

Distribution of Dissolved and Particulate Fe in an Estuarine System at Bagan Pasir, Perak

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ABSTRACT

The distribution of dissolved iron (dFe) and particulate iron in the estuarine system was studied where *in-situ* water sampling stations were selected at Bagan Pasir, Perak. The concentration of dFe was 1.17 ± 0.28 mg/L on average at the estuary, while in freshwater samples its concentration was 0.08 ± 0.00 mg/L. This study found that the concentration of particulate Fe in freshwater system was higher than that in the estuary system. The Fe concentration was 0.95 ± 0.03 mg/kg and 0.80 ± 0.18 mg/kg at the freshwater and estuary systems, respectively. We have applied a distribution coefficient (K_D) in order to quantify the partitioning of Fe between the particulate ($>0.45 \mu\text{m}$) and dissolved ($<0.45 \mu\text{m}$) phases. The K_D value of Fe in the freshwater system was much higher compared to that in the estuary, where the K_D value was 12.18 in freshwater and 0.48 -1.31 in the estuary. This indicated that Fe in this area has a strong affinity with the particulate phase in a freshwater system and this is probably due to the anthropogenic input. On the other hand, Fe may exist in colloidal or organic ligands which probably originate from surface sediment or a biological process in water columns at the estuarine area.

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INTRODUCTION

Iron (Fe) acts as an important element as well as a micronutrient for marine organisms and has a key role in sustaining estuary biogeochemistry (Gledhill et al., 2004). The

bioavailability and biogeochemistry of Fe depends on the probability to form either in metal complexes or colloids (Lohan et al., 2005). Therefore, the concentration of iron influences the level of atmospheric CO₂ uptake via phytoplankton growth to maintaining the marine ecosystem. In oxygenated and highly saline waters iron has low solubility; thus, this is the reason why Fe concentration is low. Otherwise, in estuaries and rivers, Fe is mainly present in association with dissolved organic matter in areas close to the ocean. A previous research (Asmala et al., 2013) had studied characterization of riverine dissolved organic matter and the significant role it played in Fe transport capacity of the river waters and extent to which riverine iron might be maintained in solution in the marine environment. It was suggested that an increasing amount of dFe could enhance the productivity of marine systems.

Therefore, some of the dissolved species may react with suspended particles. Fe predominantly occurs in the particulate form (Costa et al., 2016; Gledhill et al., 2004) with lower dissolved concentration. Anthropogenic and many other human activities produce residue and toxic substances (mostly heavy metals) that are eventually discharged into rivers and estuaries. These subsequently flow to the open ocean (Syvitski et al., 2005). Thus, these metals are present in different components of an aquatic system such as: water body; suspended matter; bed sediments; and biota. In this way, they remain in the medium as highly toxic micro-pollutants and cause adverse effects (Schnoor, 1996). In order to better understand what controls estuarine primary production, we need to understand clearly the distribution and fractionation of trace metals in seawater. Fe is reported to be rendered more complex by ligands that can relate to some specific chemical compounds in coastal waters (Avendaño et al., 2016; Gledhill et al., 2004; Huber et al., 2011; Mawji et al., 2011; Velasquez et al., 2011).

However, most of the current trace metal studies performed in Malaysia were carried out in sediment and freshwater (Ahmad et al., 2009; Adiana et al., 2014; Koh et al., 2015; Suratman et al., 2009; Yusof et al., 2009; Yap et al., 2011). There were also a few studies conducted of Fe in estuarine areas. Billah et al. (2016) studied the distribution (Fe, Zn, Cu and Mn) and water characteristics at Miri estuary, Sarawak, by using Atomic Absorption Spectrophotometer (AAS). An earlier study by Mohamed et al. (2016) focused on fractioning of Mn, Fe and Cu in seawater at Port Dickson, Negeri Sembilan by applying Chelex 100 to a preconcentrate before determination by Inductive Couple Plasma – Mass Spectrometry (ICP-MS). However, most of these methods require complex and expensive analytical equipment, thereby limiting their potential application. This could affect the limitation of understanding of biogeochemistry of dissolved Fe in an estuarine system. Therefore, a lack of dissolved Fe data might be due to the use of an analytical method where the sample itself (seawater) has a high metric and contains higher levels of salt. There are challenges involved in analysing the salty water sample directly. It is vital to have more knowledge of estuarine systems since most estuarine areas are the main economic sources

of fresh seafood stock. This stock will be supplied to markets where humans will be the final consumer. This study was proposed so as to determine dissolved Fe in estuary water by using the current developed method (electrochemistry method), along with determination of particulate Fe. Due to the high salt content, this technique can be undertaken directly in seawater. The pre-concentration procedure is performed and followed by a potential scan towards more negative potentials and the cathodic (reductive) currents are then determined. This method is based on the measurement of current response as a function of the potential applied to a voltammetric cell.

The objectives of this study were to identify the distribution of dissolved Fe (dFe) and particulate Fe (Fe_p) in an estuarine system at Bagan Pasir, Perak and also to determine the influence of *in-situ* parameters on its fractionation distribution at an estuarine location. This is important in relation to updating our knowledge and increasing our understanding of the effect of anthropogenic and natural activities on the Fe biogeochemistry cycle and allowing us to monitor the productivity of our estuarine systems.

MATERIALS AND METHODS

Acid Wash

Sample container (1L, low-density polyethylene (LDPE)) bottles were cleaned by soaking in 30 % HNO_3 overnight followed by thorough rinsing with Milli Q to remove all the metal contaminants. All sample bottles used in this study were cleaned according to a standard protocol (Achterberg et al., 2001).

Sampling Area

The Bagan Pasir estuary is located west of Teluk Intan (Figure 1), in the state of Perak, Malaysia. The majority of the fresh water entering the estuary originates from the Tanjung Karang (Perak's main river) which drains a catchment area of approximately 14900 km².

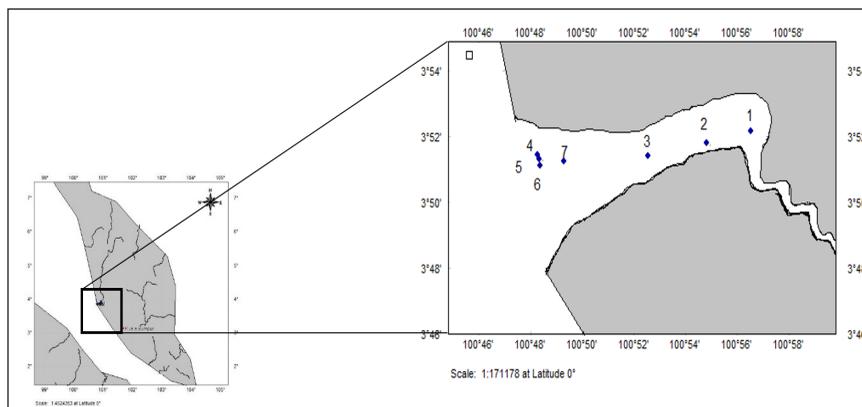


Figure 1. The sampling location at Bagan Pasir estuary, Perak on January 2018

The Bagan Pasir area is well known as a fishing village, producing about 30 different seafood supplies including pomfret, prawn, shrimp, and cockles. Most of the suppliers at the market around Selangor visit this place in order to refresh their stocks (Kelly, 2016).

Sampling Activity

Sampling was carried out in January 2018 at Bagan Pasir, Perak. The water samples were collected from seven stations (Figure 1). Our sampling stations were divided into three (3) zones based on salinity, i.e.: Zone 1 (St.1, salinity of 7.52 ppt); Zone 2 (St.3 and St.2, salinity of 13.18 ± 0.05 ppt); and Zone 3 (St.7, St.6, St.5 and St.4 salinity of 16.42 ± 2.25 ppt) (Figure 1). This classification was applied in order to identify the possible influences of salinity on Fe distribution in the water column as suggested by the United States Environmental Protection Agency (US EPA, 2006). Stations 1, 2 and 3 were a distance of 1km apart from each station; while the other stations were located near to the estuaries area with a distance of 500m apart from each station. A 1 L sample was collected at middle depth at each station by using Van Dorn water sampler and was then dispersed into a PTFE bottle for further analysis. The reading of *in-situ* parameters was recorded by using, specifically: pH meter Thermo Orion (Model 230); Dissolved Oxygen (DO) meter (YSI Model 52); salinity meter (YSI 30); Conductivity meter (Thermo Scientific Orion 3-star Plus); and Turbidity meter (Thermo Orion Model AQ4500). The in-situ parameters used during our sampling are as shown in Table 1 following.

Table 1
The in-situ parameters data during sampling at Bagan Pasir, Perak

Station	Coordinate	Sal. (ppt)	Cond. (mS)	Turbidity (NTU)	Temp. (°C)	pH	DO (mg/L)	dFe (mg/L)	Fe _p (mg/kg)	K _D
1	3.8696 100.9420	7.52	14905.00	127.00	28.80	7.05	2.81	0.08±0.04	0.95±0.03	12.18
2	3.8635 100.9136	13.21	23806.00	155.00	29.10	6.60	3.32	1.15±0.62	0.55±0.03	0.48
3	3.8567 100.8755	13.14	30794.00	97.00	29.30	6.80	6.03	0.70±0.02	0.91±0.02	1.31
4	3.8576 100.8046	13.20	39855.00	75.00	29.00	7.27	4.51	1.26±0.60	0.87±0.00	0.69
5	3.8553 100.8054	17.43	24230.00	58.00	31.60	7.45	5.26	1.26±0.64	0.71±0.02	0.56
6	3.8522 100.8060	18.41	33337.00	23.00	29.40	7.31	5.31	1.55±0.67	1.06±0.04	0.69
7	3.8542 100.8215	16.87	38261.00	0.00	29.90	7.39	4.14	1.12±0.55	0.72±0.01	0.64

Sample Treatment

About one litre of water samples (1L) was sampled using filter vacuum pump as described by Bruland et al. (2003) and Achterberg et al. (2001). A 500ml of sample for total dissolved analysis was acidified to pH 1.99 to 2.10 (a final concentration of 10%) using pure 65 % HNO₃ (RCI Premium). Total suspended solid (TSS) samples obtained from filtration of a 1L sample were allowed to dry for several days until a constant weight was attained.

Particulate Fe Analysis

A process of acid digestion was suggested by Adiana et al. (2014) with a modification. In this modification, a digestion of TSS samples was conducted by using 2 ml of HF, 3 ml of HCl and 4 ml of HNO₃ in a closed Teflon vessel on a hotplate for 30 min duration. This was followed by rinsing of the sample using 2% HNO₃ by open digestion process and adjusting the volume until 10 ml. It was then heated up again for approximately 2-3 min so as to obtain a good mixture of solution and finally made up to 25 ml with Milli-Q water. The digested sample was kept in centrifuge tubes at 4°C before determining particulate Fe by using Induced Coupled Plasma Mass Spectrometry (ICP-MS).

Inorganic Dissolved Fe Analysis

All sample preparation was carried out in a Class 100 laminar airflow bench at room temperature. Milli-Q (Millipore U.K) of 18.2M Ω ·cm resistivity was used to prepare reagents and dilutions. Iron solutions of different concentrations were prepared by diluting 1000 ppm atomic absorption standard solutions (BDH, UK) which were then acidified to pH 2 with HCl. HCl (Merck) and ammonia (EMSURE, Merck) were purchased from Fisher Scientific and were used to adjust the pH. A stock solution of 0.02 M 2-(2-Thiazylazo)-p-cresol (TAC) was prepared by dissolving TAC in 100% Methanol. The TAC was obtained from Sigma-Aldrich and had a purity rating of 97%. The pH buffer contained 1 M boric acid in 0.3 M ammonia in Milli-Q and gave pH 8.05-8.15.

Inorganic dissolved Fe analysis was conducted by using the method devised by van der Berg and Huang (1984) with some modification. A sub-sample (15 ml) of treated water sample (pH: 2) was pipetted into a polarographic cell and the pH was adjusted to 8.0 by ammonia hydroxide solution. Following this, there was an addition of 1 μ M (100 μ l) of 1M borate buffer. The solution was deaerated by bubbling with pure nitrogen gas (99.99%), and 150 μ l of 1mM of TAC solution were then added. A new mercury drop was extruded and the potentiostat was then switched on and set to 0.1V. The stirrer was started in order to initiate the collection which was carried out for 8 min. A negative scan was then made 10 s after stopping the stirrer using a fast linear sweep of 50 Mv/s. Deposition time was about 1 min in duration. The smooth reduction peak of Fe lies between -0.35 V to -0.4 V.

RESULTS AND DISCUSSIONS

The results of the Fe concentrations are presented in Table 1. We found that the salinity at St. 1 was 7.52 ppt (Table 1) which was the lowest result. St. 2, 3 and 4 were ranged between 13.14 to 13.21 ppt (Table 1) and St. 5, 6 and 7 recorded the highest salinity levels, namely, 16.87 to 18.41 ppt (Table 1). Present collected data had shown that the salinity increased from St. 1 through to St. 7 (Figure 2). Salinity refers to the effect on a biogeochemical process through chemical and physical aspects. This occurs through salinity where salt within seawater interacted with iron, thereby having the potential to experience ion exchange (Bai et al., 2012). Findings from a volunteer estuary monitoring manual stated that salinity in an estuary played a role involving flocculation of particles, where the particles that entered an estuary dissolved in fresh river water and collided with salt water. Hence, they may flocculate resulting in increased turbidity thereby influencing the distribution of Fe. From this, our results found that the dFe increase with salinity increase has been proven from the study of Jilbert et al. (2018) at Boreal estuary.

A pH at St.1 was found at 7.05 (Table 1) followed by St. 2, 3 and 4 at 6.60 to 7.27 (Table 2) which is slightly acidic. At St.7, the pH was 7.31 to 7.45 (Table 1) which is slightly more alkaline to the open sea area. This occurs because most of the dissolved minerals

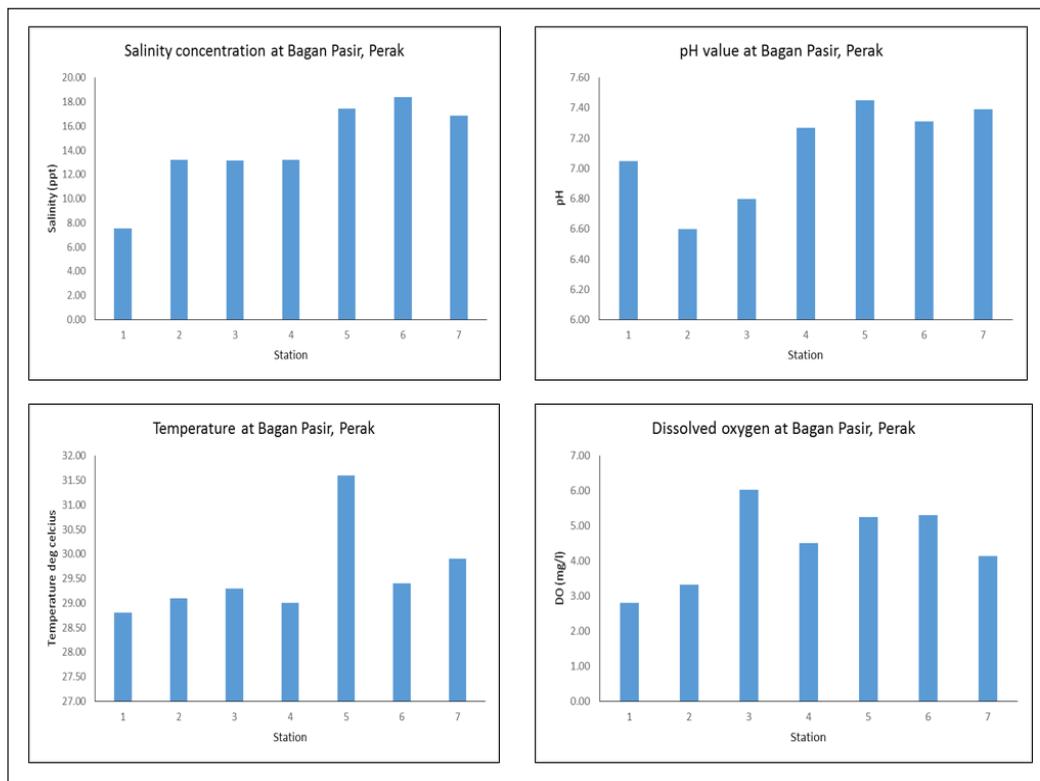


Figure 2. The in-situ parameter pattern and distribution at sampling station at Bagan Pasir, Perak

(dissolve CO_2 turns to HCO_3^-) are picked up by groundwater and carried eventually to the ocean (Sophie, 2017). The alkalinity of the water body indicated the presence of CO_3^{2-} , Ca^{2+} and Mg^{2+} . The acidity may cause a photosynthetic process and decomposition of organic matter mostly from urban runoff (Billah et al., 2016). During our sampling, the temperature recorded was also the same; ranging between 28.80 to 31.60°C. The temperate zone might not influence other parameters; while some research reported that the influence of temperature on metal transportation was not evident, but could be influenced by salinity changes (Aston et al., 2010; Biesuz et al., 1998; Zhang et al., 2013). Mokhtar et al. (2009) stated that change of temperature on surface water was a function of heat exchange on the earth's surface; hence, our recorded temperature was probably influenced by the tidal cycles since our sampling was carried out at high flow cycles.

The concentration of dissolved oxygen (DO) at St.1 was 2.81 mg/L, St.2, 3 and 4 were 3.32 to 6.03 mg/L and 4.14 to 5.36 mg/L at St.5, 6 and 7 (Table 1), respectively. This data shows an increase of DO from St.1 to St.7 (Figure 2). This could be the reason for a slower oxidative precipitation rate and scavenging of dissolved heavy metal ions by iron hydroxide formed from Fe cations simultaneously released from pore waters under low DO (Atkinson et al, 2007; Santana-casiano et al, 2004). Whereas at high DO, oxygen penetration was much stronger, Fe oxidative precipitation generated hydroxide or oxide would adsorb more dissolved heavy metal, thus leading to reduced metal release (Zhang et al., 2017).

The dFe concentration in the sample was determined by standard additions to 1ppm of Fe (III), which gave a peak current of about 114.58 nA (Figure 3). Measurements were made with 15 ml of samples which were buffered to pH 8.05 by 1 M boric acid, in the presence of 10 μM TAC as an added ligand to be binding to the natural Fe in sample. Collection was carried out using HMDE for 8 min fraction of the Fe-TAC which was adsorbed on the surface of the Hg drop. A potential scan direction is aimed toward more negative potentials and the resulting current is measured at -0.1 V. This was followed by using Differential Pulse modulation at a pulse rate of 10 pulse/s and scan rate at 10Mv/s. It was found that the maximum peak height which could produce at high iron concentrations was about 118.20 nA (Figure 3(b)). Where the resultant current-potential stripping voltammogram provides quantitative information, the height of the peak is of the standard addition method and qualitative information. The potential of the peak is an indication of the Fe analyzed. This technique is sufficiently sensitive for the direct determination of dissolved iron in seawater as it has a concentration in oceanic regions in nM range. Hence, voltammetric analysis (Figure 3(a)) may vary between samples of different ionic strength and containing different concentrations of surfactants and natural trace metal complexing organic ligands.

The dFe concentration at St.1 was 0.08 \pm 0.04; St.2, 3 and 4 were ranged between 0.70 \pm 0.02 to 1.26 \pm 0.62 mg/L and St. 5, 6 and 7 were 1.12 \pm 0.55 to 1.55 \pm 0.67 mg/L (Table 2), respectively, in our study area. Most of the stations which were located at the estuary

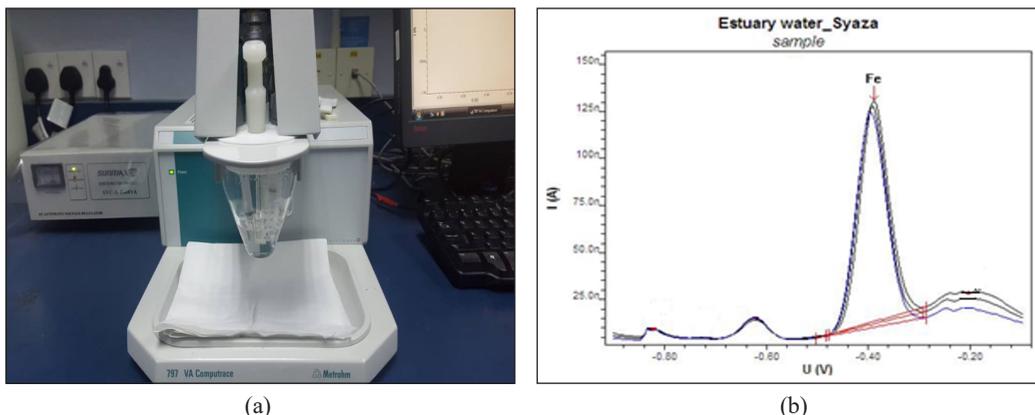


Figure 3. (a) 797 Voltammetric Analysis Computrace Stand, (b) determination of dissolved Fe using DPCSV, 10 pulse/s, 10 Mv/s. The collection time was 1 min.

had higher levels of dFe concentration (Figure 4). This indicated that the concentration of dFe was increased by salinity and DO. This could suggest that Fe input was occurring naturally in the environment. Further, it could be mobilized by anthropogenic activities consisting of mining and industrial effluents discharging from rivers into natural ecosystems like forest, mangroves, estuaries and ocean (Larison et al., 2000). Our dFe in mean was $(1.0 \pm 0.2) \times 10^3 \mu\text{g/L}$ in an estuary, which is lower than that of other studies (Table 3). This was a comparison from previous studies that were mostly focused in river areas, which are a direct source of heavy metal.

Table 2

Range of in-situ parameters and concentration of Fe in dissolved and particulate phase at Bagan Pasir, Perak

Station	Salinity (ppt)	Temperature (°C)	pH	DO (mg/L)	dFe (mg/L)	Fe _p (mg/kg)	K _D
1	7.52	28.80	7.05	2.81	0.08±0.04	0.95±0.02	12.18
2, 3 and 4	13.14-13.21	29.00-29.30	6.60-7.27	3.32-6.03	0.70±0.02-1.26±0.62	0.55±0.03-0.91±0.02	0.48-1.31
5, 6 and 7	16.87-18.41	29.40-31.60	7.31-7.45	4.14-5.36	1.12±0.55-1.55±0.67	0.71±0.02-1.06±0.04	0.56-0.69

Results from previous studies indicated that the metal concentrations were comparable. There was also general acceptance on the area that had been polluted by agricultural activities, as well as industrial, effluent discharge and human activities (Table 3). However, the fraction of riverine Fe present as discrete ferrihydrite particles had been shown to increase with rising pH, as was typically observed with increasing stream order towards the coastal zone (Neubauer et al., 2013). It was found that Fe probably did exist in colloidal form or being bound with organic ligands.

Table 3

Average concentration of Fe in dissolved (ug/l) and particulate phase (ug/l) of river water samples as noted in previous studies

Rivers	Dissolved Fe (dFe)	Particulate Fe (Fe _p)	References
Setiu	$(2.0\pm 3.4)\times 10^2$	10±13	Koh, 2015
Langat	$(1.3\pm 2.3)\times 10^3$	Nd	Yusof et al., 2009
Kelantan	Nd	$(3860\pm 30)\times 10^3$	Ahmad, 2009
World Average	50	5.8±4.8	Viers et al, 2009; Meybeck et al., 1996
Bagan Pasir estuary	$(1.0\pm 0.2)\times 10^3$	$(0.80\pm 0.18)\times 10^3$	This study

Note: *nd = no data available

Based on the correlation of Fe in a dissolved phase with in-situ parameters, we found that dFe had a significant linear relationship with salinity. In estuarine environments, elevated electrolyte strength along salinity gradients induces the flocculation of DOM (Sholkovitz et al., 1978) and Fe (Boyle et al., 1977) from river waters. This phenomenon is usually explained by the cation-induced aggregation of colloidal humic substances, which carry a net negative surface charge (Eckert & Sholkovitz, 1976). This suggests a destabilization of colloidal iron as ionic strength increases (Byrd et al., 1990). In contrast, we found that dFe did not have a significant relationship between pH, DO and temperature after $P\geq 0.05$. In the case of Fe_p, there is an indication that all the in-situ parameters do not have any influence upon Fe_p. This could indicate that there is little or no remobilization of iron in the sediments in this area.

Table 4

Correlation coefficient between dissolved and particulate Fe concentration with in-situ parameter at Bagan Pasir Perak

Parameter	R value (dFe)	R value (Fe _p)
Salinity	0.88	0.09
pH	0.37	0.30
Temperature	0.37	0.33
DO	0.46	0.32

Concentration of Fe in particulate form at the Bagan Pasir estuary can be seen in Table 1. Fe_p concentration ranged from 0.95 ± 0.03 to 1.06 ± 0.04 mg/kg in inverse relation with river levels (estuary to river). The results showed a slight variation between each station. High concentrations of particulate Fe were found at the estuary area (St.1); this is due to the turbidity maximum area and related to the estuarine dynamic circulation (Barak & Nurit, 1997). It is represented by a simple model of seawater transport and settling of particulate metal from the surface to the deep layer of water and can be carried back to the upstream and remixed with surface water (Postma, 1967). Both instances of Fe “inputs” concentration

were below the values obtained in the river in all stations, which suggests that this metal comes from upstream. It is probable that during the last two years, the stream was flooded by river waters in November, 2016 (Kelly, 2016).

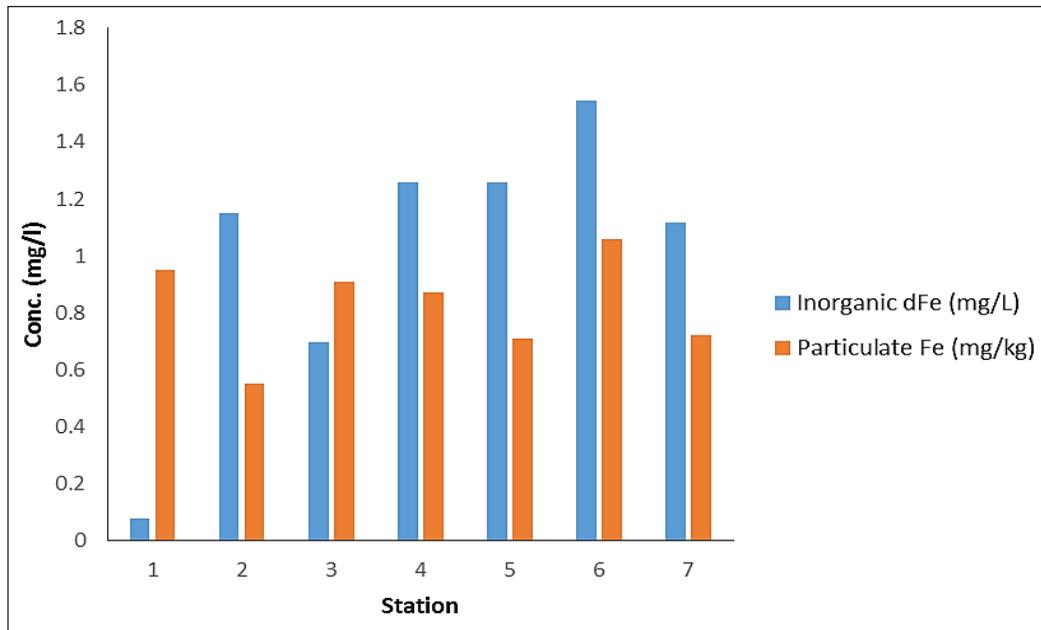


Figure 4. Distribution of dissolved and particulate Fe at Bagan Pasir estuary

A pattern of Fe was observed for this distribution in both dissolved and particulate phase as shown in Figure 4. Where the particulate phase showed a higher concentration than the dissolved phase of Fe ($Fe_p \geq dFe$) at St.1 and St.3, at other stations it displayed $dFe \geq Fe_p$ (Fig. 5). In order to find out the partitioning of a metal between the particulate ($>0.45 \mu m$) and dissolved ($<0.45 \mu m$) phases, we applied a distribution coefficient, K_D (Benoit et al., 1994; Benoit & Rozan, 1999; Munksgaard & Parry, 2001; Nguyen et al., 2005):

$$K_D = \frac{[particulate\ metal\ concentration](ug/kg)}{[dissolved\ metal\ concentration](ug/l)}$$

K_D is a measure of the tendency of an element to be associated and transported with the particulate phase. High particle reactivity for a metal would tend to increase that metal's K_D value. A partitioning coefficient in this study shows that St.1 is 12.18, St.2, 3 and 4 are 0.48 to 1.31 and St.5, 6 and 7 are 0.56 to 0.69 (Table 1), respectively. It indicated that St. 2 to St. 7 and zone 3 were lower than St.1. This could suggest that Fe at St.1 might have strong affinities for TSS and also might represent the competition between dissolved and particulate metals binding sites. This is due to anthropogenic activities and urban runoff directly from a river. However, St.2 to St.7 showed transportation particulate

to the dissolved phase. This is due to Fe in the particulate phase re-suspending from anoxic zones and coming into contact with oxygenated water where sediment suspension occurred (Hou et al, 2013). The particulate iron is dissolved by bacteria, which also release ligands for iron ions complexation and keeps them in the solution. The oxidation state of iron in an aquatic system and its redox processes are determined by the dissolved oxygen concentration. Redox reactions, complexation with inorganic and organic ligands, adsorption and precipitation are involved in the chemistry of iron in natural waters; whereas at high DO, oxygen penetration was stronger, and Fe and Mn oxidative precipitation was more rapid. Hence, the generated hydroxide or oxide would adsorb more dissolved heavy metals, thus leading to reduced metals release. Therefore, the result of both zones having low K_D values was probably due to most of the Fe possibly existing in organic ligands or colloidal forms (Byrd et al., 1990).

The organic ligands were thought to stabilize the metals through struggling with binding sites on settling particles (Mohamed et al., 2011). These results were in line with the kinetic iron studies carried out by Mayer (1982) which showed that iron agglomerates in the form of colloids during mixing of fresh water and saline water while following two (2) stages of a kinetic process. There is a first, fast stage (zone 1) with first order kinetic, relating to the interaction of iron with high molecular mass of organic matter followed by a second, slower stage (zones 2 and 3). This stage has a second order kinetic corresponding to the formation of colloidal particles which would depend on temperature and turbidity (quantity of suspended particles). This could also relate with our turbidity data, where the value decreased from a river (St.1) to 127.00 NTU. The lowest value along the estuarine area (St. 2, 3, 4, 5, 6 and 7) is 23.00 NTU respectively (Table 1).

For instance, the high value of K_D at St.1 might originate from anthropogenic activities directly linked to the river possibly resulting in multiple sources of organic matter. This indicates that most of the Fe exists in particulate phase rather than dissolved phase at St.1. Moreover, the characteristic of freshwater could reveal the condition of surrounding water. Many researchers reported that at low pH (6.0 or less), the metal release was more obvious than at middle (7.0) or high pH (more than 7.0); however, low pH value instances are very rare in a natural environment (Butler, 2009; Jing et al., 2007; Pérez-Esteban et al., 2013; Watmough et al., 2007; Yang et al., 2006). This provides an explanation to our data at Zone 1 (fresh water).

Furthermore, domestic sewage as one of the input contributors of anthropogenic activities could be the main factor. Residents in the Bagan Pasir area stated that they had no proper rubbish disposal system (Kelly, 2016). Besides, dFe at zone 1 was found to be lower, probably due to the presence of low dissolved oxygen (DO); hence, the oxidative precipitation rate would become slower. Further, scavenging of dissolved Fe ions form iron hydroxide by Fe cations released from pore water as they diffuse from sediment to water (Atkinson et al., 2007; Santana-Casiano et al., 2004).

CONCLUSIONS

Dissolved Fe and particulate Fe samples along some stations at an estuarine system at Bagan Pasir were observed in this study. Our K_D value indicated a decrease along the station due to most of the metal being predominantly in dissolved fraction with the low value of particulate fraction. Our data found that concentration of dFe was lower than Fe particulate in fresh water as opposed to the estuary area. This could suggest the possibility of existence of Fe in an estuary mostly in colloidal or in organic ligand forms. However, further investigation on these speciation of dissolved Fe is needed in order to improve our knowledge on iron biogeochemistry cycle in the estuarine system.

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