A Role of the Northeast Monsoon Seasons in the Dilution of Cu and Pb Concentrations in Sediments off Pahang, South China Sea

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ABSTRACT

Surface sediments from the Pahang waters of the South China Sea were collected from 48 stations during pre-monsoon and post monsoon seasons. The samples were analysed concentrations of Pb and Cu using the sensitive inductively coupled plasma mass spectrometry (ICP-MS). In general, the concentration of studied metals in both seasons show considerable variation spatially, which largely appeared to be controlled by natural processes. This was proven by their enrichment factors (EF) which had values significantly distributed about the unity and were considered to be dominantly terigenous in origin. In this study, the concentrations of all studied metals were relatively high in the pre monsoon season and became much lower after the post monsoon season. In the pre monsoon season, Pb showed an average value of $24.5 \pm \mu g/g$ dry weight, while Cu was $19.2 \mu g/g$ dry weight. However, during the post monsoon season, the concentrations of Pb and Cu were significantly lower at $13.1 \mu g/g$ dry weight and $6.31 \mu g/g$ dry weight, respectively. This finding indicates that the annual seasonal changes that occur in Pahang waters of the South China Sea play an important role in regulating the concentration of heavy metals.

Keywords: Heavy metal, Northeast monsoon, South China Sea

Introduction

The South China Sea is one of the largest marginal seas in the western Pacific Ocean and is surrounded by the Asian continental and several large marine islands. The South

China Sea is located in the low-latitude tropical region and the surface layer is characterised by high temperatures, low salinities and low nutrient concentrations with low primary productivity (Wang *et al.* 1995). The oceanography of the upper layer of the South China Sea is dominated by the strong monsoon system and the considerable quantities of runoff from several great rivers including the Mekong River and Pearl River (Zheng *et al.* 1993). The South China Sea is a unique environment that had had rapid economic development and rapid population increase in the coastal areas during the past two decades and with rapid degradation of marine and coastal environments.

The climate of the South China Sea is controlled by the seasonal monsoon winds and these winds are generated by the difference in atmospheric pressure between the northern (Asian continents) and the southern (Australia) hemispheric (Camerlengo & Monica 1995). Winter monsoons are characterised by continental cooling and the development of high-pressure systems over northern Asia. During the winter monsoon, northeasterly winds blow across the South China Sea and the Indian Ocean and rainfall increases in the Austral-Asian equatorial zone. Summer monsoons are characterised by continental heating, the development of a low-pressure zone over Tibet, and southerly winds that blow across southern Asia (Maged 1994). In general, the northeast (NE) winds prevail from November to March and southeast (SE) winds prevail from April to September over the South China Sea. Since the monsoonal impact to the geochemical profile of Pahang waters, the South China Sea has not been well investigated, a study of the impact of pre-monsoon and post-monsoon seasonal changes on the heavy metals (Pb and Cu) concentration and the degree of heavy metal contamination was conducted.

Materials and Method

Sampling Sites

Pahang waters are the semidiurnal tides type while the northern region of Terengganu experiences diurnal tides. Waves are generated by monsoonal wind and the highest wave energy usually occurs during the north east monsoon season in late November to early of January particularly. The water movement during the north east monsoon is mainly from the Pacific Ocean consequence of the surface water movement by the monsoonal wind. Current direction during the north east monsoon season is to the south west and in the other way round for the south west monsoon wind (Rosnan *et al.* 2002). The North East monsoonal winds are characterised by alternating periods of strong winds and periods of relatively calm conditions (Wrytki 1961). The surface sediment samples were obtained from 44 stations in Pahang waters (Figure 1) using a Smith McIntyre. Seven transects were stablished about 5 km from the coastline and heading towards the southern region of Pahang waters. Sediments were sampled in pre-monsoon and post-monsoon using the research vessel of UNIPERTAMA VII.

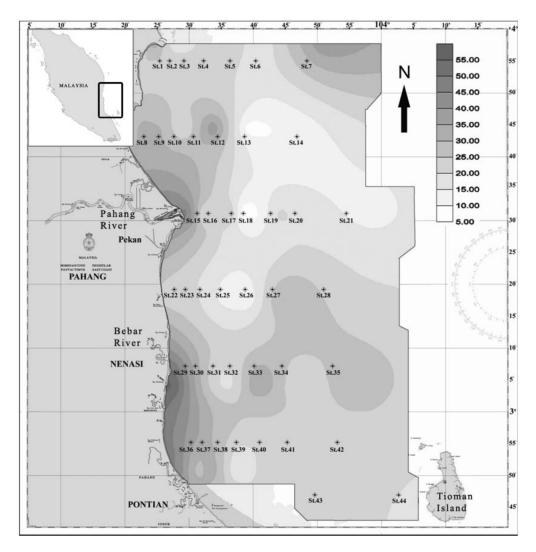


FIGURE 1a: The Distribution of Pb in Surface Sediment During the Pre-Monsoon Season

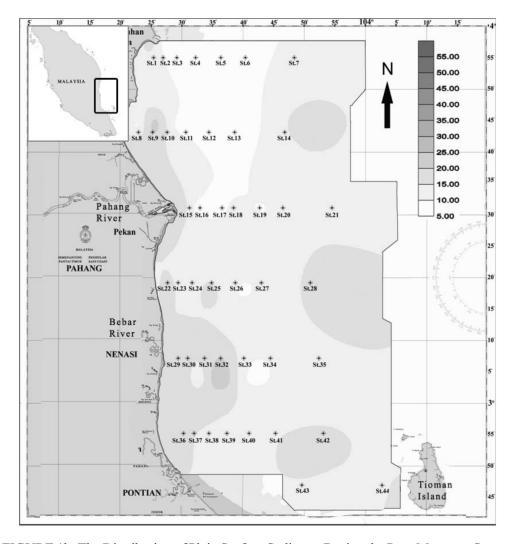


FIGURE 1b: The Distribution of Pb in Surface Sediment During the Post-Monsoon Season

Analytical Methods

The sediment samples were digested according to the published methods (Noriki *et al.* 1980; Sen Gupta & Bertrand 1995; Kamaruzzaman 1999) with some modifications. An inductively-coupled plasma mass spectrometer (ICP-MS) was used for the quick and precise determinations of Pb and Cu in the digested marine sediment. Briefly, the digestion method involved the heating of 50 mg of a $< 63 \,\omega$ m size sample in a sealed teflon vessel with mixed concentrated acids of HF, HNO₃ and HCl in the ratio of 2.5 : 3.5 : 3.5. The teflon vessel was kept at 150 °C for 3 – 5 hours. After cooling, a mixed solution of boric acid and EDTA was added, and the vessel was again heated at 150 °C for at least 5 hours. After cooling to room temperature, the content of the vessel was thoroughly

transferred into a 10 ml polypropylene test tube and was diluted to 10 ml with deionized water. A clear solution with no residue should be obtained at this stage. The precision assessed by replicate analyses was within 3%. The accuracy was also examined by analysing, in duplicate a Canadian Certified Reference Materials Project standard (DL-1a) and the results coincided with the certified values within a difference of \pm 3%.

Results and Discussions

Anthropogenic activities had caused important transformations in aquatic environments during the last 150 years. Heavy metals were among the most widespread of the various pollutants originating from anthropogenic activities, particularly from mining and smelting waste sites (Salomons 1995; Hochella *et al.* 1999). The approach most often used to determine the sources of the pollution is through the normalisation of geochemical data to a reference metal. The assumption is that the reference metal used represents a certain mineral fraction of the sediment. The reference metal must therefore be an important constituent of one or more of the major fine-grained trace metal carriers and reflect their granular variability in the sediment. The most often used reference metal is Al, which represents a chemical tracer of Al-silicates, particularly the clay minerals (Weijden 2002; Din 1992; Loring & Rantala 1992).

For a better estimation of anthropogenic input, an enrichment factor was calculated for each metal by dividing its ratio to the normalising element by the same ratio found in the chosen baseline. Table 1 shows the calculated EFs of the analysed elements with respect to those determined in the crustal abundance (Taylor 1964), employing the equation:

$$EF = (E/Al)_{sed}/(E/Al)_{crust}$$

where (E/Al)_{sed} and (E/Al)_{crust} are the relative concentrations of the respective element E and Al in the sediment and in the crustal material, respectively (Molinari *et al.* 1993, Kremling & Streu 1993). An enrichment factor close to 1 would indicate a crustal origin, while those with factors greater than 10 are considered to have non-crustal sources. Based on the calculated results obtained, Pb and Cu have EF values close to unity and may therefore be considered to be predominantly terrigenous in origin. Although the concentration of both Pb and Cu had decreased during the post-monsoon season, it was still identified as significantly enriched or moderately contaminated for both seasons as indicated by EF values. However, some high EF values found in some sampling samples may indicate some influents from the anthropogenic sources.

TABLE 1: Calculated EFs Values of Pb and Cu with Respect to Those Determined in the Crustal Abundance

| | Pb | Cu |
|---------------------|-----|-----|
| Pre-monsoon season | 2.4 | 1.1 |
| Post-monsoon season | 1.8 | 0.6 |

The distribution of heavy metals in the study area was clearly influenced by the seasonal changes of the monsoon season (NE) and the non-monsoon (SW). Statistical analysis clearly indicated significantly changes of heavy metal concentrations between the seasons of pre-monsoon and post-monsoon seasons. In this study, the average Pb concentration was significant higher during pre-monsoon compared to post-monsoon seasons with 24.5 µg/g dry weights and 13.1 µg/g dry weights, respectively (Fig. 1a and 1b). It is interesting to note that the concentration of Cu (Fig. 2a and 2b) was also high during the pre-monsoon season (19.2 µg/g dry weights) and became lower during the post-monsoon season (6.31 µg/g dry weights). This phenomena was also reported by Antonina (2001), showing some higher concentrations of Pb and Cu in the pre-monsoon season than in the post monsoon seasons. Relatively higher Pb and Cu concentrations in some coastal region during the pre-monsoon season were likely due to seabed topography which is capable of trapping metals containing sediments. Furthermore, the elevation of river discharge to the coastal areas was likely to contributes to Pb and Cu concentration throughout the study area. The contribution of these metals in the study area would likely be due to the anthropogenic activities such as boating, sand mining, and sea dumping activities (Kamaruzzaman et al. 2003).

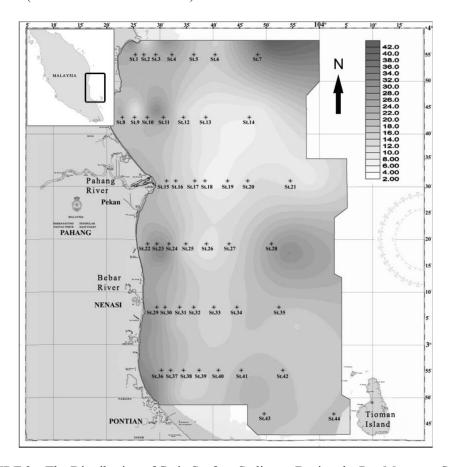


FIGURE 2a: The Distribution of Cu in Surface Sediment During the Pre-Monsoon Season

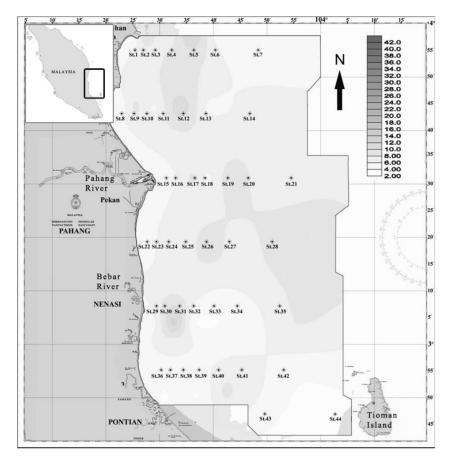


FIGURE 2b: The Distribution of Cu in Surface Sediment During the Post-Monsoon Season

On the other hand, the significant depletion of Pb and Cu concentrations that had occurred during the post-monsoon season was likely affected by the current forces of the north east monsoon. Rosnan *et al.* (2002) stated that the sediment characteristics in the South China Sea waters are mainly regulated by the transition seasons of the south west and north east monsoons. Bottom sediments are likely to experience turbulence during the north east monsoon resulting in particle re-suspension (Willison 2006). As a result, the concentrations of Pb and Cu in this study became lower compared to those during the pre-monsoon season.

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