not to be enriched in the Gulf sediment during the past 30 years (Hungspreugs and Yuangthong, 1983). However, the direct comparison between the results of this study and others in terms of leachable metal concentration should be viewed cautiously since the others do not consider the effect of grain size and dilution by metal-poor shell material (Table 11).

Table 11 Non-lattice held metal concentration in the Gulf of Thailand.

Metals	Jindasom ^a batchareon (1983)	Windom ^a et al. (1984)	Jaturanon ^a (1983)	Petpiroon ^b (1988)	This study ^c (1989)
($\mu\text{g/g}$)					
Cd	0.013-1.605		ND		0.033-0.829
Cr			11.99-26.01		5.697-27.634
Cu	0.79-13.42	2.5-24.0	1.34-18.17	3.68	
Pb	1.56-32.16		10.13-26.01	5.13	
Zn	1.66-24.17		12.89-68.13	14.52	11.14-34.62
Ni		8.8-38.0	4.01-11.68		
(mg/g)					
Fe		12-33	2.39-4.44		5.57-17.63
Mn		0.5-0.9	0.19-0.63		0.22-0.86
Al		15-61			

- a : Upper Gulf of Thailand
 b : Rayong, Chanthaburi and Trat
 c : The whole Gulf of Thailand

4. Bulk Metal Content

Bulk metal content may also be used in studying the metal partitioning in sediment. In this study Neutron Activation Analysis,

a non-destructive method, is employed. The data are presented in Appendix P. The concentrations are calculated on carbonate-free basis in order to reduce dilution effect of the metal-poor shell materials. The samples are sieved prior to analyses, thus help reducing the grain size effect.

Among the 4 metals analysed only Mn shows the trend of having lower concentration in the Lower Gulf of Thailand. It is very unfortunate that in order to establish a partitioning pattern from total metal concentration each element must be analyzed for its total concentration as well. However, Cd and Zn can not be determined by the neutron activation method due to their theoretical limitation. Therefore, only partitioning pattern for Cr can be established. Using the enrichment factors (EF) (Kemp et al., 1976) calculated by either using the abundant values in shale or in near-shore mud the EFs of 73 samples never exceed 2.4. The low value of EF indicate that Cr is not enriched, by associating itself with non-residual fraction in the Gulf of Thailand sediment.

The analytical result of Fe and Mn are used only for the purpose of establishing the amount of oxyhydroxide present in each sample. The patterns of correlation between these compounds and the leachable metal contents are described in the previous section. The high amount of both Fe and Mn in sediment do not really indicate that the sediments are contaminated. This is because Fe and Mn are the second and third most abundant elements in the earth crust. This is confirmed by their EFs of having values less than 1 for Fe and 1.5 for Mn.

Comparison between the results of total metal concentration from this work with the others is not likely to yield a very useful comparison (Table 12). Because the analytical value of total metal analysis is strongly dependent upon the types and strength of reactant and also digestion technique. In addition, the dilution effect from metal-poor sediment materials and grain size effect must be accounted for.

Table 12 Total metal contents in the Gulf of Thailand.

($\mu\text{g/g}$)	Cd	Cu	Zn	Pb	Cr
Chanpongsang (1982) ^a	0-2.37	4.40-17.43	21.22-164.07	ND	
Menasveta & Cheevapara-napiwat (1981) ^b	0.45-1.75	3.75-37.50	35.0-95.0	20.2-28.3	
Idthikasem et al. (1981) ^c	0.04-0.18	3.1-23.0	7.3-95.0	14-42	
Polpasert et al. (1979) ^c	0.93-5.70	2.63-12.08	15.98-37.81	14.03-84.51	6.57-19.71

a : Chao Phraya Estuary

b : Mouth of 4 major rivers

c : Upper Gulf of Thailand

5. Sequential Leaching Analysis

As mentioned earlier in Chapter I (section Methodology (4)) that the results from total sediment analysis and leaching do give us some informations on the partitioning pattern. Up to this point, it can now be established that the 3 metals are not enriched in the non-residual fraction and Cd, being a soft acceptor, is the metals that is least likely to be incorporated into sediments. In addition, Cd is the least abundant metals among the three (Table 13), thus

making its concentration in non-residual fraction lower than the other twos.

Table 13 Elemental abundance of the earth crust and sediment ($\mu\text{g/g}$) (Salomons and Förstner, 1984).

	Cd	Cr	Zn
Mean crust	0.11	100(?)	75
Mean sediment	0.17	72	95
Average shale	0.22	90	95
Deep-sea clay	0.42	90	165
Shallow water sediment	-	60	92
River suspended sediment	1	100	350
Sandstone	0.05	35	30
Limestone	0.03	11	20
Soil	0.6	84	60

The experiment 1 as described in Chapter I (section Methodology (4.2)) is carried out in order to test the practicality and suitability of the sequential extraction procedure designed. This procedure is based on the one designed by Robbins et al. (1984). It is found that among the 4 fractions namely: exchangeable, carbonate and sorbed; oxyhydroxides; organic bound and residual fractions) extracted organic fraction give rise to a difficulty while measuring Cd with GFAAS. This is due to the low surface tension of the SDS which made the injected solution spreaded throughout the furnace resulting in very low and erratic absorbant reading. In addition, the comparison of the effectiveness in extracting metals from organic fraction between the SDS and acidified H_2O_2 (Figure 23, 24, 25) show that SDS may not be efficient enough. On the other hand, one may argue that higher metal content extracted by acidified extract may not mean that the acidified H_2O_2 is more efficient than the SDS but rather indicate the ability of poorly-buffered acidified H_2O_2 to release some

metals from the residual fraction, particularly in organic-rich or sulfide-rich sediment (Presley et al., 1972; Langeveld, Van der Gaast and Eisma, 1978; Tessier et al., 1979, 1982). However, the sum of the first 3 fraction excluding non-residual (with organic fraction extracted by acidified H_2O_2) is always relatively smaller than leachable metal contents. This may be an indication that either acidified H_2O_2 does not result in overestimation of organic fraction or the hot acid leaching method always overestimates the non-residual fraction.

Since the SDS gives rise to a difficulty in AA measurement, acidified H_2O_2 is used instead of the SDS. In addition, the sample size is also increased in order to raise the metal concentration in each extracts above the practical detection limit. This procedure is rather promising so that the experiment is repeated in experiment 3. The results of experiment 2 and 3 are comparable which indicate an acceptable precision for this extraction procedure (Appendix Q).

Though satisfactory result is obtained with this procedure, it is found that high strength of extrcats results in very concentrated matrixes. This kind of solution has a certain disadvantage when one measures metal contents in such solution with GFAAS. The concentrated matrix gives rise to a very high background absorbance in which the measurement must be carried out either in a diluted solution or at an alternate wavelength having lower sensitivity.

In order to raise the metal concentration in extracts above blank level whereby dilution of the extract prior to AA measurement to reduce the matrix effect is still able to produce metal concentration having reasonably high absorbant above the blank level the sediment : extractant ratio is double (1 : 10, Experiment 4). The amount of Cr and Zn extracted in carbonate fraction are lower than the previous experiment where the amount extracted in both oxyhydroxide and organic fraction are only slightly lower (Appendix Q). This is not the case for Cd because once the concentration in carbonate fraction can not be extracted completely (Figure 23, 24, 25), the left over amount produces cross contamination in the subsequent fractions. From this observation it is very likely that by decreasing the volume of extractant one will reduce the capacity of the extractant as well. Therefore, in case of Cr and Zn where their concentration are much higher than Cd the use of sediment : extractant ratio of 1 : 10 will not be able to completely extract the metals from each fractions.

It is also noted in every experiments that sediment : extractant ratio for extracting the residual fraction remains the same. With this fact in mind it is observed that Cr is the most troublesome metal among the three because in both sample 8A and 37 the residual content of Cr analyzed are scattered (low precision) while the results of Cd and Zn are quite high in precision. This may due to interferences during Cr determination with AAS.

Price (1979) indicated that Cr(III) and Cr(VI) give different responses and samples are best oxidized with perchloric acid to give Cr(VI), or reduced with H_2O_2 to give Cr(III). There is a major interference by Fe in an air acetylene flame, which can be

reduced by the presence of NH_4Cl . The depression is most significant in a fuel-rich flame, is less in fuel lean flame, and is not experienced at all in the hotter nitrous oxide-acetylene flame. The degree of depression increases gradually as the Fe concentration is increased, levelling off only when a large excess of Fe is present. This does not support the theory of the formation of a definite compound, e.g., a spinel. Furthermore, in the reverse situation, the Fe absorption is little depressed by a large excess of Cr. Aspiration of Cr/Fe solutions will cause relatively large solid particles, which after reduction by the flame gases consist of Cr (boiling point 2480°C) in a matrix of Fe (boiling point 3000°C). These are not completely vaporized and the atomization efficiency of the Cr is low. In the reverse situation-iron in a matrix of Cr-the Cr vaporizes at a lower temperature and the Fe is atomized.

It is obvious that doubling the sediment : extractant ratio does affect the amount of metal extracted. However, the effect of the strength of each reactant is yet to be investigated. Therefore, in the experiment 5 while keeping the sediment : extractant ratio at the same level as in experiment 4 (1 : 10) the strength of each extractant is lower by half. The following are observed (Appendix Q):

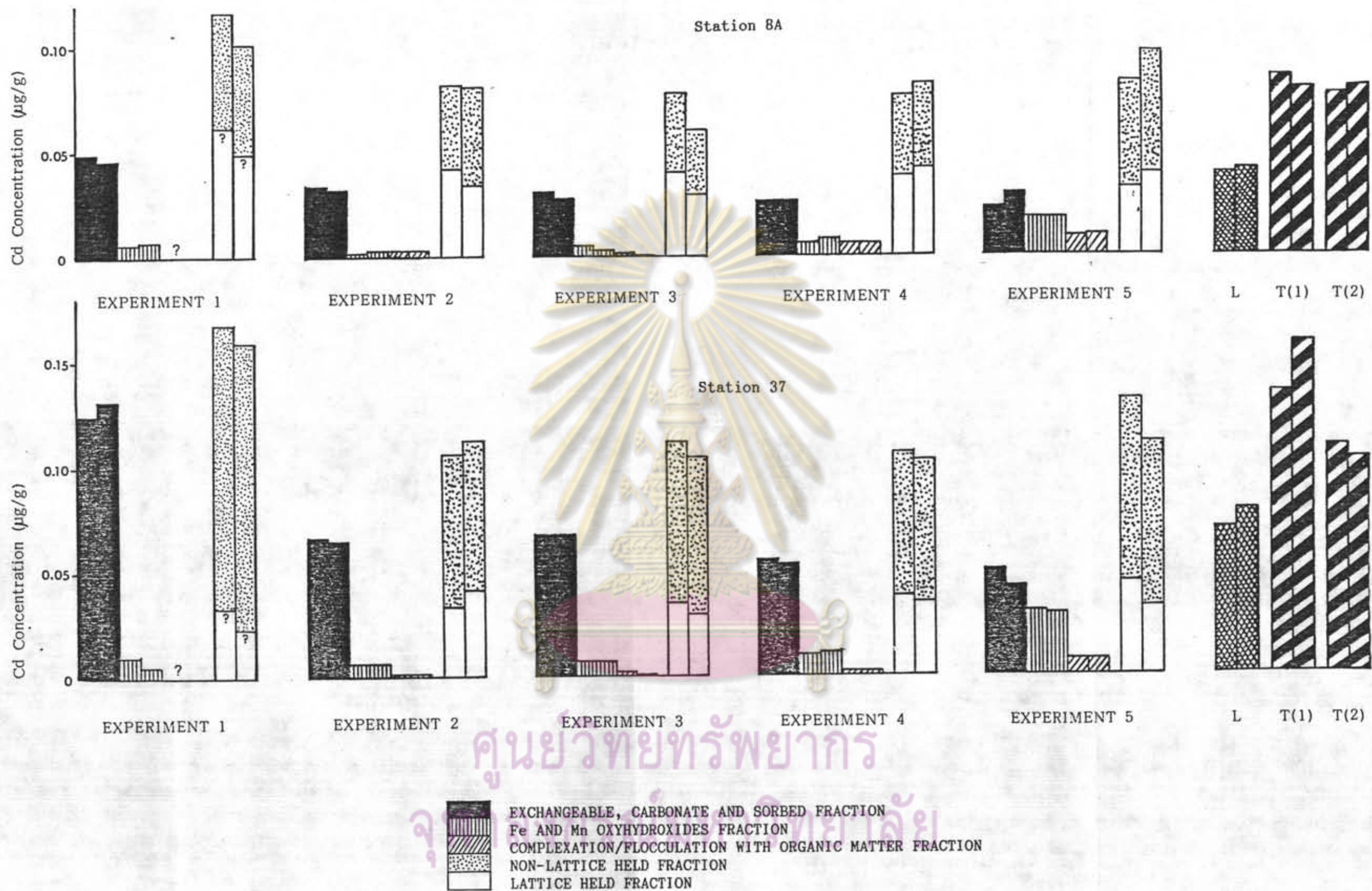
In case of Cd it is now quite certain that eventhough the amount of Cd associated with non-residual fraction, is relatively lower than the other two. The strength and capacity of every extractant to be used must be considered with great care. Sediment : extractant ratio greater than 1 : 20 will greatly reduce the capacity of the 1 M NaOAc-HOAc, pH 5.0 in extracting Cd associated with

exchangeable, carbonate and sorbed fraction. In addition, lowering the strength of extractant is also not recommended. The use of 1 M $\text{NH}_2\text{OH}\cdot\text{HCl}$ -Na-citrate, pH 5.0 and acidified H_2O_2 seem to have more than enough strength and capacity to completely extract Cd from oxyhydroxide and organic fraction even at sediment : extractant ratio of 1 : 10. This is confirmed in this experiment when the half strength extractant are used that they are still able to cope with the amount of Cd increased by cross contaminated from the first fraction.

Cr and Zn are associated with sediment in considerably higher amount than Cd. Therefore, once the first fraction can not be completely extracted the amount left over will cross contaminate with the subsequence 2 fraction, making the amount of metal to exceed the capacity of $\text{NH}_2\text{OH}\cdot\text{HCl}$ -Na-citrate and acidified H_2O_2 at half capacity (sediment : extractant ratio = 1 : 10) and at half strength (original concentration are lowered by half).

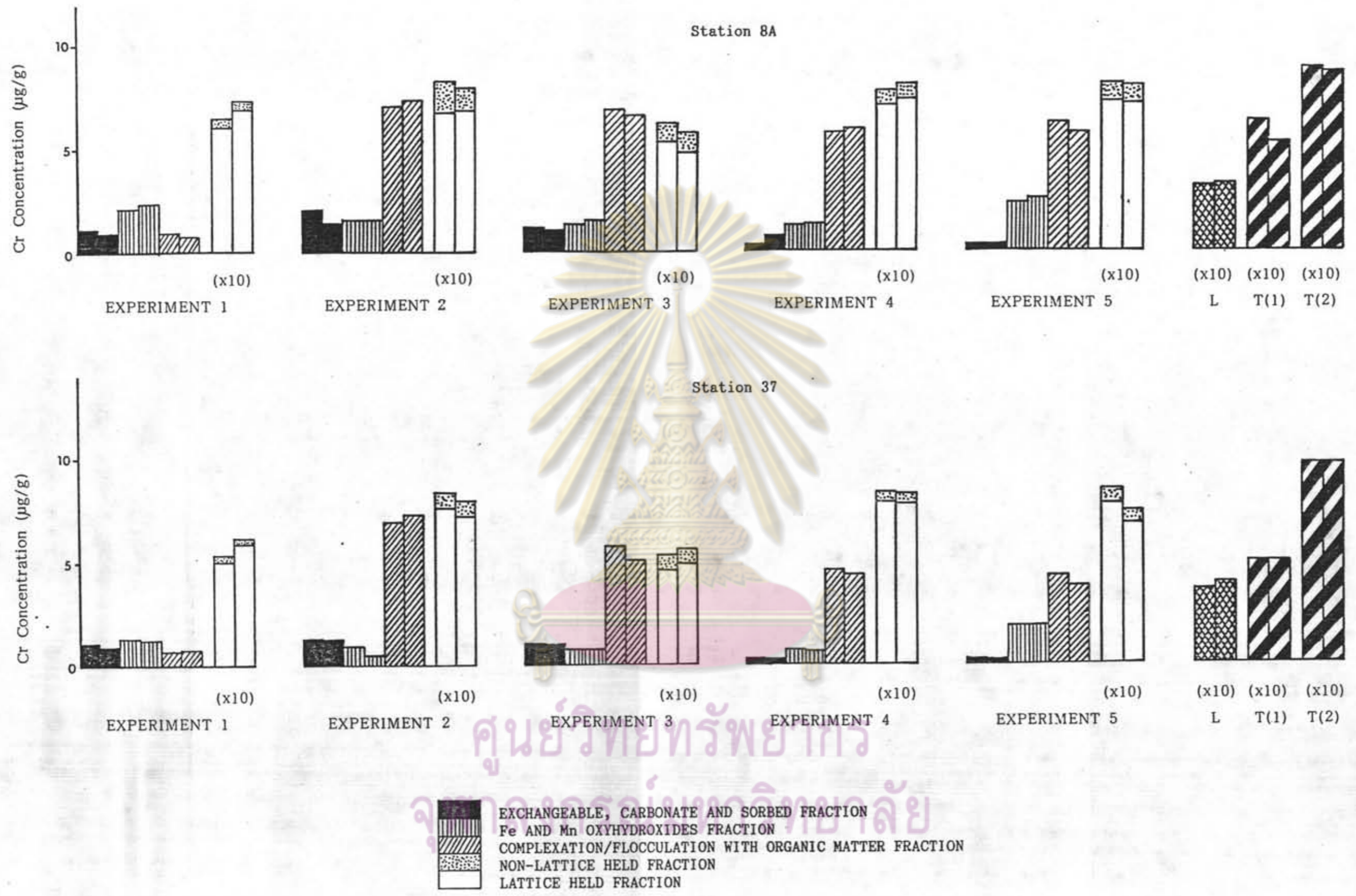
Comparison between the sum of 3 fractions (carbonate sorbed, oxyhydroxides and organic fractions) and non-residual fraction obtained from a single leaching, it is amazing to find that they are not comparable. The result of single leaching may be either higher (Cr and Zn) or lower (Cd) than the sum.

It is possible that 1 N HNO_3 at 1 : 20 sediment : extractant ratio is too strong and at high temperature (above 100 °C in this experiment) may not have only release exchangeable and adsorbed cation, dissolving disorder hydroxy species, metal-humate complexes and carbonate mineral but also partially dissolved some silicate mineral (Pickering, 1981). Normally, the extractant should be weakly acidic



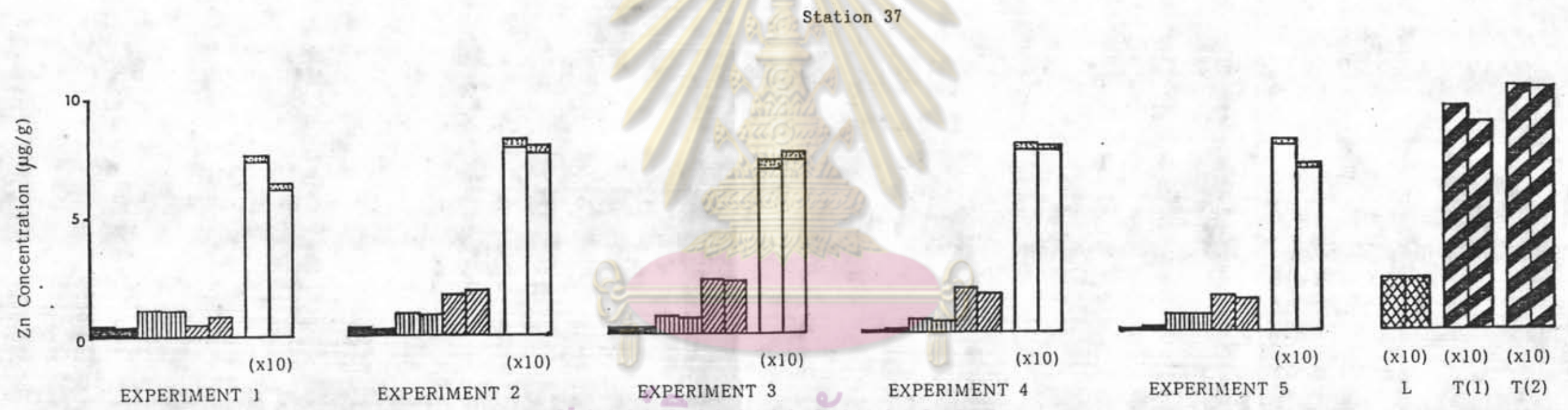
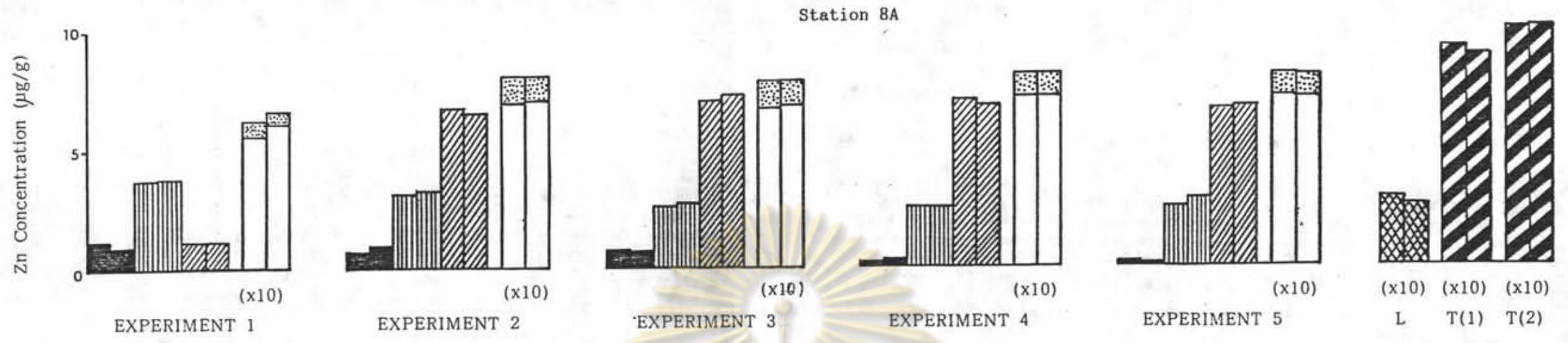
L : Single leaching experiment
 T(1) and T(2) : Total digestion

Figure 23 Histograms of Cd concentration of each experiment of sequential leaching (µg/g).



L : Single leaching experiment
 T(1) and T(2) : Total digestion
 (x10) : the concentration is 10 times greater than the one on the scale.

Figure 24 Histograms of Cr concentration of each experiment of sequential leaching (µg/g).



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	EXCHANGEABLE, CARBONATE AND SORBED FRACTION
	Fe AND Mn OXYHYDROXIDES FRACTION
	COMPLEXATION/FLOCCULATION WITH ORGANIC MATTER FRACTION
	NON-LATTICE HELD FRACTION
	LATTICE HELD FRACTION

L : Single leaching experiment
 T(1) and T(2) : Total digestion
 (x10) : the concentration is 10 times greater than the one on the scale.

Figure 25 Histograms of Zn concentration of each experiment of sequential leaching (µg/g).

in order to ensure a minimum extract on silicates. Therefore, in this case it is very likely that Cd which is always presented in a relatively larger amount in non-residual fraction than in residual fraction may be leached into solution both from the non-residual and residual fraction. Eventhough, Cd in the residual fraction is leached along with the non-residual the sum total may not differ much from the non-residual fraction alone as the contribution from residual fraction is relatively small (Figure 23, 24, 25). In the case of the Cr and Zn in which the sum total of non-residual fraction obtained from sequential leaching are always lower than the leachable amount (single leach) do give a strong support that single hot-acid leached is capable of partial leaching of residual fraction. Cr and Zn are more abundant than Cd and always present in higher concentration. In addition, the amount of this 2 metals are presented at relatively higher in residual than in non-residual fractions (Figure 26, 27, 28).

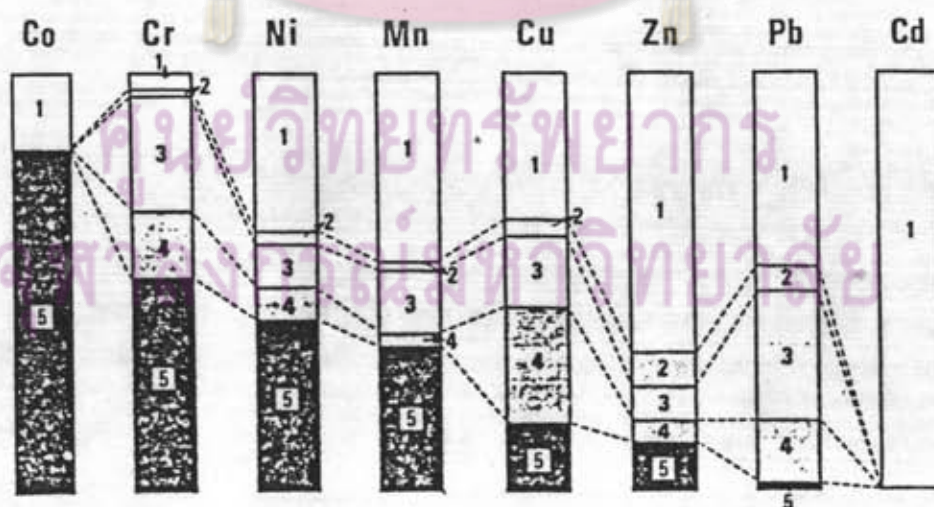


Figure 26 Mode of occurrence of trace metals in Standard Reference Material 1648 (urban particulate matter). (Drawn after Lum et al., 1982). 1. Exchangeable fraction, 2. Surface oxide and carbonate-bound fraction, 3. Associated with Fe-Mn oxides, 4. Organically bound fraction, 5. Residual fraction. (After Salomons and Förstner, 1984)



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Figure 27 The speciation of trace metals in 18 different river sediments (After Salomons and Förstner, 1980; cited by Salomons and Förstner, 1984).

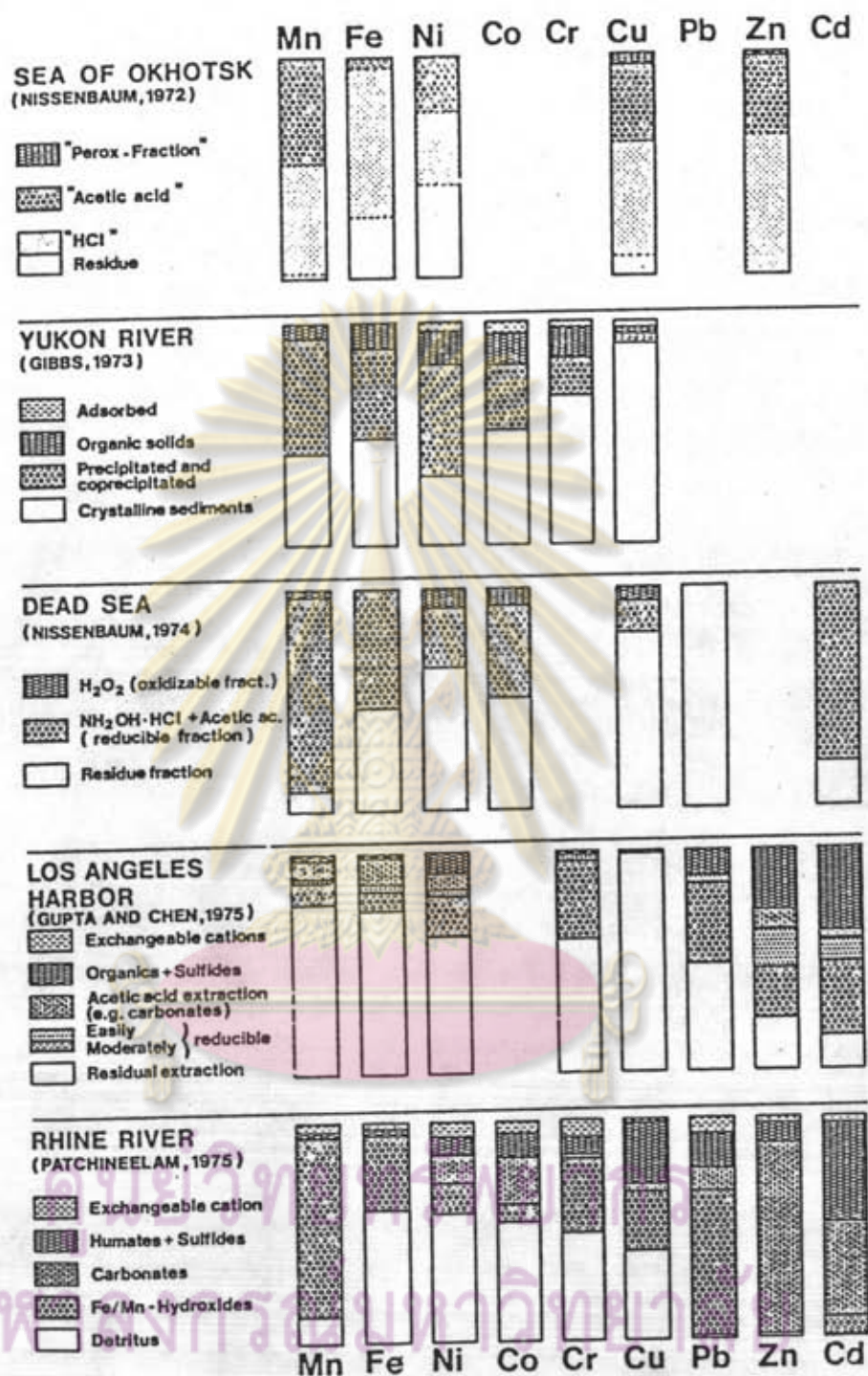


Figure 28 Chemical associations of heavy metals in sediments from natural and polluted aquatic environments (After Förstner and Wittmann, 1981).

Therefore, when 1 N hot HNO_3 partially dissolves some silicate the contribution of these 2 metals from residual fraction to the leachable content makes it higher than the sum of 3 fractions obtained from sequential leaching.

As mentioned earlier in this chapter that the acidified H_2O_2 tends to overestimate the amount of metals associated with organic fraction. However, the findings that single leaching is also capable of partial leaching of metals from residual fraction should be sufficient in giving more credibility to the use of acidified H_2O_2 . Since the acidified H_2O_2 , even though can partially dissolve some silicate, still doesn't overestimate the amount of metals extracted significantly.

Previous partitioning study of metal in the Gulf sediment by Jaturanon (1983) is somewhat incomparable to the result of this study due to the followings :

- 1) Grain size and dilution effect are not considered.
- 2) The use of dilute, unbuffered NH_2OH (0.04 M $\text{NH}_2\text{OH}\cdot\text{HCl}$ + HOAc) is not capable of dissolving Fe-oxyhydroxides completely (Chester and Hughes, 1967; Chao, 1972) and its acid pH will cause partial dissolution of aluminosilicates and also results in much greater degree of Fe dissolution than does the increasing the $\text{NH}_2\text{OH}\cdot\text{HCl}$ concentration (Chao, 1972). Therefore, it is likely that Jaturanon's results of oxyhydroxides fractions are overestimated.
- 3) Prevention of contamination is very poor which may result in overloading the extractants thus, causing cross contamination.