Aluminium Normalization of Heavy-Metal data from Estuarine and Coastal Sediments of the Gulf of Thailand

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Abstract

Sediment samples were collected from 20 stations along the coastal line of the Gulf of Thailand. Trace metal concentrations were then determined using an atomic absorption spectrophotometer for Al, Fe, Mn, while Zn, Cr, Cu, Pb, Cd, Ag,and Ni were analysed using an inductively coupled plasma atomic emission spectrophotometer. Each metal was then normalized using Al as the reference element. Two of the metals, namely Zn and Cr were shown to covary strongly with Al, with correlation coefficient (r^2) ranging between 0.88-0.90. Four other metals also showed positive linear correlations with the reference element, with r^2 values of 0.69 for Cu, 0.60 for Fe, 0.52 for Pb, and 0.50 for Cd. The last 3 metals, Mn, Ag, Ni did not covary with Al. On the whole, it was concluded that for most cases, Al can be used to normalize granular variability in trace-metal analyses of the coastal sediments of the Gulf of Thailand and the adjacent area such as Straits of Melaka.

1. Introduction

Although studies on heavy metals in the coastal waters of Thailand have existed for more than 20 years, the available data and publications are very limited and patchy. Most of the studies that have been conducted are on metal contents in living organisms such as fish and shellfish [1],[2],[3],[4],[5], with less on metal contents in the environment [6],[7],[8]. With regard to metal contents in the coastal sediments, both the studies by National Research Council of Thailand in the Upper Portion of the Gulf of Thailand [7],[8] and by Menasveta & Cheevaparanapiwat [6] quoted absolute values of individual metal.

Although this kind of information is useful, it has its limitation, and in some cases it may lead to erroneous conclusions. This is because particulate metals from natural and anthropogenic sources accumulate together in sediment. In order to determine the level of metal pollution in an area we need to isolate the two metal proportions and this can pose problems because sedimentary metal loads can vary by several orders of magnitude, depending on the mineralogy and grain size distribution of the area as described by Loring [9]. In order to overcome this problem, a normalization procedure is suggested. With this procedure, we will be able to calculate the natural component of the total concentration by defining the ratio of natural concentrations to that of some normalizing factor whose concentration is unaffected by human activity which would then enable us to detect and quantify any anthropogenic metal contribution to the system.

Loring [9] discussed two approaches to normalization of metals in sediment, namely, the granulometric and geochemical methods. Overall, geochemical normalization was shown to be superior because it compensates for minerological as well as the natural granular variability of the metal concentration in the sediment. There is no concensus on the appropriate sediment constituent to be used for normalization. Among those used have been aluminium, iron, lithium, total organic carbon, and grain size. However, aluminium has been widely used for normalization of trace-metal data from marine suspended matter and sediments because of its high natural concentration and minimal anthropogenic contamination and because it is a structural element of clays. Since trace elements tend to be adsorbed onto surfaces of particles, their concentrations naturally increase as particle sizes decrease. As a central component of clay, the smallest sized particles, aluminium, can serve as a measure of clay content of sediment sample with which the bulk of the trace metals are associated. Schropp and Windom [10] recommended using aluminium as a reference element to normalize sediment metals concentrations because it is highly refractory and its concentration is generally not influenced by anthropogenic sources.

One of the basic assumptions used in the metal/aluminium approach is that it cannot be applied universally. It has been shown to work for samples from the Gulf of Paria [11], [12] and more recently for estuarine and coastal sediments from southeastern United States [13]. For high latitude sediments however, use of aluminium as a metal normalizer is not recommended because in these sediments, the Al concentrations do not always vary significantly with grain size [14],[15],[16]. Thus the present study was conducted in order that a proper interpretation of metal pollution in the Southeast Asian Seas such as Gulf of Thailand can be accomplished.

2. Materials and Methods

Sampling Procedure

Twenty stations were selected along the coastal line of the Gulf of Thailand (Fig.1). At each site, replicate sediment samples were taken using the grab sampler. A small sample was then taken in the middle of the grab just beneath the top surface using a non-metallic spatula in order to reduce metal contamination from the sampler. The samples were placed in sealed plastic bags and taken to the laboratory for analysis.

Laboratory Analysis

In the laboratory the sediment samples were freeze dried after which approximately 1-g portions were finely ground. About 250 mg samples were then measured accurately into 100-ml teflon beakers followed by addition of 10 ml concentrated HNO_3 and 10 ml of concentrated HF. The samples were left to digest in the fume cabinet, overnight, at room temperature. The next morning, 3 ml of $HClO_4$ was added into the beakers and these were then placed on the hot plates set at 120 ^{o} C. Once the acids had evaporated to dryness, 2 ml of concentrated HNO_3 was added and the samples were reheated to dryness. The beakers were then set aside to cool. Finally, 2 ml of 10% HNO_3 was pipetted into the beakers, and after a few swirls to dissolve the residue, the samples were poured into plastic scintillation vials. Each beaker was then rinsed with 18 ml of double distilled water and this was added into the vials. Prior to analysis of the metals, 10 ml 1/50 dilution for Al, and 1/10 dilution for the other metals were prepared from the sample solutions. Determination of concentrations of Al, Fe and Mn was conducted using Atomic absorption spectrophotometer (Perkin Elmer 3300) while Inductively coupled plasma atomic emission spectrometer (optima 3000) was used for Cd, Cr,Ag,Cu,Zn,Pb, and Ni analysis. All the vessels and materials used for metal determinations were cleaned with acid and dried in laminar flow hood before use. In order to use the normalization procedure, a total digestion of the sediment samples is required. This was monitored by analysing a standard reference material for trace metals (MESS-1) from the National Research Council, Canada. The results are given in Table 1. The titration method of Gaudette et al.[20] was used for the determination of organic carbon in the sediments.

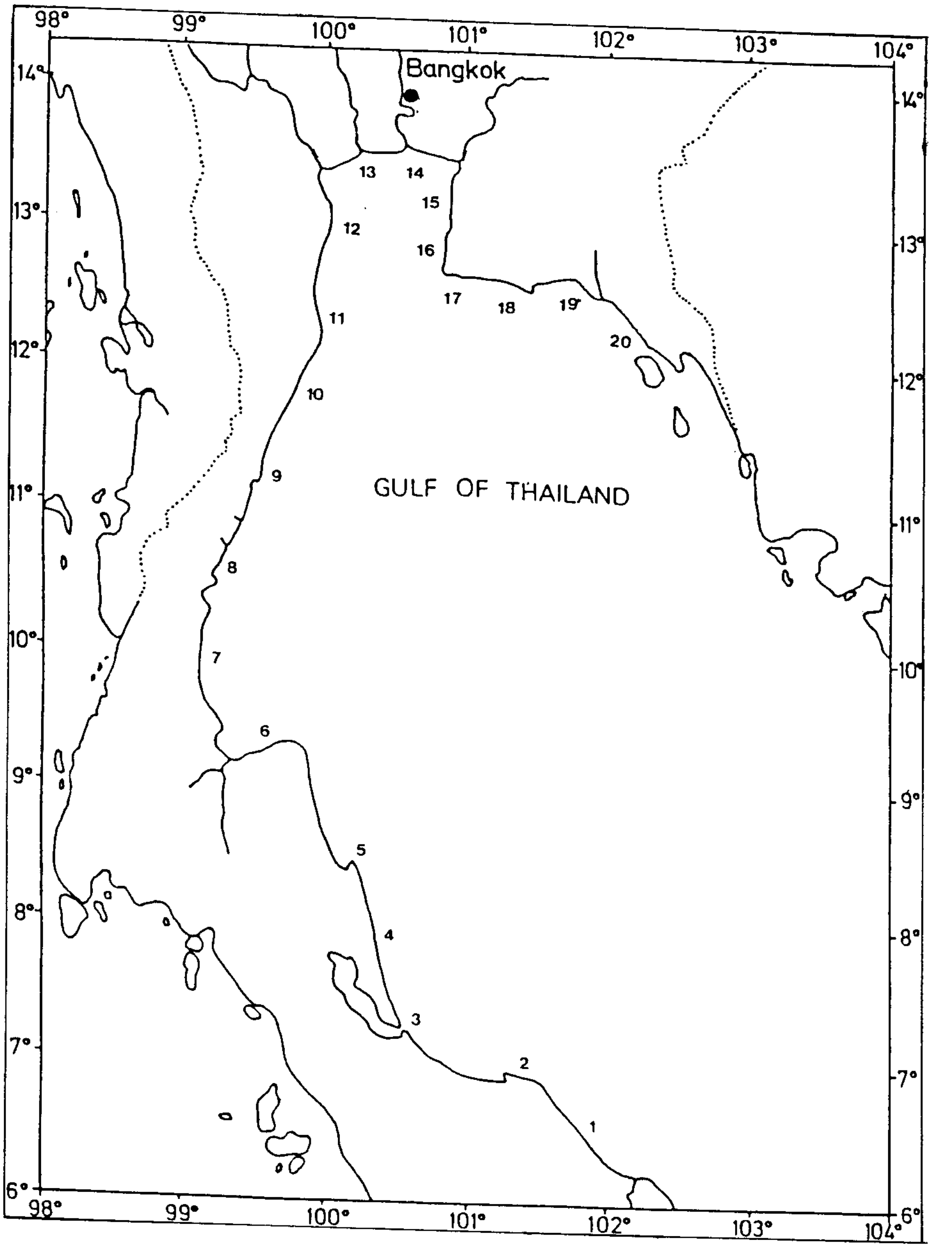


Figure 1. Map of the Gulf of Thailand showing the location of the sampling stations.

Statistical Analysis

Regression analysis was run for all the metals using Al as the independent variable. Log-transformation were first carried out for all the data in order to satisfy the assumption of constant variance and normality, as suggested by Schropp and Windom [10].

3.Results and Discussion

Figure 2 shows the scatter-plot for Zn vs. Al, Cr vs. Al, with the resultant regression line. Zn is shown here to have a very strong positive correlation with Al, with an r^2 value of 0.90. Cr is also shown here to be positively correlated with the normalizer, Al. The correlation coefficient (r^2) calculated for this metal was 0.88. The strong covariance of concentrations of Zn and Cr against Al suggest that Al should be used as the normalizer to correct the effects of changing grain size and mineralogy on concentrations of Zn and Cr in the sediments of the Gulf of Thailand.

Scatter plots and regression lines of Cu, Fe, Pb, and Cd against Al are shown in figure 3. Positive correlation between Cu, Fe, and Al is shown here, with r^2 value of 0.69 and 0.60 respectively. Pb and Cd are shown to have positive covariance with Al, as reflected by an r^2 value of 0.53 and 0.50. However, the strength of the relationship between the concentrations of these metals, is somewhat reduced as compared to Zn and Cr.

The last figure (Fig.4) indicates that Mn,Ag, and Ni do not covary with aluminium. Regression analyses here resulted in an r^2 value of 0.21 for Mn, 0.20 for Ag, and 0.14 for Ni.

On the whole, the study apparently indicates that for the sediment samples along the Gulf of Thailand, Zn and Cr covary strongly with aluminium with r^2 value ranging between 0.88-0.90. Aluminium is also shown to covary with Cu and Fe and to a lesser extent with Sn. It is also evident from this study that for these particular sediment samples, Mn, Ag, and Ni do not covary with aluminium. For the most part, the covariance of metals with Al found in this study is similar to what has been reported earlier for low latitude areas such as the Straits of Melaka [17] and the southeastern United States [13], although some differences do exist. For example, in the southeastern United States, Windom et al.[13]. indicated strong correlations between Al and Zn, Cr, Cu, Fe, and Pb, as was found in this present study. However, while Windom et al.[13]. reported strong correlations between Al and two other metals, Mn and Ni, no such covariance existed for the sediment samples collected during this study. On the contrary, Cd, which was shown not to covary with Al for the sediment samples of southeastern United States does covary with the normalizer for the Gulf of Thailand. The results found in this study are similar to what have been reported by Din [17] in the Straits of Melaka. However, the correlation coefficient between the concentrations of Cu,Fe, Pb, Cd, and Al, as reported by Din [17] is rather higher than what have been reported by this study (Table 2).

Daskalakis [21] found that the r^2 value of As,Cr,Cu,Ni,Pb,Sn,Zn with Fe and Al generally decreased at sites near population centers, implying that those elements are most likely to be present as contaminants. If this assumption is true, since the r^2 value of Cu,Fe,Pb, and Cd with Al in the Gulf of Thailand decreased relative to those found in the adjacent seas such as Straits of Melaka. It might imply that contamination by those metals in the Gulf of Thailand is much more influenced by anthropogenic input than in the Straits of Melaka.

The findings of this study indicated that for the most part, the metal/Al approach to normalization appears to work for the sediments from the Gulf of Thailand, just as it did for the sediment samples of the Straits of Melaka and southeastern United States. However, for some of the metals, including Mn, Ag, and Ni, the grain-size effect should be normalized by other means since the concentration of these metals in the Gulf of Thailand samples was not shown to covary with Al.

Normalization procedures using various other clay mineral indicator elements as well as total organic carbon have been documented in several earlier reports. Windom et al [13]. indicated that some metals, such as Cd, do covary with TOC but at a far less significant level than Al. In this study, the TOC contents in sediments were quite low (usually much less than 10 %).

Table 1. Analysis of reference material (MESS-1). All units in ppm.

Element	Certified value	This study (n=6)	% recovery	C.V.*
Zn	191±17	200.4±12	110.7	5.99
Cr	. 71±11	58.9±3	82.9	5.09
Cu	25.1±3.8	20.8±1.3	82.9	6.25
Pb	34.0±6.1	29.5±2.4	86.8	8.14
Cd	0.59±0.10	0.41±0.07	71.2	16.67
Ni	29.5±2.7	26.3±1.9	89.2	7.22

* C.V. = Coefficient of variation.

Table 2. Comparison of the correlation coefficient (r^2) between Al and other metals in the sediments from the Gulf of Thailand and Straits of Melaka.

Element	Gulf of Thailand	Straits of Melaka*
Zn	0.902	0.903
Cr	0.875	0.926
Cu	0.697	0.893
Fe	0.602	0.930
Pb	0.527	0.858
Cd	0.505	0.718
Mn	0.215	0.194
Ag	0.202	0.143
Ni	0.143	0.063

*Ref.17.

Thus its use as a normalizing factor does not look very promising. One weakness of TOC as a normalizer, however is the fact that TOC itself is subject to considerable augmentation by human activity and is often a contaminant.

Use of Fe as a reference metal to normalize for grain-size effect in estuarine and coastal sediments from the inner Virginia shelf was reported by Rule [18]. However, total Fe concentration in many nearshore sediments can be distorted by the accumulation of iron compounds in these areas and this makes it an unsuitable alternative. Srisuksawad et al [19]. reported the strong covariance of concentrations of Al, Ti and Sc in the Gulf of Thailand sediments and suggested that they should be equivalently useful normalizing elements to correct for effects of changing grain-size and mineralogy on concentrations of other metals. Loring [9] highly recommended the use of Li as a normalizing element to correct for grain-size effect, particularly for high latitude coastal sediments. In fact, even for low latitude samples he regarded Li to be as good, if not better than Al.

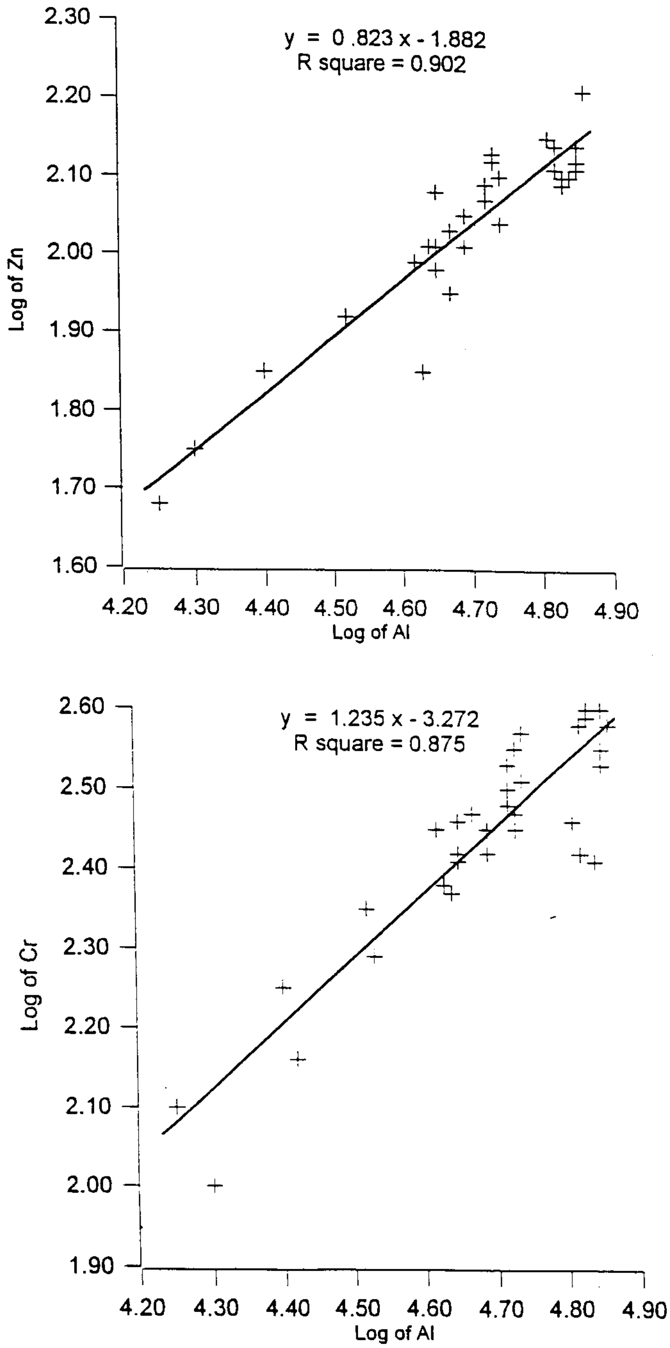


Figure 2. Zn : Al, and Cr : Al scatter plots for the coastal sediments of the Gulf of Thailand. The solid line represents the regression line.

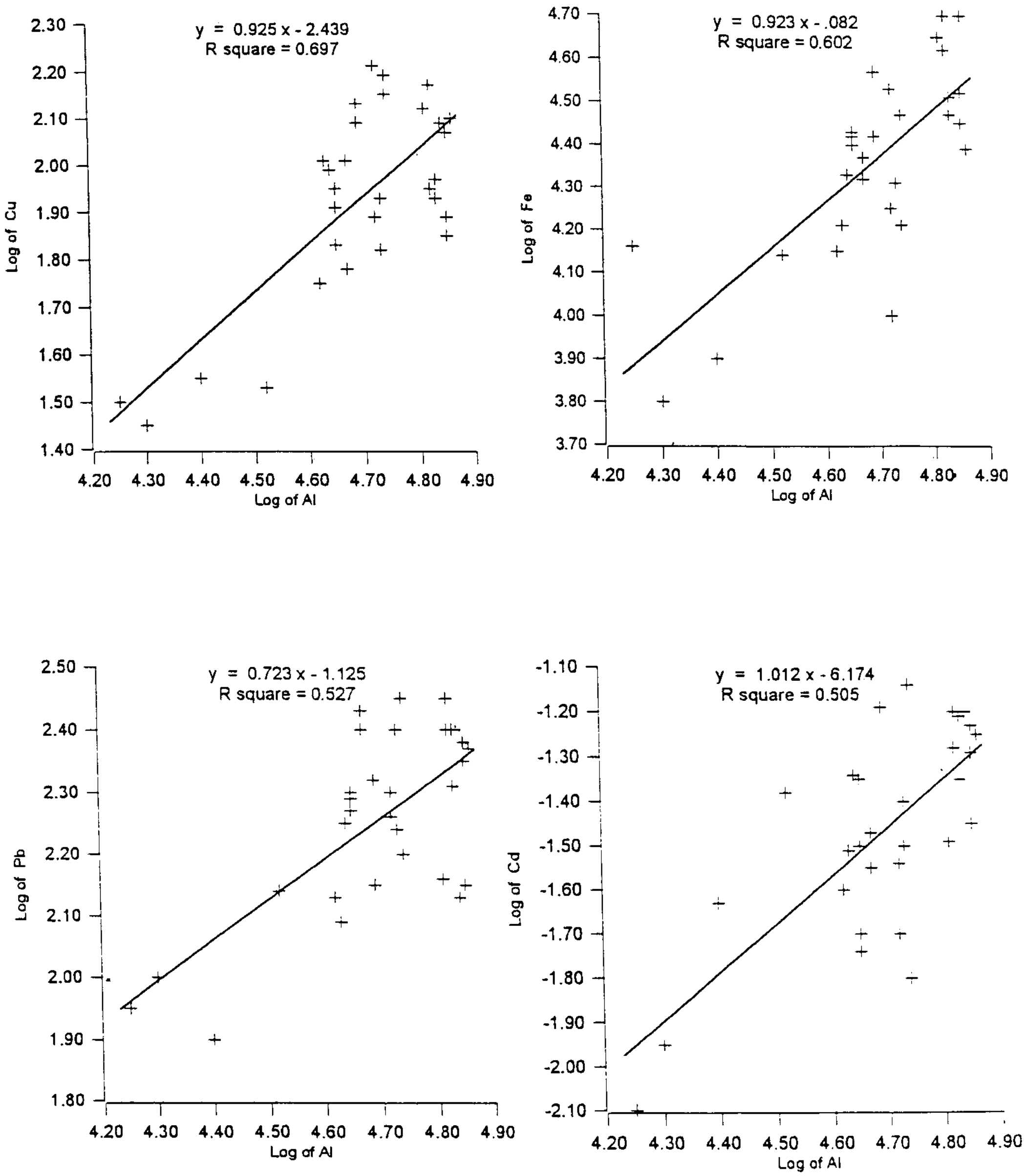
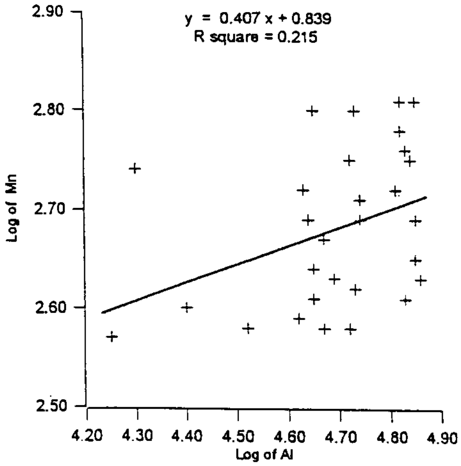
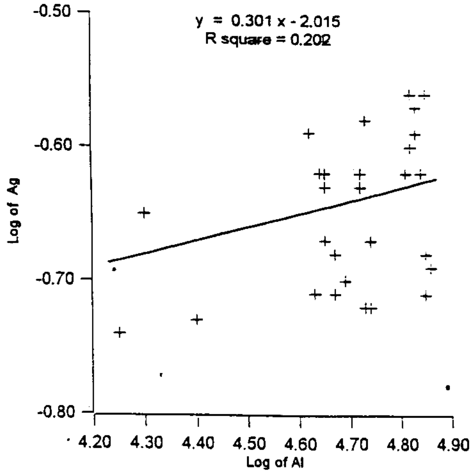


Figure 3. Cu : Al, Fe : Al, Pb : Al, and Cd : Al scatter plots for the coastal sediments of the Gulf of Thailand. The solid line represents the regression line.





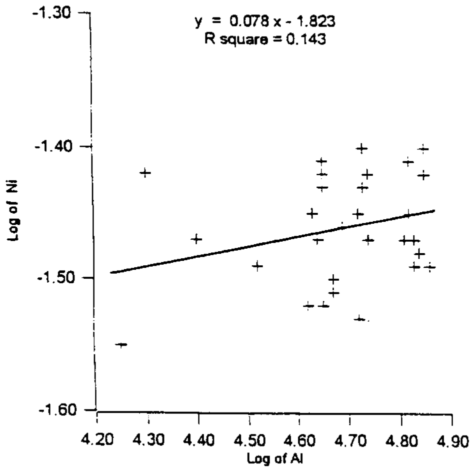


Figure 4. Mn : Al, Ag : Al, and Cr : Al scatter plots for the coastal sediments of the Gulf of Thailand. The solid line represents the regression line.

The arguments in support of Li are that apart from being a lattice component of fine-grained trace-metal-bearing minerals such as the phyllosilicates and clay minerals, it also reflects the granular variability of its host mineral component and is present in highly detectable concentrations. Moreover, levels of Li in the sediments are usually not influenced by anthropogenic inputs.

4. Conclusion

In conclusion, this study along with other recent results shows that in most cases, Al can be used as a reference element to normalize granular variability in trace-metal analyses of the coastal sediments of the South East Asian Seas such as the Gulf of Thailand. For some other metals, including Mn, Ag, and Ni, a different normalizer is recommended, Ti, Sc, and Li, being high in the list. Use of TOC as a normalizer in the area is not recommended due to its low concentration and because it is usually influenced by human activity.

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6.References

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