Seasonal variation and mobility of trace metals in the beach sediments of NW Borneo

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Abstract

Miri city has a dynamic coastal environment, mainly influenced by intensive sedimentation from the Baram River and excessive trace metal loading by the Miri River, which are significant environmental concerns. As the mobility, bioavailability, and toxicity of the trace metals in the sediments are largely controlled by their particulate speciation, the modified BCR sequential extraction protocol was applied to determine the particulate speciation of trace metals in the coastal sediments of Miri, to unravel the seasonal geochemical processes responsible for known observations, and to identify possible sources of these trace metals. The granulometric analysis results showed that littoral currents aided by the monsoonal winds have influenced the grain size distribution of the sediments, enabling us to divide the study area into north-east and south-west segments where the geochemical composition are distinct. The Cu (>84%) and Zn (82%) concentrations are predominantly associated with the exchangeable fraction, which is readily bioavailable. Pb and Cd are dominant in non-residual fractions and other metals viz., Fe, Mn, Co, Ni, and Cr are dominant in the residual fraction. Using Pearson's correlation and factor analysis, the major mechanisms controlling the chemistry of the sediments are identified as association of Cu and Zn with fine fraction sediments, sulphide oxidation in the Ssegment of the study area, atmospheric fallout of Pb and Cd in the river basins, precipitation of dissolved Fe and Mn supplied from the rivers and remobilization of Mn from the coastal sediments. Based on various pollution indices, it is inferred that the coastal sediments of NW Borneo are contaminated with Cu and Zn, and are largely bioavailable, which can be a threat to the local aquatic organisms, coral reefs, and coastal mangroves.

Keywords: BCR sequential extraction, contamination factor, geo-accumulation index, Risk assessment code, Miri coast.

1. Introduction

Globally the contamination of a coastal ecosystem by trace and heavy metals is a serious environmental problem. Trace metals such as chromium, cobalt, copper, iron, magnesium, and zinc are generally occurring at very small levels in the environment. Living organisms need very lesser quantities of some trace metals, but high levels of the same metals can be toxic. Trace metals originate from both natural (erosion and mineral weathering) and anthropogenic sources (industrial and mining activities) and are transferred into the coastal environment via river runoff, discharge of municipal and industrial effluents through small streams and atmospheric fallout (Hyun et al., 2007; Li et al., 2013; Liu et al., 2018; Nagarajan et al., 2019). Under reasonable environmental conditions, where freshwater is well-oxygenated, the concentration of trace metals is high in the sediments compared to the water column. The partitioning of trace metals between the water column and sediments results from the adsorption and complexation by clay minerals and organic matter in the sediments. Trace metal concentration in the sediments often reflects their lithological source (Govindasamy and Azariah, 1999; Gopinath et al., 2010; Prabakaran et al., 2020) but sometimes anthropogenic contamination (Barath Kumar et al., 2017; Lu and Kang, 2018; Sajimol et al., 2021). The physicochemical changes occurring in the overlying water column and within sediments remobilize the trace metals (Förstner, 1985; Chakraborty et al., 2015; Tiquio et al., 2017; Xie et al., 2019). After remobilization, various physicochemical and biological processes recycle the trace metals (Xu et al., 2017), which undergo bioaccumulation and biomagnification through a complex food web structure that initiates adverse health effects to aquatic organisms and humans (Gleyzes et al., 2002; Barath Kumar et al., 2017; Liang et al., 2018; Anandkumar et al., 2020).

The bioaccumulation and biomagnification depend on the physicochemical availability (mobility) dictated by the carrier phase with which the trace metals are associated in the sediments, and the prevailing environmental conditions (Tessier et al., 1979; Salomons and Förstner, 1980; Rauret et al., 1988; Szefer et al., 1995; Chakraborty et al., 2014; 2019; Tiquio et al., 2017). The labile form of the trace metals primarily exists in five different phases viz., exchangeable, bound to carbonates, adsorbed onto iron and manganese oxides, complexed with natural organic matter, and as sulphides (Gibbs, 1973). The mobility and bioavailability of the trace metals differ across these carrier phases. Thus, measuring the total metal concentrations is inadequate to explore the contamination status of the sediments (Cottenie et al. 1980; Gleyzes et al. 2002). Thus, earlier researchers have employed different sequential extraction procedures (Tessier et al., 1979; Ure et al., 1993; Morillo et al., 2004; Nemati et al., 2011; Chakraborty et al., 2014; Wali et al., 2015; Schintu et al., 2016; Lu and Kang, 2018; Prabakaran et al., 2019; Dong et al., 2019; Chakraborty et al., 2021; Zhao et al., 2021) of which the Tessier (1979) protocol is widely adopted.

However, the lack of standardized procedures favored the development of the BCR method (Ure et al. 1993). The present work utilized the modified BCR procedure of Rauret et al. (1999). The revised protocol involves the use of an increased concentration of hydroxylammonium chloride and a lower pH. This allows for a more efficient dissolution of the soil/sediment matrix in the reducible fraction, in particular, metals bound to the iron oxyhydroxide phase (Mossop and Davidson 2003). Many researchers (Morillo et al., 2004; Cuong and Obbard, 2006; Nemati et al., 2011; Alshemmari et al., 2012; Chakraborty et al., 2015; Schintu et al., 2016; Akhbarizadeh et al., 2017) have successfully applied this modified BCR sequential extraction protocol to investigate bioavailability, mobility and toxicity of trace metals in the coastal sediments.

The Miri coast of the Sarawak consists of scenic geological structures, such as rock cliffs, arches, caves, stacks, beach rocks, a recreational waterfront area, and coral reefs (Miri-Sibuti Coral Reef National Park; MSCRNP, which makes them regularly visited hotspot areas for local and foreign travelers. Apart from the coastal ecosystems, three rivers (Baram River: the 2nd longest River in Sarawak and Miri, and Sibuti Rivers are minor rivers) that originate inland of Sarawak and confluence in the South China Sea and deliver a vast amount of sediments to the South China Sea. Compared to these three rivers, the Baram River contributes a much higher sediment flux to the Miri coast. Research on the alluvial sediments on the Miri coastal belts, which delineate the source and nature of these sediments is limited (Nagarajan et al., 2013; Ismail 1993; Sim et al., 2017; Prabakaran et al., 2018).

An earlier study by Nagarajan et al. (2013) in the tourist beach sediments of Miri revealed possible anthropogenic influence based on the acid leachable trace metals in the sediments and not reported the total trace metals in the beach sediment. Later, Nagarajan et al. (2019) reported the total trace metals including Rare Earth Elements (REEs) and mainly emphasized the source rock characterization, weathering intensity and the geological processes controlling the geochemical signature of the sediments. A high rate of erosion in the catchment area of the Baram River led to enhanced sediment transport to the Miri coast, which resulted in the formation of the sand bar opposite the Baram River mouth (Nagarajan et al., 2015a, 2019). Such a sand bar modulates the alongshore transport and distribution of the sediments delivered by the Baram River to the South China Sea. The enhanced upstream erosion due to changing land use and land cover modulate sediment delivery, and dictate accretion and erosional features of the Miri coast (Anandkumar et al., 2019a), and impact the nearshore Miri-Sibuti Coral Reef National Park (Browne et al., 2019). Studies on trace metal accumulation in biological tissues were also reported from the Miri Estuary of Sarawak (Billah et al., 2017) and the Miri coastal area (Anandkumar et al., 2017, 2018, 2019) which observed a higher concentration of Cu and Zn in different tissue organs of consumable aquatic organisms such as fish, crab, and prawn, etc. Even though, there have been some studies on the trace and heavy metals in the sediments of coastal areas of Borneo, a combined method that addresses the nature of the source, the seasonal, environmental, and biological impact of the trace metals, seasonal variations and mobility of the trace metals in the sediments of adjacent coastal belts are limited. In addition, geochemical fingerprinting studies to address the impact on the coral reef ecosystem in the MSCRNP by the local rivers, as well as the adjacent coastal belts are also limited to evaluate the future threats of the reef due to high suspended sediment input with a significant amount of pollutants (e.g. Browne et al., 2019). Thus, the present study mainly focuses on measuring the sequential extraction of trace metals of various beach sediments of the Miri coast to assess their bioavailability, toxicity, the association of metals in the different sediment fractions, to identify possible sources of the contaminants, and the pollution status based on the sediment quality guidelines (SQGs).

2. Study Area

Miri is the birthplace of the Malaysian oil industries and it is located in the northern part of Sarawak in Borneo Island. The beaches in this region are exposed to several types of natural and anthropogenic influences (Nagarajan et al., 2013, 2019; Billah et al., 2016; Anandkumar et al., 2017, 2018; Prabakaran et al., 2019). The Baram, Miri, and Sibuti rivers deliver freshwater and sediments to the coastal area of the South China Sea. The sediment input from the Baram

River is much higher compared to the Miri and Sibuti rivers. A heavy rainfall, changes in the land use/land cover and increased soil erosion in the upper Baram region result in the transportation of huge quantity of sediments and organic debris through the Baram River are washed from the deforested agricultural lands, mixed with the Baram River and that is finally drains delivered to into the Miri coast of South China Sea (Nagarajan et al., 2015a; Anandkumar et al., 2019a), which harms the nearshore turbid coral reef (MCRNP; Miri-Sibuti Coral Reef National Park) exists along the north-central coastal section of Sarawak, Borneo (Browne et al., 2019). The delivered materials are carried away by freshwater influence, suspended solids and organic debris from the Baram River are diverted towards the southern Miri coast and with the help of littoral currents, are deposited on this shoreline, which affects seawater and sediment quality along the Miri coastal region. This region has a tropical climate characterized by southwest (SW) and northeast (NE) monsoons, with semidiurnal tides and a temperature range of 23 to 32˚C. The annual mean rainfall in the study area varied from 2247 to 3499 mm (Source: Jabatan Meterologi, Malaysia, Miri). The tidal range on the Sarawak coast ranges between 1.2 m (at Kuala Baram) and 3.6m (at Pulau Lakir) (Sharifah Mastura, 1992).

The study area comprises a stretch of around 75 km from the Kualabaram in the northeast to Bungai Beach in the southwest. One of the famous dive locations the Miri-Sibuti Coral Reefs National Park well-known for live corals and rich in marine biodiversity, such as fish, marine mammals, molluscs, and crustaceans are located in the offshore region of the study area. Timber processing, ship-building, fiberglass boat companies, concrete curling, tire industries and oil palm plantation estates are also commonly observed in the coastal area of Miri city. The major industries are located in the Kualabaram area (north of the city), the Piasau Industrial Estate (central part of the city), Krokop suburbs and the Miri River Estuary (Nagarajan et al. 2014). A major contributor to untreated wastewater comes from the squatter houses on the banks of the Miri River (Tang and Lee, 2010). The study area (**Figure 1**) consists of ten beaches, A) Kuala Baram River mouth/Estuary (KBE), B) Fish Landing Center (FLC), C) Lutong Beach (LB), D) Piasau Boat Club Beach (PBC), E) Miri River Estuary (MRE), F) Park Everly Beach (PVB), G) Tanjong Lobang Beach (TB), H) Esplanade Beach (ESP), I) Kampong Baraya Beach (KPB) and J) Bungai Beach (BB). Amongst, LB, PBC, MRE, PEB, TB, ESP and BB are important tourist beaches and related activities are common.

3. Methodology

3.1. Sample collection and analysis

A total of 57 beach sand samples were collected during monsoon (MON; December 2013; n=26) and post-monsoon seasons (POM; June 2014; n=31) during low tides. Using a clean plastic scoop, sediment samples were collected from 0-10cm depth, transferred to the polyethylene bags, labelled, transported to the laboratory and stored under refrigeration at 4ºC. Before sample processing, all the samples were thawed to attain ambient temperature. After removal of organic debris, the sediments were washed with distilled water to remove sea salt and then dried in the oven at 60ºC to attain complete dryness. Then, the sediments were homogenized for chemical analyses by cone and quartering and ground to ≤63 μm using an agar mortar and pestle. The modified BCR sequential extraction of Rauret et al. (1999) was adopted for the extraction of exchangeable, reducible, and oxidizable fractions of trace metals. Complete digestion of the samples was achieved using an ODLAB Graphite Block Acid Digestion System using a mixture of aqua regia and HF (5 ml HNO_3 + 15 ml HCl + 6 ml HF; Loring and Rantala, 1992). The detailed methodology of using the modified BCR sequential extraction process has been provided in the supplementary material. Calcium carbonate and organic carbon in the sediment samples were determined by using the standard protocol by Gaudette et al. (1974) and (Muller, 1969) respectively.

The trace metals in the sediment extracts and the seawater were analyzed by Atomic Absorption Spectrometer (Perkin Elmer, 400 AAanlyst) using an air-acetylene stream at Curtin University, Malaysia and the operational condition is presented in **Table S1**. MESS-3 and BCR-701 reference materials were used for quality control during AAS analysis. The results of the CRMs are listed in **Table S2** and **Table S3.** Triplicate analysis of all the samples was made to reduce uncertainty in the results. The quality control (QC) was maintained by bracketing each set of five samples with an internal standard. Recalibration was done whenever necessary. The overall mean recovery rates for trace metals ranged between 87% and 105%.

The surface seawater samples (5 L) were collected at all sampling locations from Kuala Baram to Bungai Beach along with the sediments in acid-cleaned plastic jerry cans and brought to the laboratory. These samples were filtered through an 11 µm filter on acid-cleaned polycarbonate filtration assembly, acidified to pH < 2 and stored until further analysis for the trace metals (Prabakaran et al., 2020). The acidification of the seawater releases the mobile fraction of the trace metals from the suspended particles, which are bioavailable. From the analytical results of water and sediments (bulk and sequential extraction analysis), the partition coefficient (Kd) values for the trace metals were calculated. The Kd values are redefined here as the ratio of the trace metals in the sediment to that in 11 microns filtered water acidified to pH < 2 (Prabakaran et al., 2020). For the analysis of trace metals, the seawater samples were analyzed using liquid-liquid extraction (Mentasti et al., 1989). Seawater samples for the analysis of nutrients (nitrate, ammonium, and phosphate) were collected in separate 500 mL containers and got analyzed within 48 hours using HACH kits (Methods 8192, 8155, and 8048) with a HACH DR-2800 spectrophotometer. The pH values were measured using a HACH pH meter. Turbidity was measured by using a portable turbidity meter (HACH 2100Q). The DO was measured by using a DO probe (YSI Pro 20). All the portable analyzers were calibrated prior to the field trip. The HCO_3^- and SO_4^{2-} were measured using standard procedures (APHA, 2005).

3.2. Risk Assessment indices

Several methods are available to calculate the enrichment of metals and to evaluate the natural and anthropogenic origin of metals in the sediments and have been used in various studies with different sedimentary environments (Muller, 1969; Hakanson, 1980; Szefer et al., 1995; Chen and Selvaraj, 2008; Jayaprakash et al., 2012; Islam et al., 2017; Celis-Hernandez et al., 2018; Nagarajan et al., 2019; Prabakaran et al., 2019; Orani et al., 2019; Dash et al., 2021). Among them, contamination factor (CF) suggested by Pekey et al. (2004), geo-accumulation index (I_{geo}) by Muller (1969) and Pollution Load Index by Tomlinson et al. (1980) were used in this study to assess the risk associated with the trace metals. The trace metal concentrations of the Upper Continental Crust (UCC: McLennan, 2001) and Post Archean Australian Shale (PAAS: Taylor and McLennan, 1985) were considered as the background values.

4. Results and Discussion

4.1 Sediment texture

The Miri beach sediments were mainly composed of fine sand and silt; the coarse fraction was lesser than 1%. Based on grain size analysis the study area is divided into two segments –

the northeastern (NE) and the southwestern (SW) segments. The fine sand dominates in the NE segment while silt is predominant in the SW segment. The Kualabaram River mouth/Estuary (KBE), Fish Landing Center (FLC), Lutong Beach (LB), Piasau Boat Club Beach (PBC) and, Miri River estuary (MRE) fall under the NE segment, whereas, Park Everly Beach (PVB), Tanjong Lobang Beach (TB), Esplanade Beach (ESP), Kampong Baraya Beach (KPB), Hawai Beach (HWB) and Bungai Beach (BB) belong to the SW segment (**Figure 1**). During the MON, the average of fine sand (62%) is lesser compared to that of during the POM season (73%). However, silt is recorded as more dominant during the MON (38%) than during the POM season (27%) (**Table 1**). The silt was dominant near the river discharge areas notably, at the Baram and Miri river mouths and adjacent areas. Coarse sand was only observed in the SW segment (**Table 1**).

4.2 Distribution of carrier phases and trace metals in the sediments

The calcium carbonate content ranges from 0.52% to 2.51% (Avg. 1.33%) during the MON season and 0.49% to 6.33% (avg.1.78%) during the POM season (**Table 1**). The organic carbon (OC) content varies from 0.11% to 0.28% during the MON and 0.16% to 0.28% during the POM season, with an average of 0.24% for both seasons (**Table 1**). Higher OC content is observed at the Piasau Boat Club Beach for both seasons. The average concentrations of the trace metals in decreasing order of their concentration are as follows: Fe > Cu > Zn > Cr > Mn > Ni > Co > Pb > Cd for the MON season and Fe > Cu > Zn > Cr > Mn > Pb > Ni > Co > Cd for the POM season. The Co and Ni are recorded higher in the MON season and the rest of the metals (Cu, Pb, Cd, Zn, Fe, Mn, and Cr) have slight enrichment in the POM season (**Table 1**).

4.3. Partitioning of the trace metals

Among the metals analyzed Cu, Cd, Pb and Zn are mainly associated with non-residual fractions (acid extractable/exchangeable fraction, reducible fraction, and oxidizable fraction) during both seasons, and the remaining metals (Co, Cr, Fe, Mn, and Ni) are associated with the residual fraction. The distribution of trace metals in different fractions is presented in **Figure 2** (MON) and **Figure 3** (POM) and the average values of each metal associated with each fraction of different beaches are summarized in **Table 2**.

4.3.1. Acid extractable/exchangeable fraction (F1)

Fraction 1 represents the trace metals in the acid exchangeable, and carbonate bound fractions (Rauret et al., 1999; Nemati et al., 2011), that are together known as "acid extractable". A significant part of Cu and Zn are associated with this fraction at 85 % and 83% during MON and 84 % and 82% during POM, respectively. A higher proportion of Cu and Zn was observed at Lutong Beach and Fish Landing center during MON and POM seasons respectively and the lower proportions were noticed near the Miri River Estuary during MON season. The acid-extractable Pb associated with this fraction varies between 22% and 49.5% during MON and POM seasons, respectively. A higher proportion of Pb in the F1 fraction was noticed from Bungai Beach at 37.59% and 63.69% for the MON and POM seasons, respectively. The major associations of Cu, Zn, and Pb in this fraction imply high mobility and bioavailability. The mean proportions of Cd, Co, Ni, Fe, Mn and Cr in this fraction were 4.70%, 13.15%, 6.25%, 8.00%, 31.40% and 3.95% during MON and 16.39%, 10.18%, 6.40%, 9.04%, 27.16% and 2.48% during POM seasons, respectively. Thus the mobility and bioavailability of Cd, Co, Ni, Fe, Mn, and Cr are comparatively lesser than Cu, Zn, and Pb. The concentration of the trace metals in F1 fraction can be ordered as: Cu > Zn > Pb > Mn > Co > Fe > Ni > Cd > Cr (MON) and Cu > Zn > Pb > Mn > Cd > Co > Fe > Ni > Cr (POM).

4.3.2. Reducible fraction (F2)

This fraction consists of trace metals bound to amorphous Fe and Mn oxides and hydroxides (Rauret et al., 1999; Nemati et al., 2011), which become dissolved under reducing conditions (Morillo et al., 2004). The concentration of metals in this fraction for both seasons can be summarized as: Pb > Fe > Mn > Co > Cu > Cr > Zn > Ni > Cd (MON) and Pb > Cd > Fe > Mn > Cu > Co > Zn > Cr > Ni (POM). Among the metals, Pb associated with this fraction varies between 27% and 26% during the MON and POM season, respectively. The higher Pb concentration (32%) in this fraction is recorded from the Miri River estuary area for both seasons. An increase in the Pb concentration of this fraction was observed at three river mouths for both seasons (i.e. the Miri River, the Lutong River, and the Baram River) indicating a supply of Pb from these river basins. A negligible amount of Fe was associated in the reducible form [16% (MON) and 14% (POM)].

4.3.3. Oxidizable fraction (F3)

The organic- and sulphide-bound fraction of trace metals are extracted in the F3 fraction (Rauret et al., 1999; Nemati et al., 2011). The association of metals in this fraction for both seasons can be summarized as follows: Cd > Cr > Co > Ni > Fe > Pb > Mn > Zn > Cu (MON) and Cd > Cr > Co > Ni > Mn > Pb > Zn > Cu > Fe (POM). Cadmium concentration in this fraction was higher in many samples and was recorded at 55% during MON and 44% during POM season. In addition to Cd, Co [19.27% (MON) & 17.06 (POM)], Ni [16.36% (MON) & 15.89% (POM)] and Cr [26.26% (MON) & 16.92% (POM) were also significantly associated in this phase. Cu (1.55%; MON) and Fe (1.04%; POM) were partially associated with this fraction. The presence of Fe in the oxidizable fraction is very low for both seasons (< 2%).

4.3.4. Residual fraction (F4)

The trace metals in the residual fraction are associated with silicate mineral lattices (Rauret et al., 1999; Nemati et al., 2011) and their average concentration can be summarized as follows: Fe > Ni > Cr > Co > Mn > Pb > Cd > Zn > Cu (MON) and Fe > Cr > Ni > Co> Mn > Cd> Pb > Zn > Cu (POM). A major proportion of Co [57.28% (MON) & 64.46% (POM)], Ni [73.17% (MON) & 73.61% (POM)], Fe [73.83% (MON) & 75.98% (POM), Mn [51.71% (MON) & 54.60% (POM)] and Cr [63.95% MON & 75.75% (POM)] are associated with this phase for both seasons. A higher proportion of Fe in the residual fraction was noticed in the Kuala Baram River mouth area during the MON season and at Piasau Boat Club beach during the POM season. Heavy inflow at Kuala Baram and intense wave action at Piasau beach might have enriched the sediments with heavier mafic minerals along the shore. However, mineralogical investigations are necessary to confirm this proposition.

4.4. Statistical analysis

In order to understand the geochemical processes responsible for the observed variations in the metal concentrations, factor analysis was carried out using Statistical Package for Social Sciences (SPSS, version 17). Factors were extracted using principal components and varimax rotation was also employed to determine uncorrelated factors. This is essential for identifying influencing factors affecting the trace metals concentration within the water (**Table 3 and 4** for MON and POM season respectively) and sediment column. Factors with eigenvalues > 1 were considered for interpretation. A detailed explanation of the statistical treatment of the data and the factor analysis is described in the supplementary material.

4.4.1. Factor analytical results for the MON season sediments: SW Part (Bungai beach to Esplanade Beach)

Five factors accounted for 91.6% variance in the data (**Table 3**). Factor 1 is characterized by positive loadings of Cu, Zn, and silt, indicating these trace metals are mainly associated with the fine fraction of the sediments. There is also evidence of the formation of extremely fine particles during the formation of metal sulphides (Lewis, 2010), and this may be one of the reasons for the observed loading of Cu and Zn with silt fraction. The observed negative loading of Co and the positive loading of silt on the first factor implies desorption of Co from clay minerals supplied by the river under the influence of seawater (Turner and Milward, 2002). The presence of Cu, Zn, and Co in the sediments of the SW segment of the study area was due to leaching from the hinterland and hence their source was identified to be natural. The factor-2 is explained by high positive loading of Cr, and water column HCO_3^- and moderate positive loadings of SO_4^{2-}, $CaCO_3$ and Ni. The association of Cr with the water column parameters (i.e. HCO_3- and SO_4^{2-}) implies sulphide oxidation in the sediments. During sulphide oxidation, Cr within the anoxic sediments could become oxidized and then diffuses towards a water-sediment interface and finally be released into the water column (Murray et al., 1983; Gaillard et al., 1986; Douglas et al., 1986). This Cr mobilization process can be best understood from its longitudinal profile, where its concentration in the sediments decreased as it moved towards the SW where sulphide oxidation was found to be a dominant process. Such sulphide oxidation occurring in the coastal area of Miri would also release sedimentary Ni to the water column as inferred from its negative loading on the factor-2 (Naylor et al., 2004). The factor-3 is positively loaded with Pb, Cd and negatively loaded with Ni and silt. The metals Pb and Cd are particle reactive (Tang et al., 2002; García-Rico et al., 2011) and may be affected by biological processes occurring in the water column (James et al., 1993; Tappin et al., 1995; Cotté-Krief et al., 2002). The negative correlation (-0.64; $P<0.05$) between the water column PO_4 and the oxidizable fraction of Pb in the sediments did not point to such a biological control on its concentration in the sediments. Moreover, Cd does not exhibit any correlation with PO_4 (**Table S4**). However, the data shows water column PO_4 levels were less significantly associated with the levels of the residual fraction of Co (0.43; $P<0.15$), Fe (0.45; $P<0.15$) and the reducible fraction of Mn (0.42; $P<0.15$) in the sediments (**Table S4**)and the values of correlation coefficients were not high, thus implying the leaching of phosphate minerals from the sediments. The variability in the content of Ni and silt that was accountable for factor-3 as detrital origin, which can be interpreted as a riverine supply of Ni with silt but the source for Pb and Cd was not of riverine origin as both Ni and silt are oppositely loaded with Pb and Cd. Therefore, it can be inferred as atmospheric fallout from forest fires, which is quite common in Borneo and SE Asia and this may be the source for these metals in the coastal sediments as well as in emergent trees of the tropical forests (Wooster et al., 2012). The factor-4 was positively loaded with Fe and Mn and negatively loaded with $CaCO_3$ implying the flocculation of dissolved Fe and Mn as their respective hydrous oxides and further precipitation to the sediments (Sholkovitz, 1978, 1979; Boyle, et al. 1977; Karbassi et al., 2013). The factor-5 was positively loaded with Pb and pH, ascribing the effect of water column pH on the adsorption of Pb to the sediments (Impellitteri et al., 2002; Wang et al., 2009).

4.4.2. Factor analytical results for MON sediments: NE part (Tanjong Beach to Kualabaram River mouth/estuary)

The factor model explains five factors that accounted for 91.3% variance in the data (**Table 3**). The factor-1 was positively loaded with Fe, Mn, silt and negatively loaded with fine sand, organic carbon, water column HCO_3^- and Co. This factor is interpreted to be “water column energy". During this season the river water input was greater, which has delivered a greater amount of sediments to the coastal region. Upon entering the sea, riverine Fe and Mn adsorbed onto the silt fraction could be deposited near the river mouth whereas, fine sand and organic debris would be transported from other areas by littoral currents. Thus, riverine Fe, Mn, Co, organic carbon, fine sand, and silt are differentiated in the sediment and water column. Such a kind of metal removal from the water column was observed in large and middle-size estuaries in China (Zhang and Liu 2002). Therefore, it is evident that Fe and Mn distribution in the NE segment (stations 10-26) was dominated by water column energy, while in the SW segment (stations 1-9) they are controlled by flocculation. The factor-2 is positively loaded with Cu, Zn, and Pb, and organic carbon and Co exhibit moderate negative loading in this factor. Water column chemistry may play a role in the metal distribution. Thus, the correlation of the trace metals' partition coefficients (Kd) with water column parameters were calculated (**Table S13**). There is a positive correlation between Cu with other metals i.e. Zn (0.93; $P<0.01$), SO_4^{2-} (0.52; $P<0.05$), NO_3- (0.53; $P<0.05$); and Zn with Mg (0.42; $P<0.05$), SO_4^{2-} (0.41; $P<0.1$) and NO_3- (0.53; $P<0.1$) (**Table S13**). From these observations, it is clear that organic complexation is affected by ionic interactions and competitive binding is responsible for the observed variations in the concentrations of Cu, Zn, Pb, and Co in the sediments (e.g. Zirino and Yamamoto, 1972; Tipping, 1981; Davis, 1984; Millward and Liu, 2003; Hatje et al., 2003; Ciffroy et al., 2003; Garnier et al., 2006). It has been demonstrated by Balistrieri and Murray (1982), that the major ion chemistry may affect the adsorption of trace metals from seawater. Balls (1989), has shown in the coastal water, the partition coefficient (Kd) decreases in the order Pb, Hg > Cu, Zn, Ni > Cd, and this sequence applies within the given area though, the values of partition coefficient may vary from place to place. In this series, Pb tends to be in the particulate phase and Cd tends to be in the solution phase. Thus, the observed correlation between Cu and Zn (0.93; $P<0.01$; Table S13) could be ascribed to their adsorption or, complexation with particulate matter. Whereas, the positive correlation between Cu and SO_4^{2-} (0.52; $P<0.05$), Cu and NO_3-N (0.53; $P<0.05$), Zn and Mg^{2+} (0.42; $P<0.05$) is due to weak ionic interactions (Table S13). The release of Cu, Zn, Pb, and Co due to sulphide oxidation in the river basin, and their transport and deposition in the coastal sediment, was the main source for these metals.

The factor-3 was positively loaded with Cd, turbidity, Ni, and Mn and negatively loaded with Cr. A Significant positive correlation was observed between the partition coefficients of Cd and Fe (0.86; $P<0.01$), and, Cd and the water column PO_4- (0.93; $P<0.01$), both in the exchangeable fraction (**Table S9**). A similar relationship existed between the partition coefficients of Cd and Ca^{2+} (0.78; $P<0.01$) in the reducible fraction (**Table S10**). At the same time, Cd in the oxidizable fraction exhibited a significant negative correlation with turbidity (-0.63; $P<0.01$) (**Table S11**). A negative correlation was also observed between Cd and Zn (-0.62; $P<0.01$) in the exchangeable fraction (**Table S9**). The $CaCO_3$ content of the sediment was positively correlated with the oxidizable fraction of Cd ($r=0.46$; $P<0.05$; **Table S5**). From these observations, it can be inferred, the variability of Cd in the sediment was mainly associated with its interaction with Fe in the carbonate phase and PO_4-, Ca^{2+} in the water column. The relationship between Cd and turbidity in the factor model (**Table 3**) mainly arose from its oxidizable fraction in the sediments. This can be explained as the formation of ferric hydroxide layers on silicate and carbonate fragments (Whitney, 1975), over which Mn oxides can become coated (Hem, 1977), and trace metals could be adsorbed onto these surfaces. Under such a situation, ionic interactions, competitive binding, and organic complexation may control the adsorption-desorption processes. The high loading of Cd and turbidity on the factor-3 should then be interpreted as resuspension of the sediments, which is quite possible due to the currents set by the riverine water along the coast (Nagarajan et al., 2015a). Under such a scenario, the organics brought by the river water deplete oxygen levels in the water column and render Cr in the sediments immobile. This explains its negative loading on factor-3 (**Table 3**). The moderate positive loading of Ni and Mn was due to their remobilization from the sediments along with Cd.

The factor-4 was positively loaded with pH, salinity, Co, HCO_3-, and turbidity. Under the seawater environment, Co mainly exists as a free ion (Wen et al. , 2011; Raymont 1980). The loading of Co implies its adsorption onto the sediment particles with increasing pH, salinity, and HCO_3-. The loading of turbidity arises from enhanced adsorption of Co under increasing suspended sediment concentration (Hansen and Leckie, 1998). The loading of bicarbonate and turbidity can be explained as due to the riverine input. The factor-5 was loaded only with water column SO_4^{2-} and moderate negative loading of Pb. This was due to the effect of SO_4^{2-} on Pb adsorption to the sediments. Balistrieri and Murray (1982) demonstrated the adsorption of SO_4^{2-} alters the electrostatic conditions on the surface of goethite (α-FeOOH) and increases the adsorption of trace metals, including Pb, in the seawater. Ferrihydrite and goethite are naturally occurring iron hydroxide minerals, which are highly reactive and capable of exerting control over the concentrations of nutrients and trace metals in the natural environment (Van Der Zee et al., 2003; Marchand and Rancourt, 2009; Bosch et al., 2010; Chesne and Kim, 2014).

4.4.3. Factor analytical results for POM sediments: SW part (Bungai beach to Esplanade Beach)

The factor model is accounted for 84.6% variance in the data with four factors (**Table 4**). The factor-1 is loaded with Cu, Fe, $CaCO_3$, and silt. The loading of Cu, Fe, and $CaCO_3$ together with silt is due to the formation of an iron hydrous oxide coating on calcium carbonate and its adsorption of Cu (Whitney, 1975; Cravotta III, 1994). The factor-2 is explained by the positive loadings of Pb, pH, and SO_4^{2-}, which can be explained by the effect of pH on sulphide oxidation (Steger and Desjardins, 1980; Heidel and Tichomirowa, 2011; Hampton et al., 2011) or, its formation (Smieja-Król et al., 2015). The factor-3 is loaded with Mn and Cr; moderate loadings are observed for Cu and $CaCO_3$. This can be explained as due to the formation of $MnCO_3$ during organic matter oxidation resulting in the conversion of Mn-oxides in the sediment into $MnCO_3$. This is implied by the fact $MnCO_3$ has a very large stability field if a high concentration of dissolved Mn is present (Hem 1977). As the Baram River supplies large amounts of silt and humus material, which are buried along the coast (up to 1m thick below the beach sediments and on the beach), intense organic matter oxidation mediated through Mn-oxide reduction, is possible and it may have significantly contributed to the high level of dissolved Mn in the sediments. This is the plausible mechanism for the formation of $MnCO_3$. The association of Cr with Mn indicates the adsorption of reduced Cr (i.e., Cr (III)) by Mn-oxides and its oxidation to Cr (VI) (Namieśnik and Rabajczyk, 2012). Similarly, the adsorption of Cu, though, to a lesser extent, by Mn-oxides is responsible for its observed loading. On factor-4, Ni and HCO_3- are loaded and are interpreted as desorption of Ni upon contact with the seawater (Edmond et al., 1985; Windom et al., 1991; Shiller and Boyle, 1991).

4.4.4. Factor analytical results for POM sediments: NE part (Tanjong Beach to Kualabaram River mouth/estuary)

The factor model explains 3 factors that accounted for 74.2% variance in the data (**Table 4**). The first factor was loaded with Ni, Fe, and silt and can be explained as riverine input of Ni was adsorbed onto an iron oxide coating on clay minerals (Xu and Axe, 2005). The second factor was loaded with Cu and Zn. These trace metals belong to the group of chalcophile elements and their association on the factor-2 indicates that they are leached out during sulphide oxidation in the river basin and delivered to the sea. The third factor was loaded with Co, Mn and HCO_3- and implied desorption of riverine particulate Co and Mn upon mixing with the seawater (Ackroyd et al., 1986; Takata et al., 2010).

4.5. Sediment quality assessment

The contamination factor (CF) was calculated for all the metals analyzed in sediments for both seasons (**Figure 4A** and **4B)**. The range and average CF values vary from 0.04 to 8.69 for the MON season and 0.07 to 12.55 for the POM season respectively. The CF values of the trace metals can be ranked in the decreasing order as Cu>Zn>Co>Pb>Cr>Ni>Fe>Mn for the MON season and Cu>Zn>Pb>Cr>Ni>Co>Fe>Mn during the POM season. The beach sediments from the Miri coast are highly contaminated by Cu during both seasons (CF=8.69 in the MON and CF=12.55 during the POM season). The Lutong Beach (MON) and Fish Landing Center (POM) is recorded the highest CF values for Cu. In addition to Cu, the beach sediments are moderately contaminated by Zn and Pb at selected locations. The CF values for remaining trace metals such as Cr, Co, Fe, Mn, and Ni are < 1 for both seasons and are considered as less/no contamination by these metals.

The calculated geo-accumulation Index (I_{geo}) values for the beach sediments are presented in **Figures 5A and 5B** for the MON season and the POM season respectively. The I_{geo} values suggest that the sediments of the Miri coast remain uncontaminated by Fe, Mn, Cr, Pb, Zn, Co, and Ni for both seasons. The I_{geo} values for all the trace metals fall under classes 1- 4 **(Table S20)**. In contrast, Cu in both (1.85 to 3.12 during the MON season and 1.55 to 4.04

during the POM season) seasons and Zn (-0.38 to 1.28) in the POM season shows positive I_{geo} values. Overall, ~ 78.85% of metals (Fe, Mn, Cr, Pb, Co, and Ni) during the MON and 73.39% metals during the POM season are recorded the I_{geo} values < 0. Zn alone at nearly 8.65% during the MON and 11.69% during the POM season shows the I_{geo} values between 0 and 1 and is classified under Class 2 (uncontaminated to moderately contaminated). The remaining 12.50% of Cu during the MON and 14.92% during the POM season show the I_{geo} values in the range of 2 - 4 (Class 3 and 4) indicate that the sediments are moderate to strongly contaminated by this metal. Also, the average I_{geo} value of Cu, (I_{geo} values = 4 - 5; class 6) 0.48% during the MON and 4.84% during the POM season indicates that the sediments are strong to extremely contaminated by Cu.

The calculated PLI values range from 0.62 to 0.74 (avg. 0.69) for the MON season, and 0.63 to 0.97 (avg. 0.76) for the POM season respectively. All the samples show PLI values <1, which implies no contamination. Nevertheless, Cu (most of the locations) and Zn (selected locations) show higher contamination factors and I_{geo} values. These observations are further confirmed by ERL-ERM values of Cu. Prabakaran et al. (2019) observed the PLI values > 1 for Cu and it is the only metal that exhibits enrichment in the Lower Baram River sediments followed by Zn. Cu and Zn are also highly bioavailable as major fractions of them associated with exchangeable fractions, which has been led to accumulating more Zn and Cu in the fish, shrimps and bivalves in the study area (Anandkumar et al., 2017, 2018, 2019).

4.6. Ecotoxicological effects of total trace metals

The level of ecotoxicological effects for the trace metals along the Miri coast for both seasons is presented in **Table S21**. Trace metal concentrations of less than ERL values are considered to have little or no adverse effects on sediment-dwelling fauna. In contrast, metals exceeding ERM values can cause adverse health effects to aquatic organisms (Long et al., 1995). Among the analyzed metals, only Cu exceeded the SQGs values, whereas all the remaining metals; Cd, Cr, Ni, and Zn, were less than ERL values or between ERL and ERM values (**Figure 6a and b**). Lead and Cr concentrations were less than ERL values in all samples during the MON season. Most of the samples recorded concentrations below the ERL values for Cd (96%), Ni (77%) and Zn (88%). During the MON season, samples were recorded Cu, Cd, Ni and Zn concentrations between ERL and ERM values (92% for Cu, 4% for Cd, 23% for Ni, and 13% for Zn). In the case of Cu, 8% of samples exceeded the ERM value and may cause adverse biological effects.

During the POM season, a similar trend was maintained as MON season, however, 55% of the samples showed Cu concentrations between ERL and ERM values and 45% of the samples were enriched with Cu (i.e. > ERM values) indicating possible adverse biological effects. This is further confirmed by the recent studies on aquatic organisms, which have accumulated more Zn followed by Cu (Anandkumar et al., 2017, 2018, 2019). The average concentrations of metals in the individual beaches of the Miri coast were compared with other SQGs such as the Threshold Effect Low (TEL), Lowest Effect Level (LEL) and Severe Effects Level (SEL) values (**Table 5**). Amongst all the analyzed metals, Cu concentration in all beach samples exceeded the maximum permissible value of SEL (110 µg/g), while all other metals were under the acceptable limits of SQGs values for both seasons.

4.7. Risk Assessment Code (RAC)

The risk assessment code is defined as the concentration of metals associated with carbonates and exchangeable fractions in the sequential extraction process (% F1 of BCR). The

RAC was determined for the analyzed nine metals and the values were interpreted in agreement with the RAC classifications (**Table S22**) described by Perin et al. (1985).

In general, a low or no risk is indicated by Cd, Ni, Fe, and Cr (except some locations) during the MON and Ni, Fe, Cr during the POM season (**Table S23**), which were confirmed by their RAC values. A medium-risk is associated with Pb, Co during the MON season and Cd, Co, and Mn during the POM season. A high to very high risk is associated with Mn, Cu, and Zn during the MON season and Cu, Zn, Pb, and Mn during the POM season. Though these metals show a high risk in the beach sediments, which were naturally derived from the hinterland of the study area as the river basins predominantly consist of sedimentary to meta-sedimentary (low-grade metamorphism) rocks, deposited in shallow and deep water conditions (i.e. turbidites of the Rajang Group and Miocene sedimentary rocks of sandstone, shale with minor coal and mud laminations) respectively.

4.8. Comparison with background values

The average total concentrations of the present study (both seasons), were compared with the background values of different sedimentary rocks exposed along the coastal region of Miri, river sediments, UCC and PAAS values (**Table 6)**. The concentrations of Cu, Cd, and Zn in both seasons and Pb in the POM season were comparatively higher than UCC values, whereas Ni, Cr, Co, Fe and Mn concentrations in the surface sediments for both seasons were lower than the UCC. Similarly, except Cu and Zn all other metals in the Miri beach sediments recorded lesser compared to PAAS values. Also, these metals are recorded higher than the Cu and Zn values recorded in source area and coastal area geological formations (**Table 6**).

The observed Cu concentration in the present study for both seasons was several folds higher than those Cu values reported for sedimentary rocks from the coastal region, such as the deep water turbidities (29.5 µg/g and 28 µg/g in the Kelalan Formation and the Belaga Formation respectively), Sibuti Formation (65.30 µg/g), the Tukau Formation (43.0 µg/g), the Lambir Formation (77 µg/g;) and the Miri Formation (16.3 µg/g) (**Table 6**). The average Cu concentration was eight and four times higher in the MON season and 12 and 6 times higher during the POM season compared to the UCC and PAAS values respectively (UCC - 25 µg/g; McLennan, 2001; PAAS: 50 µg/g; Taylor and McLennan, 1985) and background metal concentration of the Upper Baram River sediments (25.71 µg/g during the MON season and 36.72 µg/g during the POM season in <2mm fraction; 19.52 µg/g during the POM season in <63µm fraction; Prabakaran et al., 2019) and other geological formations exposed in the source region and adjacent to the coastal area. The association of Cu and Zn indicates both natural and anthropogenic sources have contributed to the concentrations of these metals on the Miri coast. A similar observation has been reported from the Lower Baram River as estuarine processes are also controlling the distribution of these metals. In addition, the Miri River is also contributing to their source as this river crisscrosses the Miri city and industrial areas and finally discharges into the SCS within the NE section of the study area. Thus, the Cu values recorded in the present study are influenced mainly by the natural lithogenic source, however, additional input from the Miri River through the anthropogenic activities that take place in the urban area. Also, based on the BCR sequential analysis, it is clearly indicated that Cu and Zn are readily bioavailable and may lead to high bioaccumulation in the aquatic organisms and coral reef system of this region.

5. Conclusion

The modified BCR sequential extraction method was adopted for the first time in the study area to analyze the potential mobility of trace metals and their seasonal variations in the sediment samples collected from the different beaches of the Miri coast. The sediments are predominantly composed of fine sand (SW segment) and are followed by silt (NE segment). The association of trace metals in the exchangeable fraction (the most mobile and bioavailable) can be ranked as Cu > Zn > Mn > Pb > Co > Fe > Ni > Cd > Cr (MON) and Cu > Zn > Pb > Mn > Cd > Co > Fe > Ni > Cr (POM). Cu and Zn were dominant in the exchangeable fraction for both seasons. Pb and Cd were also dominant in the non-residual fraction (F1+F2+F3) for both seasons. Cadmium was the only metal showing a high proportion in the oxidizable fraction for both seasons. Mn showed intermediate mobility and was mainly associated with residual fraction. Iron, Co, Ni, and Cr were mainly associated with the residual fraction for both seasons and will not involve in the remobilization process under normal environmental conditions.

Amongst the metals analyzed, Fe, Mn, Co, Cr, and Ni were influenced by natural sources, such as weathering of the parental rocks, and sediments were mainly derived from the Baram River, Miri River and Sibuti River into the SCS along the Miri coast. Copper, Cd, Pb, and Zn were derived from both natural sources as well as man-made activities in the study area. These metals have a higher chance to leach from sedimentary rocks such as sandstone, shale, siltstone with clay seams, coal laminae, pyrite concretions and then enrich their concentration in the adjacent coastal regions in the SW segment of the study area. Pb and Cd were also found derived from atmospheric fallout, particularly during the wildfire/haze episodes in the Borneo/Miri region.

Based on the geochemical indices, the beach sediments were contaminated with Cu, followed by Zn and both may pose some biological threats to the aquatic organism in the near future, which was confirmed by the RAC values. In this study, Cu in 8% and 45% of the samples during the MON and the POM season respectively exceeded the ERM values and hence, may cause biological adverse effects. Finally, the concentration of analyzed trace metals was comparable to the UCC values, except for Cu and Zn in all locations for both seasons and Pb in certain sampling locations during the POM season. All the remaining trace metals were below the UCC and PAAS values.

Conflict of Interest

The authors declare that there are no conflicts of interest

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References

Ackroyd, D.R., Bale, A.J., Howland, R.J.M., Knox, S., Millward, G.E., Morris, A.W., 1986. Distributions and Behaviour of Dissolved Cu, Zn and Mn in the Tamar Estuary. Estuarine, Coastal Shelf Sci. 23 (5), 621-640. https://doi.org/10.1016/0272-7714(86)90103-4.

Ahmed, N., Siddiqui N.A., Nagarajan, R, Ramkumar, Mu, Jamil, M., Usman, M., Sajid, Z., Rahman, A.H., 2021. Geochemistry of Eocene Bawang Member turbidites of the Belaga Formation, Borneo: Implications for provenance, palaeoweathering, and tectonic setting. Geol. J. 56, 2477–2499. https://doi.org/10.1002/gj.4062

Akhbarizadeh, R., Moore, F., Keshavarzi, B., Moeinpour, A., 2017. Microplastics and potentially toxic elements in coastal sediments of Iran's main oil terminal (Khark Island). Environ. Pollut. 220, 720-731. https://doi.org/10.1016/j.envpol.2016.10.038

Alshemmari, H., Ali, L., Alotaibi, Y., 2012. Trace metal speciation in marine sediments from Sulaibikhat Bay, Kuwait. Aquat. Ecosyst. Health Manage. 15, (sup1), 33-40. https://doi.org/10.1080/14634988.2012.669185

Anandkumar, A., Nagarajan, R., Prabakaran, K., Rajaram, R., 2017. Trace metal dynamics and risk assessment in the commercially important marine shrimp species collected from the Miri coast, Sarawak, East Malaysia. Regional Stud. in Marine Sci. 16, 79–88. https://doi.org/10.1016/j.rsma.2017.08.007.

Anandkumar, A., Nagarajan, R., Prabakaran, K., Chua, H.B., Rajaram. R., 2018. Human health risk assessment and bioaccumulation of trace metals in fish species collected from the Miri coast, Sarawak, Borneo. Mar. Pollut. Bull. 133, 655-663. https://doi.org/10.1016/j.marpolbul.2018.06.033.

Anandkumar, A., Nagarajan, R., Prabakaran, K., Chua H.B., Rajaram, R., Li, J., Du, D., 2019b. Bioaccumulation of trace metals in the coastal Borneo (Malaysia) and health risk assessment. Mar. Pollut. Bull. 145, 56-66. https://doi.org/10.1016/j.marpolbul.2019.05.002.

Anandkumar, A., Vijith, H., Nagarajan, R., Jonathan, M.P., 2019a. Evaluation of Decadal Shoreline Changes in the Coastal Region of Miri, Sarawak, Malaysia. In: Krishnamurthy, R.R., Jonathan, M.P., Srinivasalu S., Glaeser B., (Eds.), Coastal Management: Global Challenges and Innovations, Academic Press, London, United Kingdom, pp. 95-119. https://doi.org/10.1016/B978-0-12-810473-6.00008-X

Anandkumar, A., Li, J., Prabakaran, K., Jia, Z.X., Leng, Z., Nagarajan, R., Du, D., 2020. Accumulation of toxic elements in an invasive crayfish species (*Procambarus clarkii*) and its health risk assessment to humans. J. Food Compos. Anal. 88, 103449. https://doi.org/10.1016/j.jfca.2020.103449.

APHA, 2005. Standard Methods for the Examination of Water and Wastewater. 21st Edition, American Public Health Association/American Water Works Association/Water Environment Federation, Washington DC.

Balls, P.W., 1989. The partition of trace metals between dissolved and particulate phases in european coastal waters: a compilation of field data and comparison with laboratory studies. Neth. J. Sea Res. 23 (1), 7-14. https://doi.org/10.1016/0077-7579(89)90037-9

Balistrieri, L.S., Murray, J.W., 1982. The Adsorption of Cu, Pb, Zn, and Cd on Goethite from Major Ion Seawater. Geochim. Cosmochim. Acta 46(7), 1253-1265. https://doi.org/10.1016/0016-7037(82)90010-2

Billah, M.M., Kamal, A.H.M., Hoque, M.M., Bhuiyan, M.K.A., 2016. Temporal Distribution of Water Characteristics in the Miri Estuary, East Malaysia. Zool. Ecol. 26 (2), 134-140. https://doi.org/10.1080/21658005.2016.1148960

Bosch, J., Heister, K., Hofmann, T., Meckenstock, R.U., 2010. Nano sized Iron Oxide Colloids Strongly Enhance Microbial Iron Reduction. Appl. Environ. Microbiol. 76 (1), 184-189. https://doi.org/10.1128/AEM.00417-09

Boyle, E.A., Edmond, J.M., Sholkovitz, E.R., 1977. The Mechanism of Iron Removal in Estuaries. Geochim. Cosmochim. Acta 41 (9), 1313-1324. http://dx.doi.org/10.1016/0016-7037(77)90075-8.

Browne, N, Braoun, C, McIlwain, J, Nagarajan, R, Zinke, J., 2019. Borneo coral reefs subject to high sediment loads show evidence of resilience to various environmental stressors. PeerJ 7, e7382. https://doi.org/10.7717/peerj.7382

Celis-Hernandez, O., Rosales-Hoz, L., Cundy, A.B., Carranza-Edwards, A., Croudace, I.W., Hernandez-Hernandez, H., 2018. Historical trace element accumulation in marine sediments from the Tamaulipas shelf, Gulf of Mexico: An assessment of natural vs anthropogenic inputs. Sci. Total Environ. 622, 325-336. https://doi.org/10.1016/j.scitotenv.2017.11.228

Chakraborty, P., Raghunadh Babu, P.V., Vudamala, K., Ramteke, D., Chennuri, K., 2014. Mercury speciation in coastal sediments from the central east coast of India by modified BCR method. Mar. Pollut. Bull. 81 (1), 282-288. http://dx.doi.org/10.1016/j.marpolbul.2013.12.054.

Chakraborty, P., Ramteke, D., Chakraborty, S., 2015. Geochemical partitioning of Cu and Ni in mangrove sediments: relationships with their bioavailability. Mar. Pollut. Bull. 93 (1–2), 194-201. http://dx.doi.org/10.1016/j.marpolbul.2015.01.016.

Chakraborty, S., Chakraborty, P., Sarkar, A., Kazip, A., Mascarenhas-Pereira, M.B.L., Nagender Nath, B., 2019. Distribution and geochemical fractionation of lead in the continental shelf sediments around India. Geol. J. 54 (3), 1190-1204. https://doi.org/10.1002/gj.3218.

Chakraborty, S., Parthasarathi C., Ed Hathorne, Arindam, S., Linsy, P., Martin, F., Nagender Nath, B., 2021. Evidence for increasing anthropogenic Pb concentrations in Indian shelf sediments during the last century. Sci. Total Environ 760, 143833. https://doi.org/10.1016/j.scitotenv.2020.143833.

Chen, C.T., Selvaraj, K., 2008. Evaluation of elemental enrichments in surface sediments off southwestern Taiwan. Environ. Geol. 54 (6), 1333-1346. https://doi.org/10.1007/s00254-007-0916-2

Chesne, R.B., Kim, C.S., 2014. Zn (II) and Cu (II) Adsorption and Retention onto Iron Oxyhydroxide Nanoparticles: Effects of Particle Aggregation and Salinity. Geochem. Trans. 15 (1), 6. https://doi.org/10.1186/1467-4866-15-6

Ciffroy, P., Garnier, J.M., Benyahya, L., 2003. Kinetic partitioning of Co, Mn, Cs, Fe, Ag, Zn and Cd in fresh waters (Loire) mixed with brackish waters (Loire Estuary): experimental and modelling approaches. Mar. Pollut. Bull. 46 (5), 626-641. https://doi.org/10.1016/S0025-326X(02)00517-9

Cottenie, A., Camerlynck, R., Verloo, M., Dhaese, A., 1980. Fractionation and determination of trace elements in plants, soils and sediments. In: Varmavuori, A. (Ed.), 27th International Congress of Pure and Applied Chemistry. pp.45-53. https://doi.org/10.1016/B978-0-08-023936-1.50007-1

Cotté-Krief, M. H., A. J. Thomas, and J. M. Martin. 2002. Trace metal (Cd, Cu, Ni and Pb) cycling in the upper water column near the shelf edge of the European continental margin (Celtic Sea). Mar. Chem. 79 (1), 1-26. https://doi.org/10.1016/S0304-4203(02)00013-0.

Cravotta III C.A. 1994., Secondary iron-sulfate minerals as sources of sulfate and acidity—the geochemical evolution of acidic ground water at a reclaimed surface coal mine in Pennsylvania. In: Alpers, C.N., Blowes, D.W., (Eds.), Environmental geochemistry of sulfide oxidation. Am. Chem. Soc. Symp. Series 550, pp.345–364, Washington, D.C.

Cuong, D.T., Obbard, J.P. 2006. Metal speciation in coastal marine sediments from Singapore using a modified BCR-sequential extraction procedure. Appl. Geochem. 21(8), 1335-1346. https://doi.org/10.1016/j.apgeochem.2006.05.001

Dash, S., Borah, S.S., Kalamdhad, A.S., 2021. Heavy metal pollution and potential ecological risk assessment for surficial sediments of Deepor Beel, India. Ecol. Indic. 122, 107265. https://doi.org/10.1016/j.ecolind.2020.107265.

Davis, J.A., 1984. Complexation of trace metals by adsorbed natural organic matter. Geochim. Cosmochim. Acta 48 (4), 679-691. https://doi.org/10.1016/0016-7037(84)90095-4.

Dong, H., Feng, L., Qin, Y., Luo, M., 2019. Comparison of different sequential extraction procedures for mercury fractionation in polluted soils. Environ. Sci. Pollut. Res. 26, 9955–9965. https://doi.org/10.1007/s11356-019-04433-6.

Douglas, G. S., Mills, G.L., Quinn, J.G., 1986. Organic Copper and Chromium Complexes in the Interstitial Waters of Narragansett Bay Sediments. Mar. Chem. 19 (2), 161-174. https://doi.org/10.1016/0278-4343(85)90019-6.

Edmond, J. M., A. Spivack, B. C. Grant, H. Ming-Hui, C. Zexiam, C. Sung, and Z. Xiushau. 1985. "Chemical Dynamics of the Changjiang Estuary." Cont. Shelf Res. 4 (1), 17-36.

Förstner, U., 1985. Chemical Forms and Reactivities of Metals in Sediments. In Leschbar, R., Davis, R.D., Hermite, P.L. (eds.) Chemical Methods for Assessing Bio-Available Metals in Sludges and Soils. pp.1-30. Elsevier Applied Science Publ. London.

Gaillard, J.F., Jeandel, C., Michard, G., Nicolas, E., Renard, D., 1986. Interstitial Water Chemistry of Villefranche Bay Sediments: Trace Metal Diagenesis. Mar. Chem. 18 (2), 233-247. https://doi.org/10.1016/0304-4203(86)90011-3

García-Rico, L., Tejeda-Valenzuela, L., Jara-Marini, M.E. Gómez-Álvarez, A., 2011. Dissolved and Particulate Metals in Water from Sonora Coast: A Pristine Zone of Gulf of California. Environ. Monit. Assess. 176 (1-4): 109-123. https://doi.org/10.1007/s10661-010-1570-9

Garnier, J.M., Ciffroy, P. Benyahya, L., 2006. Implications of short and long term (30 days) sorption on the desorption kinetic of trace metals (Cd, Zn, Co, Mn, Fe, Ag, Cs) associated with river suspended matter. Sci. Total Environ. 366 (1), 350-360. https://doi.org/10.1016/j.scitotenv.2005.07.015.

Gaudette, H.E., Flight, W.R. Toner, L., Folger, D.W., 1974. An Inexpensive Titration Method for the Determination of Organic Carbon in Recent Sediments. J. Sediment. Res. 44 (1) 249-253. https://doi.org/10.1306/74D729D7-2B21-11D7-8648000102C1865D

Gibbs, R.J., 1973. Mechanisms of Trace Metal Transport in Rivers. Science 180 (4081), 71-73. DOI: 10.1126/science.180.4081.71

Gleyzes, C., Tellier, S., Astruc, M., 2002. Fractionation studies of trace elements in contaminated soils and sediments: a review of sequential extraction procedures. TrAC Trends Anal. Chem. 21(6-7), 451-467. https://doi.org/10.1016/S0165-9936(02)00603-9

Gopinath, A., Nair, S.M., Kumar, N.C., Jayalakshmi, K.V., Pamalal, D., 2010. A Baseline Study of Trace Metals in a Coral Reef Sedimentary Environment, Lakshadweep Archipelago. Environ. Earth Sci. 59 (6), 1245-1266. https://doi.org/10.1007/s12665-009-0113-6

Govindasamy, C., Azariah, J., 1999. Seasonal Variation of Heavy Metals in Coastal Water of the Coromandel Coast, Bay of Bengal, India. Indian J. Mar. Sci. 28, 249-256.

Hakanson, L., 1980. An Ecological Risk Index for Aquatic Pollution Control. A Sedimentological Approach. Water Res. 14 (8), 975-1001. https://doi.org/10.1016/0043-1354(80)90143-8

Hampton, M.A., Plackowski, C., Nguyen. A.V., 2011. Physical and Chemical Analysis of Elemental Sulfur Formation During Galena Surface Oxidation. Langmuir 27 (7), 4190-4201. https://doi.org/10.1021/la104755a

Hansen, A.M., Leckie, J.O., 1998. Time-dependent adsorption in near coastal marine sediments: a two-step model. Adv. Water Resour. 21, 523–531. https://doi.org/10.1016/S0309-1708(97)00039-0

Hatje, V., Payne, T.E., Hill, D.M., McOrist, G., Birch, G.F., Szymczak, R., 2003. Kinetics of Trace Element Uptake and Release by Particles in Estuarine Waters: Effects of Ph, Salinity, and Particle Loading. Environ. Int. 29 (5): 619-629. https://doi.org/10.1016/S0160-4120(03)00049-7

Heidel, C., Tichomirowa, M., 2011. The isotopic composition of sulfate from anaerobic and low oxygen pyrite oxidation experiments with ferric iron—new insights into oxidation mechanisms. Chem. Geol. 281 (3), 305-316.

Hem, J. D. 1977. Reactions of Metal Ions at Surfaces of Hydrous Iron Oxide. Geochim. Cosmochim. Acta 41 (4), 527-538. https://doi.org/10.1016/0016-7037(77)90290-3

Hyun, S., Lee, C.H., Lee, T., Choi, J.W., 2007. Anthropogenic Contributions to Heavy Metal Distributions in the Surface Sediments of Masan Bay, Korea. Mar. Pollut. Bull. 54 (7), 1059-1068. http://dx.doi.org/10.1016/j.marpolbul.2007.02.013.

Impellitteri, C.A., Lu, Y., Saxe, J.K., Allen, H.E., Peijnenburg. W.J.G.M., 2002. Correlation of the Partitioning of Dissolved Organic Matter Fractions with the Desorption of Cd, Cu, Ni, Pb and Zn from 18 Dutch Soils. Environment Int. 28 (5), 401-410. https://doi.org/10.1016/S0160-4120(02)00065-X

Islam, M.A., Al-Mamun, A., Hossain, F., Quraishi, S.B., Naher, K., Khan, R., Das, S., Tamim, U., Hossain, S.M., Nahid, F., 2017. Contamination and ecological risk assessment of trace elements in sediments of the rivers of Sundarban mangrove forest, Bangladesh. Mar. Pollut. Bull. 124(1), 356-366. https://doi.org/10.1016/j.marpolbul.2017.07.059

Ismail, A., 1993. Heavy Metal Concentrations in Sediments Off Bintulu, Malaysia. Mar. Pollut. Bull. 26 (12), 706-707. http://dx.doi.org/10.1016/0025-326X(93)90556-Y.

James, R.H., Statham, P.J. Morley, N.H., Burton, J.D., 1993. Aspects of the Geochemistry of Dissolved and Particulate Cd, Cu, Ni, Co, and Pb in the Dover Strait. Oceanol. Acta 16 (5-6), 553-564.

Jayaprakash, M., Nagarajan, R., Velmurugan, P.M., Sathiyamoorthy, J., Krishnamurthy, R.R., Urban, B., 2012. "Assessment of trace metal contamination in a historical freshwater canal (Buckingham Canal), Chennai, India. Environ. Monit. Assess. 184 (12), 7407-7424. https://doi.org/10.1007/s10661-011-2509-5

Karbassi, A.R., Bassam, S.S., Ardestani, M., 2013. Flocculation of Cu, Mn, Ni, Pb, and Zn During Estuarine Mixing (Caspian Sea). Int. J. Environ. Res. 7 (4), 917-924. https://doi.org/10.1016/S0269-7491(96)00047-4

Barath Kumar, S., Padhi, R.K., Mohanty, A.K., Satpathy, K.K., 2017. Elemental Distribution and Trace Metal Contamination in the Surface Sediment of South East Coast of India. Mar. Pollut. Bull. 114 (2), 1164-1170. https://doi.org/10.1016/j.marpolbul.2016.10.038

Lewis, A.E., 2010. Review of Metal Sulphide Precipitation. Hydrometallurgy 104 (2): 222-234. https://doi.org/10.1016/j.hydromet.2010.06.010

Li, G., Hu, B., Bi, J., Leng, Q., Xiao, C., Yang, Z., 2013. Heavy Metals Distribution and Contamination in Surface Sediments of the Coastal Shandong Peninsula (Yellow Sea). Mar. Pollut. Bull. 76 (1–2), 420-426. http://dx.doi.org/10.1016/j.marpolbul.2013.08.032.

Liang, X., Song, J., Duan, L., Yuan, H., Li, X., Li, N., Qu, B., Wang, Q., Xing, J., 2018. Source identification and risk assessment based on fractionation of heavy metals in surface sediments of Jiaozhou Bay, China. Mar. Pollut. Bull. 128, 548-556. https://doi.org/10.1016/j.marpolbul.2018.02.008

Liu, Q., Wang, F., Meng, F., Jiang, L., Li, G., Zhou, R. 2018. Assessment of metal contamination in estuarine surface sediments from Dongying City, China: Use of a modified ecological risk index. Mar. Pollut. Bull. 126, 293-303. https://doi.org/10.1016/j.marpolbul.2017.11.017

Long, E.R., MacDonald, D.D., Smith, S.L. Calder, F.D., 1995. Incidence of adverse biological effects within ranges of chemical concentrations in marine and estuarine sediments. Environ. Manage. 19 (1), 81-97. https://doi.org/10.1007/BF02472006.

Loring, D.H., Rantala, R.T., 1992. Manual for the geochemical analyses of marine sediments and suspended particulate matter. Earth Sci. Rev. 32(4), 235-283. https://doi.org/10.1016/0012-8252(92)90001-A

Lu, Z.B., Kang, M., 2018. Risk assessment of toxic metals in marine sediments from the Arctic Ocean using a modified BCR sequential extraction procedure. J. Environ. Sci. Heal. Part A. 53(3), 278-293.

MacDonald, D.D., Ingersoll, C.G., Berger, T.A., 2000. Development and Evaluation of Consensus-Based Sediment Quality Guidelines for Freshwater Ecosystems. Arch. Environ. Contam. Toxicol. 39 (1), 20-31. https://doi.org/10.1007/s002440010075.

Marchand, P., Rancourt, D.G., 2009. General Model for the Aqueous Precipitation of Rough-Surface Nanocrystals and Application to Ferrihydrite Genesis. Am. Mineral. 94 (10), 1428-1439.

McLennan, S.M., 2001. Relationships between the trace element composition of sedimentary rocks and upper continental crust. Geochemistry, Geophys. Geosystems. 2 (4). https://doi.org/10.1029/2000gc000109.

Mentasti, E., Nicolotti, A., Porta, V., Sarzanini, C., 1989. Comparison of different pre-concentration methods for the determination of trace levels of arsenic, cadmium, copper, mercury, lead and selenium. Analyst 114 (9), 1113-1117. https://doi.org/10.1039/AN9891401113.

Millward, G.E., Liu. Y.P., 2003. Modelling Metal Desorption Kinetics in Estuaries. Sci. Total Environ. 314-316, 613-623. https://doi.org/10.1016/S0048-9697(03)00077-9

Morillo, J., Usero, J., Gracia, I., 2004. Heavy Metal Distribution in Marine Sediments from the Southwest Coast of Spain. Chemosphere 55 (3), 431-442. http://dx.doi.org/10.1016/j.chemosphere.2003.10.047.

Mossop, K.F., Davidson, C.M., 2003. Comparison of original and modified BCR sequential extraction procedures for the fractionation of copper, iron, lead, manganese and zinc in soils and sediments. Anal. Chim. Acta 478(1), 111-118. https://doi.org/10.1016/S0003-2670(02)01485-X

Muller, G., 1969. Index of Geoaccumulation in Sediments of the Rhine River. GeoJournal 2, 108-118.

Murray, J.W., Spell, B., Paul, B., 1983 The Contrasting Geochemistry of Manganese and Chromium in the Eastern Tropical Pacific Ocean. In: Wong, C.S., Boyle, E., Bruland, K.W., Burton, J.D., Goldberg, E.D., (Eds.) Trace Metals in Sea Water. NATO Conference Series (IV Marine Sciences), vol 9. Springer, Boston, MA. https://doi.org/10.1007/978-1-4757-6864-0_37.

Nagarajan, R., Armstrong-Altrin, J.S., Kessler, F.L., Hidalgo-Moral, E.L., Dodge-Wan, D., Taib, N.I., 2015b. Provenance and Tectonic Setting of Miocene Siliciclastic Sediments, Sibuti Formation, Northwestern Borneo. Arab. J. Geosci. 8 (10), 8549-8565. https://doi.org/10.1007/s12517-015-1833-4.

Nagarajan, R., Jonathan, M.P., Roy, P.D., Wai-Hwa, L., Prasanna, M.V., Sarkar, S.K., and Navarrete-López, M., 2013. Metal Concentrations in Sediments from Tourist Beaches of

Miri City, Sarawak, Malaysia (Borneo Island). Mar. Pollut. Bull. 73 (1), 369-373. http://dx.doi.org/10.1016/j.marpolbul.2013.05.036.

Nagarajan, R., Jonathan, M.P. Roy, P.D. Muthusankar, G., Lakshumanan, C., 2015a. Decadal Evolution of a Spit in the Baram River Mouth in Eastern Malaysia. Cont. Shelf Res. 105, 18-25. http://dx.doi.org/10.1016/j.csr.2015.06.006.

Nagarajan, R., Roy, P.D., Jonathan, M.P., Lozano, R., Kessler, F.L., Prasanna, M.V., 2014. Geochemistry of Neogene Sedimentary Rocks from Borneo Basin, East Malaysia: Paleo-Weathering, Provenance and Tectonic Setting. Chem. Erde. 74 (1), 139-146. https://doi.org/10.1016/j.chemer.2013.04.003

Nagarajan, R., Armstrong-Altrin, J. S., Kessler, F. L., Jong J., 2017a. Petrological and geochemical constraints on provenance, paleo-weathering and tectonic setting of clastic sediments from the Neogene Lambir and Sibuti Formations, NW Borneo (Chapter 7). In: Rajat Mazumder (Ed.), Sediment Provenance: influences on compositional change from source to sink Elsevier Amsterdam, Netherlands. pp.123-153. http://dx.doi.org/10.1016/B978-0-12-803386-9.00007-1

Nagarajan R., Roy, P.D., Kessler, F.L., Jong, J., Vivian D., Jonathan, M.P., 2017b. An integrated study of geochemistry and mineralogy of the Upper Tukau Formation, Borneo Island (East Malaysia): Sediment Provenance, Depositional Setting and Tectonic Implications. J. Asian Earth Sci. 143:77-97. https://doi.org/10.1016/j.jseaes.2017.04.002

Nagarajan, R., Anandkumar, A., Hussain, S.M. Jonathan, M.P., Ramkumar, Mu., Eswaramoorthi, S., Saptoro, A., Chua, H.B., 2019. Geochemical characterization of beach sediments of the NW Borneo, SE Asia: Implications on provenance, weathering intensity and assessment of coastal environmental status. In: Ramkumar, Mu., Arthur

James, R., Menier, D., Kumaraswamy, K., (Eds.). Coastal Zone Management: Global Perspectives, Regional Processes, Local Issues. pp.279-330. Elsevier, https://doi.org/10.1016/B978-0-12-814350-6.00012-4

Namieśnik, J., Rabajczyk, A., 2012. Speciation Analysis of Chromium in Environmental Samples. Crit. Rev. Environ. Sci. Technol. 42 (4), 327-377. https://doi.org/10.1080/10643389.2010.518517

Naylor, C., Davison, W., Motelica-Heino, M., Van Den Berg, G.A., Van Der Heijdt. L.M., 2004. Simultaneous release of sulfide with Fe, Mn, Ni and Zn in marine harbour sediment measured using a combined metal/sulfide DGT probe. Sci. Total Environ 328 (1), 275-286. https://doi.org/10.1016/j.scitotenv.2004.02.008

Nemati, K., Bakar, N.K.A., Abas, M.R., Sobhanzadeh, E., 2011. Speciation of Heavy Metals by Modified BCR Sequential Extraction Procedure in Different Depths of Sediments from Sungai Buloh, Selangor, Malaysia. J. Hazard. Mater. 192 (1), 402-410. http://dx.doi.org/10.1016/j.jhazmat.2011.05.039.

Orani, A.M., Vassileva, E., Renac, C., Schmidt, S., Angelidis, M.O., Rozmaric, M., Louw, D., 2019. First assessment on trace elements in sediment cores from Namibian coast and pollution sources evaluation. Sci. Total Environ. 669, 668-682. https://doi.org/10.1016/j.scitotenv.2019.03.059

Pardo, R., Barrado, E., Lourdes, P., Vega. M., 1990. "Determination and Speciation of Heavy Metals in Sediments of the Pisuerga River. Water Res. 24 (3), 373-379. http://dx.doi.org/10.1016/0043-1354(90)90016-Y.

Pekey, H., Karakaş, D., Ayberk, S., Tolun, L., Bakoğlu, M., 2004. Ecological risk assessment using trace elements from surface sediments of Izmit Bay (Northeastern Marmara Sea)

Turkey. Mar. Pollut. Bull. 48(9-10), 946-953. https://doi.org/10.1016/j.marpolbul.2003.11.023

Perin, G., Craboledda, L., Lucchese, M., Cirillo, R., Dotta, L., Zanette, M. L., Orio, A.A., 1985. Heavy Metal Speciation in the Sediments Northern Adriatic Sea - a New Approach for Environmental Toxicity Determination. In: T.D. Lekkas (Ed.), Heavy Metal in the Environment, Vol. 2, CEP Consultant, Edinburgh, pp. 454-456.

Persaud, D., Jaagumagi, R., Hayton, A., 1993. Guidelines for the Protection and Management of Aquatic Sediment Quality in Ontario. Toronto: Ontario Ministry of the Environment and Energy. 27p. http://hdl.handle.net/10214/15797

Prabakaran, K., Nagarajan, R., Eswaramoorthi, S., Anandkumar, A., Franco, F.M., 2019. Environmental significance and geochemical speciation of trace elements in Lower Baram River sediments. Chemosphere, 219, 933-953. https://doi.org/10.1016/j.chemosphere.2018.11.158

Prabakaran, K., Eswaramoorthi, S., Nagarajan, R., Anandkumar, A., Franco, F.M., 2020. Geochemical behaviour and risk assessment of trace elements in a tropical river, Northwest Borneo. Chemosphere 252, 126430. https://doi.org/10.1016/j.chemosphere.2020.126430.

Ramasamy, N., Franz, L.K., Jong, J., Ramkumar, Mu., Abdulmajid Muhammad A., Vivian D., Lalitguha, S., Naltalie, V., Kovin, S., Desianne, K.S., 2021. Geochemistry of the Palaeocene-Eocene Upper Kelalan Formation, NWBorneo: Implications on palaeoweathering, tectonic setting, and provenance. Geol. J. 56, 2500–2527. https://doi.org/10.1002/gj.3950

Rauret, G., Lopez-Sanchez, J.F., Sahuquillo, A., Rubio, R., Davidson, C., Ure, A., Quevauviller, P., 1999. Improvement of the BCR three step sequential extraction procedure prior to the certification of new sediment and soil reference materials. J. Environ. Monit. 1 (1), 57-61. https://doi.org/10.1039/A807854H

Rauret, G., Rubio, R., López-Sánchez, J.F., Casassas, E., 1988. Determination and Speciation of Copper and Lead in Sediments of a Mediterranean River (River Tenes, Catalonia, Spain). Water Res. 22 (4), 449-455. https://doi.org/10.1016/0043-1354(88)90039-5

Raymont, J.E.G., 1980. Plankton & Productivity in the Oceans: 2nd Edition, Vol. 1: Phytoplankton. Pergamon, England, 489p.

Sajimol S., Roy, P.D., Lakshumanan, C., Nagarajan, R., 2021. Evaluation of metals and trace elements in sediments of Kanyakumari beach (southernmost India) and their possible impact on coastal aquifers. Mar. Poll. Bull. 169 112527. https://doi.org/10.1016/j.marpolbul.2021.112527

Salomons, W., Förstner, U., 1980. Trace Metal Analysis on Polluted Sediments: Part II: Evaluation of Environmental Impact. Environ. Technol. 1 (11), 506-517. https://doi.org/10.1080/09593338009384007

Schintu, M., Marrucci, A., Marras, B., Galgani, F., Buosi, C., Ibba, A., Cherchi, A., 2016. Heavy Metal Accumulation in Surface Sediments at the Port of Cagliari (Sardinia, Western Mediterranean): Environmental Assessment Using Sequential Extractions and Benthic Foraminifera. Mar. Pollut. Bull. 111 (1), 45-56. https://doi.org/10.1016/j.marpolbul.2021.112414

Sholkovitz, E.R., 1978. The flocculation of dissolved Fe, Mn, Al, Cu, Ni, Co and Cd during estuarine mixing. Earth Planet. Sci. Lett. 41 (1), 77-86. https://doi.org/10.1016/0012-821X(78)90043-2

Sholkovitz, E.R., 1979. Chemical and Physical Processes Controlling the Chemical Composition of Suspended Material in the River Tay Estuary. Estuarine, Coastal Marine Sci. 8 (6), 523-545. https://doi.org/10.1016/0302-3524(79)90033-1

Sharifah Mastura, S.A., 1992. The Coastal Zone in Malaysia: Processes, issues and management plan. Background paper), Malaysian National conservation Strategy, Economic Planning Unit, Kuala Lumpur. 31p.

Shiller, A.M., Boyle, E.A., 1991. Trace Elements in the Mississippi River Delta Outflow Region: Behavior at High Discharge. Geochim. Cosmochim. Acta 55 (11), 3241-3251. https://doi.org/10.1016/0016-7037(91)90486-O

Smieja-Król, B., Janeczek, J., Bauerek, A., Thorseth. I.H., 2015. The Role of Authigenic Sulfides in Immobilization of Potentially Toxic Metals in the Bagno Bory Wetland, Southern Poland. Environ. Sci. Pollut. Res. 22 (20), 15495-15505. https://doi.org/10.1007/s11356-015-4728-8

Steger, H.F., Desjardins. L.E., 1980. Oxidation of Sulfide Minerals; V. Galena, Sphalerite and Chalcocite. Canadian Mineral. 18 (3), 365-372.

Szefer, P., Glasby, G.P., Pempkowiak, J., Kaliszan, R. 1995. Extraction Studies of Heavy-Metal Pollutants in Surficial Sediments from the Southern Baltic Sea Off Poland. Chem. Geol. 120 (1), 111-126. https://doi.org/10.1016/0009-2541(94)00103-F

Takata, H., Aono, T., Tagami, K., Uchida, S., 2010. Processes Controlling Cobalt Distribution in Two Temperate Estuaries, Sagami Bay and Wakasa Bay, Japan. Estuarine, Coastal Shelf Sci. 89 (4), 294-305.

Tang, D., Warnken, K.W., Santschi, P.H., 2002. Distribution and Partitioning of Trace Metals (Cd, Cu, Ni, Pb, Zn) in Galveston Bay Waters. Mar. Chem. 78 (1), 29-45. https://doi.org/10.1016/S0304-4203(02)00007-5

Tang, F.E., Lee, V.Z. 2010. CNRGT6: A Study of Coastal Areas in Miri, Sarawak." In: Soom, M.A.M. (Ed.), World Engineering Congress 2010, Proceedings of Conference on Natural and Green Technology. pp.56-65. International Association of Engineers (IAENG), Kuching, Sarawak, Malaysia.

Tappin, A.D., Millward, G.E., Statham, P.J., Burton, J.D., Morris, A.W., 1995. Trace Metals in the Central and Southern North Sea. Estuarine, Coastal Shelf Sci. 41 (3), 275-323. https://doi.org/10.1006/S0272-7714(85)70068-7

Tessier, A., Campbell, P.G.C., Blsson, M., 1979. Sequential Extraction Procedure for the Speciation of Particulate Trace Metals. Anal. Chem. 51 (7), 844-851. https://doi.org/10.1021/ac50043a017

Tipping, E. 1981. The Adsorption of Aquatic Humic Substances by Iron Oxides. Geochim. Cosmochim. Acta 45 (2), 191-199. https://doi.org/10.1016/0016-7037(81)90162-9

Tiquio, M.G.J., Hurel, C., Marmier, N., Taneez, M., Andral, B., Jordan, N., Francour, P., 2017. Sediment-bound trace metals in Golfe-Juan Bay, northwestern Mediterranean: Distribution, availability and toxicity. Mar. Pollut. Bull. 118(1-2), 427-436. https://doi.org/10.1016/j.marpolbul.2017.02.065

Tomlinson, D.L., Wilson, J.G., Harris, C.R., Jeffrey, D.W., 1980. Problems in the assessment of heavy-metal levels in estuaries and the formation of a pollution index. Helgol. Meeresunters. 33(1), 566-575. https://doi.org/10.1007/BF02414780

Turner, A., Millward, G.E., 2002. Suspended Particles: Their Role in Estuarine Biogeochemical Cycles. Estuarine, Coastal Shelf Sci. 55(6), 857-883. https://doi.org/10.1006/ecss.2002.1033.

Ure, A.M., Quevauviller, P., Muntau, H., Griepink, B., 1993. Speciation of Heavy Metals in Soils and Sediments. An Account of the Improvement and Harmonization of Extraction Techniques Undertaken under the Auspices of the BCR of the Commission of the European Communities. Int. J. Environ. Anal. Chem. 51 (1-4), 135-151. https://doi.org/10.1080/03067319308027619

Van Der Zee, C., Roberts, D.R., Rancourt, D.G., Slomp, C.P., 2003. Nanogoethite Is the Dominant Reactive Oxyhydroxide Phase in Lake and Marine Sediments. Geology 31 (11), 993-996. https://doi.org/10.1130/G19924.1

Wali, A., Kawachi, A., Bougi, M.S.M., Dhia, H.B., Isoda, H., Tsujimura, M., Ksibi, M., 2015. Effects of Metal Pollution on Sediments in a Highly Saline Aquatic Ecosystem: Case of the Moknine Continental Sebkha (Eastern Tunisia). Bull. Environ. Contam. Toxicol. 94 (4), 511-518. https://doi.org/10.1007/s00128-015-1469-9

Wang, S., Hu, J., Li, J., Dong, Y., 2009. Influence of Ph, Soil Humic/Fulvic Acid, Ionic Strength, Foreign Ions and Addition Sequences on Adsorption of Pb (II) onto Gmz Bentonite. J. Hazard. Mater. 167 (1), 44-51. https://doi.org/10.1016/j.jhazmat.2008.12.079

Wen, L.S., Santschi, P.H., Warnken, K.W. Davison, W., Zhang, H., Li, H.P., Jiann, K.T., 2011. Molecular Weight and Chemical Reactivity of Dissolved Trace Metals (Cd, Cu, Ni) in

Surface Waters from the Mississippi River to Gulf of Mexico. Estuarine, Coastal Shelf Sci. 92 (4), 649-658. https://doi.org/10.1016/j.ecss.2011.03.009

Whitney, P.R., 1975. Relationship of Manganese-Iron Oxides and Associated Heavy Metals to Grain Size in Stream Sediments. J. Geochem. Explor. 4 (2), 251-263. https://doi.org/10.1016/0375-6742(75)90005-9

WHO, 1991. International Programme On Chemical Safety, Environmental Health Criteria 124, Lindane, 155p.

Windom, H., Byrd, J. Smith, R., Hungspreugs, M., Dharmvanij, S., Thumtrakul, W., Yeats, P., 1991. Trace Metal-Nutrient Relationships in Estuaries. Mar. Chem. 32 (2), 177-194. https://doi.org/10.1016/0304-4203(91)90037-W

Wooster, M.J., Perry, G.L.W., Zoumas, A., 2012. Fire, Drought and El Niño Relationships on Borneo (Southeast Asia) in the Pre-Modis Era (1980–2000). Biogeosciences 9 (1), 317-340. https://doi.org/10.5194/bg-9-317-2012

Xie, M., Alsina, M.A., Yuen, J., Packman, A.I., Gaillard, J.F., 2019. Effects of resuspension on the mobility and chemical speciation of zinc in contaminated sediments. J. Hazard. Mater. 364, 300-308. https://doi.org/10.1016/j.jhazmat.2018.10.043

Xu, Y., Axe, L. 2005. Synthesis and characterization of iron oxide-coated silica and its effect on metal adsorption. J. colloid interface sci. 282(1), 11-19. https://doi.org/10.1016/j.jcis.2004.08.057

Xu, L., Wang, T., Wang, J., Lu, A., 2017. Occurrence, speciation and transportation of heavy metals in 9 coastal rivers from watershed of Laizhou Bay, China. Chemosphere, 173, 61-68. https://doi.org/10.1016/j.chemosphere.2017.01.046

Zhang, J., Liu, C.L., 2002. Riverine Composition and Estuarine Geochemistry of Particulate Metals in China—Weathering Features, Anthropogenic Impact and Chemical Fluxes. Estuarine, Coastal Shelf Sci. 54 (6), 1051-1070. https://doi.org/10.1006/ecss.2001.0879

Zhao, M., Shenghui Z., Haitao H., Pan, D., 2021. Heavy metals in sediments of Yellow Sea and East China Sea: Chemical speciation, distribution, influence factor, and contamination. J. Oceanol. Limnol. https://doi.org/10.1007/s00343-020-0237-9

Zirino, A., Yamamoto, S., 1972. A Ph-Dependent Model for the Chemical Speciation of Copper, Zinc, Cadmium, and Lead in Seawater. Limnol. Oceanogr. 17 (5), 661-671. https://doi.org/10.4319/lo.1972.17.5.0661

List of Figures

Figure 1 Location map of the study area showing the sample locations

Figure 2. The average percentage of metals in different fraction of beach sediments of Miri coast during the MON season

Figure 3. The average percentage of metals in different fraction of beach sediments of Miri coast during the POM season

Figure 4. Level of CF values for beach sediments during (a) the MON season and (b) the POM season.

Figure 5. Geo-accumulation index (I_{geo}) value of analyzed metals during (a) the MON season and (b) the POM season.

Figure 6. Biological effects of selected trace metals on living organisms based on the guideline values (a) the MON season and (b) the POM season (Long et al. 1995)

List of Tables

Table 1. Granulometry, organic carbon, calcium carbonate (in %) and total trace metal concentrations (μg.g^{-1}) of the Miri beach sediments

Table-2. Average concentration of trace metals associated with each fraction in the sediments of various beaches in the study area

Table 3 Rotated Component Matrix components for SW and NE segments of the study area during the MON season

Table 4 Rotated Component Matrix components for SW and NE segments of the study area during the POM season

Table 5. Comparison of total trace metal concentrations (FR 01+FR 02+FR 03+FR 04) in different beaches of the Miri coast with the eco-toxicological values used to determine marine sediment quality

Table 6. The summary of total trace metal (FR 01+FR 02+FR 03+FR 04) concentrations (μg g^{-1}) in sediments of the Miri coast sediments and comparison with UCC, PAAS, geological formations exposed in the source area/coastal area, and sediments from adjacent rivers

List of Supplementary Tables

Table S12 Correlation of partition coefficient (Kd) of total trace metals with the water column parameters in the SW segment during the MON season

Table S13 Correlation of partition coefficient (Kd) of total trace metals with the water column parameters in the NE segment during the MON season

Table S14 Correlation of partition coefficient (Kd) of trace metals in the exchangeable fraction (F1) with the water column parameters during the POM season

Table S15 Correlation of partition coefficient (Kd) of trace metals in the reducible fraction (F2) with the water column parameters during the POM season

Table S16 Correlation of partition coefficient (Kd) of trace metals in the oxidizable fraction (F3) with the water column parameters during the POM season

Table S17 Correlation of partition coefficient (Kd) of total trace metals with the water column parameters in the SW segment during the POM season

Table S18 Correlation of partition coefficient (Kd) of total trace metals with the water column parameters in the NE segment during the POM season

Table S19a. Pearson Correlation analysis for the water samples during the monsoon season

Table S19b. Pearson Correlation analysis for the water samples during the post-monsoon season

Table S20. Ranges of Geo-accumulation Index

Table S21. Guideline values and biological effects of heavy metals (after Long et al., 1995)

Table S22. Criteria of Risk Assessment Code (Perin et al., 1985)

Table S23. Comparison of RAC values for all the beaches in the MON season and POM season