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RESEARCH NOTES

HIGH CONCENTRATIONS OF CU AND ZN IN THE SURFACE SEDIMENTS ARE NOT NECESSARILY RELATED TO HIGH TOTAL ORGANIC MATTER IN THE SEDIMENTS: AN EVIDENCE OF THE METAL DATA IN THE IGNITED SEDIMENTS OF THE INTERTIDAL AND DRAINAGE AREAS

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Fine-grained sediments tend to have relatively high metal concentrations, due in part to the high specific surface of the smaller particles. This enrichment is mainly due to surface adsorption and ionic attraction (Chen and Stevenson, 1986). However, in order to confirm and to enhance the understanding about this knowledge, the following comparative study and correlation analysis between mud and sandy sediments and between polluted and unpolluted sediments with different loss of ignitions were conducted. The objective of this study is to investigate and to prove that the high concentrations of Cu and Zn are not necessarily related to high total organic matter in the sediments.

It has been well-established that organic matter is one of the important controlling factors in the abundance of heavy metal concentrations in the sediments (Rubio *et al.*, 2000). In the litearature, most researchers use loss on ignition (LOI) as a method to determine the total organic matter in the sediments or soils. According to some researchers (Dean, 1974; Bengtsson and Enell, 1986), LOI is a common and widely used method to estimate the organic and carbonate content of sediments. The weight loss during the reactions is easily measured by weighing the samples before and after heating and is closely correlated to the organic matter and carbonate matter is oxidised at 500–550ºC to carbon dioxide and ash. Dean (1974) evaluated the method and concluded that LOI provides a fast and inexpensive means of determining carbonate and organic contents of clay-poor calcareous sediments and rocks with precision and accuracy comparable to other, more sophisticated geochemical methods. In view of that, the present study used 550ºC to ignite the sediment in order to get the LOI, as a proxy of total organic loss.

The sediment samples were dried for 24 hours at 105ºC and then ignited for 4 hours at 550ºC for the determination of the loss on ignition as an indirect index of organic matter content (Hakanson, 1980).

In this study, the 105ºC dried sediment samples were ignited at 550ºC for 18 hours to determine the total organic matter. The concentrations of Cu, Zn and Fe between the 105ºC dried and 550ºC ignited sediments were determined. The non-resistant and resistant fractions of Cu and Zn were determined by sequential extraction technique (SET) based on the methodology suggested by Badri and Aston (1983) that was modified by Yap *et al.* (2002). The SET consisted by of four geochemical fractions, namely easily, freely or leachable (EFLE), acid-reducible, oxidisable-organic and resistant. The summation of EFLE, acid-reducible and oxidisable-organic fractions would constitute the non-resistant fraction of metals (Yap *et al.*, 2002). Comparisons of between two different types of samples were done by using t-test, in the STATISTICA software.

The relationships between metal concentrations and total organic matter of the intertidal sediments (based on 18 sites) were presented in Fig. 1. Significant correlations were found between total organic matter -Cu ($R = 0.71$, $p < 0.01$) and total organic matter - Zn ($R = 0.85$, $P < 0.001$). This indicated that the concentrations of Cu and Zn in the sediments were highly dependent on the types of sediments in which high

metal concentrations were found high in mostly fine-grained muddy type of sediment. The results of these correlation analysis indicated that higher concentrations of Cu and Zn were found in the sediment containing higher organic matter content more usually found in the muddy type of sediments than in the sandy sediment due to higher surface area (Epstein, 1972; Garcia *et al.,* 1979). In addition, the different levels of Cu and Zn between the muddy and sandy types of sediments could also be a result of differences in the compaction, inorganic and organic contents that would modulate the metal concentrations (Garcia *et al.,* 1979).

Fig. 2 shows the difference in the concentrations of Cu and Zn in two different types of sediment, namely mud and sand collected from Kuala Muda. The results indicated that the metal levels in the non-resistant and resistant fractions were higher in the muddy type of sediments than those of the sandy type. From Fig. 2, it is evidenced that the sandy sediments contained much lower concentrations of nonresistant, resistant and total Cu and Zn when compared to muddy sediments. These results clearly indicated that the muddy sediments had higher organic matter that was bound to Cu and Zn when compared to sandy sediments. Since these sand and mud were collected from the same site at Kuala Muda, these results had led us to conclude that the muddy sediment had higher metal concentrations than in the sandy sediments. However, is there an exception from this theoretical thinking of anthropogenic metals overload of the total organic matter in the sediment samples? To answer this ecotoxicological argument, concentrations of Cu and Zn between 105ºC dried and 550ºC ignited sediments were determined and the results are shown in Fig. 3.

From Table 1 and Fig. 3 and Fig. 4, there is no significant (P> 0.05) difference of Cu and Zn concentrations between 105ºC dried and 550ºC

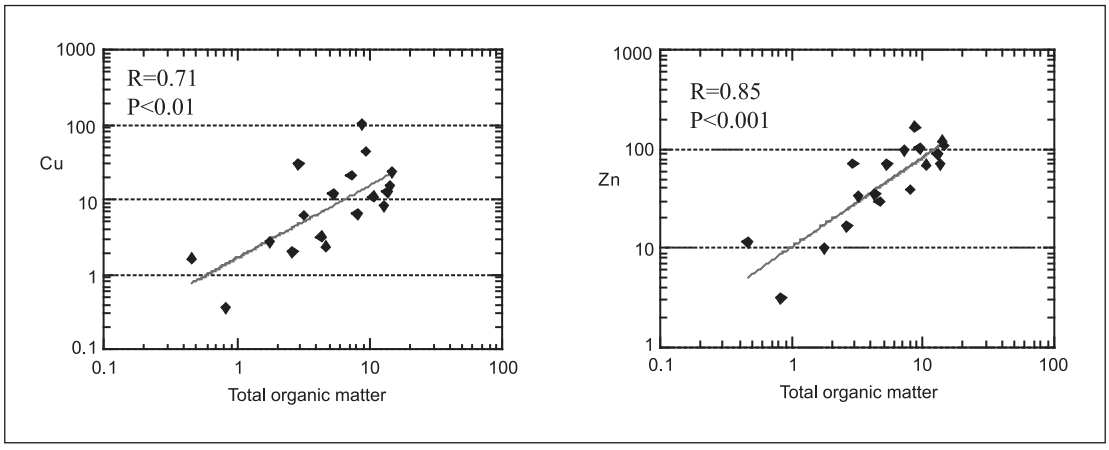

Fig. 1. Relationships between total organic matter and total concentrations of Cu and Zn in the intertidal sediments (N= 18). The correlation coefficients were based on $\log_{10}$ (mean) for both total organic matter and metals. Values given are the correlation coefficients (r) with their levels of significance ($^{ns}p > 0.05$, $^{*}p < 0.05$, $^{**}p < 0.01$, $^{***}p < 0.001$).

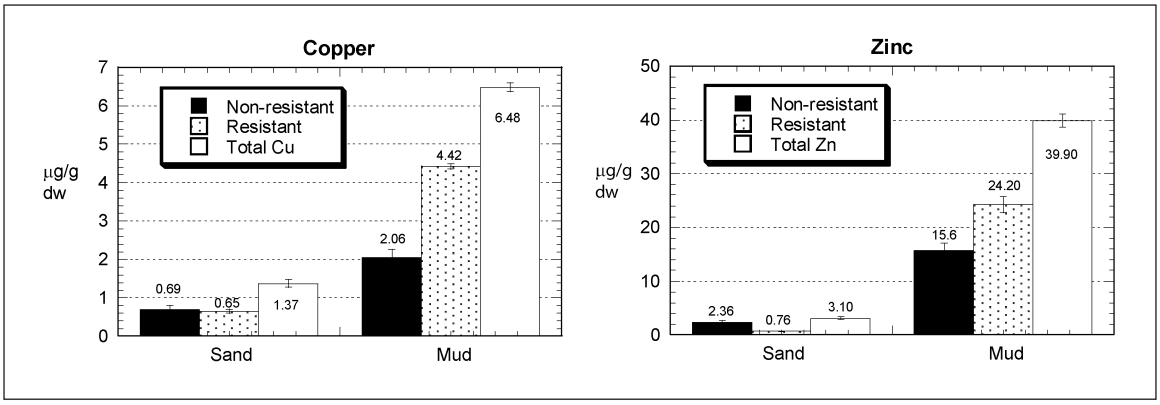

Fig. 2. Comparison of Cu and Zn concentrations between sandy and muddy sediments of the same site (an unpolluted site at Kuala Muda).

Table 1. T-test between the Cu and Zn concentrations (μg/g dry weight) between 105ºC dried sediments (total metal) and 550ºC ignited sediments

	ignited sediment				105ºC sediment				
	min	max	mean	SE	min	max	mean	SE	t-test*
Cu	1.63	104.42	20.84	5.06	4.79	119.64	24.13	5.98	P> 0.05
Zn	5.6	413.13	134.6	28.2	33.6	484.14	148.98	32.96	P> 0.05
TOM	0.57	13.41	4.89	0.74					

Note: * based on mean concentrations of metals.

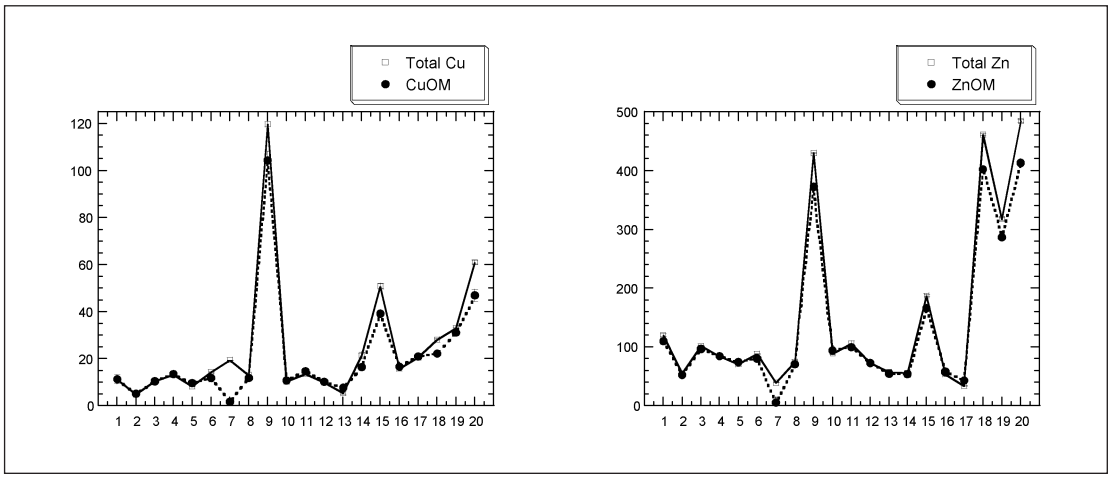

Fig. 3. Comparison of Cu and Zn concentrations (μg/g dry weight) between 105ºC dried sediments (Total metal) and 550ºC ignited sediments (metal OM).

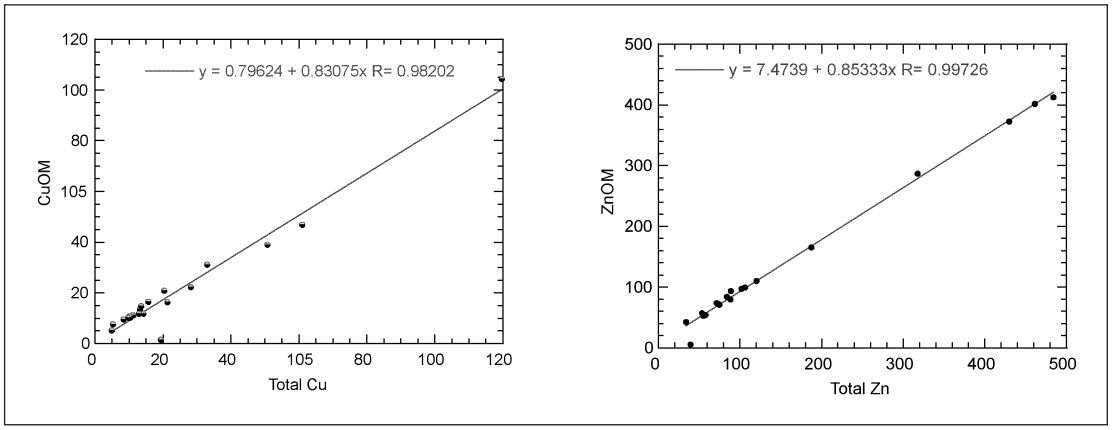

Fig. 4. Relationships of Cu and Zn concentrations (μg/g dry weight) between 105ºC dried sediments (total metal) and 550ºC ignited sediments (metal OM).

ignited sediments. Fig. 3 shows that there are strong correlations of Cu and Zn between 550ºC ignited and 105ºC sediments. This indicates that although the total organic matter in the ignited sediment is lost, the metal concentrations is not lost but are still stay within the ignited sediment and are similar to those sediments dried at 105ºC. These results also indicated that the boiling points for Cu and Zn are higher than 550ºC and therefore the both metals were not lost through vaporization. These results are interesting from several chemical points of view. Since the boiling point temperature for the two metals are above 900ºC [Cu: 2595ºC and Zn: 907ºC] (Anon, 2005), the ignition at 550ºC did not cause any loss of Cu and Zn since the ignition temperature was lower

than the boiling points for both metals. The 550ºC had caused the loss of ignition which was a proxy of total organic matter. This indicates that although high concentrations of Cu and Zn are related to high total organic matter, due to higher binding affinity of metals to organic surfaces, incineration at 550ºC will not cause the loss of the bonded metals. It can be concluded that loss of total organic matter is not related to the concentrations of Cu and Zn. These metals will be stored in the ignited sediments even after 550ºC ignitions. This finding is useful to explain the argument that high concentrations of metals in the sediments might not necessarily be related to the high total organic matter.

The 550ºC ignited sediments are considered sediments without any organic matter since the total organic matter is lost through ignition at 550ºC. By conducting this study, results showed that the ignited sediments were still having the similar pattern of metal concentrations to those sediments dried at 105ºC as shown in Fig. 1. In fact, significant and high correlation coefficients of metal concentrations between 105ºC and 550ºC ignited sediments are found as shown in Fig. 4.

From Table 2, the comparison of Cu and Zn concentrations is shown between a polluted site at Kurau Town and an unpolluted site at Kurau drainage receiving paddy field water. It is clearly shown that all the different geochemical fractions in the Kurau drainage sediments had significantly ($P< 0.05$) lower concentrations of Cu and Zn even though the unpolluted site at Kurau drainage recorded significantly ($P< 0.05$) higher percentage of total organic matter than that in the polluted site at Kurau Town. This is evidence that high organic matter might not necessarily be related to high concentrations of Cu and Zn.

Previous studies have supported differing conclusions as to whether increases in sediment organic matter yield higher metal concentrations. The presence of organic matter can potentially increase sediment metal concentrations by adsorption of metals from surrounding media onto plant litter, as well as contribution of the metals directly contained in the particulate organics (Knight and Pasternackref, 2000). Generally, metals tend to accumulate in the clay fraction of the soil because clay-sized particles have a large number of ionic binding sites due to a higher amount of surface area (Epstein, 1972; Garcia *et al.*, 1979). Epstein (1972) further maintained that metals could be tightly bound to organic matter content of the soil, which is gradually released during the process of mineralisation. However, all the above theoretical points of view are questioned when the high anthropogenic inputs of Cu and Zn overload the

Table 2: Comparison of heavy metal concentrations [µg/g dry weight] (Cd, Cu, Pb and Zn) between two different sediment types with different total organic matter [TOM in %]

Variable	Kurau Town		Kurau Drainage		P of t-test
	Mean	Std Error	Mean	Std Error	
Total organic matter	8.44		13.41		P< 0.05
Cu					
Total aqua-regia	119.64	1.10	10.24	0.52	P< 0.05
Summation of SET	127.91	1.42	14.51	0.18	P< 0.05
EFLE	0.30	0.00	0.24	0.01	P> 0.05
Acid-reducible	0.17	0.00	0.09	0.01	P< 0.05
Oxidisable-organic	67.01	1.99	2.25	0.04	
Resistant	105.43	0.55	11.94	0.16	P< 0.05
Resistant Cu PCT	47.26	0.95	82.29	0.06	
Non resistant Cu PCT	100–47.26		100–82.29		
Zn					
Total aqua-regia	429.46	1.19	88.74	2.06	P< 0.05
Summation of SET	329.21	2.13	122.71	1.49	P< 0.05
EFLE	51.93	0.40	4.85	0.01	P< 0.05
Acid-reducible	63.35	0.21	20.20	0.41	P< 0.05
Oxidisable-organic	86.58	0.34	39.14	0.27	P< 0.05
Resistant	127.36	2.28	58.51	0.80	P< 0.05
Resistant Cu %	38.68	0.45	47.68	0.07	
Non resistant Cu %	100–38.68	0.45	100–47.68	0.07	

Note : 1) Summation of SET is the total concentrations of EFLE, Acid-reducible, oxidisable organic and resistant fractions.
2) EFLE : Easily, freely, leachable or exchangeable
3) % of resistant or non-resistant is based on summation of SET.

role of total organic matter as a major factor of high metal concentrations due to higher binding affinity.

In conclusion, based on 1) comparison of Cu and Zn concentrations between 105ºC dried and 550ºC ignited sediments and 2) significantly high concentrations of Cu and Zn in the low total organic matter of the polluted sediments than those in the high total organic matter sediment, those two findings imply that high metal concentrations found in the sediments are not necessarily related to high total organic matter in the sediments.

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