



## CHAPTER I

### INTRODUCTION

#### BACKGROUND

Sediments are important carrier for trace metals in hydrological cycle. They can also reflect the current quality of the aquatic system as well as the historical development of certain hydrological and chemical parameters. Comparative analysis of total concentration of longitudinal and vertical profiles can be helpful in determining metal anomaly in zone of mineralization (Rose *et al.*, 1981), as well as from pollution sources (Solomon and Forstner, 1984). The study of dated sediments cores has also proved to be especially useful as it provides historical records of the natural background levels and the man-induced accumulation of metal.

In case that a short term or past pollution event is not or only insufficiently traceable from water analysis, sediment analysis plays an important role within the framework of environmental forensic investigation (Meiggs, 1980). In addition to what mentioned above sediment is not only an indicator medium, but also depending on environmental condition, sinks and sources for metal in the surface water. This is because metals are not necessarily fixed permanently by sediments, but may be recycled via biological and chemical agents, both within the sedimentary compartment and also back into the water column (James, 1978). The recycling of mineralised organic matter and pore-fluid transfer processes are essential component of models that are devised to describe the nutrient and pollutant dynamics of aquatic system.

Generally, metals are largely associated with silt and clay fractions of detrital sediments as a result of chemical and physical weathering of parent rocks where metal minerals degrade into the finer fraction. Authigenic

processes during transport and deposition and post-depositional diagenetic processes alter the elemental chemistry of source material to produce the final sediments. These processes include chemical reactions (for example, dissolution, precipitation and sorption) induced by changes in pH, oxidation potential, and chemical speciation that result from natural biogeochemical cycles and inputs of material from a myriad of natural and contaminant sources. The metal content of sediments is thus a composite of natural and contaminant source materials and reaction products and is mostly associated with the fine-grained fraction.

Since fine-grained sediments, or the fine-grained fraction of a mixed sediment, is potentially a sensitive indicator of sediment contamination, therefore pollution assessment is made difficult by the need to differentiate contaminant levels from background levels in sediments of different origins and textural characteristics (Hanson *et al.*, 1993).

Metals in sediment come from lithogenic (natural) and anthropogenic (man-made) input. Thus, it is very difficult, by using total digestion techniques, to distinguish between these two sources. Therefore, there have been various attempts e.g. Chester & Hughes (1976); Chester & Messiha-Hanna (1970); Agemain & Chau (1976) cited by Chester and Voutsinou (1981) to fractionate the metals found in sediments. But perhaps the most useful one from a practical point of view, is that which fractionates between lattice-held (assumed that comes from natural processes, or residual) and non-lattice-held (assumed that comes from human activity, or non-residual).

Residual metal is herein defined as those which is part of the silicate matrix of the sediments and is located mainly in the lattice structures of the component minerals (Gibbs, 1973).

Non-residual metal is those which is not part of the silicate matrix and has been incorporated into sediments from aqueous solution by processes such as adsorption and organic complexation (Gibbs, 1973), including those originate from polluted waters (Chester and Voutsinou, 1981).

Eventhough, the techniques of partial or partial extraction are more suitable in assessing trace metal pollution in sediments. But, most of them are complex and time-consuming comparing with the total digestion technique. The following are summary of advantages and disadvantages of the two main categories of digestion techniques used in assessing trace metal pollution in sediment.

*Total Digestion* : This techniques will often yield data on the both lithogenic and anthropogenic metal in sediment. Samples are often digested with a mixed, high concentration acids as shown in table 1.1.

This kind of techniques is rather simple and less time-consuming than partial extraction. Moreover, it involves less handling, thus, making it less prone to contamination. However, the analytical results cannot be used directly for pollution assessment but have to go through comparison procedure involving the use of reference elements eg. Windom *et al.*, 1984; Din, 1992; Loring, 1992; Hanson *et al.*, 1993.

*Leaching* : The analysis of non-residual fraction often yields more meaningful data on the extent of trace metal pollution than those of the total sediment (Chester and Voutsinou, 1967). The most simple selective dissolution technique separates residual and total non-residual fractions by a single leaching of sediment samples with an acid.

The analysed data by leaching method can be used directly in assessment of metal pollution. However, factor affecting leaching techniques are numerous, eg. disaggregation, mixing of sample and leach, buffered extractant, readsorption, temperature and time, extraction sequence, chemical reactivity and kinetic effects (Sompongchaiyakul, 1988).

In addition, the more sophisticated techniques may involved many extraction steps which are very time-consuming and risky to contamination.

Table 1.1 Procedures for total digestion method.

Procedure	Reference
HCl+HF+HNO <sub>3</sub> +HClO <sub>4</sub> (ashing at 400° C)	Bruland <i>et al.</i> (1974)
250 mg of sediment sample + 10 ml HNO <sub>3</sub> + 5 ml HF+ 3ml HClO <sub>4</sub>	Windom <i>et al.</i> (1989)
HF+HNO <sub>3</sub> +HClO <sub>4</sub>	Agemian and Chau (1975) Trefry and Presley (1976) Taylor (1979) Donazzolo <i>et al.</i> (1981) Abu-Hilal (1987) Windom <i>et al.</i> (1984) Zwolsmam <i>et al.</i> (1993)
HCl+HF+HNO <sub>3</sub>	Bernas (1968) Rantala and Loring (1975) Okamata and Fuwa (1984) Abu-Hilal (1993) Hanson <i>et al.</i> (1993)
500 mg of sediment sample + 10 ml HNO <sub>3</sub> + 5 ml HF+ 15ml HCl(digestion bomb)	Subramanian & Mohanachandran (1990)
500 mg of sediment sample + 0.25 ml HNO <sub>3</sub> + 6 ml HF+ 0.75ml HCl (90° C)	Macdonald <i>et al.</i> (1991)
HNO <sub>3</sub> +H <sub>2</sub> SO <sub>4</sub> +HClO <sub>4</sub>	Kramer <i>et al.</i> (1991)
500 mg of sediment sample + 10 ml HNO <sub>3</sub> +10 ml HF+ 3ml HClO <sub>4</sub>	Din (1992)
200 mg of sediment sample + HNO <sub>3</sub> +HF+ HClO <sub>4</sub>	Presley <i>et al.</i> (1992)

Table 1.2 Procedures of leaching method for metals in non-residual fraction.

Procedure	Reference
8N HNO <sub>3</sub> for 2 hour	Carmody <i>et al.</i> (1973) Pavoni <i>et al.</i> (1987)
5 g of sediment sample + 75 ml of 0.5 N HCl	Chester and Voutsinou (1981)
1 g of sediment sample +1 ml of 1 N HNO <sub>3</sub> 150°C , 10 min	Hungspreugs and Yuangthong (1983)
0.5 M HCl	Abu-Hilal (1987)
0.25 g of sediment sample + 10% HNO <sub>3</sub>	Windom <i>et al.</i> (1984) Greenaway and Rankine-Jone (1992)

No matter what technique is used in sample preparation, after the determination of metal concentrations in sediments, the metal data are compared and interpreted (Forstner and Salomon, 1980) for pollution assessment.

Comparison which may be used in assessing the extent of anomalous (antropogenic) trace metal concentrations in sediments is done by looking at their magnitude in relation to baseline, or 'natural', levels. However, this is particularly difficult for coastal zone because sediments can be deposited under such a wide variety of environments. For example, factors such as redox conditions, which can exert a considerable influence on the geochemistry of a sediment, and dilution by trace metal-poor components, such as calcium carbonate, can vary greatly from place to place (Chester and Voutsinou, 1981). Without correction for variable background levels, meaningful comparisons of metal concentrations often are impeded by large levels of bias and variability (Hanson *et al.*, 1993).

Forstner and Wittmann (1984) have considered the problems inherent in the selection of a sediment baseline material for environmental studies and have proposed a number of criteria which should be fulfilled in order to best satisfy the principal requirements. These criteria include :

- 1) the baseline material should have a grain size, material composition and origin which are similar to recent deposits;
- 2) it should be uncontaminated by anthropogenic influences;
- 3) a large number of analyses of the material should be available.

In practice, it is almost impossible to adequately fulfill all these criteria in a single baseline material. Forstner and Wittmann (1984) have proposed that shales seem to offer the best compromise for a generally acceptable baseline sediment. There are, however, even more critical problems involved in the selection of a baseline material against which to compare the concentrations of non-residual trace metals in sediments. For example, the analysed data for shales given most literatures are of total samples (Chester and Voutsinou, 1981), thus, sediment samples have to be analysed by total digestion method as well before comparing with shales.

However, even though samples are digested by the same techniques either total digestion and partial digestion, direct comparison of the analyzed data is still doubtful. This is because of the different in grain size and mineral compositions between each samples.

For example, metals are not homogeneously distributed over the various grain-size fractions, and large differences in total metal concentrations are observed in sediment samples from a single locality (Forstner and Solomons, 1980). As for the difference in mineral compositions, it has been shown by many researchers that metals appear to be favorably associated with certain fractions of sediments. In case that the sediment sample under consideration composes largely of metal-poor components eg. quartz and carbonate. Total digestion of this type of

sediment often yields a relatively low metal contents than those sediments compose largely with silt and clay.

A variety of approaches for reducing natural variability has been used to improve the statistical power of data intercomparison (Hanson *et al.*, 1993). Metal concentrations are often normalized to a conservative component whose levels are unaffected by contaminant inputs, for example, grain size, Al, Fe, Ni and Li (De Groot *et al.*, 1976; Forstner and Wittmann, 1984; Luoma, 1990; Trefry *et al.*, 1976; Wu, 1984; and Loring, 1990).

In 1992, Loring compared normalization method, namely, the granulometric and geochemical methods for metal data in sediment. It was found that overall geochemical normalization was superior than granulometric method because it compensates for the mineralogical as well as the natural granular variability of metal concentration in sediment.

Geochemical 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 sediment enrichment factor (SEF) (Kemp *et al.*, 1976) is employed as :

$$SEF_s = \frac{(E_s/R_s) - (E_a/R_a)}{(E_a/R_a)}$$

$E_s$  : The observed elemental concentration in sediments

$E_a$  : The average observed elemental concentration in sediments

$R_s$  : The reference element concentration in sediments

$R_a$  : The average reference element concentration in sediments

Where  $SEF_s$  is the enrichment factor of an element "s" in the analysis material relative to a reference element 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 .

The most commonly used reference 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 and Al concentrations do not always vary significantly with grain size (Loring, 1977). Therefore, the use of enrichment factors relative to reference element is possible to estimate the partitioning of an element between the residual fraction of sediments providing the ratios are known for aluminosilicate residual minerals.

Schropp and Windom, (1988) have described criteria of reference elements that can be used to normalize sediment metals concentrations as follows :

- It is the most abundant naturally occurring metal.
- It is highly refractory.
- Its concentration is generally not influenced by anthropogenic.

In Thailand, sediment study has also been used in assessing impact of trace metals in marine environment.

The early works reported metal contents in sediments on different bases that cannot be compared directly. These include the works of Polprasert *et al.* (1979), AIT (1980), Idthikasem *et al.* (1981), who worked on total metals in sediments from the Upper Gulf of Thailand.

Other works that used total digestion method as well but trying to assess metal pollution by comparison with average sediment reported by Rankama and Sahama (1960) are :

Menasveta and Sawangwong (1979) who studied distribution of heavy metals in the Chao Phraya river estuary,

Menasveta and Cheevaporanapiwat (1981) who worked on sediments from the mouth of the four rivers, Mae Klong, Ta Chin, Chao Phraya and Bang Pakong, and

Chanpongsang (1982) studied the Chao Phraya estuarine sediments.

The interpretation may be doubtly useful, considering the problems inherent in the selection of baseline material for sediment study.



Table 1.3 Reference element used for interpretation of metal in sediment.

Reference Elements	Reference
Al	Windom <i>et al.</i> (1984) Schropp and Windom (1988) Subramanian <i>et al.</i> (1988) Subramanian <i>et al.</i> (1989) Windom <i>et al.</i> (1989) Hungspreugs and Yuangthong (1983) Subramanian & Mohanachandran (1990) Din (1992) Hanson <i>et al.</i> (1993) Gagnon <i>et al.</i> (1993)
Fe	Trefry and Presley (1976) Sinex and Wright (1988) Trefry <i>et al.</i> (1992)
Mn	Subramanian <i>et al.</i> (1988) Zwolsman <i>et al.</i> (1993)

Apart from direct comparison with baseline (natural) material, another approach of assessing metal pollution is also employed. A number of researcher (Clifton and Hamilton, 1979; Keinonen *et al.*, 1989; Swart *et al.*, 1991; Macdonald *et al.*, 1991 cited by Meankumnird, 1996) used coring method for sample collection and constructed vertical profiles of metals in relation with depth and/or age. The method eliminates the problem of selecting baseline material because it can be reasonably assumed that sediment at depth was deposited in the same sedimentary environments as those of surface sediments but without any human influence. Though, this approach may look promising but it still depends on many assumptions, for example : the works of Jaturanon (1983), Hungspreugs and Yuangthong

Hungspreugs and Yuangthong (1983) and Meankumnird (1996). These works employ normalization technique to help adjusting analysed data for comparison by assuming that Al is the most suitable normalizer but do not test the assumption.

In the last approach for interpreting sediment data analyzed by total digestion method, sediment enrichment factor values (SEF) were used as an indicator for antropogenic input in sediments. However, baseline material which is used in SEF calculation may not represent the composition of land-derived components in Thailand because

1. the lack of baseline data for elemental abundance in Thailand
2. suitable reference elements for using in SEF calculation have never been studied.

The works of Dharmvanij (1987) and Meankumnird (1996) both used average world sediment and average crust reported by Bowen (1979) and Turekian and Wedepohl (1961) for calculation.

It is obvious that metal concentrations in sediments analyzed by total digestion techniques cannot yield any useful information for pollution study without proper interpretation. Thus, the problems related to using sediment for assessment of metals pollution in Thailand fall into, at least two major aspects.

- Which reference element(s) is (are) suitable for interpretation of sediment data in the Gulf of Thailand.
- What are the average values of elemental compositions of crustal materials in Thailand. These values can be used for SEF calculation which will help predicting anomaly in metal content for pollution assessment.

#### RELATED RESEARCHES

Schropp and Windom (1988) described an approach for interpreting metals concentration in coastal sediments along the coast of Florida. The interpretive tool is based on the relatively constant natural relationships that exist between metals and aluminium. "Clean" coastal sediments from

throughout Florida were collected and their metal contents determined. Metal/aluminium regressions and prediction limits were calculated and diagrams of metal/aluminium relationship constructed. Metal data from coastal sediments can be plotted on these diagrams to determine whether measured metal concentrations represent natural concentrations or metal enrichment. Over 450 sediment samples from estuarine and coastal marine areas of the southeastern United States remote from pollution sources were analyzed for trace metals. Although these sediments are compositionally diverse, As, Co, Cr, Cu, Fe, Pb, Mn, Ni, and Zn concentrations covary significantly with Al, suggesting that natural aluminosilicate minerals are the dominant natural metal bearing phases. Cd and Hg do not covary with Al apparently due to the importance of the contribution of natural organic phases to their concentration in sediment. It is suggested that the covariance of metals with Al provides a useful basis for identification and comparison of anthropogenic inputs to sediments.

Din (1992) studied the use of aluminium in normalizing heavy-metal data of estuarine and coastal sediments from Straits of Malaka. Sediment samples were collected from 24 stations along the Malaysian coast of the Straits of Malaka. Trace-metal concentrations were then determined using an atomic absorption spectrophotometer for Al, Fe and Mn, while Cd, Cr, Ag, Au, Cu, Zn, As, Pb, and Sn were analysed using an induced-couple plasma/mass spectrophotometer. Each metal was then normalized using Al as reference element. It was concluded that Al can be used to normalize granular variability in trace-metal analyses of the sediments of the Malaysian coast of the Straits of Malaka.

Greenaway and Rankine-Jones (1992) undertook the task of assessing the pollution status of Hellshire, Jamaica from coastal sediments. Sample were determined by instrumental neutron activation analysis. By considering the percentages of the fine components of the sediments and enrichment factors based on the average composition of representative carbonate sediments taken form the area, the sources of non marine sediments have been identified. However, enrichment factors based on the

average composition of sedimentary shale showed that the area had not been contaminated, for the elements under study, by sediments reaching the coastal area from the identified sources.

Yusof and Wood (1993) employed the elemental ratioing technique in their environmental assessment of coastal sediments. The distribution of heavy and trace elements in coastal sediments was obtained by elemental analysis techniques such as INAA and GFAAS. The elemental concentrations were expressed in terms of enrichment factors derived by the elemental ratioing method, and evaluation was done by comparison to those found in SRMs. The associated sources of polluting elements were traced from their distribution patterns and, where applicable, related to the surrounding activities. Sample to sample variation was also taken into account to establish any correlative factor.

Hanson *et al.* (1993) studied the extent of elemental contamination in estuarine and coastal environments by using geochemical and statistical modelling of sediment. Sediment of variable mineralogical, textural and metal contaminant composition from 38 estuaries along the Atlantic and Gulf of Mexico coasts of the United States were collected and analyzed for total Al, Ag, As, Cd, Cr, Fe, Hg, Mn, Ni, Pb, Se, Si, Sn, Ti, and Zn concentrations. Observed covariation of elements at 15 estuaries remote from contaminant inputs, linear regressions of metals on Al were used to model the metal content in baseline sediments. A geochemical model for the covariation was developed, verified and used to guide the statistical modelling approach. Comparison of metal concentrations predicted by the models with those occurring in uncontaminated geological materials suggests that baseline relationships are valid for the entire region sampled. Using these baseline relationships, sediment metal concentrations can be partitioned into natural and anthropogenic fractions. Models improve the comparability of metal levels in sediments by correcting for variable background concentrations that, if left uncorrected, only serve to increase total data variability and reduce detection of spatial and temporal differences.

## OBJECTIVES

1. To determine type(s) of reference element(s) suitable for interpretation of trace metal data in sediments of Mae Klong watershed for pollution study.
2. To test the study result with trace metal data from sediments in Mae Klong watershed.

## HYPOTHESIS

Enrichment factor values calculated from elemental concentration value of parent rocks in Mae Klong watershed may be compared more favorably than those of average world sediments.

## SCOPE OF THESIS

In order to achieve the above objectives, both field and laboratory works were carried out. The field work involved collection of rock and soil samples in Mae Klong watershed area and sediments in Mae Klong river estuary.

Laboratory work involved analyses of reference elements such as aluminium, iron, manganese and trace elements such as lead, copper, and zinc in rock, soil and sediment samples were analysed used AAS technique as proposed by Shapilo (1975) and X-Ray Fluorescence technique as compiled by Sangsila (1994).

## APPLICATION OF THE STUDY

1. Establish the kinds of reference elements in Mae Klong watershed suitable for interpreting analytical results of sediment by total digestion method.

2. Distinguish natural versus enriched metal concentrations in Mae Klong sediments. The degree of enrichment can also be estimated based on the deviation from the expected natural range.

3. Provide supporting data for management of metals pollution in Mae Klong river and other rivers in Thailand.



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