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GEOCHEMICAL SPECIATION OF VANADIUM AND NICKEL FROM SELECTED MANGROVE AREAS ALONG THE WEST COAST OF PENINSULAR MALAYSIA

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ABSTRACT

Continuous use of products containing vanadium (V) and nickel (Ni) along the coastal areas present potential threat to the coastal environment and biota. Hence, this study was conducted to determine V and Ni geochemical speciation in surface sediments from selected mangrove areas along the west coast of Peninsular Malaysia. The four-steps sequential extraction technique (SET) was used to extract these metals based on their leachability behaviour and describing their origin. Results showed the non-resistant fractions to be higher at all the sites for both V (highest in Kuala Gula: 76.89%) and Ni (highest in Kuala Juru: 75.44%) while resistant fractions were higher for both V(30.14%) and Ni (39.22%)in Sungai Tiga, respectively. Mean concentration of V was highest in Sungai Tiga (24.18±1.70 µg/g) in oxidizable organic and Ni in Kuala Juru (22.38±0.05 µg/g) also in oxidizable organic. There was a significant difference ($p<0.05$) between fractions in different sites.

KEY WORDS : Geochemical speciation, Sequential extraction technique, Heavy metals, Mangrove, Sediment

INTRODUCTION

Heavy metal has the capacity to bioaccumulate in aquatic ecosystems and can exert potential toxic effects (Yuan *et al.*, 2004; Li *et al.*, 2014; Khan *et al.*, 2017). As a result of the ecological importance of aquatic ecosystem and the persistence and non-biodegradable nature of pollutants, sediments are very important to be monitored in environmental evaluation (Tokalioglu *et al.*, 2000; Alkarkhi *et al.*, 2009). Ismail (1993) stressed the importance of using sediments for monitoring metal pollution in the biosphere and the effect posed by the anthropogenic activities in the environment. Sediments have been termed as the last store or sink of chemical pollutants (heavy metals inclusive), that results from various anthropogenic activities (Hope, 1997; Zulkifli *et al.*, 2010a; Abdallah, 2017).

In most cases, heavy metal studies are based on the analyses of the total metal concentration of V and Niwhich is not sufficient in providing explanations for their environmental behaviour (Ramirez *et al.*, 2005). Determination of total metal concentration can't suffice in evaluating metal contamination. As such, other more detail methods like sequential extraction technique (SET) needs to be employed. Chemical speciation of heavy metals by the use of SET is one of the methods used in evaluating metal concentrations in sediment and gives a more accurate assessment of real environmental effect (Kumar *et al.*, 2012).

Despite reported works on sequential extraction of heavy metals including V and Ni in this and other regions of the world such as the works of Yuan *et al.*, (2004); Cuong and Obbard, 2006; Zulkifli *et al.*, 2010; and Yap and Pang, 2011 there is still need for continuous monitoring of heavy metals and other contaminants as new chemicals are being discharged

into the environment. This is as a result of rapid industrial development Malaysia has recorded due to several factors, such as population increase, transportation of oil cargos, agricultural activities, mining, fishery activities etc. Hence, the present study was conducted to determine geochemical speciation of V and Ni in the sediments from selected areas of the west coast of Peninsular Malaysia.

METHODS

Surface Sediment (≤ 5cm depth) samples were collected in 2010 from four sampling areas (Bagan Lalang in Selangor, Kuala Gula in Perak, Kuala Juru in Penang and Sungai Tiga in Johor) in the west coast of Peninsular Malaysia. Information on these areas is described in Table 1. Samples were collected using a plastic scoop and placed in labelled plastic bags and taken to the laboratory. The samples were kept in a freezer at -20 °C until analysis. They were dried in an oven at 60 °C to obtain a constant dry weight, after which they were ground to a powder using mortar and pestle. It was sieved through a 63µm mesh size stainless steel sieve by shaking vigorously to produce recommended homogeneity (Ismail, 1993) and were kept in cleaned plastic bags before chemical analysis was conducted.

About1.0 g of each dried sediment sample was weighed and digested in a combined solution of nitric acid (AnalaR grade BDH 69%) and perchloric acid (AnalaR grade BDH 60%) in the ratio of 4:1, initially for 1 hour at a temperature of 40 °C and the temperature was increased and maintained at 140 °C for 3 hours (Yap *et al.,* 2002; Kadhum *et al.,* 2016). Digested samples were then diluted to 40 mL with deionized distilled water (ddH_2O). It was then filtered through Whatman's No. 1 filter paper into 100 mL sample bottles and kept until metal analyses.

Geochemical fractions of V and Ni were determined in the sediment using a modified sequential extraction technique (SET) described by Badri and Aston (1983). The technique involves four fractions:

(1) Easily, freely and leachable or exchangeable fraction (EFLE). In this, about 10 g of the sample was shaken continuously in 50 mL of 1.0 M ammonium acetate (NH_4CH_3COO) solution for 3 hours adjusted to pH 7 at room temperature.

(2) Acid-reducible. The residue obtained in the first step was also shaken continuously for 3 hours in 50 mL of 0.25 M hydroxylammonium chloride ($NH_2OH.HCl$) which was acidified to pH 2 with HCl at room temperature.

(3) Oxidisable – organic. In this step, the residue from acid-reducible was oxidized in a water bath with 30% H_2O_2 at 90-95 °C. The residue was then shaken with 50 mL of 1.0 M NH_4CH_3COOH continuously for 3 hours and acidified with HCl to pH 2 at room temperature.

(4) Resistant Fraction. The third step residue was digested using a combined solution of concentrated nitric acid (HNO_3) (AnalaR grade, BDH 69%) and perchloric acid (AnalaR grade, BDH 60%) in the ratio of 4:1 at 40 °C for an initial 1 hour. The temperature was increased to 140 °C for 3 more hours.

Residue left for each fraction preceding the next step was weighed before carrying out fractionation. It was then rinsed with 20 mL of dd H_2O and filtered through Whatman's No 1 filter paper in a funnel. The filtrate was kept in glass sample bottles until metal analysis. And for each step of the sequential extraction procedure, a blank solution was prepared in the same way as the procedure in ensuring both the samples and chemicals used were free of contamination. The filtrates were analyzed for V and Ni with the use of inductively coupled plasma

Table 1. Location, coordinates and description of the sampling sites

No.	Sampling site	Coordinate	Description of site
1	BaganLalang, Selangor	N 02° 36.669' E101°41.100'	Mangrove, fish jetty, agricultural, aquaculture and recreational area
2	Kuala Gula, Perak	N 04° 56.2502 E100° 28.1082	Northern section of Matang Mangrove Forest, Important Bird Area (IBA) for local and migratory shorebirds, shipping activities, fishing activities, aquaculture
3	Kuala Juru, Penang	N 05° 19.683' E100° 22.949'	Mangrove remnant surrounded by industrial area, port, urban development, and aquaculture
4	Sungai Tiga, Johor	N 01° 25.841' E 104°00.281'	Agricultural, fish jetty and oil plantation

optical emission spectrometry (ICP-OES) Spectrometer Model; Optima 2000 and all data were presented in microgram per gram dry weight (µg/g). In order to check for accuracy of the sample or if they are contaminated, the blank solution was prepared from acid solution without samples. Also, in order to ensure recovery and sensitivity of the instrument that was used, a quality control sample standard was prepared from 1,000mg/L of stock solutions of V and Ni and was analyzed for every 10 samples.

Analysis of variance using Portable IBM SPSS Statistics version 21 showed a significant difference ($p \leq 0.05$) between fractions in different sites.

RESULTS

Table 2 shows the mean metal concentrations, standard error (±SE) of the geochemical fractions (EFLE, acid-reducible, oxidizable organic and resistant), total concentrations (Σf1-f4), aqua-regia and recovery of both V and Ni for each of the sampling sites. EFLE fractions for V and Ni in the surface sediment ranged from 0.38-1.60 and 0.18-1.50 µg/g, respectively. For acid-reducible fractions, the range for V was 1.75-5.88 µg/g and Ni was 0.93-4.78 µg/g. The oxidizable organic fractions for V and Ni ranged from 9.43-24.18 and 5.23-22.38 µg/g respectively. The resistant fractions for V and Ni ranged from 6.08-11.35 and 3.56-9.23 µg/g respectively. Mean concentrations of heavy metals observed were generally higher in resistant fractions when compared to individual non-resistant fractions except for oxidizable organic fractions for both V and Ni which were higher.

Figure 1 shows percentage (%) resistant and non-resistant fractions of both V and Ni in surface sediments from the study areas. For V, the non-resistant fractions were 70.47% in BL, 76.89% for KG, 72.61% for KJ and 69.86% for ST. Resistant fraction, on the other hand, were 29.53% in BL, 23.11% in KG, 27.39% in KJ and 30.14% in ST. As for Ni, the percentages for non-resistant fractions stands at 73.03% for BL, 71.15% for KG, 75.44% for KJ and 60.78% for ST, while resistant were 26.97% for BL, 28.85% for KG, 24.56% for KJ and 39.22% for ST

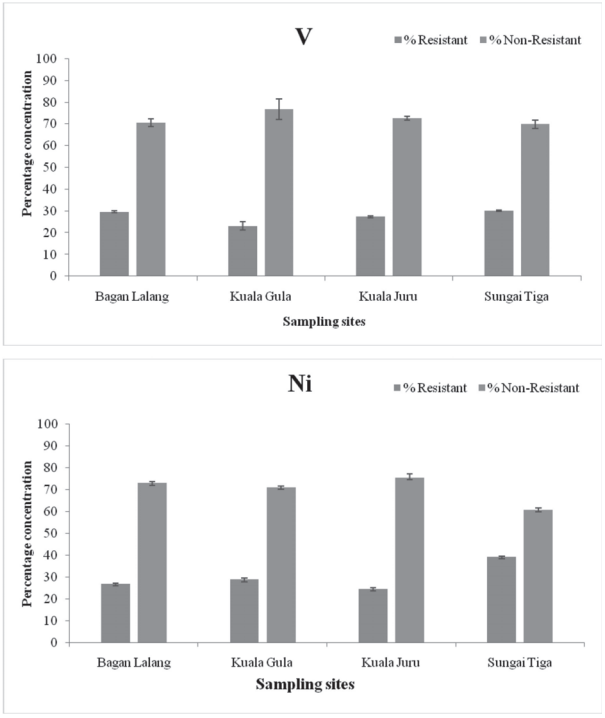

Fig. 1. Percentage (%) resistant and non-resistant fractions of V and Ni in surface sediments from selected mangrove areas of the west coast of Peninsular Malaysia

Table 2. Mean concentrations (±SD; n=3) of geochemical fractions and aqua-regia of V and Ni (µg/g dw) of surface sediments from selected mangrove areas of the west coast of Peninsular Malaysia

Metal	Site	Non-Resistant			Resistant (F4)	Σ (F_1-F_4)	Aqua Regia	Recovery (%)
		EFLE (F1)	Acid-reducible (F2)	Oxidisable organic (F3)				
V	Bagan Lalang	1.60±0.30^{b}	3.48±0.05^{ab}	9.43±1.45^{a}	6.08±0.45^{a}	20.59	20.02±2.48	102.85
	Kuala Gula	0.63±0.00^{a}	3.05±2.03^{ab}	17.95±2.63^{b}	6.50±1.90^{ab}	28.13	26.79±2.30	105.19
	Kuala Juru	0.50±0.03^{a}	5.88±0.63^{b}	13.58±0.13^{a}	7.53±0.48^{a}	27.49	28.78±2.54	95.52
	Sungai Tiga	0.38±0.05^{a}	1.75±0.20^{ab}	24.18±1.70^{b}	11.35±0.28^{b}	37.66	33.81±0.57	111.39
Ni	Bagan Lalang	0.28±0.08^{a}	1.53±0.35^{ab}	7.83±0.05^{b}	3.56±0.05^{b}	13.2	11.94±0.84	110.55
	Kuala Gula	0.18±0.10^{a}	0.93±0.18^{a}	16.40±0.20^{d}	7.10±0.50^{bc}	24.61	21.63±0.56	113.78
	Kuala Juru	1.50±0.10^{b}	4.78±1.70^{b}	22.38±0.05^{e}	9.23±0.38^{c}	37.89	34.79±1.31	108.91
	Sungai Tiga	0.53±0.05^{a}	0.95±0.28^{a}	5.23±0.60^{a}	4.33±0.28^{a}	11.04	10.79±1.20	102.32

*same alphabets are not significant at $p>0.05$

respectively. Non-resistant fraction or the most altered fraction comprised the first three fractions; EFLE, acid-reducible and oxidisable-organic. Percentage concentrations were generally higher in non-resistant fractions (EFLE +acid-reducible + oxidisable-organic) than the resistant fraction. Higher percentages in the non-resistant fractions could be due to anthropogenic inputs around the sampling sites.

The concentration for V at Bagan Lalang was 20.02±2.48 µg/g, Kuala Gula 26.79±2.30 µg/g, Kuala Juru 28.78±2.54 µg/g and Sungai Tiga 33.81±0.57 µg/g respectively. For Ni, the concentrations were; Bagan Lalang 11.94±0.84 µg/g, Kuala Gula 21.63±0.56 µg/g, Kuala Juru 34.79±1.31 µg/g and Sungai Tiga 10.79±1.20 µg/g respectively. Mean range for V for all the sites was 20.02 – 33.81 µg/g and 10.79 – 34.79 µg/g for Ni as well.

DISCUSSION

The concentrations of metals reported in this study are well within the ranges reported by most investigations carried out in and around the west coast of Peninsular Malaysia and few regions of the world. Zulkifli *et al.* (2010b) reported a similar level of vanadium in western Johor strait but with higher concentrations in the eastern Johor strait. The highest concentration of vanadium was rerecorded in Sungai Tiga in Johor and thus justifying their report that Johor strait is a hotspot for trace elements concentration. Vanadium was relatively lower than the average concentration reported by Wood *et al.* (1997) along Johor strait between Malaysia and Singapore. Concentrations of Ni were higher in Kuala Juru when compared to the levels reported by most workers in the study area except at eastern Johor which follows asimilar pattern of concentration. Studies by Nemati *et al.* (2011) in Sungai Buloh, Malaysia, Wood *et al.* (1997) in Johor strait between Malaysia and Singapore, Mat *et al.* (1994) in Penang, Malaysia, all reported lower concentrations of Ni than the present study.

Higher total concentrations of both V and Ni in Sungai Tiga and Kuala Juru respectively reported could be attributed to industrial discharges from the various industries located in those areas. Such industries located in Prai industrial area, for example, discharge their effluents into the Kuala Juru River and other canals which empty their contents into the sea via a pump house (Seng *et al*., 1987). There are other sources of anthropogenic inputs from shipping activities with petroleum unloading, quarry works in the coastal areas as well as domestic discharges together with fishing activities which explained why the sites recorded higher levels of metal concentrations. Industries such as chemical plants, rubber based industries, paper products, textiles, agricultural products, electronics, food processing and canning, timber products have been reported by Alkarkhi *et al.* (2009) to be operating in Juru area. A lot of jetties and fishing villages are situated near the sampling locations which contributed to the anthropogenic input of heavy metals in the sites. Some related studies in the west coast of Peninsular Malaysia have reported high levels of heavy metals in the sediments close to the sources of industrial discharges of textiles, plastic factories, electroplating, battery manufacture and much more (Mat *et al*., 1994; Naji *et al.*, 2010; Nemati *et al.*, 2011).

Although the levels of both V and Ni are not very high in the study area, elevation of their concentrations could pose possible effects on both biota and the ecosystem. It (V) is one of the so-called essential elements (Nriagu, 1998) and is beneficial to normal cell growth in trace quantity. Toxicity of this metal arises when its concentration increased to higher levels (Colina *et al*., 2005). Effects of V in both ecosystem and biota have been well documented (Sivaperumal *et al*., 2007; Soares *et al*., 2008; Karageorgis *et al*., 2009). Toxicity of Ni is more pronounced especially at higher concentrations in fish and other organisms as it accumulates in organs like lungs (Ptashynski and Klaverkamp, 2002; Leonard *et al.,* 2009).

Most of the concentration levels of both V and Ni reported in this study are either within the ranges or higher than those reported in this region and elsewhere. Although the use of total concentration (aqua-regia) and metal speciation using sequential extraction techniques have given light on the contamination level of the metals in the study area, it is recommended that more pollution indices be used to explain further on the degree of contamination or the pollution level of the study area.

CONCLUSION

Although V and Ni concentrations of present study are within the ranges reported by most investigations, however, their presence is more in the non-resistant forms, which is available to be

release, absorb and accumulated by biota of the mangrove ecosystem. This could potentially cause mangrove ecosystem degradation if concentration of these metals exceed the threshold limit of specific organisms. Hence, further monitoring and ecotoxicological assessment should be conducted to reveal V and Ni impacts on the mangrove ecosystem in long term.

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