

DISSOLVED FE (III) SPECIATION IN TROPICAL COASTAL WATER: IN CASE OF NORTHEAST MONSOON EFFECT

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Abstract: The distribution of total dissolved iron (dFe) and natural organic Fe (III) binding ligands (FeL) were determined in the east coast of Peninsular Malaysia. This study was carried out during the pre- (October 2015) and post- (April 2016) Northeast Monsoon. Seawater samples were analyzed by using a competitive ligand equilibration–adsorptive cathodic stripping voltammetry method. The [dFe] in October 2015 (3.0 – 25.0 nM) was lower than in April 2016 (40.4 – 940.4 nM) due to a longer Northeast Monsoon 2015/2016 period. We recorded a similar distribution of [FeL] to those [dFe]. In October 2015, its concentration was 4.2 - 25.8 nM, which was lower than in April 2016 (43.3 - 948.6 nM). However, the speciation data shows that the distribution of [FeL]/[dFe] ratio and Log *K* value were slightly similar during the two seasons. This indicated that [FeL] was always in excess of [dFe] and the presence of high stability of organic ligands class (L_1 : Log *K* 13). Our present results suggested that the Northeast monsoon system results to the ligand saturation state in the water column, especially during the post-monsoon season. These organic ligands play an important role in Fe biogeochemistry cycle by binding any input of Fe (III) and remain it in the water column.

Keywords: Northeast monsoon, organic ligands, dissolved Fe, speciation, coastal water.

Introduction

In marine environment, iron (Fe) becomes bioavailable to microorganism as Fe (II). Its production is related to the free Fe (III) ion concentration and complexation properties of organic ligands in seawater. For these reasons, Fe (III) complexation by dissolved organic matter is crucial and needs to be considered in order to identify the biological Fe cycle in seawater.

The Fe (III) organic complexation (FeL) is complexed by organic ligands in the marine environment and nearly ubiquitous feature of dissolved iron (dFe) speciation in seawater. Previous studies (Mohamed *et al.*, 2011; Ibsanmi *et al.*, 2011; Kondo *et al.*, 2012) have suggested that more than 99% of dFe is strongly binding to these natural organic ligands (L_T). This complex increases the solubility of dFe, prevents oxyhydroxide precipitation (Hutchins *et al.*, 1999) and increases its residence time in the water column (Fan, 2008). Without

this FeL complex, Fe (III) solubility could decrease to approximately 0.15 - 0.20 nmol/L in coastal seawater (Kuma *et al.*, 1996). Therefore, determination of FeL speciation is crucial in order to gain information on Fe (III) bioavailability in coastal water.

Fe bioavailability is highly sensitive to assumptions regarding to the dissolved concentration of Fe (III) that bioavailable for phytoplankton to growth (.....regarding the dissolved concentration of.....that is bioavailable for plankton to grow...Is this what you mean? Or else you need to make it clearer.). When forced to representations of Malaysia's climate, it might be large changing to this Fe (III) distribution (*Please take a look and try to make the message clearer*). We speculated that these changes may exert selective pressure on the phytoplankton growth and productivity, especially in the coastal area. One of the changes is a seasonal monsoon event which induces changing of physicochemical properties such as

pH, salinity, DO etc., (Mohamed *et al.*, 2019b), nutrient conditions and chlorophyll distribution (Chl-a) (Mohamed *et al.*, 2019a). Unfortunately, we have limited information on this due to limited available data in the area, especially on dFe speciation data.

In addition, Gledhill *et al.* (2015) have suggested this FeL is likely to be influenced by pH changing. Decrease of pH reduces a binding strength of the complex between Fe (III) and natural organic ligands. Therefore, it will affect the bioavailability of Fe (III) for biological uptake. However, this study is an initial report based on modelling and laboratory simulation. Therefore, further studies by extending it to a real marine environment would provide a more information and better understanding on that relationship.

According to a previous study conducted in the area by Godon and Mohamed (2016), they found a spatial and seasonal Fe distribution. It may have significant effects on its bioavailability which resulting to the primary productivity. However, this impact is challenged to determine because of biogeochemical mechanisms in coastal waters and the fact that many aspects of Fe cycling and distribution have not yet been fully understood, especially in the tropical area. The Fe biogeochemistry cycle is more dynamic and complicated due to coastal area, anthropogenic input and sediment impacts. Furthermore, the concentration of natural organic Fe (III) ligands due to many different types of organic compounds that bind Fe to varying degrees in seawater present in the coastal area. Therefore, indirect measurements were developed to determine the concentration of FeL and the complexation capacity of Fe (III) with natural ligands (Log *K*). One of the successful methods is a competitive ligand equilibration–adsorptive cathodic stripping voltammetry (CLE–ACSV) (Croot & Johansson, 2000; Mahmood *et al.*, 2015; Su *et al.*, 2015). Hence, we take this opportunity to conduct an initial comprehensive study on the distribution of dissolved Fe and its Fe (III) speciation determination at Pulau Perhentian, Terengganu during the pre-monsoon

and post-monsoon seasons. This information will give a better understanding on the effect of the Malaysia climate on the Northeast Monsoon system on the Fe (III) bioavailability in the coastal waters and also improve in the trace metals analysis at tropical zone, by extending to the speciation analysis.

Materials and Methods

Vertical seawater samples were collected at Pulau Perhentian, Terengganu in a series of samplings. This study area was chosen because it is less affected by anthropogenic activities in the marine park and effects of the northeast monsoon. A sampling activity was conducted during the post-monsoon season in October 2015 and the pre-monsoon season in April 2016. The seawater was sampled using Van Dorm water sampler at five stations, located in transect line facing toward the South China Sea, as shown in Figure 1. The coordinate for each station and in-situ parameters in each sample were measured by using GPS MAP 78s Garmin and YSI multi prop Professional Plus respectively.

Samples of seawater from the samplers were poured directly into 1.0 L low-density polyethylene (LDPE) bottles. These samples were collected at five to six different depths at each station. A 250 mL of filter through 0.2 μm Whatman® filters (25 mm diameter, Sigma-Aldrich) and stored into polytetrafluoroethene (PTFE) bottles (Nalgene). The samples were immediately frozen at -20°C (not acidified) for total dissolved Fe and speciation analysis. All bottle samples in this study were cleaned according to a standard protocol (Achterberg *et al.*, 2001).

Total dissolved Fe concentration and Fe (III) speciation were determined by using electrochemistry analysis on a 797 VA computrace (Metrohm, Switzerland) instrument. A hanging mercury drop electrode (HMDE) was applied as the working electrode. Clean dry nitrogen gas (99.999% purity) was applied to remove all dissolved oxygen from the samples.

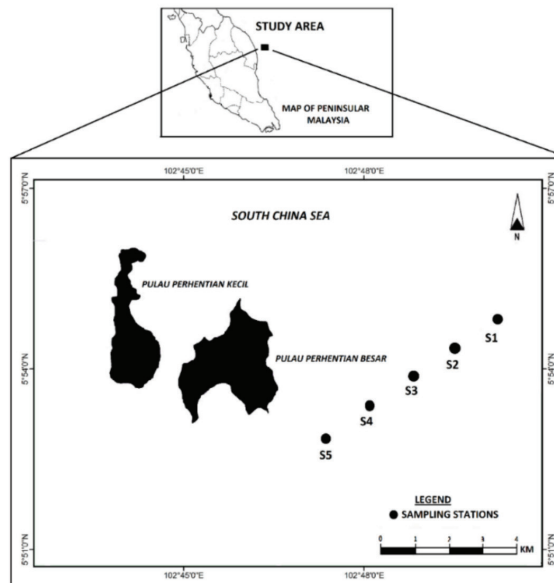


Figure 1: Seawater profile was collected at five stations (in transect line facing the South China Sea) at Pulau Perhentian, Terengganu during the pre- and post-monsoon events

Total dissolved Fe (dFe) was determined by using adsorptive cathodic stripping voltammetric (AdCSV) technique (Laglera & Monticelli, 2017). A frozen seawater sample was defrosted at room temperature and then its organic content destroyed (Mohmood *et al.*, 2015). 10 mL of sample was pipetted into a quartz voltammetric cell and added with 0.1 M of HEPES as a buffer at pH 8.05 (final concentration 5 μ M). A 0.1 M of 2,3-dihydroxynaphthalene (DHN) (final concentration of 0.4 μ M) was added into the sample before determining dFe concentration by using standard addition method.

The organic Fe-binding ligands (FeL) were measured by using a competitive ligand equilibration–adsorptive cathodic stripping voltammetry (CLE–AdCSV) method (Mohmood *et al.*, 2015).

Results and Discussion

Table 1 shows the in-situ parameters recorded during the sampling activities in October 2015 and April 2016. From the salinity data obtained, it suggested that the seawater column in April 2016 was more saline compared to the one in October 2015 (Figure 2). It ranged between 37.44 - 38.97‰ in April 2016 and 31.50 - 32.10‰ in October 2015 (Table 1). We also found that the seawater column was slightly acidic in October 2015 compared to in April 2016 (Figure 2). The pH of seawater in October 2015 ranged between 7.19 - 7.96 (Table 1), compared to pH 7.45 - 8.52 in April 2016 (Table 1). For dissolved oxygen concentration, it ranged between 5.82 - 8.68 mg/L in October 2015 (Table 1), which was higher compared to the concentration in April 2016 (Figure 2). In April 2016, its concentration ranged from 3.54 - 7.02 mg/L (Table 1). Warmer seawater was recorded in April 2016. It ranged between 28.9 - 30.28°C (Table 1) but decreased with depth (Figure 2).

Table 1: Data in-situ parameters (salinity, conductivity, turbidity, temperature, pH and dissolved oxygen) during the pre-monsoon sampling (October 2015) and post-monsoon sampling (April 2016) at Pulau Perhentian, Terengganu

Station (Total depth)	Depth (meter)	Oct-15						Apr-16														
		Salinity ppt ±	Conductivity (mS) ±	Temp. (°C) ±	pH (mol/L) ±	DO (mg/L) ±	Salinity ppt ±	Conductivity (mS) ±	Temp. (°C) ±	pH (mol/L) ±	DO (mg/L) ±											
(38.8m)	1	31.50	0.03	52.30	0.04	29.90	0.00	7.19	0.02	7.53	0.55	38.36	1.00	63.37	0.60	29.95	0.00	8.35	0.00	6.34	1.11	
	6	31.60	0.03	52.50	0.06	29.80	0.00	7.84	0.00	6.38	0.04	38.68	0.34	63.44	0.10	29.31	0.00	8.35	0.00	5.65	0.80	
	15	31.90	0.01	53.10	0.00	29.90	0.01	7.80	0.06	7.46	0.17	38.35	0.69	63.51	0.11	30.28	0.00	7.45	0.00	4.97	0.04	
	20	31.90	0.00	53.20	0.05	29.80	0.00	7.84	0.00	6.66	0.00	38.48	0.04	63.23	0.15	29.37	0.02	8.31	0.00	3.71	0.04	
	30	31.80	0.01	53.20	0.04	29.50	0.00	7.84	0.00	6.80	0.00	38.45	0.22	62.29	0.44	29.34	0.20	8.28	0.00	5.48	0.71	
(40.2m)	2	31.50	0.02	52.50	0.08	29.60	0.00	7.86	0.03	8.68	0.06	38.51	0.94	33.03	0.38	30.13	0.00	8.23	0.01	7.02	0.38	
	6	31.60	0.04	52.60	0.02	29.50	0.00	7.69	0.02	8.18	0.00	38.34	0.00	63.49	0.07	30.15	0.05	8.36	0.00	3.54	0.00	
	15	31.90	0.02	53.30	0.04	29.60	0.02	7.94	0.06	8.30	0.05	38.97	0.37	63.31	0.00	29.88	0.01	8.33	0.02	3.79	0.04	
	20	31.90	0.01	53.30	0.03	29.60	0.01	7.96	0.00	8.34	0.00	37.44	0.62	62.35	0.30	29.30	0.00	8.32	0.00	4.33	0.00	
	30	32.10	0.01	53.50	0.03	29.60	0.00	7.66	0.00	8.07	0.01	38.29	0.05	62.12	0.00	28.88	0.00	8.02	0.00	4.44	0.00	
(36.5 m)	3	31.50	0.04	52.50	0.05	29.40	0.00	7.68	0.00	6.89	0.47	38.48	0.00	63.48	0.73	29.68	0.02	8.02	0.00	4.25	0.03	
	6	31.80	0.04	53.10	0.05	29.40	0.00	7.66	0.00	6.55	0.11	38.44	0.04	63.43	0.26	29.58	0.02	8.25	0.00	4.85	0.82	
	15	31.90	0.02	53.30	0.13	29.50	0.01	7.66	0.05	7.34	0.03	38.46	0.33	63.38	0.00	29.62	0.00	8.37	0.00	4.48	0.11	
	20	32.00	0.00	53.40	0.10	29.60	0.01	7.65	0.02	7.75	0.00	38.52	0.07	63.30	0.04	29.70	0.01	8.35	0.00	4.45	1.11	
	30	32.10	0.00	53.50	0.20	29.50	0.00	7.63	0.00	7.54	0.00	38.44	0.20	62.57	0.03	29.22	0.00	7.45	0.01	4.56	0.00	
(33.3m)	4	31.70	0.02	52.80	0.10	29.30	0.02	7.91	0.00	6.43	0.02	38.45	0.47	63.47	0.00	29.85	0.00	8.33	0.00	6.14	0.03	
	6	31.90	0.02	53.40	0.00	29.50	0.03	7.50	0.04	6.30	0.58	38.33	0.42	63.31	0.00	29.90	0.00	8.49	0.00	4.61	0.00	
	15	32.00	0.00	53.40	0.33	29.40	0.00	7.45	0.01	6.78	0.00	38.17	0.39	62.97	0.36	29.97	0.00	8.37	0.00	4.74	0.50	
	20	31.99	0.01	53.30	0.71	29.50	0.00	7.32	0.00	6.92	0.00	38.23	0.47	62.54	1.01	29.50	0.00	8.05	0.00	4.41	0.00	
	30	32.00	0.04	53.30	1.01	29.40	0.02	7.23	0.00	7.48	0.07											
(29.1 m)	5	6	31.90	0.05	53.10	0.08	29.30	0.02	7.53	0.01	7.05	0.83	38.38	1.22	63.31	1.06	29.95	0.50	8.52	0.01	5.80	1.00
	15	31.80	0.03	52.90	0.42	29.30	0.02	7.36	0.01	6.17	0.07	38.52	0.59	63.44	0.11	29.73	0.00	8.39	0.01	4.54	0.11	
	20	32.00	0.03	53.20	1.00	29.30	0.02	7.33	0.01	5.82	0.00	38.52	1.00	63.26	0.00	29.83	0.02	8.24	0.00	5.32	0.00	

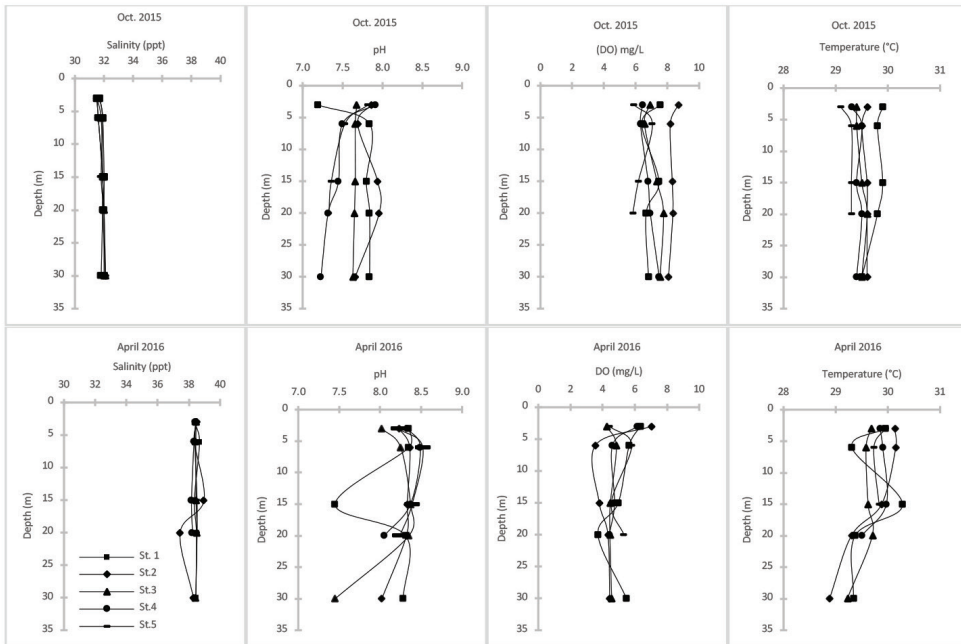


Figure 2: In-situ parameters during sampling activities in October 2015 and April 2016 at Pulau Perhentian, Terengganu

A Temperature/ Salinity (T-S) relationship was applied to our data in order to identify the different water mass properties during both periods in the region. The characteristics of water mass in April 2016 were clearly distinguishable. It was more saline with a range of temperature, compared to its salinity and temperature in October 2015. The warmer water in April 2016 might be the result of *El Niño* phenomena. According to Sang *et al.* (2016), it was among the top three strongest episodes since 1979. Its pressure level was 850-hPa which was a stronger than normal northerly flow over the South China Sea, Indochina and Borneo. Moreover, a high tide phenomenon also occurred during this period at Peninsular East Coast. Therefore, these two phenomena would have contributed to the physical-chemical conditions of the water column in April 2016.

In March 2016, one month prior to our sampling period, the north west and the east coast of Peninsular Malaysia (including our

study area) and experienced the greatest drop of in the average rainfall, from 11 - 13% to 3 - 4% (Sang *et al.*, 2016). This extremely dry condition might had contributed to the massive difference in the salinity readings in April 2016, as the least rainfall was observed in this period, compared to in October 2015.

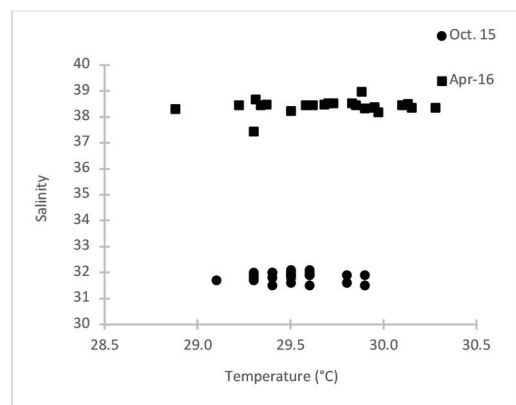


Figure 3: Temperature–salinity (T-S) plot for in-situ data from Pulau Perhentian, Terengganu in October 2015 and April 2016. The plot shows clearly a massive different physical-chemical condition between both periods

Dissolved Fe Distribution

The distribution of dFe is shown in Fig.4 below. In October 2015, its concentration ranged between 3.0 - 25.0 nM (Table 1), with an average concentration of 12.9 ± 0.0 nM ($n=15$) throughout the water column. The highest [dFe] was determined at 15 m depth (Table 2). However, its concentration was recorded higher in April 2016 compared to in October 2015. It ranged between 40.4 - 940.4 nM (Table 2), with an average concentration of 417.8 ± 0.0 nM ($n=22$). This indicated that the [dFe] in the area was seasonal and spatial throughout the water column.

During the post-monsoon season in April 2016, we found a significant difference in [dFe] throughout the water column (Figure 4). Its concentration ranged between 40.4 - 900.6 nM at the surface layer (3 m depth), 200.1 - 430.3 nM

at the middle layer (15 m) and 100.9 - 172.3 nM at the bottom layer (30 m). This indicated high [dFe] at surface water and decreased with depth during this season. The high [dFe] in surface layer might be input from bottom sediment resulting from water mixing (Adiana *et al.*, 2014; Mohamed *et al.*, 2019a). The changing surface cool water temperature in October 2015 to warmer water in April 2016 due to *El Niño* phenomenon and a longer northeast monsoon 2015/2016 period induces an imbalance and a pronounced formation of coastal upwelling process at the area (Trenberth, 2013; Zainol & Akhir, 2016; Edmunds, 2017). This process brings up nutrients along with Fe at surface sediment into upper water layer. Possibility combination between both processes could be an explanation to the increasing of [dFe] at surface water during post-monsoon season.

Table 2: Iron speciation data for Pulau Perhentian, Terengganu during our sampling periods a) October 2015 and b) April 2016. Total dissolved Fe concentration ([dFe]), total Fe binding ligand ($[L_T]$) and stability constant of Fe ligand ($\log K$) were determined, and free iron binding-ligand ($[L'] = [L_T] - [dFe]$), was calculated

a) Iron speciation data in October 2015

St.	Depth (m)	[dFe]	$[L_T]$		$\log K$		$[L']$		$[L_T]/[dFe]$	FeL (%)
		nM	nM	±	mol^{-1}	±	nM	±		
St.1	3	4.0	4.5	0.1	12.3	0.3	0.5	0.1	1.1	99.9
	6	17.0	17.8	0.1	13.4	2.4	0.8	0.1	1.0	100.0
	15	10.0	11.0	0.0	13.6	1.2	1.0	0.0	1.1	100.0
St.2	3	12.0	12.5	0.1	13.0	0.9	0.5	0.1	1.0	100.0
	6	3.0	4.2	0.1	13.4	4.5	1.2	0.1	1.4	100.0
	15	7.0	7.5	0.1	12.8	0.6	0.5	0.1	1.1	100.0
	20	15.0	15.5	0.1	13.4	4.5	0.5	0.1	1.0	100.0
	30	15.0	18.3	0.0	14.1	4.3	3.3	0.0	1.2	100.0
St.3	3	12.0	12.3	0.1	13.9	9.6	0.3	0.1	1.0	100.0
	6	22.0	22.2	0.1	13.9	3.5	0.2	0.1	1.0	100.0
	15	25.0	25.8	0.5	12.6	0.9	0.8	0.5	1.0	100.0
	20	14.0	19.7	0.1	14.1	9.6	5.7	0.1	1.4	100.0
	30	15.0	20.6	0.2	13.9	8.4	5.6	0.2	1.4	100.0
St. 4	6	10.0	10.2	0.1	12.9	1.4	0.2	0.1	1.0	99.9
	15	12.0	12.4	0.0	13.9	1.8	0.4	0.0	1.0	100.0

b) Iron speciation data in April 2016

St.	Depth (m)	[dFe] nM	[L ₇] nM	±	log K mol ⁻¹	±	[L] nM	±	[L ₇]/[dFe]	FeL (%)
St.1	3	430.7	432.8	1.9	13.7	1.9	2.1	1.9	1.0	100.0
	6	400.0	409.8	0.1	13.7	0.9	9.8	0.1	1.0	100.0
	15	400.3	403.6	0.1	14.6	1.5	3.2	0.1	1.0	100.0
	20	750.9	776.3	0.2	13.9	0.6	25.5	0.2	1.0	100.0
	30	200.4	211.7	0.1	13.8	0.7	11.3	0.1	1.1	100.0
St.2	3	900.6	929.4	0.3	14.3	1.9	28.8	0.3	1.0	100.0
	6	800.6	822.4	0.9	12.7	1.3	21.7	0.9	1.0	100.0
	15	200.1	249.0	0.4	12.9	3.0	48.9	0.4	1.2	100.0
	20	190.0	194.8	0.9	12.7	6.0	4.8	0.9	1.0	100.0
	30	172.3	172.4	0.3	14.5	4.0	0.1	0.3	1.0	100.0
St.3	3	900.5	905.0	0.8	13.6	3.9	4.5	0.8	1.0	100.0
	6	260.8	265.1	0.1	14.2	4.3	4.3	0.1	1.0	100.0
	15	400.5	403.8	0.3	13.3	1.2	3.3	0.3	1.0	100.0
	20	390.0	392.4	0.2	13.3	3.1	2.5	0.2	1.0	100.0
	30	100.9	117.0	0.4	12.9	2.5	16.1	0.4	1.2	100.0
St.4	3	40.4	43.3	0.1	12.9	2.2	2.9	0.1	1.1	100.0
	6	491.0	494.7	0.3	13.4	1.5	3.7	0.3	1.0	100.0
	15	530.3	536.2	0.6	13.6	1.8	5.8	0.6	1.0	100.0
St.5	3	70.3	71.1	0.1	13.1	1.3	0.8	0.1	1.0	100.0
	6	220.2	225.4	0.2	13.3	3.9	5.2	0.2	1.0	100.0
	15	400.3	402.8	0.4	13.0	0.7	2.5	0.4	1.0	100.0
	20	940.4	948.6	0.3	13.5	0.4	8.2	0.3	1.0	100.0

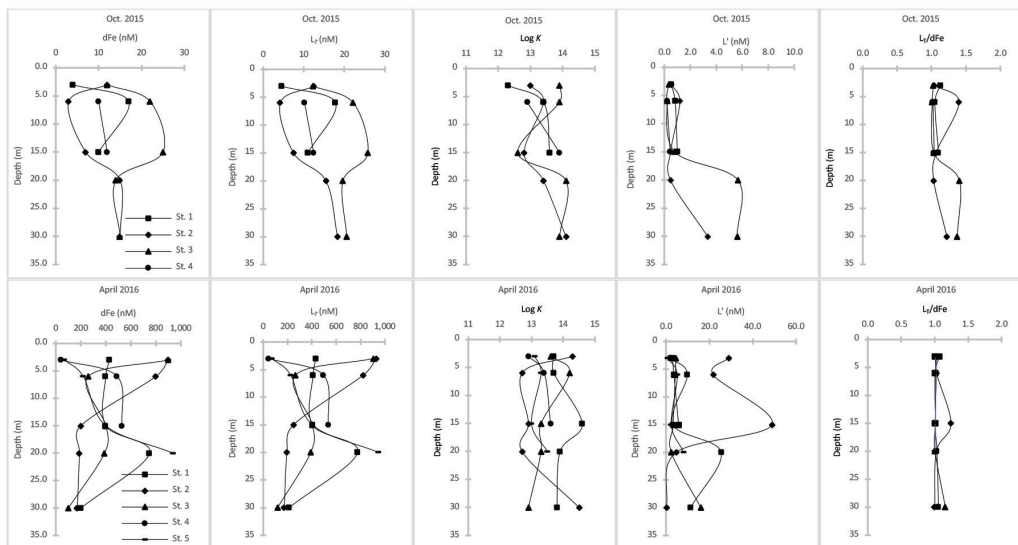


Figure 4: Distribution of dFe and its speciation in Pulau Perhentian, Terengganu in October 2015 and April 2016

Organic Ligand Distribution and Characteristics

In this present study, we have determined concentration of total organic ligand (L_T) by an assumption that a single ligand was present (Mohamed *et al.*, 2011; Gledhill *et al.*, 2015). The concentration of L_T throughout the water column in October 2015 was recorded between 4.2 ± 0.0 nM to 25.8 ± 0.5 nM (Table 2), with an average concentration of 14.3 ± 0.1 nM ($n=15$). However, a year later its concentration was higher and variable throughout the water column (Figure 4). It ranged between 43.3 ± 0.1 nM to 948.6 ± 0.3 nM (Table 2), with an average concentration of 427.6 ± 0.4 nM ($n=22$). This indicated that the $[L_T]$ in our study area was seasonal and spatial and its profile showed a similar trend to those of $[dFe]$ (Figure 4).

Interestingly, an extremely high $[L_T]$ was recorded throughout the water column in April 2016. The spatial variation of $[L_T]$ might be due to similar factors that influence the distribution of $[dFe]$. We also recorded that $[L_T]$ was always in excess of $[dFe]$ in the water column at all stations. High $[L_T]$ might be caused by the monsoon and sediment input (Buck *et al.*, 2007; Gledhill & Buck, 2012; Zhu *et al.*, 2012; Bundy *et al.*, 2014).

The concentration of excess ligand ($[L'] = [L_T] - [dFe]$) with respect to Fe corresponds to the concentration of free Fe binding sites. The $[L']$ ranged between 0.2 - 5.7 nM in October 2015 (Table 2). The distribution of L' was low in the surface layer (<15 m depth) and high in the bottom layer (>15 m depth) (Figure 4). This indicated that most of the ligand was binding to the Fe (III) in this surface layer and it was saturated in the bottom layer. This could support the probability of input ligand from surface sediment. On the other hand, a higher and variable $[L']$ was recorded in April 2016. It ranged between 0.1 - 48.9 nM throughout the water column (Table 2). This suggested that the huge input of $[dFe]$ into the water column was saturated by ligand during the period. In addition, we have recorded that more than 99% of $[dFe]$ was organically complexed (not considering Fe

(II)) throughout the water column during both seasons (Table 2). In April 2016, we found that all the $[dFe]$ exist in organic complex (100%). This high proportion of organic complexation, especially in April 2016 is due to the saturation condition of L' throughout the water column.

According to the data in Table 2, the Log K value throughout the water column in October 2015 and April 2016 ranged between 12.3 - 14.1 and 12.7 - 14.6, respectively. The average value for Log K was 13.4 ± 3.6 ($n=15$) and 13.5 ± 2.2 ($n=22$) in October 2015 and April 2016, respectively. This indicated the presence of similar strong organic Fe (III) binding ligand class (L_1) at our study area during both seasons, resulted in low concentrations of free Fe^{3+} (ca. $pFe^{3+}=11-13$) (Table 2). Moreover, the binding capacities recorded during our study was in the range of previously reported ($\sim 9 - 14$) by Laglera and van den Berg (2009). This range of Log K is similar to a humic-like substance in seawater and it has been suggested that humic substance (HS) can account for the majority of the total ligand pool in the coastal waters (Stolpe *et al.*, 2010; Stolpe & Hasselov, 2010; Hassler *et al.*, 2011). These humic substances are high in terrestrial ^{land} and also found in the colloidal fraction, which is quite refractory. Hassler *et al.* (2011) have suggested that the complex of Fe-humic acid is available to phytoplankton. However, information on this complex is poorly defined in Malaysia's coastal waters. An effort to characterize the association between Fe and HS, and the contribution of HS to the ambient ligand pool in this coastal water is needed.

In order to identify trends in Fe (III) speciation throughout the water column during the pre- and post-monsoon seasons, a ration of $[L_T]/[dFe]$ was applied to our data. It is important in order to highlight the differences in ligand saturation state as suggested by Mohamed *et al.* (2011). According to Thuroczy *et al.* (2010), when the ratio is more than one, it indicates an excess of ligands and any addition of Fe (III) into the area would be complexed by the ligands. On the other hand, a ration less than one indicates that all the ligands are saturated by Fe (III) and

additional input of Fe (III) would be removed from the water column via precipitation and scavenging processes.

The vertical profiles of the $[L_T]/[dFe]$ ratios in our study area showed a similar trend during both seasons, slightly constant ratio throughout the water column (Figure 4). In October 2015 the $[L_T]/[dFe]$ ratios were between 1.0 - 1.4, with an average of 1.1 ($n=15$) (Table 2). In April 2016, it ranged between 1.0 – 1.2 (Table 2). This could suggest that our study area is saturated with the excess of ligands and all the Fe (III) input into the water column is complexed by ligands during both seasons. It is likely that the ligands potentially control the coastal geochemistry of Fe (III) by increasing its solubility and bioavailability (Hutchins *et al.*, 1999). It also increases the residence time of Fe (III) within the euphotic zone (0.3 – 2.9 years) (Boye *et al.*, 2003; Fan, 2008). Previous study by Kuma *et al.* (1996), suggested that, with the absence of these ligands in seawater, the solubility of Fe (III) hydroxide is approximately 0.15 – 0.20 and 0.07 – 0.09 nmol/L in coastal and open ocean, respectively. Therefore, the presence of organic ligand in the area plays an important role in Fe biogeochemistry cycle and productivity.

The Log K value (≈ 13) and $[L_T]/[dFe]$ ratio (≈ 1.1) in this area was slightly similar during both seasons and indicated that the changing of physicochemical properties such as pH, DO and salinity do not affect the binding strength of natural organic Fe (III) binding ligands complex and ligand saturation state at this coastal area. Furthermore, the present of strong class ligand (L_1) has saturated any input of dissolved Fe into the water column. These saturated ligands are potentially input from sediments as resulting from water mixing during the northeast monsoon (Adiana *et al.*, 2014; Mohamed *et al.*, 2019a). An accumulated sediment is weathered and carried along with the associated porewaters into the water column when the season changes. Furthermore, the changing of season releases Fe and Fe-complexing ligands into the water column due to the shallow nature of Pulau Perhentian

(≈ 35 m depth). In addition, Jones *et al.* (2011) reported that a pore-water from the sediment was the prevailing source of ligands which accounted for a portion of dFe pool to strong ligands. Therefore, this sediment resuspension appears to be a source of Fe-binding ligands to the water column, as suggested in previous studies at Kerguelen Archipelago (Gerringa *et al.*, 2008) and Thurso Bay (Batchelli *et al.*, 2010). These organic ligands play an important role in Fe bioavailability in the east coast of Peninsular Malaysia.

Conclusion

The determination of dissolved Fe distribution and its organic ligands during the pre-monsoon and post-monsoon seasons on the east coast of Peninsular Malaysia indicated that dissolved Fe was organically complexed by strong organic Fe (III) binding ligands class (L_1) throughout the water column during both seasons. These organic ligands which are probably anticipated from sediment resuspension, increase the solubility of dFe and remain in the water column especially during the post-monsoon season. In addition, our speciation data suggested that the northeast monsoon system increases the distribution of dissolved Fe and its organic ligands in the water column but does not change its organic Fe (III)-ligand binding strength and ligand saturation state, even though it has changed the physicochemical parameters (such as pH and salinity) of water.

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