UNIVERSITI PUTRA MALAYSIA

EFFECT OF NORTHEAST MONSOON ON COPPER SPECIATION AT PULAU PERHENTIAN, TERENGGANU, MALAYSIA

EDRIANNA GODON

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EFFECT OF NORTHEAST MONSOON ON COPPER SPECIATION AT PULAU PERHENTIAN, TERENGGANU, MALAYSIA

By

EDRIANNA GODON

Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfilment of the Requirements for the Degree of Master of Science

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Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirement for the degree of Master of Science

EFFECT OF NORTHEAST MONSOON ON COPPER SPECIATION AT PULAU PERHENTIAN, TERENGGANU, MALAYSIA

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December 2017

Chair : Khairul Nizam bin Mohamed @ Mohd Ramli,, PhD
Faculty : Environmental Studies

Copper (Cu) speciation was studied in the seawater at Pulau Perhentian, Terengganu, Malaysia in two different seasons, the pre- and post-Northeast monsoon. The existence of organic Cu (II) complexing ligands were determined by the application of CLE-AdCSV to determine Cu bioavailability and toxicity in the area. The existence of organic ligands (CuL) in the area helps to keeps the solubility of Cu and maintains its concentration under the toxicity level. The development method of CLE-AdCSV for Cu(II) speciation was optimized by analysing the seawater samples collected from Pulau Perhentian. Multiple series of sampling were carried out in pre- and post-monsoon season to identify the possible effect of the Northeast monsoon to the Cu(II) speciation in the area. The profile of seawater samples was analyzed from selected stations at Pulau Perhentian, Terengganu for Cu(II) speciation determination in order to determine the concentration level of Cu(II) in dissolved seawater. The analysis showed that >99.5% of total dissolved Cu (dCu) was bound to Cu (II) complexing ligands in this area. The ratio of CuL/dCu was analysed to see the ligand distributions, which showed their saturation rate with dissolved Cu. For both Nov 2015 and 2016, the CuL/dCu ratio showed low ratio (1.00-1.90, 1.00-1.20) in open ocean (St. 1 and St. 2), and varied ratios were observed in near-shore stations at St. 3, St. 4 and St. 5 (1.10-4.30). Meanwhile for both April 2016 and 2017, the ratios were in low ranges (1.02-2.31, 1.00-1.60), especially in April 2017. This finding indicated a saturated Cu-ligand complexation in the area. The concentration of natural organic Cu(II)-ligand binding (CuL) and its conditional stability constant (Log K'_{CuL}) in each sample was determined by using salicylaldoxime (SA) as competitive ligand. Our present data indicated the presence of strong natural organic Cu(II) complexing ligands in our seawater samples. Its distribution was similar to the dissolved Cu (dCu) throughout the water column, where the concentrations increased from the surface (3 m) to the middle layer (15m), before decreasing at the bottom layer. The Log K'_{CuL} was more than 12.00 throughout the water column and indicated the presence of strong natural organic ligands in our study area. Preliminary data for Cu

speciation in pre- and post-Northeast monsoon at Pulau Perhentian for two years (2015/2016 and 2016/2017) were presented here. All the results observed in saturation rate, complexation percentage, and the conditional stability constant, Log K'_{CuL} and the pCu data suggested that the dissolved Cu in the study area are taken up by marine organisms, thus preventing the free Cu^{2+} ions to be produced. The complexing capacity of the species in the area were also highlighted in the results, which gave an indication of the ability of the organisms to absorb dissolved Cu and render it non-toxic, by complexing with dissolved Cu. In addition, the presence of dominant diatoms species might had also influence Cu bioavailability in the area. This initial study on Cu(II) speciation has suggested that more than 99% of dissolved Cu was complexed to the natural organic ligands which prevents the toxicity of Cu(II) to the marine organisms.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk Ijazah Master Sains

KESAN MONSUN LAUT KEPADA KOMPLEKSASI KUPRUM DI PULAU PERHENTIAN, TERENGGANU

Oleh

EDRIANNA GODON

Disember 2017

Pengerusi : Khairul Nizam bin Mohamed @ Mohd Ramli, PhD
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Kajian kompleksasi Kuprum (Cu) dijalankan di air laut Pulau Perhentian, Terengganu, Malaysia pada dua musim yang berlainan, iaitu sebelum dan selepas Monsun Barat Daya. Kehadiran ligan (Cu) organik dikaji melalui aplikasi CLE-AdCSV untuk mengukur bioavailabiliti dan toksisiti Cu di kawasan kajian. Ligan organik ini mebantu mengekalkan kelarutan Cu dan seterusnya menghalang toksisiti Cu. Kaedah CLE-AdCSV kemudian dibangunkan dan dioptimumkan sesuai dengan keadaan air laut di tempat kajian. Kemudian beberapa siri sampling dijalankan untuk mengambil sampel air laut pada sebelum dan selepas monsun untuk mengkaji kesan monsun Barat Daya kepada kompleksasi Cu. Profil daripada sampel air laut telah dianalisis dari beberapa stesen di Pulau Perhentian, Terengganu untuk kajian kompleksasi Kuprum (II) untuk mengenalpasti tahap kepekatan Cu(II) didalam air laut. Hasil analisis menunjukkan bahawa >99.5% daripada keseluruhan Cu terlarut adalah terikat kepada ligan kompleks di kawasan tersebut. Nisbah CuL/dCu kemudian dianalisis untuk melihat taburan ligan dan kadar tepu diantara CuL dan dCu. Untuk kedua2 Nov 2015 dan 2016, nisbah CuL/dCu adalah rendah (1.00-1.90, 1.00-1.20) di kawasan laut terbuka (St.1 dan 2) dan bervariasi di kawasan berdekatan pantai St. 3, 4 dan 5 (1.10-4.30). Sementara itu bagi April 2016 dan 2017, nisbah didapati dalam julat yang rendah (1.02-2.31, 1.00-1.60), terutama bagi April 2017. Ini menunjukkan bahawa kompleksasi ligan-Cu adalah tepu bagi kawasan berkenaan. Kepekatan ligan organik Kuprum (II) semulajadi (CuL) dan *conditional stability constant* (Log K'_{CuL}) di dalam setiap sampel diukur dengan menggunakan kaedah *competitive ligand exchange–adsorptive cathodic stripping voltammetry (CLE-AdCSV)* dengan ligan pesaing *salicylaldoxime,* (SA). Data terkini menunjukkan kehadiran ligan organik Kuprum (II) semulajadi di dalam semua sampel air laut. Taburannya adalah sama dengan Kuprum terlarut (dCu) disemua kolum air, dimana kepekatannya meningkat dari permukaan (3m) ke lapisan tengah (15m), sebelum menurun ke lapisan bawah (30m). Bacaan Log K'_{CuL} adalah lebih daripada 12.00 disemua kolum air, memberi gambaran kehadiran ligan organik semulajadi yang kuat di

kawasan kajian ini. Kajian awal dalam analisis kompleksasi Kuprum(II) mencadangkan bahawa lebih daripada 99% Kuprum terlarut telah dikompleks dengan ligan semulajadi organik yang menghalang toksisiti Kuprum(II) kepada organisma marin. Data awal untuk kompleksasi Cu sebelum dan selepas Monsun Barat Daya di Pulau Perhentian untuk dua tahun, (2015/ 2016 dan 2016/2017) dibincangkan disini. Semua keputusan yang diperoleh dari kadar tepu, peratus kompleksasi dan *conditional stability constant*, Log K'_{CuL} dan data pCu menunjukkan bahwa Kuprum terlarut di kawasan kajian digunakan oleh organisma marin, lalu menghalang pembentukan ion Cu^{2+}. Kapasiti kompleksasi oleh sepsis di kawasan tersebut juga dibincangkan, dimana hasil kajian memberi indikasi abiliti organisma untuk menyerap Kuprum terlarut dan menghalang toksisiti. Sebagai tambahan, kehadiran diatom sebagai spesis phytoplankton dominan juga mungkin mempengaruhi bioavailabiliti Kuprum di kawasan ini.

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Philippians 4:13

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LIST OF ABBREVIATIONS

CLE-AdCSV	Competitive Ligand Exchange–Adsorptive Cathodic Stripping Voltammetry
K_{CuL}	Conditional Stability Constant
SA	Salicylaldoxime
CuL	Cu-ligand complex
dCu	Dissolved Cu
IUPAC	International Union of Pure and Applied Chemistry
GC-ICP-MS	Gas Chromatography - Inductively Coupled Plasma Mass Spectrometry
ASV	Anodic Stripping Voltammetry
AdCSV	Adsorptive Cathodic Stripping Voltammetry
LDPE	Low Density Polyethylene
PTFE	Polytetrafluoroethylene
NEM	Northeast Monsoon
SWM	Southwest Monsoon
DOC	Dissolved Organic Carbon
DOM	Dissolved Organic Matter
SPM	Suspended Particulate Matter
FEP	Fluorinated Ethylene Propylene
CSC	Conditional Stability Constant

CHAPTER 1

INTRODUCTION

1.1 Introduction

Some trace metals such as copper (Cu), iron (Fe), zinc (Zn), manganese (Mn) are vital for the organisms' growth by behaving as micronutrients for primary producers. In marine environment, usually these trace metals are found in low concentration (picomolar to nanomolar), where their roles are important in ocean biogeochemistry (Sunda, 2012). Marine organisms such as phytoplankton, macro algae bacterioplankton and fungi also require the micronutrients for many enzymatic reactions (Vraspir and Butler, 2009).

Basic physical differentiation of trace metals is either in particulate or dissolved forms, but they can also be found in other chemical and physical forms. The widely used definition to differentiate between both is by using the 0.4 mm or 0.2 mm filter size (Fig 1.1). The particulate forms of the metals involve those which are soaked to particles surfaces, absorbed in the biogenic origin particles or in the meld of minerals. Meanwhile, dissolved forms are those of potentially colloids or soluble trace metals fixation. Colloids, both organic and inorganic in nature, are produced abiotically or biotically and involve small organisms such as bacteria and viruses, and are frequently defined as the >0.02 and <0.4 µm fraction (Aiken *et al*., 2011).

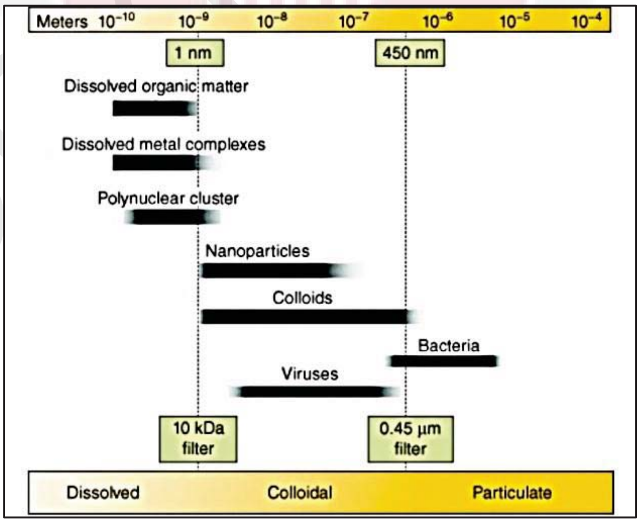

Figure 1.1: Sizes for various fractions in natural water sample and the typical constituents of the fractions. Typical filtrations use either a 0.2 or 0.45 µm pore size.

(Source: Aiken *et al.* (2011) *Environmental Science & Technology* 45: 3196-201, Copyright (2011), American Chemical Society).

Ocean biogeochemical cycle generally includes the transformations that occur in a substance as it goes through Earth's lithosphere, biosphere, hydro-sphere, and atmosphere (Raven *et al.,* 2006). The flux and subsequent rate, as well as the composition of trace metals are important to understand their biogeochemistry in the ocean. Atmospheric and riverine inputs are known as the two major sources of trace metals in the surface ocean, as shown in Fig. 1.2 (Donat and Bruland, 1994). Industrial and domestic waste, urban runoff and sewerage discharges are also possible to introduce the trace metals in aquatic environment but usually point sources are the ones that lead to increased concentrations (Whitby *et al.,* 2017).

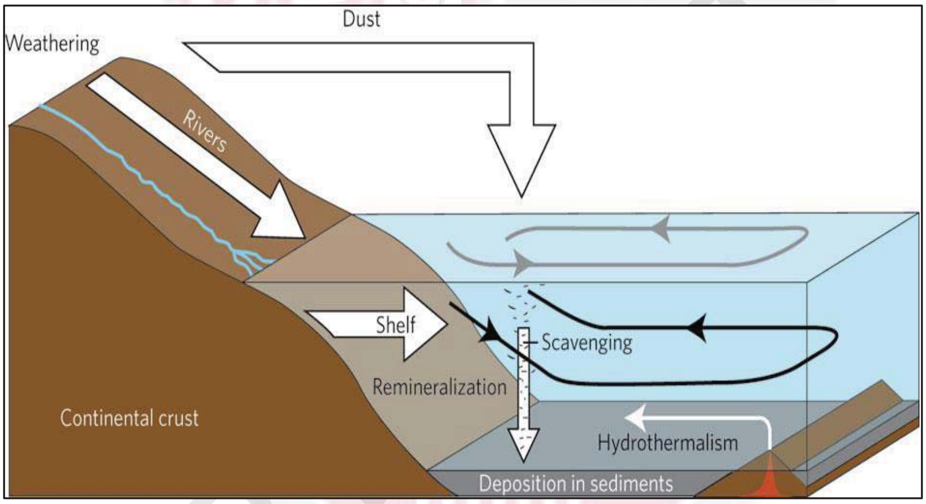

Figure 1.2: Diagram of dissolved and particulate trace metals origins in seawater which include rivers, shelf sediment and dust, but less impact from hydrothermal inputs. After the trace metals reach the sea water, biogeochemical cycling occurs, and causes vertical transport and fractionation from surface to bottom waters. In addition, the metals are distributed or transported by the water circulation (Frank, 2011).

The first-hand input of this metals to open ocean is usually affected by deposition of atmospheric dust and long-range transport. While volcanic activity and continental dust serve as the natural sources, waste incineration and fossil fuel burning are mostly the anthropogenic sources (Chester and Jickells, 2012). The movement of dust particles in the atmosphere is significantly dependent on the condition of the grassland, forests, lands or desert in an area, which in turn are affected by climate, weathering process or geological aspects (Bruland and Lohan, 2003)

The Southeast Asian countries (Fig. 1.3), are governed by monsoon season, which is defined as a 'huge-scale seasonal turn-around of wind order' (Serreze and Barry, 2010). These areas greet maximums summer rainfall and nearly twofold rainfall maximums. The season does not only affect Asian countries, but also goes past the tropical latitudes and can also impact other non-monsoonal regions (Serreze and Barry, 2010).

The two-major monsoon order are distinctly named the southwest monsoon (SWM) or the summer monsoon, and northeast monsoon (NEM) or the winter monsoon. NEM starts from November to March, and SWM starts from late May to September. October is the changing month from SWM to NEM seasons (Cruz *et al.,* 2012).

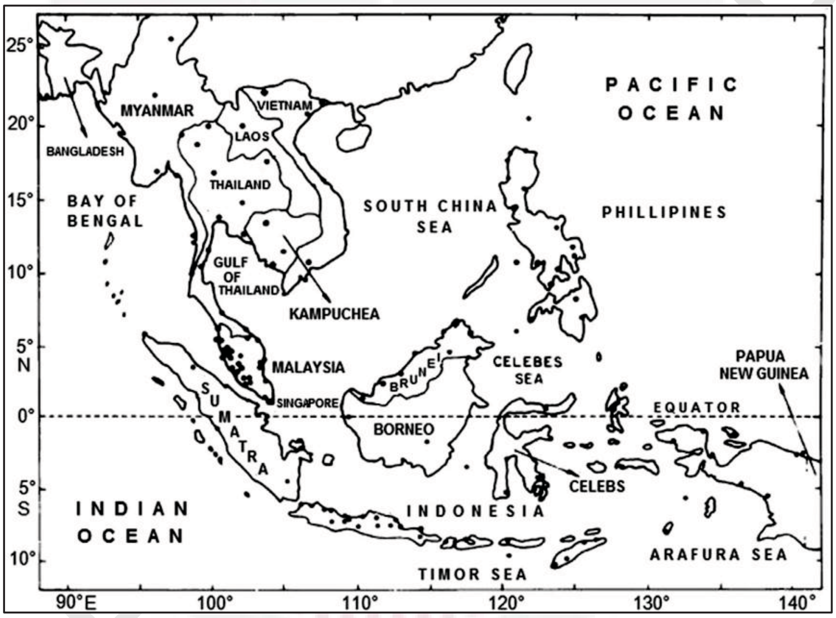

Figure 1.3: Southeast Asia region (Kripalani and Kulkarni, 1997).

In Peninsular Malaysia, the NEM maintains the easterly or north-easterly winds of 10 to 20 knots but the winds may achieve up to 30 knots or more during periods of strong cold surges. Light and inconsistent winds are observed during the two inter-monsoon seasons but the monsoon carries winds that affect the vertical and upwelling process in the seawater because of the movement from the wind stress curl between air and the seawater surface (Adiana *et al*., 2014; Mohamed and Amil, 2015). Previous study by Adiana *et al.* (2014) only highlighted the impact of Northeast monsoon on metals distribution in sediment, but not in dissolved or complexed phase. This condition triggers the need to conduct the study to see the relationship between the monsoon season to the trace metal distribution and speciation processes, as well as the impact on the biogeochemistry cycling in the water column, especially Cu, due to its toxicity and bioavailability functions.

1.2 Problem Statement

A number of heavy metals data in the South China Sea (SCS) had already been published elsewhere, but the database lists at www.elsevier.com/scopus shows that from 1968 to 2012, approximately only ten percent of studies on heavy metals have been discussed for southern part of SCS (Adiana *et al*., 2014).

More importantly, most of the studies focus on marine organisms and sediments (Shazili *et al.* 2006) and lack of analysis was done on particulate and dissolved metals in seawater because of their trace concentrations (Jiménez *et al*. 2002). Unfortunately, speciation data has not been available in the country yet, due to the lack of research in this area. Reactivity and bioavailability of metals are determined by its speciation process and affect their biogeochemical cycling in the marine environment, hence speciation analysis is necessary in order to understand its reactivity in the environment such as its toxicity (for Cu) and biological availability.

Pulau Perhentian's status as a Marine Park in the area highlights the needs to conduct the study as an indication of its ecosystem health. This area is affected by the Northeast monsoon season, which carry wind over about maximum of 30 knots and affects the vertical and upwelling activities thus lifting nutrient-rich water to the ocean surface water (Mohamed and Amil, 2015). Generally, trace metals speciation in the upper layer is governed by the complexation of strong organic ligands (Bruland *et al*., 1991), produced by phytoplankton in the water column (Croot *et al.,* 2000). Since speciation is controlled by the natural ligands produced by phytoplankton, an analysis is required to determine the effect of monsoon season to metal speciation at the study area.

1.3 Research Objectives

The overall aim of this research is to study the effect of Northeast monsoon on bioavailability of Cu to understand the effect of seasonal monsoon in the biogeochemical cycle of Cu at Pulau Perhentian, Malaysia.
The definite objectives are:

1. To study the distribution of total dissolved Cu at Pulau Perhentian, Malaysia in order to identify the influence of Northeast monsoon.

2. To determine Cu(II) speciation at Pulau Perhentian, Malaysia to by modifying the existing method to measure the Cu-ligand complex and the conditional stability constant in the seawater.

3. To quantify the degree of Cu(II) speciation to understand its toxicity threats by measuring the amount of free cupric ions, Cu^{2+}, saturation rate and its conditional stability constant.

1.4 Research Questions

Based on the research objectives above, the underlying research questions are as follows:

1. What are the role or effect(s), if any, of the Northeast monsoon on total dissolved Cu distribution at Pulau Perhentian?

2. Is there any presence of natural Cu(II) organic ligands in dissolved phase at Pulau Perhentian?

3. What are the degree of Cu(II) speciation and its toxicity threats, if any, during pre-and post-monsoon season at Pulau Perhentian?

1.5 Scope of study

This study generally covers the area as follows:

1- This study focuses on Cu speciation at Pulau Perhentian during pre-and post-monsoon season by using the current method, competing ligand exchange-adsorptive cathodic stripping voltammetry (CLE-AdCSV) as an initial study of its kind in the area. CLE-AdCSV is a very sensitive voltammetric technique that is accurate for detection limit of the order 10^{-11} M for dissolved copper concentration in water samples. Data collection was taken both during pre-and post-monsoon to compare the results obtained in lab analysis. The influencing parameters include the dissolved Cu concentration, total Cu concentration, natural ligands concentration, as well as the conditional stability constant, log K, to quantify the free cupric ions concentration, Cu^{2+} in the water sample. The stability constant was influenced by the chemical properties of both metal ions and organic ligands. The concentration of organic ligand in seawater was among important parameter to know the ecological roles of these ligands and their possible origins.

2- This study also involves the identification of toxicity threats (if any), posed by free Cu^{2+} ions in the water column as a result of weak speciation process. Toxicity levels are determined by the pCu activity and the free Cu^{2+} concentrations in the sample, in which are quantified by using van den Berg linearization formula, after the lab analysis using CLE-AdCSV.

1.6 Significance of study

Copper speciation analysis is necessary to understand its reactivity in marine environment, for example its toxicity and bioavailability, as well as the geochemical behavior of its species. Diatoms are among vital phytoplankton responsible for most marine photosynthesis, thus playing significant role in ocean carbon cycling.

As one of the essential nutrients for biological functions, concentration and speciation, trace metal Cu may directly influence the distribution of phytoplankton species in the ocean. Utilization and biological uptake of this element is related to its chemical interactions, which include interactions with the phytoplankton themselves. Interestingly, any changes to carbonate, hydrogen and hydroxide ions concentrations in carbon pump process may directly affect the speciation of metal complexes with dissolved organic matter (Stockdale *et al.,* 2016).

As a Marine Park itself, the health of the ecosystem at Pulau Perhentian requires a close monitoring of its trace metals' concentrations, especially Cu, as it can affect both in bioavailability and toxicity to microorganisms in the area. Previously, a limited condition of phytoplankton growth during pre-northeast monsoon was reported in a study (Mohamed and Amil, 2015). This raises a question whether the phytoplankton can produce strong natural organic ligands during the season, and whether the concentration of natural ligands are sufficient for Cu complexation, thus eliminating the toxicity threat it brings.

By using the current technology, this study hopes to provide a preliminary data for future comparisons of Cu distribution and speciation in seawater for pre-and post-NEM in southern SCS.

1.7 Thesis organization

Following this chapter, the remaining chapters of the thesis are outlined below:

Chapter 2 (Literature Review) details on the topics covered throughout the study that consists of the fundamentals background of Cu toxicity and bioavailability in seawater, the history of Cu speciation by other methods and by CLE-AdCSV, the production of natural ligands by phytoplankton, and Cu(II) speciation with natural ligands.

Chapter 3 (Methodology) presents the research design for this study in detail. The laboratory analysis in this study consist of sample treatment and preparation, as well as using CLE-AdCSV. The data collected experiments were analyzed using van den Berg linearization formula after the analysis.

Chapter 4, 5 and 6 (Results and Discussion) discuss the findings of the distribution of dissolved Fe, Al and Cu; the determination of Cu speciation by using CLE-AdCSV; and finally, the effect of Northeast monsoon on Cu speciation at Perhentian Island, Terengganu. All the findings are presented in profile graphs for easy comparisons and discussions. This chapter also highlights the answers for all the research questions in this study.

Chapter 7 (Conclusions) summarizes the major findings of the study in the fulfilment of the research objectives. Recommendations for future studies in this field are also included.

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