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Spectrometry and Chemometrics Interpretation of Metals in the Sulu and Celebes Seas of Malaysian Waters During PMSE 09' Expedition

[1]G. Adiana, [2]B. Joseph, [2]N.A.M. Shazili, [3]M. Mohamad and [1]H. Juahir
[1]East Coast Environmental Research Institute (ESERI),
Universiti Sultan Zainal Abidin (UniSZA), Gong Badak Campus,
21300 Kuala Nerus, Terengganu, Malaysia
[2]Institute of Oceanography and Environment, Universiti Malaysia Terengganu,
21030 Kuala Nerus, Terengganu, Malaysia
[3]Faculty of Business Management and Accountancy, Universiti Sultan Zainal Abidin (UnisZA),
Gong Badak Campus, 21300 Kuala Nerus, Terengganu, Malaysia

Abstract: A research expedition was carried out off the Borneo Island coastal in order to define the current level and behavior of metals in the water column of Sulu and Celebes Seas. Water samples were collected at 37 stations off Sabah and Sarawak coasts. Samples were then pre-concentrated using Chelex-100 resin, preserved on-board ship prior transportation to the laboratory and finally, analyzed using Inductively Coupled Plasma Mass Spectrometry (ICP-MS). Overall, the vertical profiling of metals showed no distinctive patterns. In the meantime, the Principal Component Analysis (PCA) showed a group of bioactive metals and abundance metals in the upper continental crust. Additionally, PCA showed the decrease in of temperature and salinity led to increase of Dissolved Oxygen (DO) in depth. Besides that, the elements partitioning exhibits that Chromium (Cr), Nickel (Ni), iron (Fe) and lead (Pb) has the strongest adsorption onto Suspended Particulate Matter (SPM) whereas Cadmium (Cd), Zinc (Zn) and Aluminium (Al) showed the weakest bond with SPM. In brief, data collected throughout the present research has evidence the influenced of land-based contaminants into the water column as well as the physico-chemical characteristics of Sulu and Celebes Seas off Malaysian waters.

Key words: Dissolved metals, particulate metals, chemometrics, Borneo Island, Sulu Sea, Celebes Sea

INTRODUCTION

Metals universally exist in the environment. Their existence in the seawater is well known in both dissolved and particulate forms. Elements released from natural and anthropogenic sources will interact with the ambient natural processes in the water column leading to metal complexation and transformation into element species (Ong *et al*., 2015; Bing *et al*., 2016; Ghazali *et al*., 2016). Some of the elements will uptake and bio-accumulate in marine organisms whereas others will be circulated between water column and surface sediment. Their composition in the seawater is influenced by many processes which include atmospheric deposition (dry or wet), land based run-off, riverine flush-out, water-surface sediment interactions as well as biological and physical-chemical processes (Jimenez *et al*., 2002; Camel, 2003; Mokhtar *et al*., 2003; Valdes *et al*., 2005; Fonseca *et al*., 2013; Sindern *et al*., 2016). Generally, elements are depleted in the surface water and enriched with depth suggesting that the elements vertical distribution is strongly controlled by biogeochemical cycling process associated with gravitational settlement and decomposition (Cuong *et al*., 2008). Besides that, metals uptake by marine organisms result in metal depletion in the surface water. Metals then return to the water column through dead organisms while fecal pellets sink into the deeper water and are mineralized.

Sulu and Celebes Seas are marginal basins that are a part of Western Pacific Ocean and both is separated by Sibutu-Basilan Ridge. Sulu is encompassing by Southwest Philippines, Northwest Palawan, Celebes Sea, Borneo Island, Sulu archipelago and Visayas Island. In the meantime, Celebes Seas is shelter by Sulu Sea, Sulu archipelagos, Sangihe Islands, Mindanao Island, Borneo Island and Indonesian archipelagos. Sulu Seas covers approximately 250,000 km^2 area and is isolated from South China Sea by Mindoro shallow sill with <400 m depth (Calvert *et al*., 1993; Nozaki *et al*., 1999; Norisuye *et al*., 2007; Asante *et al*., 2010; Beaufort *et al*., 2003). Since, Sulu Sea is isolated by the shallow sills this sea possesses a pure marine water column with their own

Corresponding Author: G. Adiana, East Coast Environmental Research Institute (ESERI), Gong Badak Campus,
Universiti Sultan Zainal Abidin (UnisZA), 21300 Kuala Nerus, Terengganu, Malaysia

unique chemical, physical and biological processes. Sulu Sea area contains a number of coral and volcanic atolls such as Mapun Island an this sea is extensively used for fisheries, inter-island trading and tourisms (DeVantier *et al*., 2004). In the meantime, Celebes Sea covers approximately 380,000 km^2 area and opens to Java Sea through Makassar Strait (DeVantier *et al*., 2004; Obata *et al*., 2007; Asante *et al*., 2010). This sea is separated from West Philippine Sea basin by a complex series of plate boundaries (Nicholas and Hall, 1999). Sulu and Celebes Seas are located in between Asian continent and Western Pacific warm pool which receives the highest mean temperature in the earth with the annual sea surface temperature above 29°C (Linsley, 1996; Beufort *et al*., 2003). Both seas are largely influence by the monsoon changes annually. The Sulu and Celebes Seas off Malaysian waters are hotspot areas for tourism as they offer numerous Scenic Islands with the natural beauty of the corals (Mohamad *et al*., 2012; Mahadzirah *et al*., 2014).

Numerous multidisciplinary research have been carried out to investigate the uniqueness of Sulu and Celebes Seas. An article published by Nozaki *et al.* (1999) discussed on the vertical profiling of dissolved rees which being affected by the physical and biogeochemical processes. A research by Calvert *et al.* (1993) defined the geochemistry of metals in the Sulu and South China Seas surface sediment. A part of the findings described that metal-aluminium ratio in the surface sediment decreased with increase in water depth corresponding to the changes in mineralogy and sediment texture. Asante *et al.* (2010) wrote an article on trace elements and stable isotope ratios of C^{13} and N^{15} in variety of fishes in the Sulu, Celebes and Philippine Seas. They intended to define the accumulation pattern as well as vertical and regional distribution of these elements in 22 species of pelagic and demersal fishes. In the meantime, Obata *et al.* (2007) carried out a research to investigate the characteristics of Mn, Ce and Fe in the water column of the Celebes, Sulu and Philippine Seas. Similarly, Norisuye *et al.* (2007) studied the vertical distribution of bioactive trace metals in the Sulu and South China Seas. Generally the distribution of bioactive metals in the surface water layer of both seas is influenced by water circulation, biological removal and external input. In the other hand, distribution of metals in deep water depends on topography, water circulation and supply from the coastal/fluvial waters, shelf, sill bottoms and benthic sediments.

During the period of 18th June, 2009 to 2nd August, 2009, National Oceanography Directorate, Ministry of Science, Technology and Innovation of Malaysia has funded Prime Marine Scientific Expedition 2009 (PMSE 09') with the cooperation of Royal Navy Malaysia (RMN). PMSE 09' was joined by several local universities and Malaysian government agencies to investigate marine environmental processes in order to maintain the sea health and productivity, in relation to the Coral Triangle Initiative. The research cruise was carried out using RMN survey vessel, KD Perantau across Sulu and Celebes Seas off Malaysian coastal. The area covered was divided into four sections namely Leg 1 (Port Klang to Labuan Island), Leg 2 (Labuan Island to Kota Kinabalu), Leg 3 (Kota Kinabalu to Tawau) and Leg 4 (Tawau to Kota Kinabalu). The present study covered only Leg 3 and 4 trips due to define the effect of human population, tourism and industrial activities towards these seas as well as to define the behavior of dissolved and particulate metals in correlation with water parameters.

MATERIALS AND METHODS

Sample collection: Laboratory wares were soaked in 10% of nitric acid (HNO_3) and rinsed thoroughly using Mili-Q water for sample preparation and analysis. Water samples were collected at 37 stations (Fig. 1) using Mercos all Teflon bottle sampler at possibly four water layers (1, 25, 50 and 100 m) depending on the water depth. Mercos sampler was released and drawn using man-power in order to keep the sampler as clean as possible, thus, water samples were able to collect up to 100 m deep.

Collected water samples were immediately filtered using 0.45 μm acid-washed Polytetrafluoroethylene (PTFE) membranes. Next, water samples were pre-concentrated using Chelex-100 under laminar flow cabinet. Particulate samples retained on PFTE membranes were stored in air-tight plastic container separately whereas dissolved samples were preserved using concentrated HNO_3. Both samples were kept under 4°C prior transportation to the lab. for analysis. Besides that, physical parameters were measured in-situ using well-inspected CTD Seabird.

Laboratory analysis: Pre-concentrated dissolved metals in Chelex-100 columns were treated ammonium acetate in order to remove salt content and then dissolved metals were eluted using HNO_3 (Adiana *et al*., 2011). In the meantime, particulate metals were digested using mixed concentrated Suprapur acids under Ethos Plus microwave heating. Method used to treat both type of samples are in accordance with Nearshore Seawater Reference Material for Trace Metals (CASS-5) and Estuarine Sediment. This is to ensure that accurate and precise methodologies were used in the study. Blanks were carried out using Mili-Q water and acid-washed PTFE membrane filters for

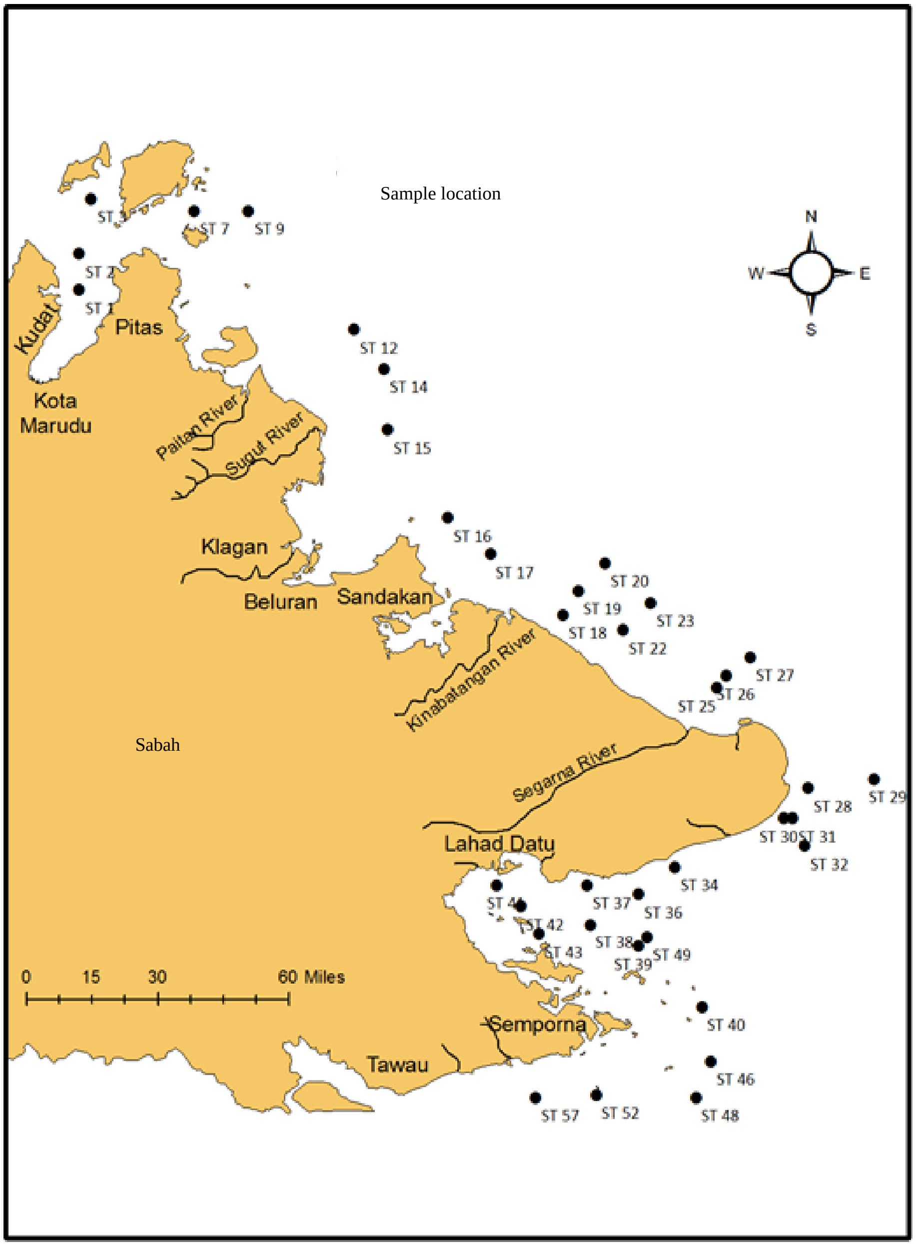

Fig. 1: Sampling location during PMSE 09' expedition

dissolved and particulate phase, respectively. Metal recovery result recorded was in the range of 93-115% for dissolved phase and 90-111% for particulate phase.

Data and statistical analysis: The concentration of dissolved and particulate metals as well as water physical parameters were imported and analysis using chemometric analysis. This comprehensive statistical approach was carried out using Microsoft Excel 2007 with XLSTAT 2014.5.03 add-in.

Principal component analysis: Principal Component Analysis (PCA) is a multivariate statistical method which has been extensively used to classify data through defining the relationship between measured variables. PCA uses variables reduction technique to minimize variables observed and can be expressed as:

$$Z_{ij} = a_{i1}x_{1j}+a_{i2}x_{2j}+a_{i3}x_{3j}+a_{im}x_{mj}$$

Where:

z = Measured value of a variable

a = Component loading

x = Component score
I = Sample number
m = Total number of factors

Normally, PCA uses Factor Analysis (FA) in order to interpret a complex and large dataset as it will define similarities between variables (Reghunath *et al*., 2002; Juahir *et al*., 2010, 2011). Eigenvalues in PCA normally defines the amount of variation in each factor. Based on the Kaiser criterion, a Principal Component (PC) is considered as statistically significant of the eigenvalues is equal or bigger than 1 (Baharuddin *et al*., 2014; Adiana *et al*., 2017). Additionally, generated Principal Components (PCs) are sometimes not readily interpreted. Hence, the PCs are urged to be rotated using varimax rotation, resulted new groups of variables namely Varimax Factors (VFs). Varimax method is an orthogonal rotation method that minimizes the number of variables that have high loadings on each factor. This method simplifies the interpretation of the factors and gives the clearest separation of factors compared to other rotation method. According to Liu *et al*. (2003), the VF coefficient having a correlation >0.75, 0.75-0.50 and 0.50-0.30 are considered as strong, moderate and weak significant factor loadings correspondingly. In the present study, PCA/FA for metals group was applied to 15 variables of normalized dataset.

Metals partitioning: Partitioning of metal between the particulate (>0.45 μm) and dissolved (<0.45 μm) phase is commonly quantified in terms of the distribution coefficient, K_D (Benoit *et al*., 1994; Benoit and Rozan, 1999; Munksgaard and Parry, 2001; Nguyen *et al*., 2005):

$$K_D = \frac{[\text{Particulate metal concentration}]\ (\mu g/kg)}{[\text{Dissolved metal concentration}]\ (\mu g/L)}$$

K_D is the measurement of the tendency of an element to be associated and transported with the particulate phase where the magnitude of K_D could indicate the strength of the suspended activity. High particle reactivity for a metal tends to increase that metal's K_D value.

Enrichment factor: Enrichment Factor (EF) is an assessment to quantify the level of anthropogenic influences according to their background value (Dung *et al*., 2013; Bidai *et al*., 2016; Yao *et al*., 2016). In the present research, EF was only applied to particulate metals as it has strong correlation with the upper continental crust compared to dissolved metals. Fe was selected as the normalizer, since, it has significant correlation with most metals. EF value was calculated according to the following formula (Idris, 2008):

$$EF = \frac{(T_{Me}/T_{Fe})\ \text{sample}}{(T_{Me}/T_{Fe})\ \text{earth crust}}$$

Where:

T_{me} = Total concentration of an element in the sediment
T_{fe} = Total concentration of Fe in the sediment

According to Yao *et al*. (2016) an element is derived from crustal material and natural weathering process if its EF value is <1.5. However, if the EF value of an element is >1.5, it is derived by an anthropogenic source. Additionally, an element is enriched if its EF values is >1 but it is depleted if its EF value is smaller than 1.

RESULTS AND DISCUSSION

Figure 2 shows the range of dissolved and particulate metals in the Sulu and Celebes Seas of Malaysian waters. The lower and upper lines of the box represent the minimum and maximum value of the data set, respectively. The horizontal line drawn within the box represents the median of the data set whereas the two vertical lines extended from the box represent the standard deviation of the data set.

Overall, the median value indicated that most of the dissolved and particulate metals data were distributed towards the minimum value of the data set. Dissolved Cr, Cu and Pb as well as particulate metals have a wide range of data. Generally, minimum concentration of most dissolved metals was found in the 100 m water layer of stations ST57, ST40 and ST48 whereas minimum concentration of particulate metals was largely distributed on the surface water of station ST40. The maximum concentration of dissolved and particulate metals was found at stations closest to the Borneo Island coasts, namely at stations ST37, ST7 and ST26.

On the whole, Pearson correlation showed that, on the surface water (1 m), dissolved and particulate Cd showed significant correlation ($p<0.01$) with dissolved and particulate Pb. In the meantime, dissolved and particulate Ni and Cu were significant correlated ($p<0.01$) with particulate Cr, Mn, Fe and Co. On the 25 and 50 m water layers, particulate Mn, Fe, Co and Ni were significantly correlated ($p<0.01$) between themselves whereas particulate Cd was also significant correlated ($p<0.01$) with particulate Pb on both water layers.

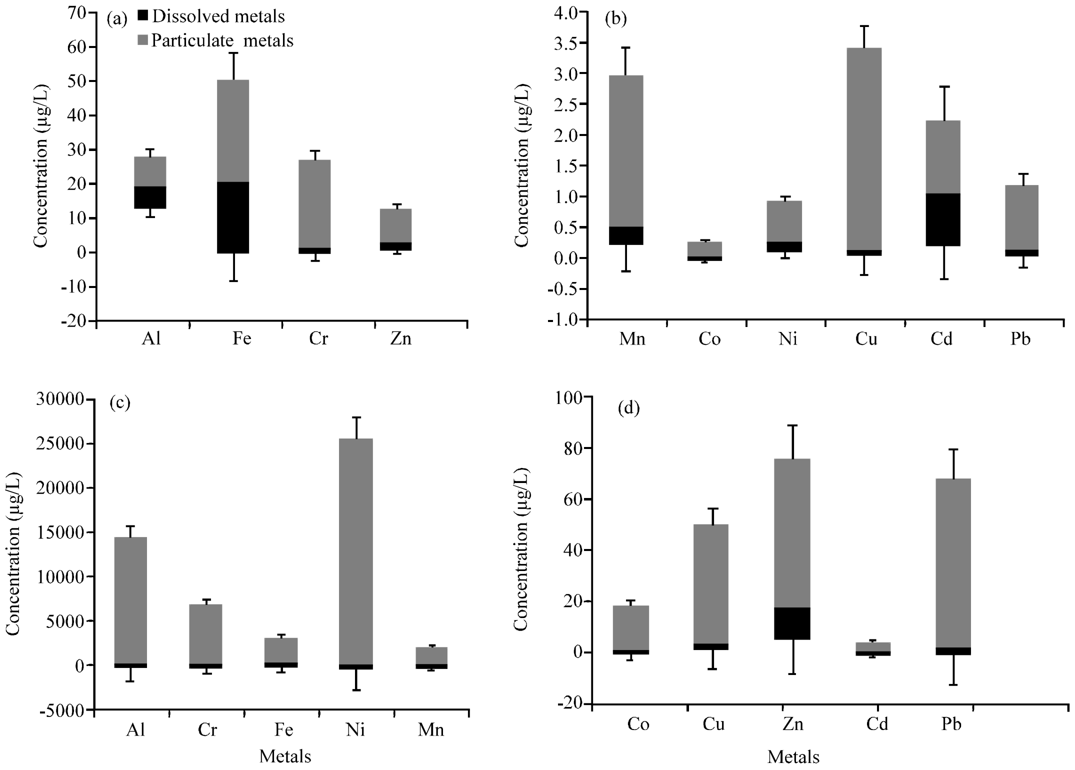

Fig. 2: a-d) Concentration range of dissolved and particulate metals in the Sulu and Celebes Seas

Meanwhile, Pearson correlation for 100 m water layer showed that most of dissolved metals (except for Al) were significantly correlated ($p<0.05$) between themselves.

The distribution of maximum concentration of metals in the Sulu and Celebes Seas of Malaysian waters during the PMSE 09' expedition provides evidences on the contribution of metals from the mainland into the seas. It is found that stations closest to the mainland of Sabah namely the Darvel Bay as well as within the vicinity of riverine flushed outs have the highest concentration. Darvel Bay, the largest bay on the east of Sabah received input from two main districts of Sabah namely Lahad Datu and Semporna. Vertical profiling of metals concentration with depth did not show any distinguished vertical distribution pattern due to water samples were collected at the surface layer of the seas, i.e., <200 m deep. According to Asante *et al*. (2010), a marine basin is classified as a deep sea if its water layer is more than 200m. Besides that, in the surface water layer, the distribution of metals tends to mix up and it will only show a stable reading once the deep water layer is reached (Calvert *et al*., 1993; Norisuye *et al*., 2007; Asante *et al*., 2010). However, minimum concentration of particulate metals on the surface water column evidence the sinking of particulate metals in both seas due to gravity settlement.

Pearson correlation matrix of all collected data proved the fact that Ni and Cu in both phases was originated from geogenic sources as they were significantly correlated with abundance metals in the earth crust, namely Al, Fe and Mn on all water layers. In contrast, the significant correlation between Cd and Pb on all water layers verified the anthropogenic behavior of both metals in the Sulu and Celebes Seas of Malaysian waters.

PCA was utilized on the raw dataset in order to delineate compositional patterns between the metals and physical parameters. Besides that, PCA could identify factors that influence the distribution of elements throughout all water layers. The elements were divided into two groups namely Dissolved Metals (DM) and Particulate Metals (PM). Four Principal Components (PCs) were acquired for PM, whereas five PCs were obtained for DM; with eigenvalues larger than 1. Total variance in the data set sum up to approximately 74.2 and 82.4%, respectively (Table 1).

Based on Table 1, the first PCA, DM showed that VF1 describes 23.1% of the total variance amongst the five Variable Factors (VFs), showing moderate negative loadings on Cr, Co Cu and DO, plus a weak positive loading on Fe and a moderate positive loading on temperature. Co, Cu, Fe and Cr are classified as bioactive trace metals in the seawater. Their critical role as

Table 1: Loadings of variables on the Varimax rotated PCs for metals data during the PMSE 09

	DM					PM				
Variables	VF1	VF2	VF3	VF4	VF5	VF1	VF2	VF3	VF4	VF5
Al	0.210	0.185	-0.529	0.374	0.406	0.542	-0.074	-0.441	-0.102	0.051
Fe	0.490	0.233	-0.362	-0.101	-0.369	0.307	0.927	0.101	-0.043	-0.078
Cr	-0.743	0.643	0.005	-0.007	0.128	0.604	-0.048	-0.352	-0.389	0.070
Mn	0.166	0.128	-0.544	-0.483	-0.224	0.190	0.958	0.170	0.038	-0.094
Co	-0.613	0.752	-0.108	0.046	0.025	0.241	0.943	0.185	0.019	-0.097
Ni	0.398	0.280	-0.455	0.432	-0.145	-0.458	0.271	-0.606	0.028	-0.068
Cu	-0.734	0.658	-0.032	-0.005	0.099	0.375	0.175	-0.114	-0.331	0.673
Zn	0.178	-0.085	-0.021	0.593	-0.037	0.657	0.089	-0.381	0.041	-0.127
Cd	-0.042	-0.506	-0.247	0.187	0.614	0.649	-0.145	-0.431	0.509	-0.151
Pb	0.130	0.325	-0.021	0.679	-0.280	0.659	-0.131	-0.438	0.493	-0.188
Conductivity	0.422	0.322	0.788	0.091	0.005	0.416	-0.100	0.693	0.466	0.244
DO	-0.716	-0.531	-0.379	0.104	-0.209	-0.716	0.230	-0.633	0.023	0.028
Salinity	-0.468	-0.326	0.582	0.288	-0.299	-0.473	0.200	0.060	0.709	0.399
Temperature	0.745	0.546	0.229	-0.153	0.245	0.745	-0.248	0.563	-0.158	-0.106
SPM	-0.115	-0.112	0.282	0.028	0.278	-0.471	-0.089	0.433	-0.047	-0.431
Eigenvalue	3.47	2.77	2.22	1.55	1.13	4.17	3.00	2.68	1.53	0.980
Variability (%)	23.10	18.45	14.82	10.31	7.51	27.81	19.99	17.88	10.18	6.540
Cumulative (%)	23.10	41.55	56.37	66.68	74.19	27.81	47.80	65.69	75.87	82.410

micronutrients to plankton have been well discussed widely (Lane *et al*, 2005; Norisuye *et al.*, 2007; Biller *et al.*, 2013; Su *et al.*, 2017). In the present study, VF1 proved that these dissolved transition metals showed some influence on DO. On the contrary, temperature was inversely related to DO. This is due to at low temperature, solubility of oxygen in the seawater increased (Badran, 2001; Rasheed *et al.*, 2003; Wheeler *et al.*, 2003; Manasrah *et al.*, 2006). VF2 of DM accounts 18.45% of the total variance with strong positive loading on Co, moderate positive loadings on Cr and Cu as well as moderate negative loading on Cd. Similar to VF1, Co, Cr, Cu and Cd are accounted as bioactive metals but in the present study, Cd may not be included as bioactive metals as it showed opposite behavior compared to Cu, Cr and Co. In some cases, even though Cd acts as micronutrient and is also known as toxic transition metal at trace level. Plankton may uptakes Cd because it closely resembles phosphate as an essential micronutrient to them (Ripperger and Rehkamper, 2007; Cox *et al.*, 2014).

In the meantime, VF3 enlighten 14.82% of the total variance has strong positive loading on conductivity, moderate positive loading on salinity, moderate negative loadings on Al and Mn, weak positive loading on SPM and weak negative loading on Fe. Al, Fe and Mn are the abundance element in the upper continental crust with the concentration of 7.7, 3.1 and 0.05% correspondingly (Wedepohl, 1995). These elements have opposite relationship with salinity, conductivity and SPM. Salinity measured the amount of salts in the water whereas conductivity is the measurement of the water ability to conduct electrical current. In the seawater, salt ions such as Na^+, K^+ and Cl^- are the conductors for conductivity (Team, 2004). Therefore, seawater salinity and conductivity measurement are closely related. VF4 and VF5 with 10.31 and 7.51% of the total variance respectively described moderate positive loadings on Zn, Pb and Cd as well as weak positive loadings on Ni and SPM.

PCA for PM (Table 1) displayed that VF1 clarifies 27.81% of the total variance has strong positive loading on temperature, moderate positive loadings on Al, Cr, Zn, Cd and Pb, moderate negative loadings on DO and weak negative loadings on SPM. Similar to VF1 of DM, DO and temperature are related in this study. At the same time, Al, Cr, Zn, Cd and Pb showed opposite relationship with DO and SPM in this water. VF2 enlighten 19.99% of the total variance, accounts strong positive loadings on Fe, Mn and Co. VF3 elucidates17.88% of the total variance showing moderate positive loadings on conductivity and negative loadings on Ni, exhibit the inverse relationship between conductivity and Ni. On the other hand, VF4 and VF5 for PM describe 10.18 and 6.54% of the total variance and have moderate positive loadings on salinity and Cu.

Besides defining the relationship of metals with physical parameters of the Sulu and Celebes Seas, metals partitioning between dissolved and particulate phases is another matter that need to be discussed. Partitioning of metals between these two phases could influence the fate and behavior of metals in the marine environment (Grassi *et al.*, 2000). Particulate metals are metals that are attached to the sorption site of SPM in the water column which will be transported elsewhere in the aquatic system through SPM scavenging. The partitioning of metals between dissolved and particulate phase in the aquatic environment depends on several parameters such as DO, pH, salinity, specific element ion, metal concentration, nature of the particle and particle concentration (Munksgaard and Parry, 2001). In the present study, partitioning is purposely made to define the changes of the metals in different water layers. The percentage of metals partitioning between dissolved and particulate phase in the Sulu and Celebes Seas of Malaysian waters is shown in Fig. 3.

Generally, throughout all water layers, all REEs and Cd were found to be more than 99% in the dissolved phase whereas Al, Cr and Zn were in the range of 75-80% in the dissolved phase out of the total concentration. The percentage of dissolved Mn throughout all water layers was similar which approximately 70% and dissolved Pb was in the range of 60-70% out of the total concentration in all water layers. In the meantime, across all water layers and out of total concentration, Fe and Co were 50-60% in the dissolved phase, dissolved Ni was in the range of 45-55% and Cu was found approximately 45% in the dissolved phase.

Partitioning coefficient (K_D) is a measure of the tendency of an element to be associated and transported along the particulate phase. High particle reactivity for a metal would tend to increase that metal's K_D value. The expression is defined by the partitioning of metals between the particulate (>0.45 μm) and dissolved (<0.45 μm) phases. The average partitioning coefficient values in the Sulu and Celebes Seas throughout the PMSE 09' expedition decreased in the following order below:

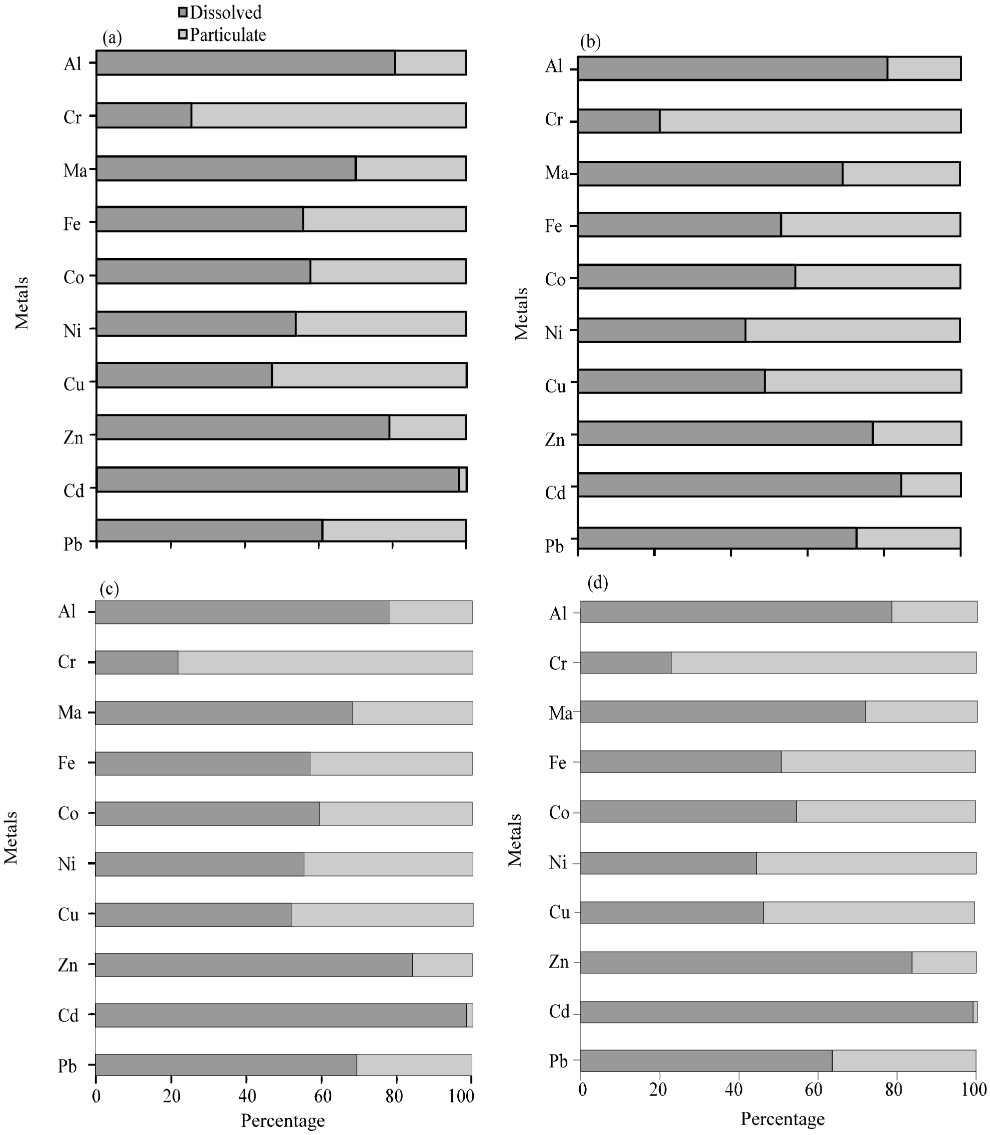

Fig. 3: Partitioning of dissolved and particulate metals in the Sulu and Celebes waters: 1 m; b) 25 m; c) 50 m and d) 100 m

- 1 m: Cr>Pb>Ni>Cu>Al>Fe>Co>Mn>Zn>Cd
- 25 m: Cr>Ni>Fe>Mn>Cu>Pb>Co>Zn>Al>Cd
- 50 m: Cr>Ni>Pb>Cu>Fe>Co>Mn>Al>Zn>Cd
- 100 m: Fe>Cr>Ni>Cu>Pb>Co>Mn>Al>Zn>Cd

Based on the average K_D values of all sampling stations, Cr, Ni and Fe showed the highest log K_D value which has the strongest SPM adsorption in all water layers. In the meantime, the mean log K_D of Pb on 1, 50 and 100 m proved that Pb is strongly bonded with SPM but on 25 m water layer, Pb has the weakest bond towards SPM. In all water layers, Cd and Zn have the weakest SPM adsorption. Al has a weak SPM adsorption in 25, 50 and 100 m water layers but it has the strongest adsorption at the surface layer (1 m). On the other hand, Mn has the weakest bond towards SPM for 1, 50 and 100 m water layers, however, strongest Mn adsorption onto SPM was on the 25 m water layer. According to Bibby and Webster-Brown (2006), elements which has lowest log K_D in the aquatic system had the least affinities for SPM and this could probably be due to salinity. Salinity affects partitioning of metals through complexation, electrostriction and competition for binding sites between metals and salt ions in seawater. According to Turner and Millward (2002), decreasing values of salinity moving away from the sea into the river could increase the magnitude of K_D by one or two orders for some selected metals. The sequence orders of K_D found in the present study were generally consistent with the literature (Jean-Francois *et al*., 1994; Weng and Wang, 2014).

Besides that, negative correlation between log K_D with SPM was recorded for all metals whereas for the 25 m water layer, most metals are negatively correlated with SPM except for Al, Co, Cu and Zn. In the meantime, most studied metals are negatively correlated with SPM for 50 and 100 m water layers except for Ni. Similar positive correlation between log K_D with SPM were found in Waikato and Kaipara Rivers in New Zealand, Sagami and Wakasa Bays in Japan as well as Danshuei River Estuary in Taiwan (Jiann *et al*., 2005; Bibby and Webster-Brown, 2006; Takata *et al*., 2010). The apparent positive correlations for the metals were likely due to desorption reactions in conditions when SPM concentrations were low. At low SPM concentrations there is increased competition SPM with Cl-ions, thus lowering K_D values.

The inverse relationship of log K_D with SPM was found in North Australian coast (Munksgaard and Parry, 2001), Lake Balaton, Hungary (Nguyen *et al*., 2005) and Port Jackson estuary, Australia (Hatje *et al*., 2003) as well as Jiulong and Jiuzhen estuaries, China (Weng and Wang, 2014). The inverse dependency of log K_D to SPM is termed as "Particle Concentration Effect" (PCE). This is attributed to heterogeneity effects of particle size and composition, including the presence of colloidal organic matter (Benoit *et al*., 1994; Tang *et al*., 2002). PCE can be obtained if the concentrations of colloids increase in proportion to the quantity of suspended macro-particles, hence causing a decrease in the apparent partition coefficient with increasing SPM (Benoit *et al*., 1994). However, even with low concentration of SPM, the inverse correlation can also be observed sometimes. This can be explained as the dependency of log K_D to salinity (Takata *et al*., 2010).

Table 2: EF values of particulate samples in the sulu and celebes seas

Metal/Station	1 m	25 m	50 m	100 m
Al				
ST14	2.18	-	-	-
ST20	-	-	0.49	-
ST37	-	-	0.63	-
ST48	-	0.13	-	-
Cr				
ST26	343	-	-	-
ST57	-	-	475	399
Mn				
ST17	2.13	-	-	-
ST19	1.23	-	-	-
ST41	3.21	-	-	-
ST43	-	-	2.93	-
Co				
ST28	-	2.87	-	-
ST41	10.07	-	-	-
Ni				
ST26	128	-	-	-
Cu				
ST12	51	-	-	-
ST31	-	114	-	-
ST37	196	-	254	-
Zn				
ST23	39	-	-	-
ST26	-	-	74	-
ST32	104	-	-	-
ST34	-	60	-	-
ST48	-	29	-	-
Cd				
ST26	-	-	1950	-
ST38	1605	-	1450	-
ST43	-	1791	-	-
ST52	-	1337	-	-
Pb				
ST26	-	-	245	-
ST38	212	-	181	-
ST43	-	219	-	-
ST52	-	144	-	-

Besides the partitioning of dissolved and particulate phases, assessment of anthropogenic particulate metal could be estimated according to normalization and EF tests (Christophoridis *et al*., 2009; Dung *et al*., 2013; Yao *et al*., 2016). In the normalization test, normalization graph of all metals were plotted against Fe as it has the most significant correlation with other metals. In the normalization graph if the plotted element falls within 95% confidence radius the element is considered to be associated with natural concentration but if the plotted element falls outside of the 95% confidence level, it is considered to be associated with anthropogenic influence. In the present study, samples which were considered as anthropogenic derivatives were then calculated for their EF values as listed in Table 2. The EF value could signify the elemental contamination and estimate the anthropogenic level of an element based on its background value. Based on the average value of calculated EF for particulate samples in the Sulu and Celebes Seas in Table 2, the grey highlighted cells, i.e., Al at station ST48 on the 25 m water layer, station ST20 and ST37 on the 50 m water layer as well as Mn on the surface water of station ST19 were derived from crustal material and natural weathering process, EF<1.5 (Yao *et al*., 2016). In the meantime, other metals (non-highlighted cells in Table 2) with the EF values of bigger than 1.5 (Yao *et al*., 2016) were contributed by anthropogenic sources. Based on Table 2, the bold highlighted EF values (Al at stations ST48 on the 25 m water layer as well as ST20 and ST37 on the 50 m water layer) showed depletion behavior because their calculated EF values are <1 (Viers *et al*., 2009) whereas the non-bold EF values of more than 1 showed enrichment behavior (Viers *et al*., 2009) of these metals.

CONCLUSION

The present study showed high concentration of metals was distributed at stations closed to Borneo coastal namely the Darvel Bay and areas within the vicinity of riverine flushed-out. For the meantime, the minimum concentration of metals was found on the surface water layer (1 m) which enlightened the gravity settlement of particulate metals in the Sulu and Celebes Seas off Malaysian coasts. The vertical profiling of metals in both seas showed no specific pattern as the 100 m water layer is still classified as surface water for the Sulu and Celebes Seas.

In general, Pearson correlation conducted pointed out that Ni and Cu were originated from geogenic sources as they showed significant correlation with abundance metals in the upper continental crust whereas Pb and Cd were known to be derived from anthropogenic sources. Statistical analysis of PCA has identified the bioactive trace metals in the studied area namely Co, Cu, Fe, Cr and Cd. Besides that, PCA also revealed that DO, temperature, salinity and conductivity are closely related. Additionally, PCA highlighted a correlation between the upper continental crust abundance metals, i.e., Al, Fe and Mn with conductivity and SPM.

As for metals partitioning between dissolved and particulate elements, generally Cr, Ni, Fe and Pb showed the strongest adsorption towards SPM whereas Cd, Zn and Al has the weakest bond with SPM. Most of the log K_D of elements showed negative correlation with SPM or also known as PCE that is a heterogeneity effect of particle size and composition including the presence of colloidal organic matter. Lastly, the EF values for particulate metals highlighted metals which are derived from anthropogenic sources at some stations on certain water layers. Concisely, the collected hydrographic data and the concentration of metals verify the anthropogenic input from land-based and physico-chemical characteristics of both seas off Malaysian.

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REFERENCES

Adiana, G., H. Juahir, B. Joseph and N.A.M. Shazili, 2017. Tracing the sources of lead (Pb) in Brunei Bay, Borneo by using integrated spectrometry ICP-MS and chemometric techniques. Mar. Pollut. Bull., 123: 232-240.

Adiana, G., N.A.M. Shazili and M.A. Marinah, 2011. Cadmium, manganese and lead distribution in the South China Sea off the South Terengganu Coast, Malaysia during post-monsoon and pre-monsoon. J. Sustain. Sci. Manage., 6: 181-192.

Asante, K.A., T. Agusa, R. Kubota, H. Mochizuki and K. Ramu *et al*., 2010. Trace elements and stable isotope ratios (ä13C and ä15N) in fish from deep-waters of the Sulu Sea and the Celebes Sea. Marine Pollut. Bull., 60: 1560-1570.

Badran, M.I., 2001. Dissolved oxygen, chlorophyll a and nutrients: Seasonal cycles in waters of the Gulf of Aquaba, Red Sea. Aquat. Ecosyst. Health Manage., 4: 139-150.

Baharuddin, N., N.A. Saim, S.M. Zain, H. Juahir and R. Osman *et al*., 2014. Characterization of spatial patterns in river water quality using chemometric techniques. Sains Malaysiana, 43: 1355-1362.

Beaufort, L., T. De Garidel-Thoron, B. Linsley, D. Oppo and N. Buchet, 2003. Biomass burning and oceanic primary production estimates in the Sulu Sea area over the last 380 kyr and the East Asian monsoon dynamics. Marine Geol., 201: 53-65.

Benoit, G. and T.F. Rozan, 1999. The influence of size distribution on the particle concentration effect and trace metal partitioning in rivers. Geochim. Cosmochim. Acta, 63: 113-127.

Benoit, G., S.D. Oktay-Marshall, A. Cantu II, E.M. Hood and C.H. Coleman *et al*., 1994. Partitioning of Cu, Pb, Ag, Zn, Fe, Al and Mn between filter-retained particles, colloids and solution in six Texas estuaries. Marine Chem., 45: 307-336.

Bibby, R.L. and J.G. Webster-Brown, 2006. Trace metal adsorption onto urban stream suspended particulate matter (Auckland region, New Zealand). Appl. Geochem., 21: 1135-1151.

Bidai, J., G. Adiana and N.A.M. Shazili, 2016. Particle sizes effect of the elements in the South China Sea sediment off Pahang coastal during the Northeast monsoon (pre-) and the Southwest monsoon (post-) periods. Environ. Earth Sci., 75: 614-625.

Biller, D.V., T.H. Coale, R.C. Till, G.J. Smith and K.W. Bruland, 2013. Coastal iron and nitrate distributions during the spring and summer upwelling season in the central California current upwelling regime. Cont. Shelf Res., 66: 58-72.

Bing, H., Y. Wu, J. Zhou, R. Li and J. Wang, 2016. Historical trends of anthropogenic metals in Eastern Tibetan Plateau as reconstructed from alpine lake sediments over the last century. Chemosphere, 148: 211-219.

Calvert, S.E., T.F. Pedersen and R.C. Thunell, 1993. Geochemistry of the surface sediments of the Sulu and South China Seas. Marine Geol., 114: 207-231.

Camel, V., 2003. Solid phase extraction of trace elements. Spectrochim. Acta Part B At. Spectrosc., 58: 1177-1233.

Christophoridis, C., D. Dedepsidis and K. Fytianos, 2009. Occurrence and distribution of selected heavy metals in the surface sediments of Thermaikos Gulf, N. Greece. Assessment using pollution indicators. J. Hazard. Mater., 168: 1082-1091.

Cox, A.D., A.E. Noble and M.A. Saito, 2014. Cadmium enriched stable isotope uptake and addition experiments with natural phytoplankton assemblages in the Costa Rica Upwelling Dome. Marine Chem., 166: 70-81.

Cuong, D.T., S. Karuppiah and J.P. Obbard, 2008. Distribution of heavy metals in the dissolved and suspended phase of the sea-surface microlayer, seawater column and in sediments of Singapore's coastal environment. Environ. Monit. Assess., 138: 255-272.

DeVantier, L., A. Alcala and C. Wilkinson, 2004. The Sulu-Sulawesi Sea: Environmental and socioeconomic status, future prognosis and ameliorative policy options. AMBIO J. Hum. Environ., 33: 88-97.

Dung, T.T.T., V. Cappuyns, R. Swennen and N.K. Phung, 2013. From geochemical background determination to pollution assessment of heavy metals in sediments and soils. Rev. Environ. Sci. BioTechnol., 12: 335-353.

Fonseca, E.M., J.B. Neto, C.G. Silva, J.J. McAlister and B.J. Smith *et al*., 2013. Stormwater impact in Guanabara Bay (Rio de Janeiro): Evidences of seasonal variability in the dynamic of the sediment heavy metals. Estuarine Coastal Shelf Sci., 130: 161-168.

Ghazali, A, N.A.M. Shazili, J. Bidai and H. Shaari, 2016. The spatial distribution of Al, Fe, Cu, Cd and Pb in the surface sediment of Brunei Bay, Borneo during the southwest and northeast monsoons. J. Sustainability Sci. Manage., 11: 93-106.

Grassi, M.T., B. Shi and H.E. Allen, 2000. Partition of copper between dissolved and particulate phases using aluminum oxide as an aquatic model phase: Effects of pH, solids and organic matter. J. Braz. Chem. Soc., 11: 516-524.

Hatje, V., S.C. Apte, L.T. Hales and G.F. Birch, 2003. Dissolved trace metal distributions in port Jackson estuary (Sydney Harbour), Australia. Marine Pollut. Bul., 46: 719-730.

Idris, A.M., 2008. Combining multivariate analysis and geochemical approaches for assessing heavy metal level in sediments from Sudanese harbors along the Red Sea coast. Microchem. J., 90: 159-163.

Jean-Francois, C., D. Cossa, D. Auger and I. Truquet, 1994. Trace metal distribution, partition and fluxes in the seine estuary (France) in low discharge regime. Marine Chem., 47: 145-158.

Jiann, K.T., L.S. Wen and P.H. Santschi, 2005. Trace metal (Cd, Cu, Ni and Pb) partitioning, affinities and removal in the Danshuei River estuary a macro-tidal, temporally anoxic estuary in Taiwan. Marine Chem., 96: 293-313.

Jimenez, M.S., R. Velarte and J.R. Castillo, 2002. Performance of different preconcentration columns used in sequential injection analysis and inductively coupled plasma-mass spectrometry for multielemental determination in seawater. Spectrochim. Acta Part B At. Spectroscopy, 57: 391-402.

Juahir, H., S.M. Zain, A.Z. Aris, M.K. Yusoff and M.B. Mokhtar, 2010. Spatial assessment of Langat river water quality using chemometrics. J. Environ. Monit., 12: 287-295.

Juahir, H., S.M. Zain, M.K. Yusoff, T.T. Hanidza and A.M. Armi *et al*., 2011. Spatial water quality assessment of Langat River Basin (Malaysia) using environmetric techniques. Environ. Monit. Assess., 173: 625-641.

Lane, T.W., M.A. Saito, G.N. George, I.J. Pickering, R.C. Prince and F.M.M. Morel, 2005. Biochemistry: A cadmium enzyme from a marine diatom. Nature, 435: 42-42.

Linsley, B.K., 1996. Oxygen-isotope record of sea level and climate variations in the Sulu Sea over the past 150,000 years. Nature, 380: 234-237.

Liu, C.W., K.H. Lin and Y.M. Kuo, 2003. Application of factor analysis in the assessment of groundwater quality in a blackfoot disease area in Taiwan. Sci. Total Environ., 313: 77-89.

Mahadzirah, M., M. Morliyati, I. Mamat and M. Mamat, 2014. Modelling positive development, life satisfaction and problem behaviour among youths in Malaysia. World Appl. Sci. J., 32: 231-238.

Manasrah, R., M. Raheed and M.I. Badran, 2006. Relationships between water temperature, nutrients and dissolved oxygen in the Northern Gulf of Aqaba, Red Sea. Oceanologia, 48: 237-253.

Michalke, B., 2003. Element speciation definitions, analytical methodology and some examples. Ecotoxicol. Environ. Saf., 56: 122-139.

Mohamad, M., A.M. Ali, A.N.I. Ghani, A.R. Abdullah and S. Mokhlis, 2012. Positioning Malaysia as a tourist destination based on destination loyalty. Asian Soc. Sci., 9: 286-292.

Mokhtar, M., M.T. Latif and L.Y. Heng, 2003. Kimia Air. Utusan Publications & Distributors Sdn. Bhd, Malaysia, Pages: 103.

Munksgaard, N.C. and D.L. Parry, 2001. Trace metals, arsenic and lead isotopes in dissolved and particulate phases of North Australian coastal and estuarine seawater. Marine Chem., 75: 165-184.

Nguyen, H.L., M. Leermakers, M. Elskens, F. De Ridder and T.H. Doan *et al*., 2005. Correlations, partitioning and bioaccumulation of heavy metals between different compartments of Lake Balaton. Sci. Total Environ., 341: 211-226.

Nichols, G. and R. Hall, 1999. History of the Celebes Sea Basin based on its stratigraphic and sedimentological record. J. Asian Earth Sci., 17: 47-59.

Norisuye, K., M. Ezoe, S. Nakatsuka, S. Umetani and Y. Sohrin, 2007. Distribution of bioactive trace metals (Fe, Co, Ni, Cu, Zn and Cd) in the Sulu Sea and its adjacent seas. Deep Sea Res. Part II Topical Stud. Oceanogr., 54: 14-37.

Nozaki, Y., D.S. Alibo, H. Amakawa, T. Gamo and H. Hasumoto, 1999. Dissolved rare earth elements and hydrography in the Sulu Sea. Geochim. Cosmochim. Acta, 63: 2171-2181.

Obata, H., T. Doi, Y. Hongo, D.S. Alibo and H. Minami *et al*., 2007. Manganese, cerium and iron in the Sulu, Celebes and Philippine Seas. Deep Sea Res. Part II Topical Stud. Oceanogr., 54: 38-49.

Ong, M.C., B. Joseph, N.A.M. Shazili, A. Ghazali and M.N. Mohamad, 2015. Heavy metals concentration in surficial sediments of Bidong Island, South China Sea off the East Coast of Peninsular Malaysia. Asian J. Earth Sci., 8: 74-82.

Rasheed, M., M.I. Badran and M. Huettel, 2003. Particulate matter filtration and seasonal nutrient dynamics in permeable carbonate and silicate sands of the Gulf of Aqaba, Red Sea. Coral Reefs, 22: 167-177.

Reghunath, R., T.R.S. Murthy and B.R. Raghavan, 2002. The utility of multivariate statistical techniques in hydrogeochemical studies: An example from Karnataka, India. Water Res., 36: 2437-2442.

Ripperger, S. and M. Rehkamper, 2007. Precise determination of cadmium isotope fractionation in seawater by double spike MC-ICPMS. Geochim. Cosmochim. Acta, 71: 631-642.

Sindern, S., M. Tremohlen, L. Dsikowitzky, L. Gronen, J. Schwarzbauer *et al*., 2016. Heavy metals in river and coast sediments of the Jakarta Bay region (Indonesia)-Geogenic versus anthropogenic sources. Marine Pollut. Bull., 110: 624-633.

Su, H., R. Yang, A. Zhang, Y. Li and S. Qu *et al*., 2017. Characteristics of trace metals and phosphorus in seawaters offshore the Yangtze River. Marine Pollut. Bull., 124: 1020-1032.

Takata, H., T. Aono, K. Tagami and S. Uchida, 2010. Processes controlling cobalt distribution in two temperate estuaries, Sagami Bay and Wakasa Bay, Japan. Estuarine Coastal Shelf Sci., 89: 294-305.

Tally, L.D., G.L. Pickard, W.J. Emery and J.H. Swift, 2011. Physical Properties of Seawater. In: Descriptive Physical Oceanography: An Introduction, Tally, L.D., G.L. Pickard, W.J. Emery and J.H. Swift (Eds.). Academic Press, Boston, Massachusetts, USA., pp: 29-66.

Tang, D., K.W. Warnken and P.H. Santschi, 2002. Distribution and partitioning of trace metals (Cd, Cu, Ni, Pb, Zn) in Galveston bay waters. Marine Chem., 78: 29-45.

Team, C.W., 2004. Electrical conductivity/salinity fact sheet, FS-3.1. 3.0 (EC). The Clean Water Team Guidance Compendium for Watershed Monitoring and Assessment, Version, 2, California State Water Resources Control Board (SWRCB), Sacramento, CA.

Turner, A. and G.E. Millward, 2002. Suspended particles: Their role in estuarine biogeochemical cycles. Estuarine Coastal Shelf Sci., 55: 857-883.

Valdes, J., G. Vargas, A. Sifeddine, L. Ortlieb and M. Guinez, 2005. Distribution and enrichment evaluation of heavy metals in Mejillones Bay (23° S), Northern Chile: Geochemical and statistical approach. Marine Pollut. Bull., 50: 1558-1568.

Viers, J., B. Dupre and J. Gaillardet, 2009. Chemical composition of suspended sediments in World Rivers: New insights from a new database. Sci. Total Environ., 407: 853-868.

Wedepohl, K.H., 1995. The composition of the continental crust. Geochimica Cosmochimica Acta, 59: 1217-1232.

Weng, N. and W.X. Wang, 2014. Variations of trace metals in two estuarine environments with contrasting pollution histories. Sci. Total Environ., 485: 604-614.

Wheeler, P.A., A. Huyer and J. Fleischbein, 2003. Cold halocline, increased nutrients and higher chlorophyll off Oregon in 2002. Geophys. Res. Lett., 30: 1-4.

Yao, Q., X. Wang, H. Jian, H. Chen and Z. Yu, 2016. Behavior of suspended particles in the Changjiang Estuary: Size distribution and trace metal contamination. Marine Pollut. Bull., 103: 159-167.