

Seasonal Distribution of Dissolved Copper(II) Ions at Tropical Coastal Water: In Case of Pulau Perhentian, Terengganu

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Abstract: Seawater samples from Pulau Perhentian, Terengganu were analysed for Cu(II) speciation concentration. Samples were collected during pre- and post-monsoon seasons, in order to measure the concentration of dCu (dissolved Cu) and CuL (Natural Organic Cu(II) Binding Ligands) by using CLE-AdCSV (Competitive Ligand Exchange-Adsorptive Cathodic Stripping Voltammetry). High [dCu] and [CuL] were determined during pre-monsoon seasons due to a long NEM (Northeast Monsoon) period along with a strong El Niño phenomenon. Water mixing during this period was suggested to be responsible for an input of Cu from bottom sediment into the water column. The Cu(II) speciation analysis has identified the presence of strong class ligands (L1), and it controls the distribution of free Cu^{2+} ions. Therefore, the presence of Cu^{2+} ions is below the toxicant level and it functions more towards the bioavailability for microorganisms. Furthermore, there is no significant effect between pre- and post-monsoon season on the dissolved Cu(II)-speciation in the study area, except an influence from the El Niño phenomenon which is unclear as of yet.

Key words: Bioavailability, dissolved, NEM, speciation, toxicity.

1. Introduction

Malaysia is influenced by the seasonal monsoon system [1]. During November to March, the NEM (Northeast Monsoon) (winter) occurs and follows by southwest monsoon (summer) from May to September. The NEM event is a natural phenomenon and results in changes in coastal water chemistry, something that has not been fully understood yet. This change possibly results in the change of the biogeochemical cycle of trace metals and will inevitably affect the marine organisms.

Recent research has suggested that monsoon events have important but unknown effects on trace metal speciation. According to Gledhill, et al. [2], the changing of physico-chemical parameters (pH) of seawater could change metal speciation either increase the toxicity or decrease bioavailable forms of metals.

Therefore, knowledge on the impact of monsoon events on the trace metal speciation is crucial to understand clearly the influences of the current issues of climate change in Malaysia's coastal water. In fact, it is challenging for the scientific due to analytical method of organic complexation determination and its complexity of the controlling processes.

In seawater, the speciation of metals is affected by the presence of hydrogen ions. Consequently, a changing in the seawater pH can alter the speciation of metals. This could affect the metal bioavailability and toxicity. According to previous studies by Campbell, et al. [3] and Gledhill, et al. [2], free metal ion concentration controls the trace metals toxicity and bioavailability. Moreover, a changing in pH will affect these free ionic forms [4]. Among the important factors affecting the bioavailability of Cu are salinity, pH, natural organic matter and alkalinity [5, 6]. Millero, et al. [4] have suggested that the sites for complexation of the organic particle surface become weak to bind metals and produce free metals

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that cause toxicity at low pH. However, if pH increases, fewer binding sites on natural organic matter become protonated, allowing Cu to form more Cu-complexes, thus declining the bioavailability of copper [6, 7].

According to Brand, et al. [8], free Cu^{2+} ion at low concentration (10^{-12} M) will be toxic to marine phytoplankton and cyanobacteria growth rates. This free Cu^{2+} ion is affecting the Zn^{2+} and Mn^{2+} uptake by phytoplankton [9]. While, diatom and various zooplanktons also will be affected at Cu^{2+} concentrations above $\sim 10^{-11}$ M [8, 9]. The presence of natural Cu(II)-organic ligands can decrease the Cu^{2+} free ion concentration and its toxicity [10]. However, this complexation could dissociate by decreasing pH, resulting in more bioavailable Cu, also toxic to other organisms. Millero, et al. [4] have suggested that the Cu^{2+} free ion will increase by 30% at pH 7.5, as in estuarine waters [11].

The speciation study especially Cu which has nutrient and toxic effect on microorganism, has been studied [12-14]. It is important for us to more understand its toxicity level, bioavailability and geochemical behavior in natural water [15]. According to Sunda and Guillard [16], free hydrated Cu^{2+} ion species is controlling the Cu bioavailability in marine water. Furthermore, this species is all complexed (> 99%) by organic ligands in seawater [17-20]. Therefore, by determining the natural organic Cu complex, we could more understand its biogeochemistry cycle in seawater.

In Malaysia, the speciation study especially with respect to the monsoon season has not been conducted yet. However, current study on trace metals distribution by Godon and Mohamed [21] has suggested a significant difference of total dissolved trace metals concentration between pre- and post-monsoon events at Pulau Perhentian. They found an increase in the dissolved trace metals concentration throughout the water column during post monsoon, due to the water mixing and turbulence, resulting in the re-suspension of bottom sediments. In their study,

they have recorded the significant change of seawater pH between both seasons. The wide range and acidity of pH (7.1-7.9) was recorded during pre-monsoon season, and a constant and alkaline pH (8.2-8.3) was found during post-monsoon throughout the water column. This might be affecting the bioavailability and toxicity of trace elements in the area. Unfortunately, there is a lack of trace metals speciation data during their study. Therefore, this present study was conducted to determine the dissolved trace metal along with their speciation at coastal water.

The objective of this research is to study the possible influence of the NEM event on the dCu (Dissolved Cu(II)) and CuL (Natural Organic Cu(II) Binding Ligands) distribution at Pulau Perhentian, in order to identify its bioavailability and/or toxicity level.

2. Material and Methods

Seawater for this study was collected during two series of sampling activities in November 2015/April 2016 and November 2016/April 2017 at Pulau Perhentian. The seawater profile samples were collected by using a Van Dorm water sampler at five stations located in transect line facing towards South China Sea, as shown in Fig. 1. The coordinate for each station and in-situ parameters in each sample were measured by using GPS (Global Positioning System) MAP 78s Garmin and YSI multi prop Professional Plus, respectively.

A seawater sample from the sampler was filled up directly into 1.0 L LDPE (Low-Density Polyethylene) bottles. It was collected at 5-6 different depths in each station and filtered through 0.2 μm pore size filters (Whatman®, Sigma- Aldrich). The samples for dCu and Cu speciation (CuL) analysis were stored into PTFE (Polytetrafluoroethene) bottles (Nalgene) and frozen at -20 °C (not acidified). All the bottles for this analysis were cleaned according to a standard protocol as suggested by Achterberg, et al. [22].

An added ligand solution was prepared by 0.01 M SA (Salicylaldoxime) in 0.1 M HCl. A standard solution

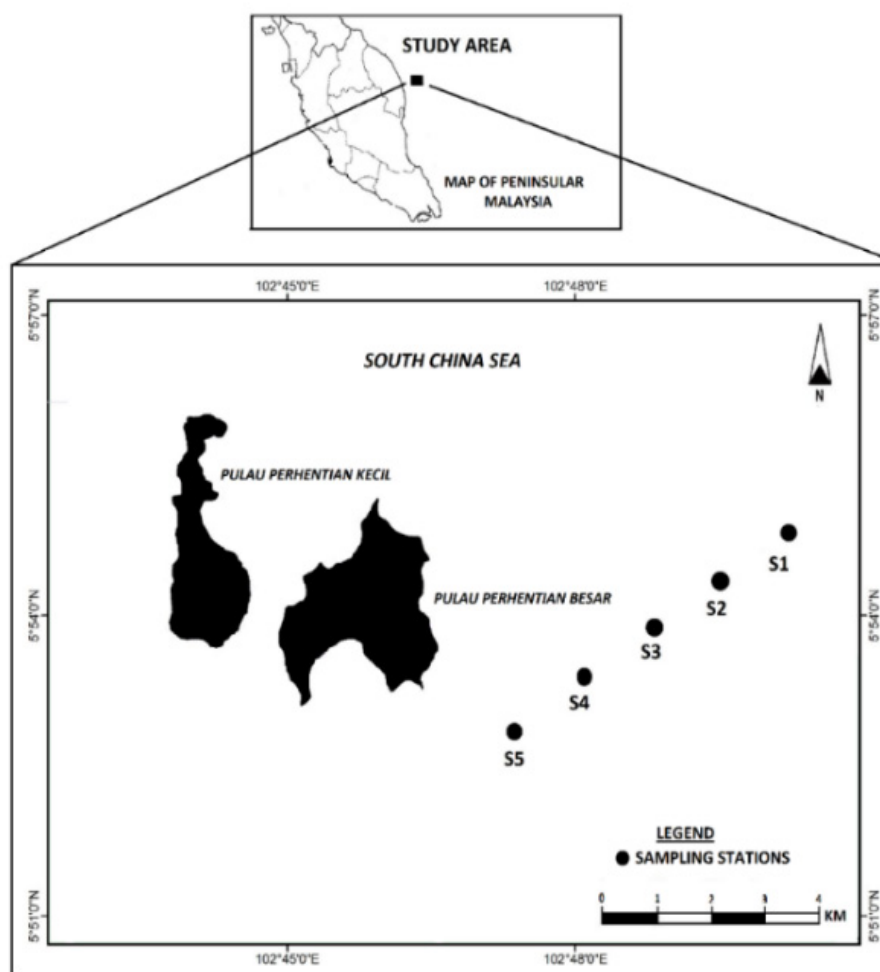


Fig. 1 Location of our sampling stations at Pulau Perhentian, Terengganu, Peninsular Malaysia during sampling activities. The sampling points were in transect line, facing towards the South China Sea. Each station was approximately 2 km apart, with St. 1 being farthest from the island.

for Cu (10^{-6} M) was prepared in 0.01 M HCl and 1.5 M of boric acid solution was prepared for buffering the sample at pH 8.05 [20, 23, 24].

CuL in seawater samples were determined by CLE-AdCSV (Competitive Ligand Exchange-Adsorptive Cathodic Stripping Voltammetry) [18, 25]. A seawater sample (120 mL) was added with borate buffer (final concentration 0.01 M) and left for 1 h before addition of SA as competing ligand. Then, the samples were sub-samples (10 mL) into 11 PTFE bottles and were added with Cu standard in increasing concentration between 0-35 μ M. The 11 PTFE bottles were left overnight at room temperature for equilibration reaction. Labile copper(II) concentration

(which reacted to added ligand SA) in each subsample was determined by using Metrohm Model VA 797 automated HMDE (Hanging Mercury Drop Electrode). The instrument setting and calculation of [CuL] and $\log K$ was followed by Godon, et al. [18]. The voltammetric cells were not rinsed with Milipore water between titrations, but the same order of cells was maintained, in order to avoid adsorption onto the cell walls and to condition the cells with copper [26].

A total dCu in seawater sample was determined by using standard addition method after UV-irradiation [18]. A 10 mL of sample was added with borate buffer (final concentration 0.01 M) and SA (final concentration 25 μ M) before analyzing.

3. Results and Discussion

There were a few series of sampling activities conducted in November 2015/April 2016 and November 2016/April 2017. Authors had done seawater sampling before (pre-) and after (post-) the monsoon event. Our sampling during November was classified as pre-monsoon, and April, as post-monsoon. This sampling approach was applied to identify the possibility of the monsoon effect on [dCu] and [CuL] in terms of its bioavailability and/or toxicity level. Unfortunately, we could not manage to collect all the seawater profiles during pre-monsoon (November 2015 and November 2016) due to the unexpected extreme weather conditions during the sampling series.

The in-situ parameters during both seasons were compared to identify the possible changes in the waterbodies during the monsoon, which might be affecting the chemical condition of the seawater. The physicochemical characteristics of the water column during both seasons in the study area were published by Mohamed, et al. [27] and Moffet, et al. [28]. According to the study, warmer seawater was recorded during pre-monsoon (29.8-29.9 °C) compared to post-monsoon (29.3-29.4 °C), due to the strong land sea breeze and precipitation. They also highlighted that the pH throughout the water column had remained alkaline during both the seasons. A slightly constant pH was recorded during pre-monsoon resulting in the factors like the removal of CO₂ by photosynthesis through bicarbonate degradation, reduction in salinity and temperature, and the decomposition of organic matter. During the study, they recorded a slightly low salinity during the pre-monsoon season (31.0-32.0 ppt), as compared to the salinity during post-monsoon (37.1-39.0 ppt). The distribution of dissolved oxygen was observed to be more consistent during pre-monsoon (4.0-5.9 mg/L), as compared to post-monsoon (3.7-6.3 mg/L).

3.1 Distribution of [dCu] and [CuL]

In November 2015, the distribution patterns of [dCu]

and [CuL] were quite similar, where the concentrations were high in the surface (3 m) and maximum in the middle layer (15 m), before decreasing at the bottom layer (Fig. 2), except for St. 5. Due to some limitations in the laboratory analysis, we could not determine [dCu] and [CuL] in all the depth for St. 4. Some analysis failed due to technical errors from the voltammetry machine that we had been using in the laboratory, thus leaving the data empty. Unfortunately, a few data at St. 1 and St. 2 in April 2016 were unavailable for discussion due to unforeseen circumstances during analysis.

In November 2015, the [dCu] ranged between 1.28 to 16.58 nM. The highest [dCu] was recorded at the bottom layer (16.58 nM) at St. 1 (Table 1; Fig. 2), which is far away from the island. On the other hand, the [CuL] was recorded between 3.61 to 20.07 nM. The highest [CuL] was found at the surface layer (5 m depth) at St. 2 (20.07 nM) (Table 1; Fig. 2), which is also far away from the island. In April 2016, we found a higher [dCu] and [CuL] in our study area. Their concentrations were in the range of 3.12 to 9.61 nM, and 3.68 to 13.05 nM, for dCu and CuL, respectively. This indicates that the [dCu] and [CuL] during pre-monsoon have a wide range of concentration.

A year later, in November 2016, the data collected were only at St. 1 and St. 2 (Fig. 2), and the profiles of [dCu] and [CuL] were found to be quite similar for both stations. Its concentration declined from the surface (3 m) to the middle layer (15 m). The [dCu] was recorded to be between 4.81 and 11.05 nM throughout the water column. Similar to the [CuL], it ranged between 4.88 and 11.78 nM (Table 2). Both [dCu] (11.05 nM) and [CuL] (11.78 nM) were recorded the highest at the surface layer (5 m depth) at St. 2 (Fig. 3). Meanwhile, in April 2017, we had determined the [dCu] and [CuL] throughout the water column from five stations. They ranged between 5.19 and 13.24 nM, and 5.60 and 13.66 nM for [dCu] and [CuL], respectively. This indicated that the [dCu] and [CuL] were higher in April 2017, as compared to their concentrations in November 2016.

Table 1 Cu speciation data at Pulau Perhentian, Terengganu in Nov. 2015 (pre-monsoon) and April 2016 (post-monsoon).

St.	Depth	[dCu]		L_T		$\log K'$		L		CuL		CuL/dCu		Cu ²⁺		pCu	
		(*Depth)	(m)	(nM)	(nM)	(mol ⁻¹)	(nM)	(%)	(%)	(M)	(M)	(M)	(M)				
		Nov. 15	Apr. 16	Nov. 15	Apr. 16	Nov. 15	Apr. 16	Nov. 15	Apr. 16	Nov. 15	Apr. 16	Nov. 15	Apr. 16	Nov. 15	Apr. 16	Nov. 15	Apr. 16
St. 1 (33.40 m)	3	4.11	na	4.79	na	12.22	na	0.68	na	99.9	na	1.2	na	3.64×10 ⁻²²	na	11.44	na
	6	6.13	na	6.16	na	12.86	na	0.03	na	99.5	na	1.0	na	2.82×10 ⁻²¹	na	10.55	na
	15	5.44	na	6.63	na	12.34	na	1.19	na	100	na	1.2	na	2.09×10 ⁻²²	na	11.68	na
	30	16.58	na	18.95	na	12.21	na	2.37	na	100	na	1.1	na	4.31×10 ⁻²²	na	11.37	na
St. 2 (32.50 m)	3	8.74	na	10.45	na	12.57	na	1.71	na	100	na	1.2	na	1.37×10 ⁻²²	na	11.86	na
	6	14.01	na	20.07	na	12.11	na	6.06	na	100	na	1.4	na	1.79×10 ⁻²²	na	11.75	na
	15	6.13	na	11.49	na	12.49	na	5.36	na	100	na	1.9	na	3.70×10 ⁻²³	na	12.43	na
	20	4.31	na	5.27	na	12.81	na	0.96	na	100	na	1.2	na	6.95×10 ⁻²³	na	12.16	na
St. 3 (32.74 m)	30	2.18	na	9.66	na	12.92	na	7.48	na	100	na	4.4	na	3.50×10 ⁻²⁴	na	13.46	na
	3	11.89	9.61	15.17	10.1	12.66	12.09	3.28	0.49	100	99.8	1.3	1.05	7.93×10 ⁻²³	1.59×10 ⁻²¹	12.10	10.80
	6	3.14	9.45	13.47	13.05	12.25	12.04	10.33	3.6	100	100	4.3	1.38	1.71×10 ⁻²³	2.39×10 ⁻²²	12.77	11.62
	15	1.28	8.3	3.65	10.59	12.71	12.13	2.37	2.29	100	100	2.9	1.28	1.05×10 ⁻²³	2.68×10 ⁻²²	12.98	11.57
St. 4 (34.23 m)	20	4.22	5.4	9.35	12.45	12.55	12.05	5.13	7.05	100	100	2.2	2.31	2.32×10 ⁻²³	6.82×10 ⁻²³	12.63	12.17
	30	5.21	7.5	5.97	8.73	12.57	12.6	0.76	1.23	100	100	1.1	1.16	1.84×10 ⁻²²	1.53×10 ⁻²²	11.73	11.81
	3	2.92	8.12	6.44	9.19	12.89	12.55	3.52	1.07	100	100	2.2	1.13	1.06×10 ⁻²³	2.13×10 ⁻²²	12.97	11.67
	20	3.25	4.12	8.44	5.24	12.42	12.96	5.19	1.12	100	100	2.6	1.27	2.38×10 ⁻²³	4.03×10 ⁻²³	12.62	12.39
St. 5 (23.76 m)	30	3.41	3.12	3.61	3.68	12.52	12.27	0.2	0.56	99.8	99.9	1.1	1.18	5.15×10 ⁻²²	2.99×10 ⁻²²	11.29	11.52
	3	2.94	8.19	5.47	9.11	12.25	12.38	2.53	0.92	100	100	1.9	1.11	6.53×10 ⁻²³	3.71×10 ⁻²²	12.18	11.43
	6	3.22	9.23	5.52	9.37	12.46	12.31	2.3	0.14	100	99.7	1.7	1.02	4.86×10 ⁻²³	3.23×10 ⁻²¹	12.31	10.49
	15	2.32	6.79	3.68	7.41	12.61	12.76	1.36	0.62	100	100	1.6	1.09	4.18×10 ⁻²³	1.90×10 ⁻²²	12.38	11.72
	20	3.87	5.49	6.11	6.64	12.73	12.5	2.24	1.15	100	100	1.6	1.21	3.22×10 ⁻²³	1.50×10 ⁻²²	12.49	11.82

dCu concentration ([dCu]), total Cu binding ligand ([CuL]) and stability constant of Cu ligand ($\log K$) were determined, and free Cu binding-ligand ($[L'] = [CuL] - [dCu]$) are presented. na = not available.

* *Depth* is real depth of water column at each station.

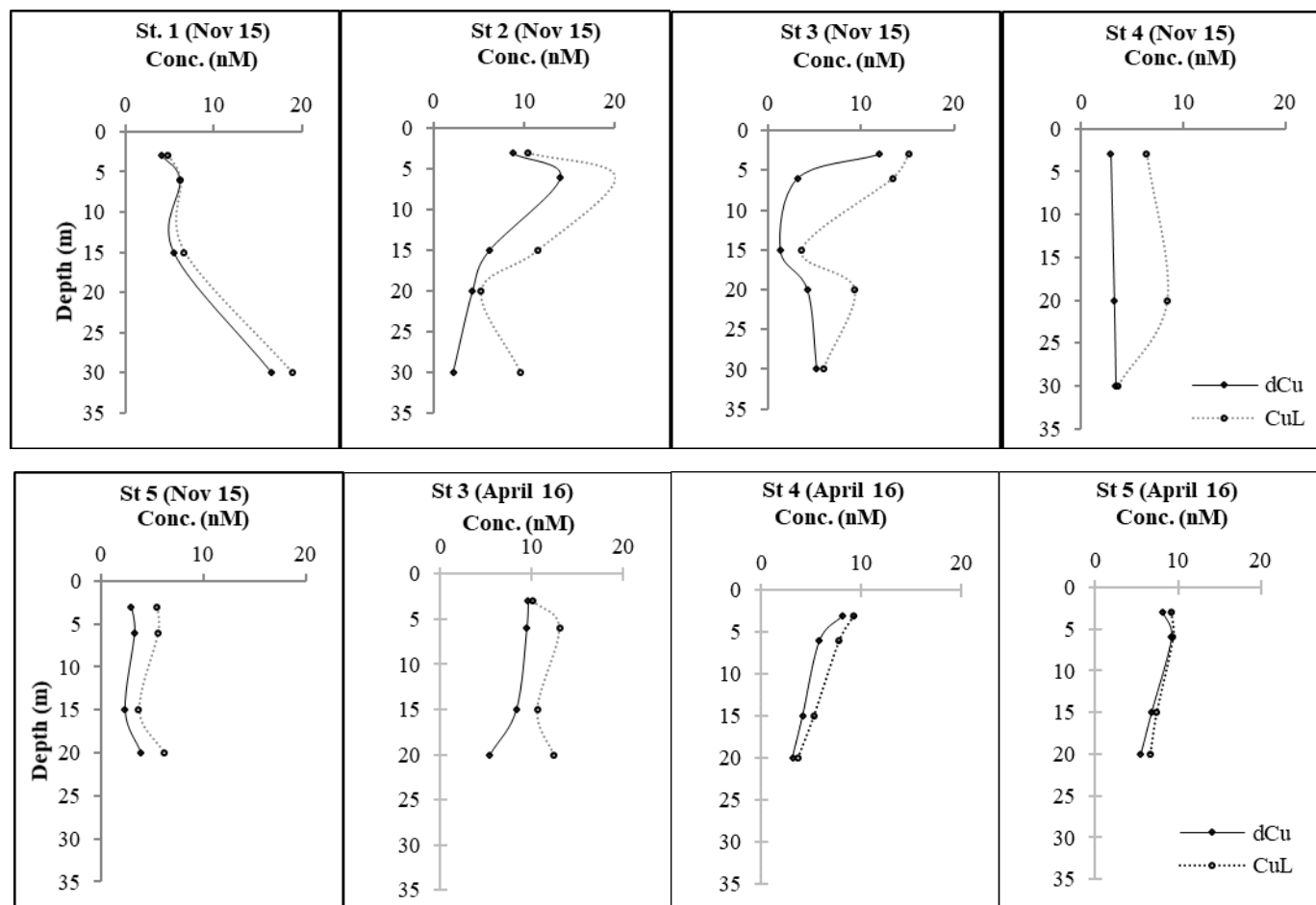


Fig. 2 The concentration of CuL and dCu at all stations at Pulau Perhentian, Terengganu during pre-monsoon (Nov. 2015) and post-monsoon (April 2016) seasons.

Table 2 Cu speciation data at Pulau Perhentian, Terengganu in Nov. 2016 (pre-monsoon) and April 2017 (post-monsoon).

St	Depth (m)	[dCu] (nM)		L_T (nM)		$\log K'$ (mol ⁻¹)		L (nM)		CuL (%)		CuL/dCu		Cu ²⁺ (M)	pCu (M)		
		Nov. 16	Apr. 17	Nov. 16	Apr. 17	Nov. 16	Apr. 17	Nov. 16	Apr. 17	Nov. 16	Apr. 17	Nov. 16	Apr. 17	Nov. 16	Apr. 17		
St. 1 (35.60 m)	3	9.01	5.98	9.29	7.23	12.13	12.10	0.28	1.25	99.7	100.0	1.0	1.21	2.39×10 ⁻²¹	3.80×10 ⁻²²	10.62	11.42
	6	7.12	10.08	7.61	10.29	12.14	12.12	0.49	0.21	99.9	99.6	1.1	1.02	1.05×10 ⁻¹²	3.64×10 ⁻²¹	10.98	10.44
	15	6.79	5.48	7.56	6.11	12.60	12.00	0.77	0.63	100.0	99.8	1.1	1.11	2.22×10 ⁻²²	8.70×10 ⁻²²	11.65	11.06
	30	4.81	8.24	4.88	8.34	12.55	12.58	0.07	0.10	99.6	99.7	1.0	1.01	1.94×10 ⁻²¹	2.17×10 ⁻²¹	10.71	10.66
St. 2 (32.90 m)	3	10.59	7.33	10.68	7.35	12.00	12.01	0.09	0.02	98.9	95.1	1.0	1.00	1.18×10 ⁻²⁰	3.58×10 ⁻²⁰	9.93	9.45
	6	11.05	12.08	11.78	13.34	12.38	12.45	0.73	1.26	99.9	100.0	1.1	1.22	6.31×10 ⁻²²	3.24×10 ⁻²²	11.20	11.49
	20	8.21	9.87	10.25	10.28	12.01	12.36	2.04	0.41	100.0	99.9	1.2	1.06	3.93×10 ⁻²²	8.95×10 ⁻²²	11.41	11.05
	30	9.37	12.36	11.43	12.53	12.42	12.83	2.06	0.17	100.0	99.7	1.2	1.04	1.73×10 ⁻²²	1.71×10 ⁻²¹	11.76	10.77
St. 3 (25.11 m)	3	na	7.32	na	8.11	na	12.41	na	0.79	na	100.0	na	1.11	na	3.60×10 ⁻²²	na	11.44
	6	na	8.64	na	8.90	na	12.09	na	0.26	na	99.7	na	1.03	na	2.70×10 ⁻²¹	na	10.57
	15	na	6.39	na	7.94	na	12.53	na	1.55	na	100.0	na	1.24	na	1.22×10 ⁻²²	na	11.91
	20	na	9.07	na	9.38	na	12.83	na	0.31	na	99.9	na	1.28	na	2.91×10 ⁻²²	na	11.54
St. 4 (32.59 m)	3	na	7.19	na	11.42	na	12.04	na	4.23	na	100.0	na	1.59	na	1.55×10 ⁻²²	na	11.81
	15	na	6.18	na	9.95	na	12.11	na	3.77	na	100.0	na	1.61	na	1.27×10 ⁻²²	na	11.90
	20	na	12.71	na	13.66	na	12.88	na	0.95	na	100.0	na	1.24	na	1.96×10 ⁻²²	na	11.71
	30	na	5.19	na	5.60	na	12.85	na	0.41	na	100.0	na	1.08	na	1.79×10 ⁻²²	na	11.75
St. 5 (23.01 m)	3	na	6.04	na	8.75	na	12.59	na	2.71	na	100.0	na	1.45	na	5.73×10 ⁻²³	na	12.24
	6	na	11.87	na	13.36	na	12.77	na	1.49	na	100.0	na	1.13	na	1.35×10 ⁻²²	na	11.87
	15	na	6.11	na	8.02	na	12.97	na	1.91	na	100.0	na	1.31	na	3.43×10 ⁻²³	na	12.46
	20	na	13.24	na	13.42	na	12.19	na	0.18	na	99.6	na	1.01	na	4.75×10 ⁻²¹	na	10.32

dCu concentration ([dCu]), total Cu binding ligand ([CuL]) and stability constant of Cu ligand ($\log K$) were determined, and also the free Cu binding-ligand ($[L^*] = [CuL] - [dCu]$).

na = not available.

* *Depth* is real depth of water column at each station.

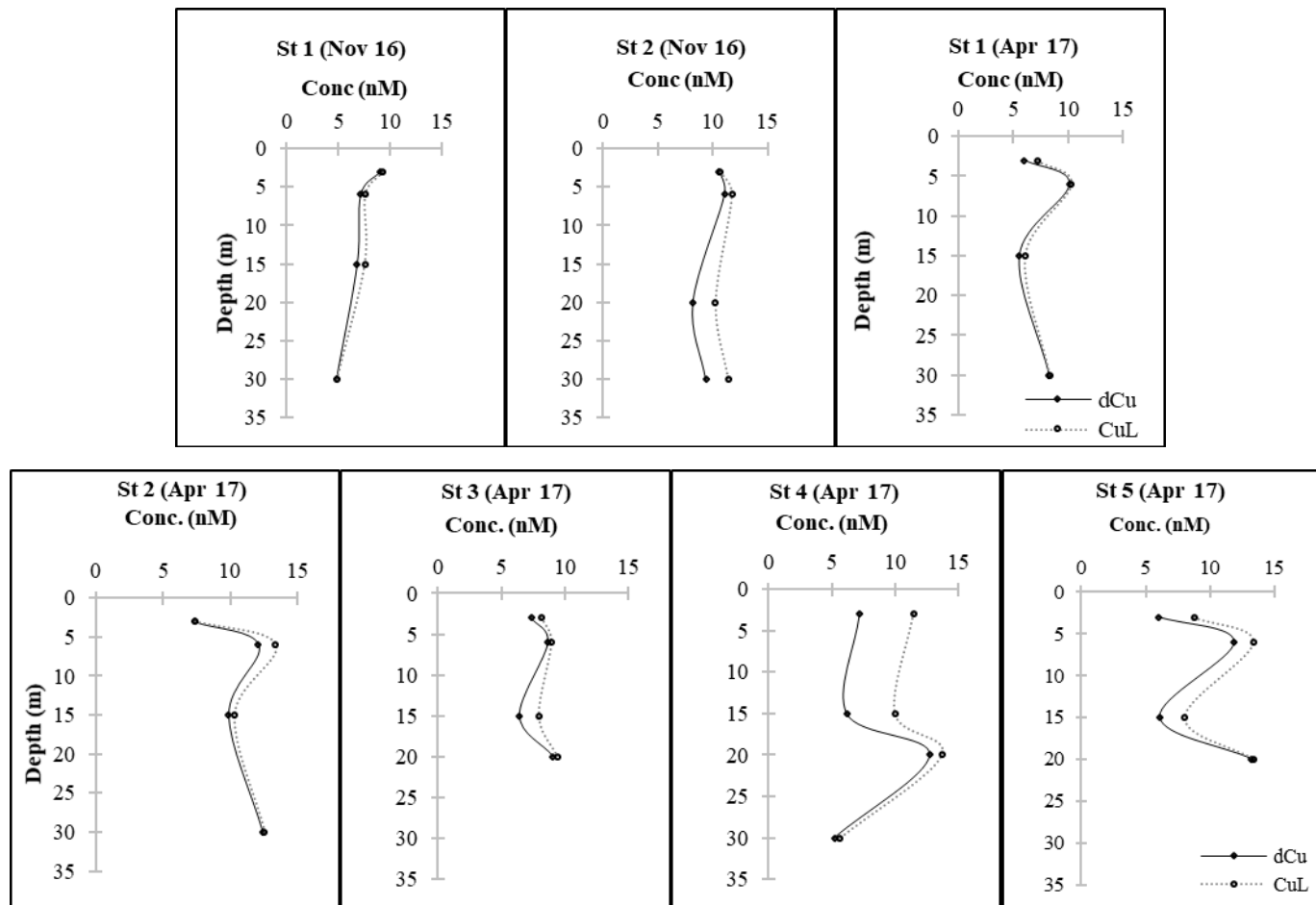


Fig. 3 The concentration of CuL and dCu at all stations at Perhentian Island, Terengganu during pre-monsoon (Nov. 2016) and post-monsoon (April 2017) seasons.

Authors' present data on [dCu] and [CuL] recorded a higher and wide range of concentrations in November 2015, compared to their concentrations in April 2016. According to Sang, et al. [29], during authors' sampling in November 2015, a longer period of NEM 2015/2016 occurred. It was the strongest episode since 1979 and was longer than usual. Furthermore, it happened along with El Niño, started at an early in October 2015, and withdrew in March 2016. This unusual phenomenon might change the chemistry of water and resulted in the [dCu] and [CuL] throughout the water column in our study area.

On the other hand, the [dCu] and [CuL] were recorded as slightly similar during both seasons in November 2016 and April 2017. This was probably due to a shorter NEM 2016/2017 as compared to the NEM 2015/2016 due to the weak La-Nina phenomena [30]. It might have affected the distribution of [dCu] and [CuL] and could also be the reason why low concentrations of dCu and CuL were recorded during the pre-monsoon seasons (November 2016).

According to a previous study in the area by Mohamed, et al. [27], they suggested that a high concentration of dissolved Al was affected by the presence of strong current velocity. This condition leads to a high re-suspension of trace elements at surface sediment into the water column, which affects their remobilization [31-33]. This was further supported by [34], where the remobilization of copper by desorption from re-suspension into the water column was a much larger flux, compared to combined point source discharges in their study area. Considering the monsoon effects (NEM 2015/2016) along with the strong El Niño phenomenon at Pulau Perhentian during sampling activities, it was not a surprise that the dissolved metal concentrations increased down the depth. Furthermore, a higher [dCu] and [CuL] at the station far away from the island's source (St. 1) probability suggested that the input of dCu in the area was originated from the bottom water, due to the water mixing which would have occurred at an earlier part of the monsoon event.

3.2 Distribution of Cu(II) Speciation

The conditional stability constant ($\log K'$) for all the stations in November 2015 showed a presence of strong class ligand (L1) with a range of 12.11 to 12.92. It also indicated that more than 99.5% of Cu^{2+} ions in this area exist as organic complexes. Interestingly, the $\log K'$ value in April 2016 was recorded to be slightly similar to the $\log K'$ value in November 2015. It ranged between 12.04 and 12.96, with more than 99.7% of dCu being complexes to the ligands throughout the water column. Furthermore, the $\log K'$ values for November 2016 and April 2017 were also recorded to be slightly similar to the previous year. The value was between 12.00 and 12.60, and 12.00 and 12.97 in November 2016 and April 2017, respectively. This indicated a strong buffering capacity in Cu(II)-ligand complexes in the area during both the seasons and suggested that the dCu is more functioned in bioavailability. These results are comparable to other studies [17, 35-38].

The [CuL]/[dCu] ratio was used to identify a saturation state of Cu(II)-organic ligands [39]. The [CuL]/[dCu] ratios showed a consistent pattern with depth and location (Tables 1 and 2). During both periods of sampling, the [CuL]/[dCu] ratio was more than 1 throughout the water column. The ratios were in ranges of 1.00 to 4.43 and 1.02 to 2.31 in November 2015 and April 2016, respectively. In November 2016, it ranged between 1.01 and 1.25, and in April 2017, between 1.00 and 1.61. An enhanced ratio during pre-monsoon, especially in November 2016, indicated a large excess of ligands condition and these ligands saturate the external inputs of Cu into the area. The high concentration of excess ligand ($[L^-] = [\text{CuL}] - [\text{dCu}]$) (Tables 1 and 2) supported this saturation condition.

In addition, the concentration of excess ligand ($[L^-]$) related to the concentration of free Cu(II)-binding sites [40]. During this study, we have recorded a higher $[L^-]$ in November 2016, with ranges of concentration between 0.03 and 10.33 nM, compared to its concentration in April 2016. This suggested that,

an external input of Cu into the study area is mostly complexed by natural organic ligands, especially during pre-monsoon. This condition could increase the Cu^{2+} solubility and keep it in a dissolved phase, since most of the ligand pool is saturated by extra Cu input.

From authors' present data, authors found that the $[\text{Cu}^{2+}]$ ranged between 10^{-21} and 10^{-24} M, and 10^{-21} and 10^{-23} M, in November 2015 and April 2016, respectively. In November 2016 and April 2017, its concentration ranged between 10^{-20} and 10^{-22} M and 10^{-20} and 10^{-23} M, respectively. This showed that $[\text{Cu}^{2+}]$ was still below the threshold limit during both the pre- and post-monsoon seasons. This could be supported by the data of $[\text{dCu}]/[\text{CuL}]$ ratio saturation during both pre- and post-monsoon seasons, since the strong relationship (more than 1 ratio) was recorded throughout the water column, thus stressing the saturated ligand-Cu(II) complexation and preventing the formation of free ions. Additionally, free Cu^{2+} concentration above 10^{-11} nM can inhibit the growth of zooplankton and phytoplankton [8, 13, 41].

A toxicity level is determined by a $p\text{Cu}$ activity ($p\text{Cu} = -\log[\text{Cu}^{2+}]$) and the free Cu^{2+} ion concentration. The $p\text{Cu}$ is a good measure of the mobility and lability of all the copper in the water system, and highly correlated to its uptake by organisms and its toxicity [42]. During pre-monsoon in November 2015, the free Cu(II) ion activities, $p\text{Cu}$, ranged from 10.55 to 11.00 (Table 1), and during post-monsoon in April 2016, the range was between

10.49 and 12.39. On the other hand, $p\text{Cu}$ activity was recorded between 9.93 and 11.76 in November 2016, and 9.45 and 12.46 in April 2017. These values were comparable to the other coastal water studies; 13.0-13.5 [43] and 12.5-12.8 [44]. This could indicate that the $p\text{Cu}$ activity in our study area was higher during post-monsoon seasons (April 2016 and April 2017), as compared to pre-monsoon seasons (November 2015 and November 2016). However, the $p\text{Cu}$ data suggested a low toxicity threat for both seasons due to the low free Cu^{2+} ions. Therefore, the Cu(II) ions in the study area was complexed by the ligands and it functioned more towards bioavailability, rather than being a toxicant.

Interestingly, the statistical analysis run on salinity, pH and dissolved oxygen (DO) to $[\text{CuL}]$ showed no statistical significance between the parameters ($p > 0.05$) for the in-situ data, thus indicating that the monsoon season has no effect on the dissolved CuL in the study area, which was contrary to what was expected and suggestion by Gledhill, et al. [2]. However, it could suggest the presence of strong natural organic ligands in buffering the Cu^{2+} ions in the water column, as resulted by the saturation ratio.

Table 3 above shows a few studies of Cu speciation in coastal area. According to the studies, our present data were in line with others and also supported the probability of dCu to function more towards bioavailability, thus eliminating the toxicity threats of free Cu^{2+} ions in the study areas.

Table 3 Cu speciation and comparison at Pulau Perhentian and other coastal areas.

Site	Salinity	dCu (nM)	$\log K$	$p\text{Cu}$ (M)	Reference
P. Perhentian (Nov. 15)	30-33	1-16	12-12.89	10-13.5	This study
P. Perhentian (Apr. 16)	38-39	3-10	12-12.96	10-12.4	This study
P. Perhentian (Nov. 16)	30-32	4-11	12-12.6	9-11.76	This study
P. Perhentian (Apr. 17)	30-32	4-13	12-12.97	9-12.46	This study
Vineyard Sound	31-32	4.4	12.75	-	Moffett, et al. [13]
Great Pond	29-32	6.3	14.08	-	Moffett, et al. [13]
Waquoit Bay	29-31	4.3	12.74	-	Moffett, et al. [13]
Bohai Bay	29-31	18-25	12-13.6	12-13.1	Li, et al. [44]
Venice Lagoon, Italy	28-29	10-25	13-15	13-13.5	Chapman, et al. [43]

4. Conclusions

Preliminary data for Cu(II) speciation during pre- and post- monsoon at Pulau Perhentian for two years (November 2015/April 2016 and November 2016/April 2017) were presented here. A strong complexing ligand was determined in our samples, present as L1 type of ligand for all sampling samples and series. The Cu speciation analysis found that the free $[Cu^{2+}]$ does not generally induce toxic effects in biota. The statistical analysis showed no significant effect of the monsoon seasons on the Cu^{2+} ions in the area, thus suggesting the vital roles of organic ligands in buffering the Cu^{2+} ions present, and allowing Cu^{2+} ions to be bioavailable to the organisms. For further study, authors recommend identifying the source of this natural ligand present in our study area.

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