



CHAPTER I INTRODUCTION

Background

Sediments are defined as solid fragmental materials, or masses of such materials, either organic or inorganic, that originate from weathering of rocks and are transported by, suspended in, or deposited by, air, water or ice, or that are accumulated by other natural agents, such as chemical precipitation from solution or secretion by organisms and that form in layers on the Earth's surface at ordinary temperature in loose, unconsolidated forms (Gary, McAfree and Wolf, 1977).

During transportation to depositional site, sediments may undergo geochemical changes. Thus, sediment composition may differ greatly from its parent rock. Geochemical alteration may continue even after the deposition due to diagenetic processes. The extent of this alteration depends on the depositional environment and the original sediment compositions.

Therefore, sediments are the result of complex processes of nature. Although they are derived from a great number of different sources, the main sources are continental areas, coasts, submarine volcanoes and marine life, while the rivers, atmosphere, icebergs, etc., act as the media of transportation toward the final resting place in the basins of the world's oceans. To understand these processes,

scientists must have information of the sediments of how they got there, where they originally came from, what kinds of changes (transformation) occurred between original source and eventual deposit, the condition under which the original deposit formed, and what changes in the sediment's environment have occurred since then. Such information is usually gleaned from the properties of the sediment sample, such as its texture and its mineral composition.

Sediments are important carriers for the trace metals in the hydrological cycle. Sediments can reflect the current quality of the system as well as the historical development of certain hydrological and chemical parameters. The study of dated sediment cores has proved to be especially useful as it provides a historical record of the natural background levels and the man-induced accumulation of metal (Salomons and Förstner, 1984). Sediments are also indicator mediums depending on environmental conditions, sinks or sources for trace metals in the surface waters. Metals are not necessarily fixed permanently by sediments. They may be recycled via biological and chemical agents between sediments and the water column.

Serious environmental damage to sediments has occurred only in very localized regions. Sediments themselves are seldom worthy of protection. But they provide a home and a food source for many organisms; it is the biota they support that require care. Moreover, sediments may serve as a source of contaminants to the water, or contaminated sediments might cause other damaging effects on people using them.

Biogeochemical processes can redistribute the contaminants, but most (metals, pesticides, hydrocarbons, etc.) show high affinity to particulates. These contaminants become associated with fine-grained materials so that their behaviour and fate are determined by particulate dynamics. Despite all the interacting processes, some portions of the particle population are deposited in coastal and estuarine areas, leaving a record of contaminant inputs.

Sediments found in marine environments can be divided into 2 broad categories according to whether they are deposited in the deep-sea or the near-shore environment. These differ in compositions, grain sizes, and depositional environments. Deep-sea sediments (pelagic sediments) have been studied in much greater detail. In contrast, less attention has been paid to near-shore sediments where depositional environments are quite variable; including estuaries, fjord, bays, lagoons, deltas, tidal flats, the continental terraces and marginal basins. These environments are geologically and oceanographically diverse and much variable than those in the deep-sea. Consequently, near-shore sediments are very heterogenous and represent the entire range of sediment presently being delivered to the ocean. Near-shore sediment composes of a number of different components which may, or may not have different sources. Recently, it has been suggested that near-shore environments are important removal sites of several elements from seawater because the accumulation rates are very much higher and the physico-chemical conditions are different from those found in open ocean. This, therefore, indicates that studies of near-shore sediments are of great importance. Golterman, Sly and Thomas (1983) said that the sediment compositions influence the water

qualities of the reservoirs by means of geochemical balance.

Metals in natural waters may be bound to the various components of sediment by a range of chemical processes (e.g., ion exchange, adsorption, compound formation, etc.). The mode of bounding and ease of release back into an aqueous phase are variable and subjected to physico-chemical changes in the natural water system. Figure 1 show how metals associated into each fraction of sediment components indicated that the metal content of soil or sediment can be distributed between a number of component phases which range in nature from fragments of the initial base rock (minerals, carbonates, sands) to accumulations of weathering products (hydrous oxide, clay minerals, organic matter) (Pickering, 1981).

In general, there are 3 principle ways in which elemental partitioning, elemental distribution in each type of sediment components, in sediment can be studied. These are : (1) by the interpretation of chemical analyses of the total sediment samples, (2) by the physical separation and subsequent analysis of the components, and (3) by the chemical separation and subsequent analysis of the components.

- Total Sediment Analyses

Total sediment analyses require the decomposition of the sediment sample by strong acids and/or strong oxidizing agents before determinations of elements can be carried out, with exception of Neutron Activation Analysis. Analytical result is the summed total of a given element in every components of a sediment sample. The most simple way of interpreting element partitioning from total sediments

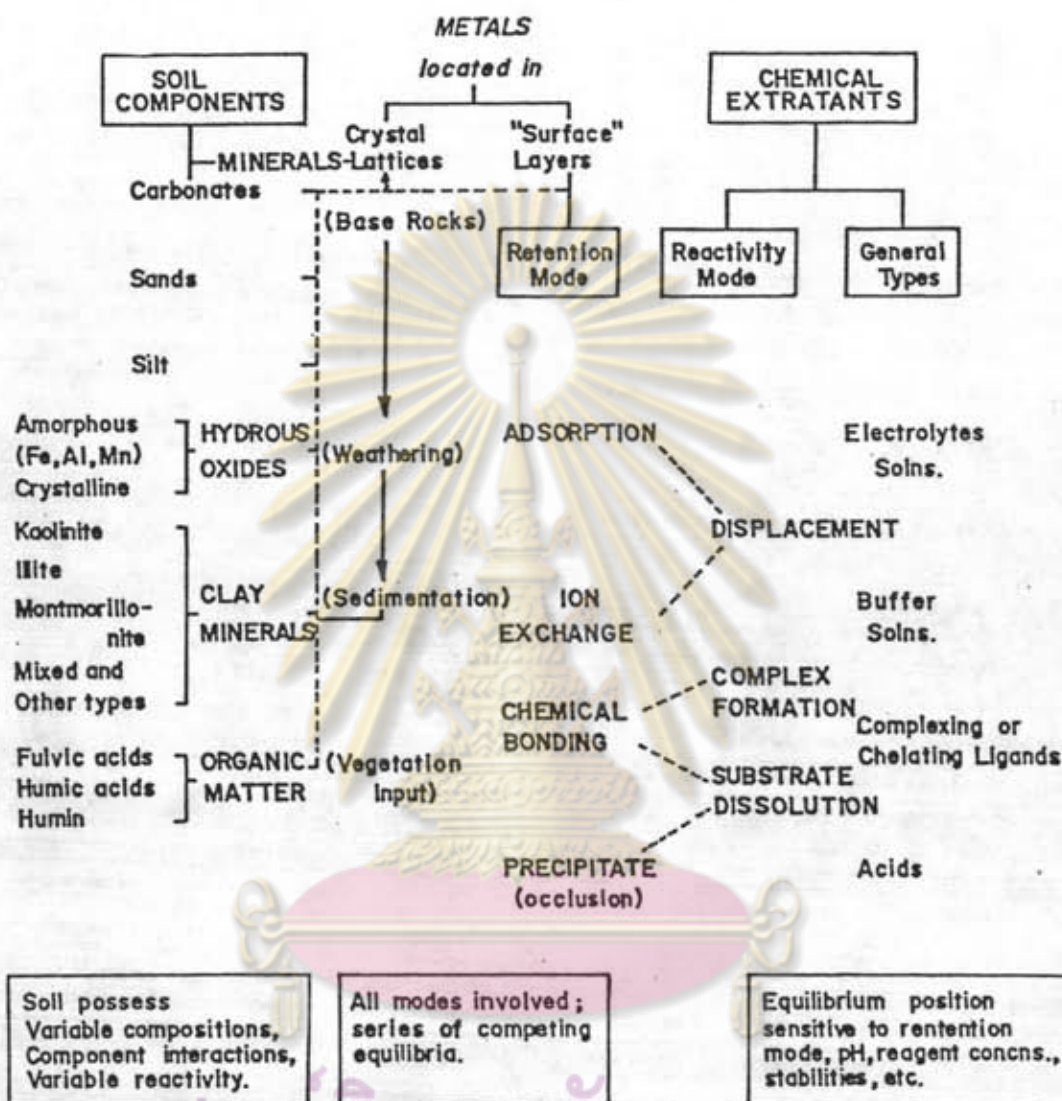


Figure 1 Diagrammatic representation of the relationship between retention mode of metal ions and nature of soil components, showing possible roles for chemical extractant solutions (after Pickering, 1981).

analyses is by expressing the results on a carbonate-free basis (Turekian and Imbrie, 1966), Quartz-free basis (Thomas, 1972), and Carbonate/Quartz-free basis (Salomons and Mook, 1977). These are attempts to correct for the dilution effects of trace element-poor materials e.g., quartz and carbonate which are present as a biogenous

fraction consisting of carbonate and siliceous shell material in sediments. Thus, the non-shell fractions of sediments can be compared directly with one another.

Another approach which may be used for the comparison of sediments of different compositions to a single baseline involves the use of specific element as an indicator of a general source material. In this approach an enrichment factor (EF) (Kemp, Thomas, Dell and Jaquet, 1976) is employed.

$$EF(x) = \frac{(\text{conc.}x / \text{conc.}Ref.) \text{ in analysis material}}{(\text{conc.}x / \text{conc.}Ref.) \text{ in source material}}$$

Where $EF(x)$ is the enrichment factor of an element x in the analysis material relative to a reference element (Ref.) and in a source material relative to reference element. For sediments, the use of indicator elements, can be taken a stage further, and rather than indicating a general elemental source, they can be used to establish the location of the elements in specific sediment fractions. In terms of distinguishing between the location of an element in either the residual (lattice-held) or the non-residual (non-lattice-held) fraction of sediments, the most commonly used indicator element is aluminium (Al). This element, in most sediments, is almost exclusively located in the lattice structures of aluminosilicate minerals or is residual in character. Therefore, the use of enrichment factors relative to Al is possible to estimate the partitioning of an element between the residual fractions of sediments providing the ratios are known for aluminosilicate residual minerals.

In practice, a baseline material, rather than individual minerals, is chosen against which to compare the element : Al ratios

of the sediments under study. The criteria in selecting a baseline material is that such a material should represent the composition of land-derived components as they are originally brought to the oceans i.e., before they have undergone any of the element enrichment processes operative in the marine environment. Shales (Förstner and Wittmann, 1981) and near-shore muds (Krishnaswami, 1976) were proposed as baseline materials. Chester and Aston (1981) believed that near-shore muds should offer the best available estimate of the baseline against which to compare the elemental composition of either deep-sea and near-shore sediments (Table 1). However, one should bear in mind that near-shore sediments are deposited under wide variety of environments which may, or may not, be the same depositional environments of the baseline materials.

Table 1 Elemental composition of the sediments (major cation in percent, %; minor and trace element mg/kg)

Element	Average shale ^(a)	Near-shore muds ^(b)
Aluminium	8.0 %	8.4 %
Iron	4.7 %	6.5 %
Magnesium	1.5 %	2.1 %
Titanium	0.5 %	0.5 %
Manganese	850	850
Chromium	90	60
Nickel	68	35
Zinc	95	92
Copper	45	56
Cobalt	19	13
Lead	20	22
Cadmium	0.22	-

(a) Turekian and Wedepohl (1961) ; (b) Wedepohl (1969, 1978)

- The Physical Separation of Sediment Components

The size of individual particles varies greatly; the coarsest materials include boulders, cobbles, gravel, and sand; the finest materials include silt and clay, and colloids which do not settle.

Within the grain size spectrum as mentioned earlier that the finer-grained fraction consisting mainly of clay materials - shows relatively high metal contents. In the silt and fine sand fractions the metal concentrations generally decrease as that fraction is dominated by quartz components with low metal contents. Consequently, metal concentrations tend to increase with decreasing grain size in many sediments. Figure 2 shows a generalized profile of the variation of a trace metal with grain size in a sediment.

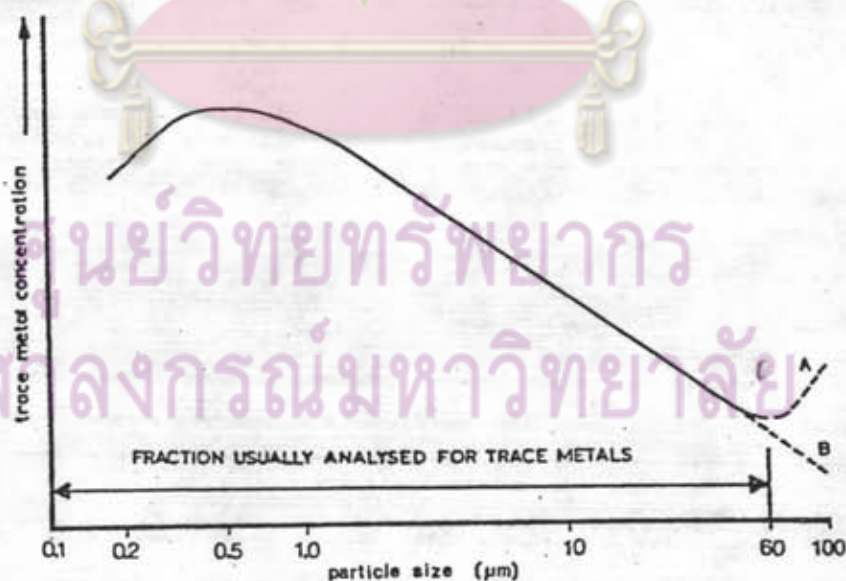


Figure 2 A generalized profile of the variation of the concentration of a trace metal with grain size in a sediment (After Förstner and Wittmann, 1981)

Therefore, the fraction $<63 \mu\text{m}$ is recommended as a normal practice for the analysis of trace metals. This is not only help in better intercomparison of results but also help reducing the grain size effect as well.

In term of trace metal partitioning study sediment will be separated into group by its size and the metal content of each sized group is analysed.

- The Chemical Separation of Sediment Components

Potentially, the chemical separation of components offers the most scientifically satisfying approach to the study of elemental partitioning in sediments because the processes by which the metals are incorporated into the various components are themselves largely chemical in nature. Most techniques employing a chemical attack on a sediment involve a leaching procedure which is specifically designed to put into solution part, or sometimes all, of the total sediment sample.

The most simple selective dissolution technique is to separate residual and total non-residual fractions by a single leaching of sediment samples with an acid e.g., Chester and Voutsinou (1981). The more elaborate techniques which have been designed to establish the distribution of non-residual elements among the components of a sediment are reviewed elsewhere e.g. Förstner and Wittmann (1981), and Salomons and Förstner (1984). The complexity of those techniques depends to a large extent on the nature of information sought.

A large amount of information is available on the distribution of trace metals determined by various operationally defined selective extraction schemes (Chester and Hughes, 1967; Presley, Kolondy, Nissenbaum and Kaplan, 1972; Nissenbaum, 1972; Bruland, Bertine, Koide and Goldberg, 1974). But all these procedures subject the sediment to drying and grinding before chemical fractionation. The oxidation and physical alternation of the sediment during drying and grinding may cause phase or fraction differentiation of elements within the sediment (Brannon, Rose, Engler and Smith, 1977).

The sediments studied to date for trace metal distribution involving chemical fractionation have consisted mainly of deep-sea sediments with little attention given to estuarine systems. Anyhow, Sholkovitz (1973) considered that rapidly deposited sediments of near-shore basins and excellent environment to relate processes of early diagenesis to interstitial water chemistry.

Objective

Since most of the sequential leaching techniques developed are designed to used for deep-sea sediment partitioning study and some has been adapted for studying in near-shore environment, there is still no sequential leaching technique originally developed for near-shore sediment study. In addition, near-shore environment varies greatly from place to place; thus, method developed for a type of near-shore sediment may not be suitable for another near-shore sediment from different environment.

Therefore, it is the prime objective of this study to develop a suitable sequential leaching technique that can be applied successfully for the sediment from the Gulf of Thailand.

Scope and Study Area

As has been mentioned previously that most of the metals associated with sediment are in the size range $<63 \mu\text{m}$, therefore, sediment samples are sieved and the silt- and clay-sized particle will be used in every experiments.

Geochemical properties of sediment such as readily oxidizable organic carbon, inorganic carbon, non-residual fraction and total metals are analysed in order to establish the trend of metal partitioning occurred in the Gulf sediments. The relationships found between metals and each geochemical property will be used in validating the sequential leaching technique developed.

It is impossible that every metals present in marine environment are tested and included in this study; therefore, only a representative from each group of metals namely chromium (Cr) for hard acceptor, zinc (Zn) for intermediate acceptor and cadmium (Cd) for soft acceptor are chosen.

Factor affecting every sequential leaching techniques are temperature, time of extraction, type of reactants, strength of reactants, sediment to extractant ratio and sequence of extraction. However, in this study only type of reactants, strength of reactants and sediment to extractant ratio are tested.

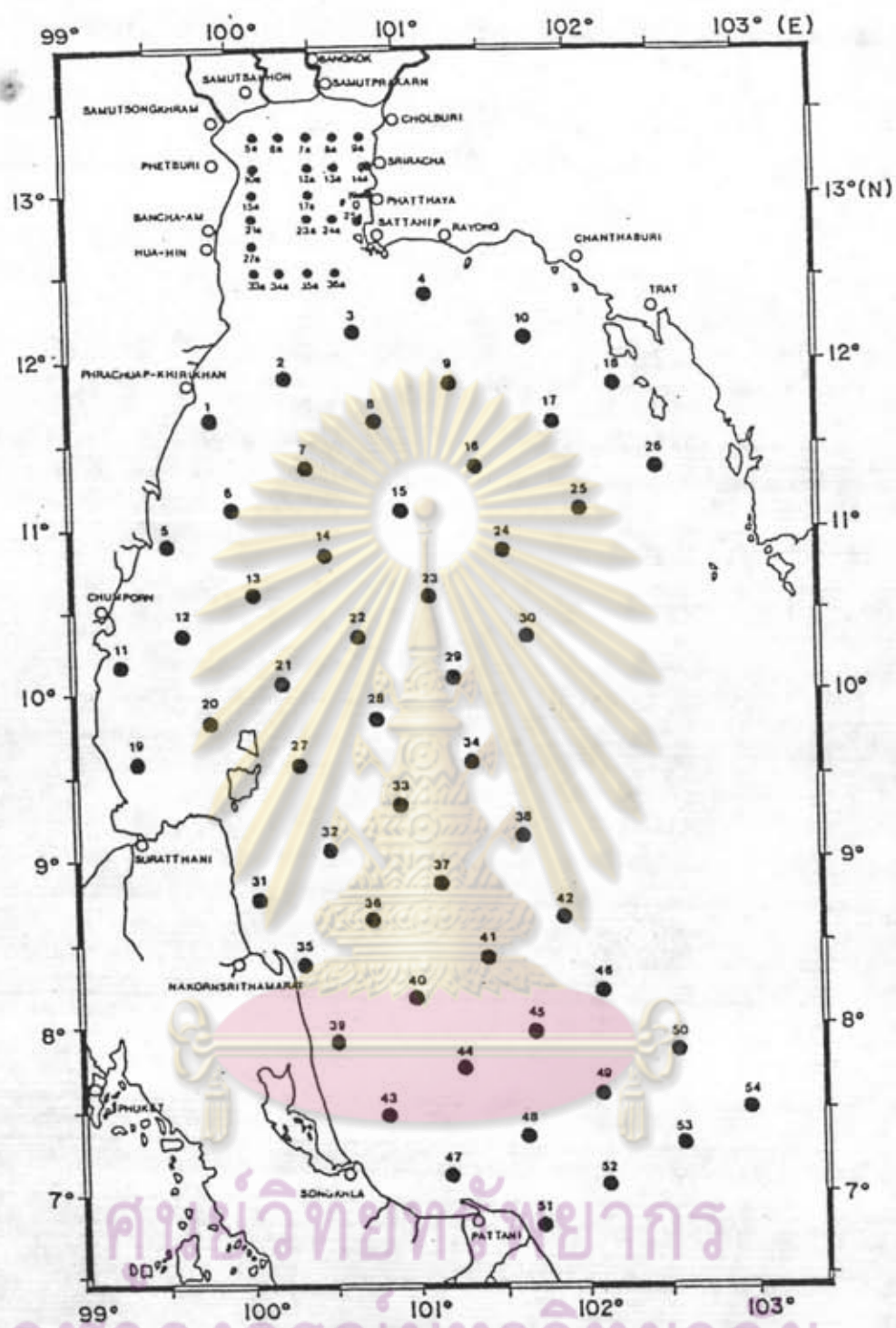


Figure 3 Sediments sampling stations in the Gulf of Thailand.

Sediment samples to be used in this study were collected from the Gulf of Thailand during March to April 1985 by the Hydrographic Department of Royal Thai Navy and Department of Fisheries using a Petersen Grab Sampler. The location of sampling is shown in Figure 3. Position of each sampling station is shown in Appendix A.

Methodology

1. Storage and Sample Preparation

Once a sediment sample is collected on board, only sediment that has not come in direct contact with the grab surface is collected into a clean plastic bag. The sample should immediately be stored at $<2^{\circ}\text{C}$ or frozen until analysis.

The frozen sample is thawed and later transferred to a clean plastic tray under the clean atmosphere. The sample is later freeze-dried. The dried sediment sample is kept in a clean plastic bag until analysis.

Usually air-drying should not have much effect on the total trace element content, but if speciation, organic-extractable trace elements, etc. are of interest, any procedure of drying may lessen the validity of the sample analysis (Maienthal and Becker, 1976). For instance, air-drying of the sample markedly affects cation exchange capacity and iron speciation, and appears to decrease the pH slightly (Schalscha, Gonzalez, Vergara, Galindo and Schatz, 1965). Furthermore, it was stated that the longer a sediment sample is kept air-dried, the greater amount of water soluble and organic material can be extracted (Birch, 1960). Drying or freezing may result in irreversible change which will also affect the complexation state of the trace metals (Hesse, 1971). In the opinion of many authors, freezing at -20°C to -30°C is the best method of storage. The drying temperature of $>60^{\circ}\text{C}$ will oxidize some organic compound (Golterman et al., 1983).

The dried sediment sample is divided into 3 subsamples. The first subsample is kept for future work at a later date and is called a reference subsample. The second subsample is used in size and mineralogical study. The third subsample is used in geochemical and sequential leaching studies.

2. Size and Mineralogical Studies

The dried sediment sample is pretreated in order to remove organic matter using a technique slightly modified from Müller (1967) and Carver (1971) (Appendix B). After removal of organic matter, the sample is wet-sieved through a 63 μm sieve. The portion that is retained on the sieve is called sand fraction while the fraction that passes through the 63 μm sieve is later analyzed for its percentage in silt- and clay-sized particles using sedimentation technique such as those described in Müller (1967) and Carver (1971) (Appendix C).

As for mineralogical analysis x-ray diffraction (XRD) technique is employed in identification and semi-quantification of major group of clay minerals. The full detail of analysis is described in Dharmvanij and Sompongchaiyakul (1987) and Appendix D.

3. Geochemical Studies

The dried sediment sample is sieved through a 70 μm nylon sieve and later analyzed for the following geochemical properties;

3.1 Readily oxidizable organic matter by chromic method (Loring and Rantala, 1977). Full detail is described in Appendix E.

3.2 Inorganic carbon by acid-base titration technique

(Gross, 1971) (Appendix F).

3.3 Metal in non-residual fraction by hot acid leaching technique (Hungspreugs, 1982) (Appendix G).

3.4 Total metal analysis by neutron activation method (Appendix H).

The geochemical study is carried out in 73 samples. After compilation and collation of these properties are completed. The Gulf of Thailand can then be divided into various sedimentary provinces and 2 representative samples from each province are chosen for sequential leaching technique study.

4. Sequential Leaching Studies

The designing of sequential leaching experiment is based on previous experimental results of many workers. The review of previous works will be fully described in Chapter II.

Sediments to be used in these experiments are sieved through a 70 μ m nylon sieve. All containers used in these experiments was polyethylene, teflon and teflon coated materials. The containers and pipette tips should be precleaned in 10% nitric acid bath for 3 days, rinsed with deionized double-distilled (DDI) water, rinse the containers in DDI water bath for 2 days, then rinse again with DDI water before let them dry in clean bench and keep the cleaned containers in plastic bags until used. Care should be taken in every step in order to prevent contamination. Clean room and clean bench provide clean atmosphere for working. Purification of analytical grade chemical reagents is required in order to reduce the

contamination of such metals in the chemical agents which can be showed in blank value (Appendix I). Electronic mechanical shaker and ultrasonic bath are used in mixing and dispersing sediment in solution. Separation of sediment from solution in each step is done by centrifugation at 4,000 rpm for 15 min. Distilled water used in all experiments is DDI water. Measuring of metal concentration is done by using an atomic absorption spectrophotometer. Every calibration curves is prepared from BDH spectrophotometric standard (using standard addition method).

4.1 Experimental Design for This Study

The sequential extraction method carried out is designed for sepecificity, to minimize manipulative losses, and to minimize variations in the proportion of ions extracted due to non-uniform or incomplete extraction, pH effect, or readsorption of solubilized ions. Theoretical considerations are reviewed in Chapter II.

- Disaggregation and Particle Dispersion Disaggregation and particle dispersion are using an ultrasonic bath.

- Separation Separation of sediment is done by centrifugation for 10-30 min at 27,000 g (or 10,000 rpm) was used, in order to settle down a pellicle of very fine material which could remain on the surface of several of the extract solutions. However, access to such centrifuge is not possible. Therefore, an ordinary centrifuge capable producing 4,000 rpm (max.) is employed instead. It is found that at 4,000 rpm all most of particle in solution is settled down, which can be observed from the clearness of supernate. Thus, it

can be assumed that least amount of particle remains in solution after centrifugation.

- Buffering Reactant Solution The type and strength of buffering reactant solution to be used are chosen and decided because of their buffering capacity and intensity.

- Readsorption Where metal concentration is expected to be high, repetitive extraction is employed to prevent the adsorption. However, single extraction is proved to be sufficient and suitable for extracting metals at low concentration from sediment.

- Extraction Sequence The sequence is designed in such a way that cross contamination of one phase with another is minimized.

Considering the storage and preparation techniques employed it is most likely that changes have happened in the exchangeable fraction (Schalscha et al., 1965) prior to analysis; thus, analyzing this fraction may not yield a meaningful result. This is because metals associated with sediment in this fraction through adsorptive bonding (Förstner and Wittmann, 1981). This kind of bonding is relatively weak and sensitive to changes in physico-chemical conditions. Therefore, adsorbed metals can easily be displaced by other cations from accessible ion exchange sites and released from weakly bonding adsorption sites. These metal released from the exchangeable fraction during storage and preparation will be present in the soluble form in which it will later change to soluble salt upon drying.

Based upon this assumption the exchangeable fraction will be extracted along with carbonate and soluble fraction and the sum of all these fractions will be considered together as one.

4.2 Experiment 1

Six samples, two from the Upper, Middle and Lower Gulf respectively, are chosen for this experiment. Each sample is run with its replicate. The sample is firstly sieved through 70 μm nylon sieve and let it dry overnight at 105 $^{\circ}\text{C}$ before weighing. Weighing should be carried out as fast as possible in order to minimize weighing error associated with moisture absorption. Sample size for each replicate is 0.5 g to be extracted by 17 ml extractant (sediment : extractant ratio is 1 : 34). 50 ml screw-capped teflon vial is chosen as a reaction vessel because it can be easily cleaned and can be put directly in the centrifuge, thus avoiding contamination during transfer and separation.

4.2.1 Extractants

1. For Carbonate, Exchangeable, Sorbed (and Salt) Fraction

- NaOAc (1.0M) + HOAc, pH 5.0 purified by passing through chelex-100 column (preparation of this column see Appendix J) before use

2. For Organic Fraction

- sodium dodesyl sulfate (SDS) (1%) + NaHCO_3 (0.2 M), pH 8.8
- NaHCO_3 (0.2 M)

3. For Oxyhydroxide Fraction

- $\text{NH}_2\text{OH}\cdot\text{HCl}$ (1.0 M) + Na-citrate (0.175 M),
pH 5.0
- 10% (w/v) $\text{Na}_2\text{-EDTA}$

4. For Residual Fraction

- HF
- HClO_4
- Suprapure HNO_3 (prepared by distilled HNO_3
(AR) in the acid distillation set)

4.2.2 Extraction Sequence

The sequence of extraction is designed in order to prevent cross contamination between fraction which are as follows:

EXTRACTANTS	REPEAT	RESULTANT FRACTION
a) NaOAc (1.0 M) + HOAc , pH 5.0	x5	carbonate, sorbed (and salt)
b) H_2O (DDI) wash (discard)	x1	
c) SDS (1%) + NaHCO_3 (0.2 M), pH 8.8 at 100 °C	x2	organic
d) SDS (1%) + NaHCO_3 (0.2 M), pH 8.8 at 25 °C	x3	
e) NaHCO_3 (0.2 M) wash (discard)	x1	
f) $\text{NH}_2\text{OH}\cdot\text{HCl}$ (1.0 M) + Na-citrate (0.175 M), pH 5.0	x5	oxyhydroxide
g) $\text{HF-HNO}_3\text{-HClO}_4$ at 200 °C		residual

4.2.3 Procedure

1. For Carbonate, Exchangeable, Sorbed (and Salt) Fraction

Extraction by acetate buffer is repeated 5 times by adding 5, 4, 3, 3 and 2 ml of extractant respectively. Care should be taken during addition of the acetate buffer due to effervescence caused by reaction of the buffer with carbonate materials. After most of the CO_2 is expelled, shake for 10 min. and disperse in a sonic bath for another 10 min. (Note : Continuous use of the bath will cause the rise in water temperature. Therefore, cooling must be provided in order to keep the water temperature at constant level). Centrifuge for 15 min. and pipette the supernate into a polyethylene bottle by means of an autopipette. Supernates from each extraction are mixed thoroughly and the final volume is obtained by weighing the solution down to at least the second decimal point.

Sediment after this extraction should be washed by adding 5 ml of DDI water, shake for 10 min. and allow to disperse in sonic bath for 10 min., then centrifuge for 15 min.. Discard the supernate by autopipette.

2. For Organic Fraction

After the first fraction is extracted and the sediment is washed, the organic fraction is extracted with the SDS solution at 100°C for the first two times and at 25°C for the remaining. Sample handling, extractant volume, separation and dispersion are carried out the same way as described in the previous

fraction. However, the sediment is washed with 0.2 M NaHCO_3 instead of DDI water.

Extraction of samples rich in organic matter with SDS-NaHCO_3 resulting in a solution with low surface tension, thus, making it very difficult in transferring the supernate quantitatively.

1 ml of 10% (w/v) $\text{Na}_2\text{-EDTA}$ chelator should be added to all SDS-NaHCO_3 extracts in order to prevent precipitation of trace metals and to convert them to the same type of metal-organic form.

SDS also crystallizes out of the NaHCO_3 (0.2 M) salt solution at temperature below 19°C . Shaking and warming the extracts is required prior to analysis as the organic matter tends to flocculate out of solution (Robbins et al., 1984).

3. For Oxyhydroxide Fraction

This fraction is successively carried out the same way as the previous fraction by using $\text{NH}_2\text{OH}\cdot\text{HCl}$ + Na-citrate solution, and the residue is washed with 5 ml of DDI water before submitting it to further analysis.

Dissolution of Mn oxyhydroxides rich samples results in vigorous foaming due to carry over of traces of SDS . Attempts to vent N_2O , produced during the reduction of Mn by NH_2OH , by cracking the seal of the cap will result in loss of a portion of the sample (Robbins et al., 1984).

4. For Residual Fraction

15 ml HF and 10 ml HNO₃ are added into the sample, allow to stay overnight. Add 3 ml HClO₄ and heat to 200 °C on hot plate until the fume of HClO₄ disappear. More HF and HClO₄ are required in some samples. Residue after this process should be completely dissolved in 10% HNO₃. Make to volume of approximately 20 ml by weighing down to the second decimal point.

4.3 Experiment 2

Upon the completion of experiment the followings are noted.

a) Having low surface tension the SDS-NaHCO₃ solution cannot be successfully injected into the graphite furnace making the result of the measurement very irratic and unreliable.

b) Concentration level in every extract is very low as observe from its absorption reading. The reading is nearly at the same level as blank.

c) All 6 samples show relatively the same partitioning pattern.

d) Metal content presents in each fraction quite low.

e) Completeness of extraction particularly for the organic and oxyhydroxide fraction is likely to be judged by the change in colour or the extract, for example during the first extraction of oxyhydroxide fraction the colour of the extract is light green which is change to colourless upon the third extrcation.

From these observation the sample size is increased to 1 g to be extracted by 20 ml extractant (sediment : extractant ratio is 1 : 20 and 1 : 23 for organic fraction). The practice of repetitive extraction for each fraction is changed to a single extraction using total volume of extractant at one time. However, the time of extraction remains the same (extraction time in this experiment equals to the sum of 5 repetitive extraction employed in experiment 1.

4.3.1 Extractants

The extraction procedure is the same as in experiment 1 except for organic fraction SDS-NaHCO₃ is changed to acidified H₂O₂. The reagents used in extraction of organic associated fraction is as follows.

- 0.02 M HNO₃
- 30% H₂O₂ acidified by HNO₃ to pH 2.0
- 3.2 M NH₄OAc in 20% (v/v) HNO₃

4.3.2 Extraction Sequence

Because of the change in the type of extractant for organic fraction; thus, the order of extraction must be reconsidered and redesigned as follows.

EXTRACTANTS	RESULTANT FRACTION
a) NaOAc (1.0 M) + HOAc, pH 5.0	carbonate, sorbed (and salt)
b) H ₂ O (DDI) wash (discard)	
c) NH ₂ OH·HCl (1.0 M) + Na-citrate (0.175 M), pH 5.0	oxyhydroxide

EXTRACTANTS	RESULTANT FRACTION
d) H ₂ O (DDI) wash (discard)	
e) H ₂ O ₂ acidified to pH 2.0	organic
f) H ₂ O (DDI) wash (discard)	
g) HF-HNO ₃ -HClO ₄ at 200 °C	residual

4.3.3 Procedure

1. For Carbonate, Exchangeable, Sorbed (and Salt) Fraction

Extractant is the same as 4.2.3(1) but only single extract is performed by using 20 ml of extractant. Commencing the process by alternating between shaking the extract for 10 min. and dispersing in sonic bath for 10 min. 5 times. Total time of extraction is 1 hour 40 minutes)

2. For Oxyhydroxide Fractions

Follow the process of 4.3.3(1) except in the type of extractant employed 4.2.3(3).

3. For Organic Fraction

3 ml of 0.02 M HNO₃ is added then follow with 5 ml acidified 30% H₂O₂. Shake for 10 min. before heating at 85 °C for half an hour then disperse for 10 min. in sonic bath. Continue heating for another half hour. Repeat the dispersing and heating process one more time (total time = 2 hours).

Add another 5 ml of acidified 30% H₂O₂, shake for 10 min. and heat at 85 °C for 0.5 hr. Alternate between

10 min. dispersing and 0.5 hr. heating until the total time of extraction is 3 hours.

Cool to room temperature before adding 10 ml of 3.2 M NH_4OAc in 20% (v/v) HNO_3 . The extract is shaken for 0.5 hr. at room temperature. Separate the supernate from residue by centrifugation at 4,000 rpm for 15 min.

4. For Residual Fraction

The same process as 4.2.3(4).

4.4 Experiment 3

Confirm the experiment 2 by using the same processes in every fraction.

4.5 Experiment 4

Using the same procedure as experiment 2, and 3, but changing in sediment : extractant ratio from approximately 1 : 20 to 1 : 10 (by using halving volume of extractants in the former experiments).

4.6 Experiment 5

Sediment : extractant ratio in this experiment was 1 : 10, but changing in concentration of extractants of carbonate and oxyhydroxides fractions to half of the former extractant concentration except in organic fraction which uses the same extractant as described in experiment 4.

4.7 Leaching and Total Analysis

4.7.1 Leaching of Non-lattice Held Metals

Cd, Cr and Zn in this fraction are leached by the same method as described in 3.3.

4.7.2 Total Metal Content

0.5 g of fine-grained sediment is digested using the same method as residual fraction.

4.8 Analysis of Metal by AAS

The extracts in the form of solution are analyzed for their metal contents by graphite furnace atomic absorption spectrophotometer (GFAAS) (for Cd) and flame atomic absorption spectrophotometer (FAAS) (for Cr and Zn). In order to minimize the matrix effect during measurement the standard addition method is employed in preparation of calibration curves.

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