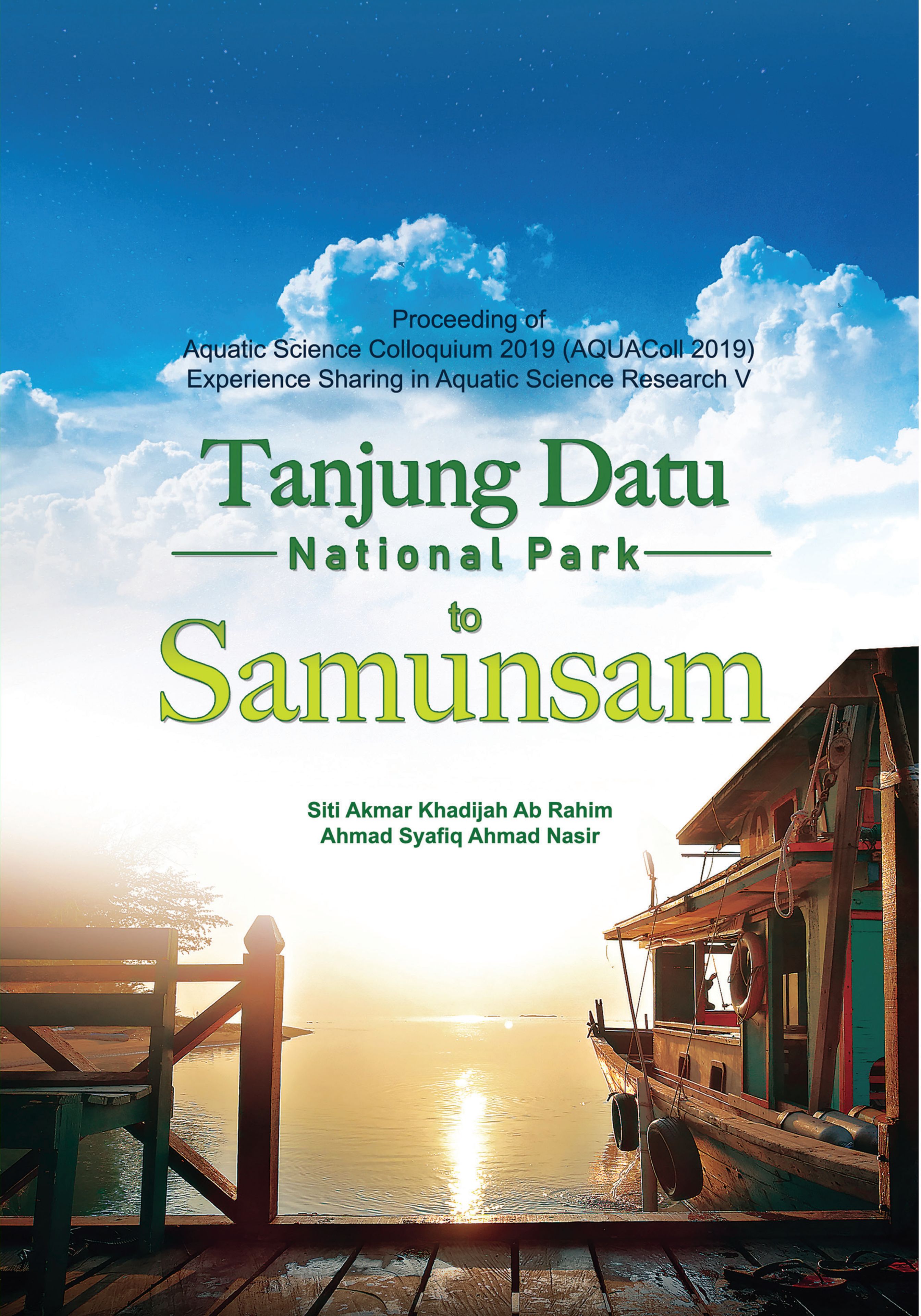

Proceeding of
Aquatic Science Colloquium 2019 (AQUAColl 2019)
Experience Sharing in Aquatic Science Research V

Tanjung Datu National Park to Samunsam

Siti Akmar Khadijah Ab Rahim
Ahmad Syafiq Ahmad Nasir

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Contents

Preface

The articles published in this proceeding are the research outcome of a joint scientific expedition in 2018 between the Programme of Aquatic Resource Science and Management, Faculty of Resource Science and Technology, Universiti Malaysia Sarawak (UNIMAS) and Sarawak Forestry Corporation Sdn Bhd (SFCSB) entitled Tanjung Datu National Park – Samunsam Wildlife Sanctuary Marine and Coastal Resources Expedition: Biodiversity Conservation and Sustainable Utilization'. The expedition was the second research collaboration between UNIMAS and SFCSB after the first 'Pulau Sampadi Marine Life Expedition' in 2012. The objectives of this expedition are: (1) to collect information and establish baseline data on the aquatic environments and its available resources from Tanjung Datu National Park to Samunsam Wildlife Sanctuary areas; (2) to contribute to the development of Sarawak Marine and Coastal Conservation Master Plan and also (3) to identify and recommend potential sustainable economic activities for the local communities.

This expedition's findings were presented during the Aquatic Science Colloquium 2019 (AQUAColl 2019) which is the fifth series of a biennial academic event that acts as a scientific platform for researchers to update, exchange and sharing of research information and findings explicitly obtained from the scientific expedition.

This AQUAColl 2019 proceeding comprises 18 research papers which reflect the aquatic and terrestrial biodiversity, physical oceanography, the status of marine pollution and socio-economic activities occurring inside or surrounding the Tanjung Datu National Park – Samunsam Wildlife Sanctuary. It is hoped that these scientific data may provide important baseline information and be beneficial towards future fisheries, oceanographic surveys and ecotourism activities in these areas.

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UNIMAS

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Prof. Dr. Ramlah Zainudin (UNIMAS)
Assoc. Prof. Dr. Devagi Kanakaraju (UNIMAS)
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Ms. Cindy Peter (UNIMAS)
Mr. Oswald Braken Tisen (SFC)

Last but not least, we thank everyone for their hard work and dedication, and we look forward to future continuous collaboration. Well done and thank you to SFC and UNIMAS!

Assessment of Selected Heavy Metals and Total Organic Carbon in Surface Sediments along Tg. Datu and Sematan Coastal Area

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Abstract

Tanjung Datu and Sematan Coastal areas were exposed to recreational activities and construction of Pan Borneo Highway, Sarawak, which may receive indirect input of heavy metals and other components into the nearby seawater. The objectives of this study were (1) to determine the concentration of selected heavy metals concentration (Al, Cd, Co, Cr, Cu, Fe, Mn, Ni and Zn) and (2) to assess the TOC in surface sediment at stations between Tg. Datu and Sematan Coastal areas. Samples were digested following the acid digestion method before analysing with the Flame Atomic Absorption Spectroscopy (FAAS, iCE 3000 Series AA) and total organic carbon analyser (TOC, Shimadzu). The results of heavy metals concentration were followed the sequences of Al (537.33 - 432.44 mg/kg) >Fe (6.81 – 110.01 mg/kg) > Cu (11.84 – 13.02 mg/kg) > Ni (5.27 – 6.50 mg/kg) > Co (3.48 – 4.35mg/kg) > Cr (0.39 – 9.18 mg/kg) > Mn (2.57 – 5.47 mg/kg) >Zn (0.38 – 3. 66 mg/kg) > Cd (0.94 – 1.09 mg/kg). For TOC, all stations were followed the sequences of Station G (1.44±0.01 %) > Station B (1.31±0.03 %) > Station C (0.51±0.02 %) > Station E (0.46±0.03 %) > Station D (0.43±0.04 %) > Station A (0.13±0.02 %). Overall, concentrations of heavy metals and TOC were considerably low. Atmospheric and land-based *inputs were the main sources for heavy metals around the sampling areas.*

Keywords: Heavy Metals concentration, Total Organic Carbon, Tg Datu, Sematan Coastal

Introduction

Tg. Datu National Park is located at the south-western most tip of Sarawak. The primary landscape constituting a narrow bridge of rugged hills towering up to 543 meter above the sea level, at its highest peak referred to as Gunung Melano. The park is covered with rain forests, fringed with pristine white sand beaches, crystal-clear waters and patches of healthy coral reefs. The international border between Malaysia and Indonesia runs along the crest of the ridge. Outside the park, on the Malaysian side of the peninsula, two villages named Kampung Telok Melano and Kampung Serabang which are located within embayment fringed by sand beaches along the largely rocky coastline. The oldest rocks of Tanjung Datu Peninsula, known as Serabang Formation.

The sediment type along this coastal area is mainly sand. The greatest contribution to reptile conservation plays role as marine turtle nesting site. Along the beach, there are turtles come ashore for nesting. Highly endangered green turtles and olive ridley turtles regularly lay their eggs on the beaches. At the national park, the activities that can do such as hiking and snorkelling. Many homestays were built for tourist that come to the national park which can lead to pollution of the sea. Tourism activities, if not properly planned and developed, could lead to negative effects on the biophysical environment such as water pollution, air pollution and ecosystem degradation (Zhong *et al.,* 2011).

Sediment analysis is vital to assessing qualities of total ecosystem of water body in addition to water sample analysis practiced for many years, because it reflects the long term quality situation independent of the current inputs (Adeyemo *et al.,* 2008). However, some research has suggested that heavy metals are stable elements that last in the environment as they do not degrade or destroyed. Therefore, heavy metals tend to accumulate in sediments and organisms (Yu *et al.,* 2000). Regular monitoring of heavy metals should be done because excess heavy metals might be harmful to the ecosystem especially aquatic life. In sediment water bodies, toxic compounds including metals tend to accumulate through complex physical and chemical adsorption mechanisms which depend on the nature of the sediment matric and the properties of adsorbed compounds (Abul Kashem *et al.,* 2007).

Continuous deposition of heavy metals in urban areas may also act as secondary source of pollution to the seawater.

Meanwhile, determination of Total Organic Carbon (TOC) is important to identify the availability of organic substances in sediments, which the contents are depending on the geographical locations, sources of pollutants and the depth of sediment layers (Ali *et al.,* 2015). The presence of TOC can influence the biogeochemical processes in the seawater including the nutrients cycling and metals cycling, chemical transport and bio-availability. TOC in sediment are the sources from the decomposition of the plants and animals or plankton or anthropogenic sources such as chemical contaminants, fertilizers of organic rich waste (Avramidis *et al.,* 2015). High concentration of nutrients and organic carbon can increase phytoplankton growth and consequently, the sedimentation of debris (Lazar *et al.,* 2012).

Therefore, the objectives of this study were to determine selected heavy metals such as Aluminium (Al), Cadmium (Cd), Cobalt (Co), Chromium (Cr), Copper (Cu), Iron (Fe), Manganese (Mn), Nickel (Ni), and Zinc (Zn); and to assess the total organic carbon (TOC) in sediment along Tanjung Datu and Sematan Coastal.

Materials and Methods

Sampling strategy

This study was conducted along Sematan to Tanjung Datu coastal area, Sarawak, Malaysia waters (Figure 1) from 14^{th} to 15^{th} of August 2018 covering 9 stations. Details of each sampling stations are shown in Table 1.

The sediments were collected by using Ekman grab at near-surface areas at 9 stations. After that, the sediments were placed in a clean resealable plastic bag and were labelled for each station. The data such as longitude and latitude, condition of the surface sediment and the weather were recorded. Then, the sediment samples were stored in the clean cooler box to avoid contamination. At the laboratory, the sediment samples were placed in a freezer at -20 °C prior for analysis.

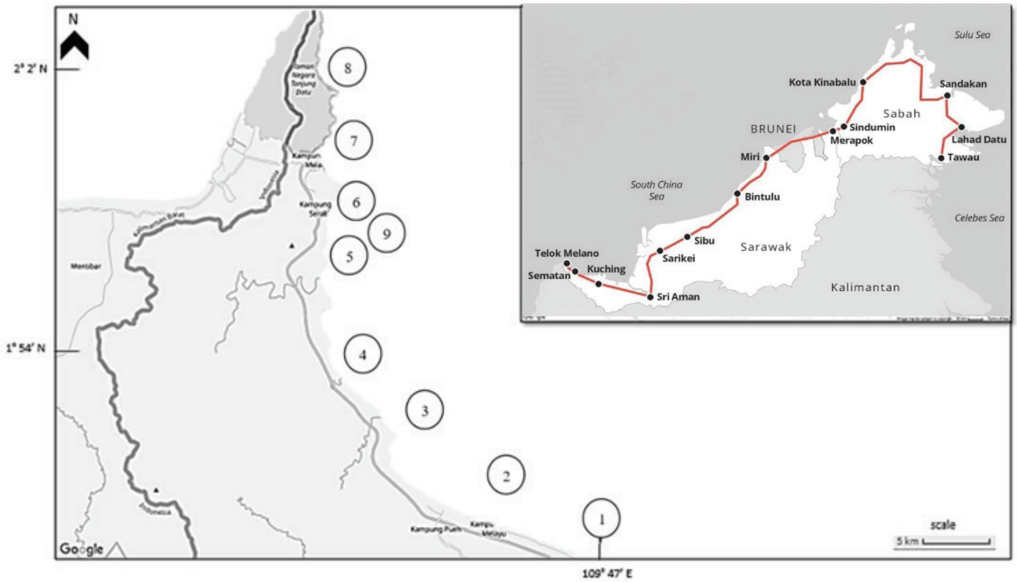


Figure 1 : Nine sampling stations along Tanjung Datu and Sematan coastal area. Red line showed the Pan Borneo highway.

Table 1 : Coordinates for the sampling locations.

Station	Date (2018)	Depth (m)	Latitude (N)	Longitude (E)
1	14th Aug	2.43	1° 49’ 25.06”	109° 47’ 03.41”
2	14th Aug	7.63	1° 50’ 59.40”	109° 44’ 19.00”
3	14th Aug	5.73	1° 52’ 50.02”	109° 41’ 56.22”
4	15th Aug	5.25	1° 54’ 27.90”	109° 40’ 08.00”
5	15th Aug	2.70	1° 57’ 15.80”	109° 39’ 19.50”
6	15th Aug	3.90	1° 57’ 23.70”	109° 39’ 45.60”
9	15th Aug	9.33	1° 58’ 40.40”	109° 39’ 44.60”

Samples digestion process

Sediments were dried out until a constant weight was obtained. Environmental Protection Agency (EPA) Acid Digestion 3050B procedure for sediment digestion was used and complete redox reaction with the addition of hydrogen peroxide (H_2O_2) (Guven and Akinci, 2011). The brief explanation of this method was as follow. Approximately 1.0 g of dried sample was taken into the conical flask with an addition of 10 mL of 65% nitric acid (HNO_3). Then, the solution was heated to ~95 °C for 30 minutes on the hot plate. 5 mL of 65% HNO_3 was continuously added until there was no brown fumes. The solution was cooled to less than 70 °C, 2 mL of deionize water and 3 mL of H_2O_2 were added. The solution was heated again until the bubble subsides. After the solution becomes cool to 70 °C, 10 mL of hydrochloric acid (HCl) was added and heated for 15 minutes until clear solution was obtained. After cooling to the room temperature, the solution was diluted to 100 mL with deionize water. The diluted sample was analysed for heavy metals and TOC.

Heavy metals analysis and Standard Calibration

Heavy metals such Al, Cd, Co, Cr, Cu, Fe, Mn, Ni and Zn in the surface sediments was determined in three replicates of each sample by using FAAS (Thermo Scientific: iCE 3000). The concentration of these metals were reported in mg/kg. Blank and replicates of standard solutions (with 3 different concentrations) were prepared for each element from 1000 ppm standard solutions (Figure 2).

Total Organic Carbon (TOC)

TOC level in the digested samples were determined using a TOC Analyser (%, Shimadzu, TOC-LCPH). The analysis was done in three replicates for each station.

Statistical Analysis

Univariate One-way analysis of variance (ANOVA) was applied to determine if there were any significant differences in the levels of heavy metals and TOC between the sampling stations. The statistical significance was fixed at 95 % confidence level. Pearson correlation analysis was used to determine the relationship between TOC and heavy metals ($p<0.05$) using IBM SPSS Statistic.

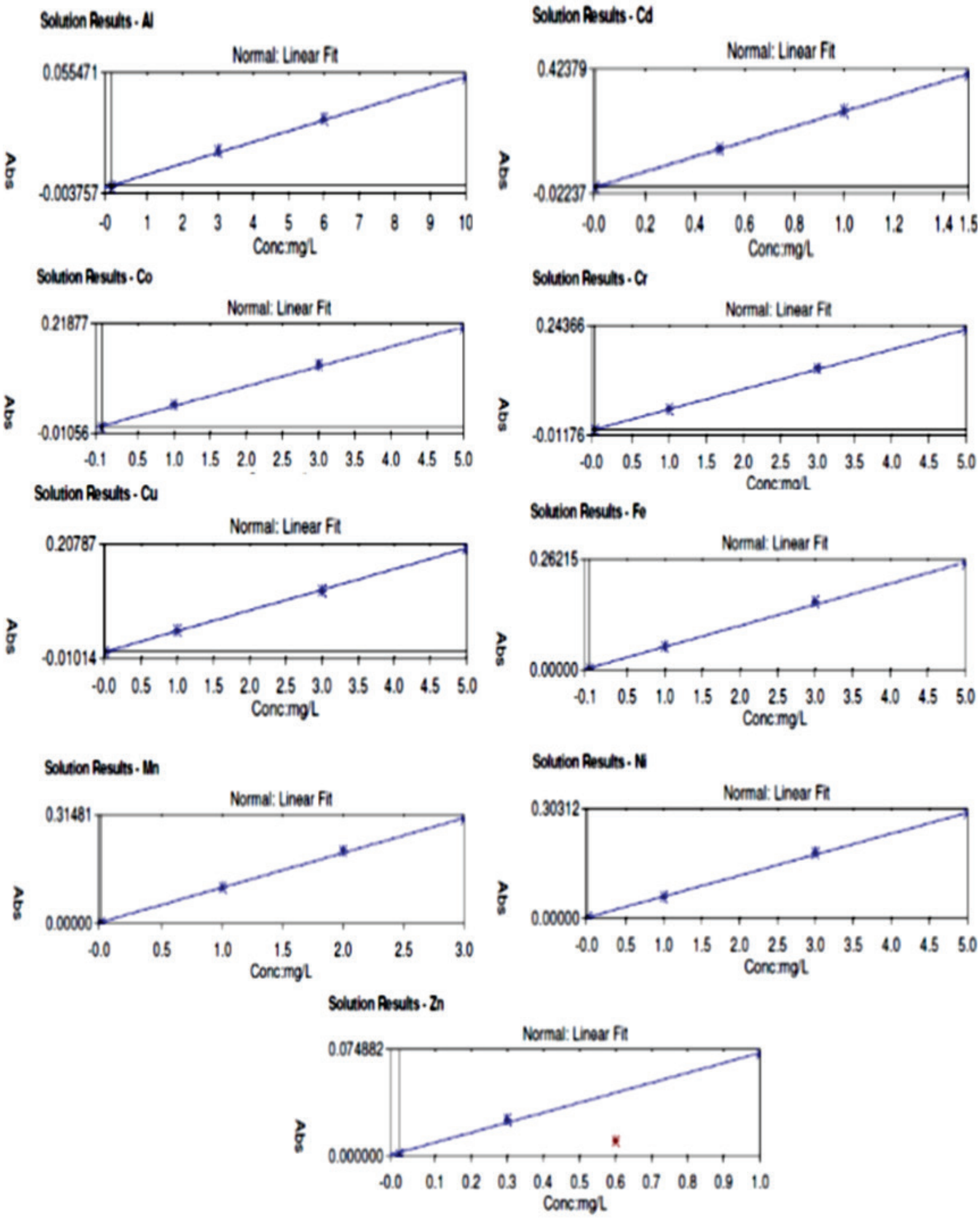


Figure 2 : Linear calibration curves for Al, Cd, Co, Cr, Cu, Fe, Mn, Ni and Zn using FAAS. The standard solution concentrations were in mg/L.

Results and Discussion

The selected heavy metal concentrations in the surface sediments from seven stations (Figures 3 and 4) varied from 537.33 to 1432.44 mg/kg for Al, 6.81 to 110.01 mg/kg for Fe, 0.38 to 3.66 mg/kg for Zn, 0.94 to 1.09 mg/kg for Cd, 5.27 to 6.50 mg/kg for Ni, 0.39 to 9.18 mg/kg for Cr, 2.57 to 5.47 mg/kg for Mn, 3.48 to 4.35 mg/kg for Co and 11.84 to 13.02 mg/kg for Cu. The average concentration of heavy metals in this study followed the order of Al >Fe > Cu > Ni > Co > Cr > Mn >Zn > Cd.

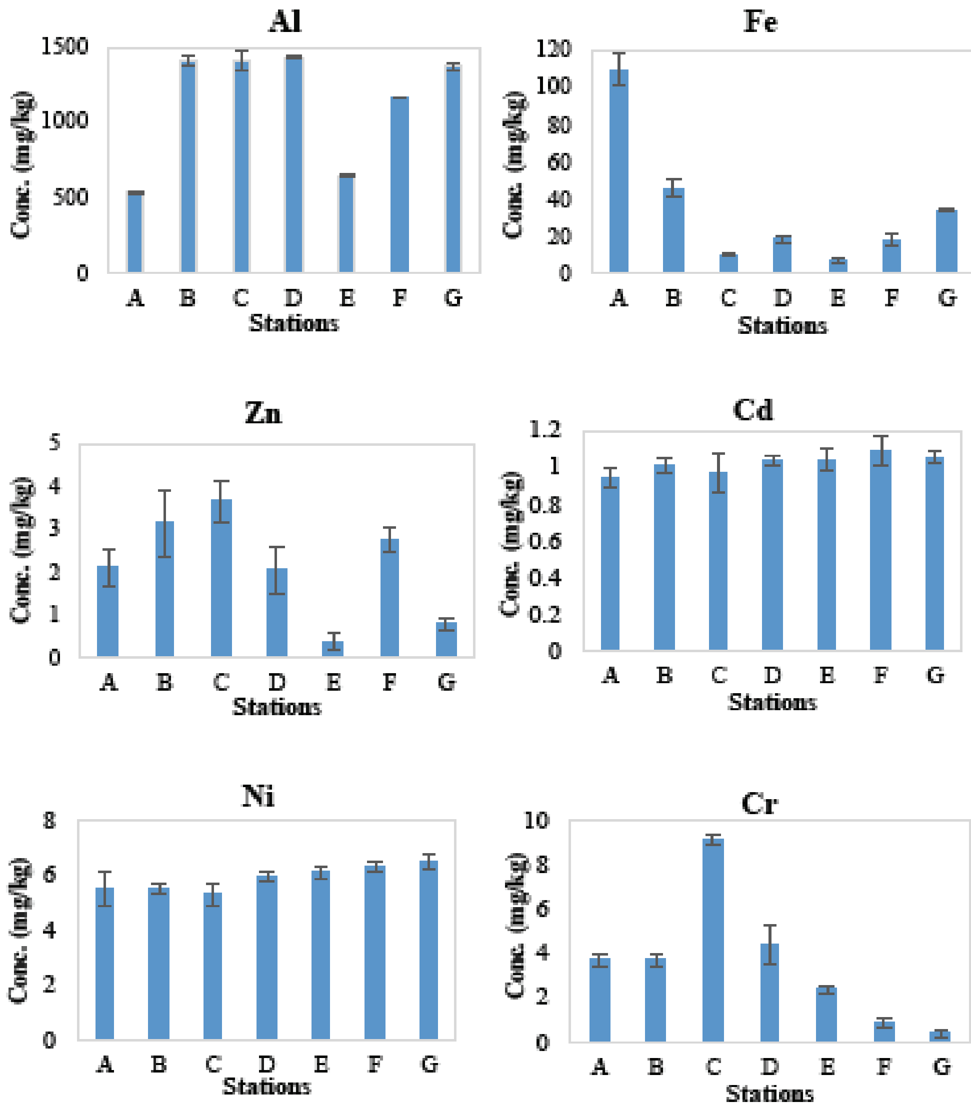
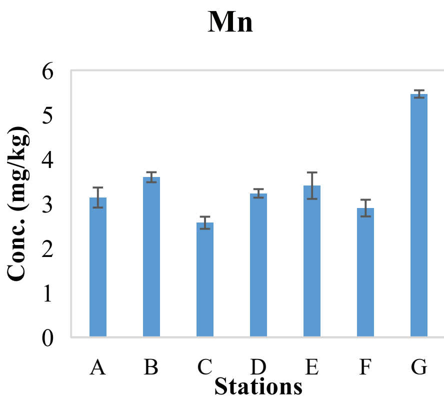


Figure 3 : Concentrations of Al, Fe, Zn, Cd, Ni and Cr of the surface sediment samples along the Sematan and Tanjung Datu coastal areas. The concentration level of each metal is different but the unit is in mg/kg.



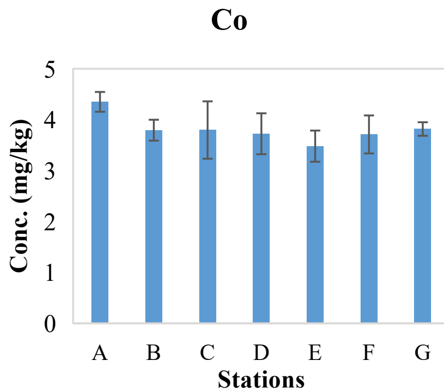
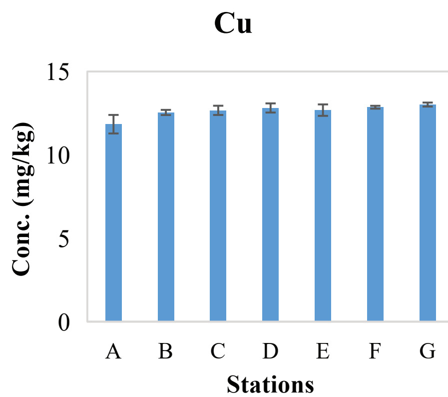


Figure 4 : Concentrations of Mn, Co and Cu of the surface sediment samples along the Sematan and Tanjung Datu coastal areas. The concentration level of each metal is different but the unit is in mg/kg.



Generally, the distribution of TOC ranged from 0.13 to 1.44 % (Figure 5). The highest concentration was found in station G that is close to Kampung Serabang (1.44±0.01 %) followed by 1.31±0.03% at station B, 0.51±0.02% at station C, 0.46±0.03% at station E, 0.43±0.04% at station D and the lowest concentration was detected in station A (0.13±0.02%), in the Sematan area.

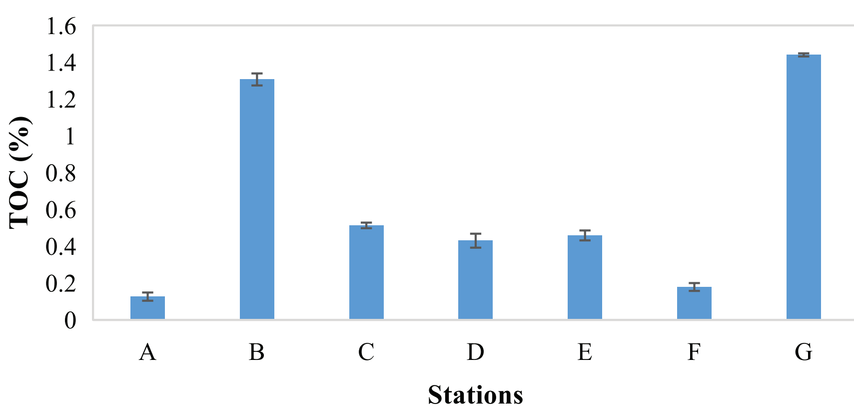


Figure 5 : TOC concentrations at all stations. The unit was in percentage (%).

Pearson correlation coefficient matrix was used to distinguish the relationship between observed heavy metals and TOC (Table 2). There were six moderate correlations and one good correlations were shown between elements Zn-Al (r = 0.73, $p<0.05$), Cr-Al (r = 0.71, $p<0.05$), Cr-Zn (r = 0.66, $p<0.05$), Mn-Ni (r = 0.65, $p<0.05$), Cu-Co (r = 0.69, $p<0.05$), TOC-Fe (r = 0.74, $p< 0.05$) and TOC-Mn (r = 0.81, $p<0.05$). The positive correlations indicate that the contents of these metals in the surface sediments probably originated from similar sources (Hossain *et al.,* 2015). Most of the metals showed a weak correlation between each other ($0 < r < 0.49$, $p<0.05$) indicating different sources. Al is an indicator of dust input in the study location. The source of Al in the study location could be from the atmospheric input as haze was spotted blanketing the study region during the sampling. However, there was no air pollution index (API) monitoring station nearby Sematan and Tanjung Datu, and the closer one is in Kuching (moderate, 51 – 100). Based on the backward trajectory data on the sampling period (Hysplit: www.ready.arl.noaa.gov), the wind direction was blown from the Kalimantan land (which many forest fire hotspots encountered) and its coastal area, which carried particulate matters to the study location.

Table 2 : Correlation between heavy metals and organic carbon in the study area.

Element	Al	Fe	Zn	Cd	Ni	Cr	Mn	Co	Cu	TOC
Al	1									
Fe	-0.20	1								
Zn	0.73	-0.08	1							
Cd	-0.36	0.26	-0.16	1						
Ni	-0.77	-0.12	-0.67	0.56	1					
Cr	0.71	-0.43	0.66	-0.39	-0.40	1				
Mn	-0.52	0.47	-0.61	0.33	0.65	-0.28	1			
Co	0.26	0.20	0.25	0.59	0.23	0.28	0.42	1		
Cu	0.50	0.30	0.40	0.32	-0.21	0.01	0.02	0.69	1	
TOC	-0.10	0.74	-0.21	0.35	0.18	-0.06	0.81	0.61	0.29	1

One-way ANOVA; $p< 0.05$.

Interestingly, stations 2, 3, 4, 6 and 9 where high concentrations of Al were recorded, located close to the ex-bauxite mining areas, along Sematan and Tanjung Serabang (Lee *et al.,* 2017). Bauxite is a rock consisting aluminium minerals, and the mining started in Sematan area in 1950s with >20 deposits had been found and ended up ~1970s (Hutchison, 2005). Munggu Belian hill in Sematan (close to stations 2, 3, and 4) made up of pyroxene andesite rocks which is a good grade of bauxite, while Bukit Gebong, contains gabbro rocks (also the Al-rich soils). Telok Serabang (that is close to stations 6 and 9) contains ferruginous greenstones which are the Al and Fe-rich soils that are low grade deposits of bauxite (Hutchison, 2005).

This also explained the noticeably high concentrations of Fe at stations 6 and 9 too. The hills around these high Al concentrations in the coastal sediments rise about 24 meters above the surrounding alluvial plain and about 1.70 Megatonnes of washed bauxite prior to mining and approximately 230,000 tonnes bauxite were still remained in these areas (Hutchison, 2005). Although these areas were the bauxite ex-mining, Al can be leached out from the soil by the wind blowing, weathering process or by the rain that wash out the soil into the coastal waters through the river or land run-off. However, Malaysian Government are against re-opening of the bauxite mining in Sematan and nearby areas.

Despite high concentrations of Al in this study, our values were still considerably low compare to values (~178.74 g/kg) from Kelantan and Johor coastal sediments (Shaari *et al.,* 2015) where their aluminium-rich sediments were due to the anthropogenic activities such as from the still active bauxite mining activity in Ramunia Bay and with the help of the run-off, the aluminium and its minerals were transported into the seawater and sinking to the sediment. Meanwhile, the logging and deforestation activities in Gua Musang may release the aluminium-rich sedimentary rocks or soils to weathering process and rainwater.

Moreover, there was ongoing road construction of Pan-Borneo Highway located in close proximity with the study location. Other heavy metal input was from the terrestrial. In this study, correlation between Mn and Fe shows a positive correlation ($r = 0.47$, $p<0.05$) suggesting that both metals maybe originated from the same sources. As the correlation of TOC-Fe ($r = 0.74$, $r<0.05$) and TOC-Mn ($r = 0.81$, $p<0.05$) were both showed a positive correlation, hence it was suggested that the sources of Fe and Mn at the study location came from the sediment and land by the river run-off and land run-off. Redox reactions may also the other possible sources for Mn and Fe due to their post-depositional concentrations were subject to alteration by the complex biogeochemical processes. The statistical analysis of one-way ANOVA shows a significant different in concentration between studied heavy metals and TOC. High concentrations of TOC were obtained in samples from stations that close to the human habitation area. Human wastes discharge may increase the availability of TOC in sediment and seawater (Ali *et al.,* 2015). However, TOC concentrations in this study are considerably low compared to the values obtained around the Langkawi Island (between 1.72 and 2.27 %; Kamaruzzaman *et al.,* 2010) and at the area of Port Klang (from 5.00 to 22.00 %; Sany *et al.,* 2013).

The concentrations of Cu, Co, Ni and Cd were found to be almost uniform. We assume that the distribution pattern of these metals are closely related to the human activities and natural sources. The possible human activities that can expose these metals into the study location are from fishing landing ports, domestic sewage sludge, motor oil, application of anti-fouling and anti-corrosive paints on the boats, application of fertilizers in the agriculture activities (Lindsey *et al.,* 2004; Kamaruzzaman *et al.,* 2008; Iyaka, 2011). Under natural conditions, these metals were found in rocks, soil, water, plants and animals. The association of Co with Mn (r = 0.42, $p<0.05$) is most likely due to the adsorption on to the Mn-oxyhydroxides.

The concentrations of metals obtained in this study was also compared with other studies. The concentrations of Cu, Cr, Ni, Zn, Fe, Al, Mn, Co in this study were lower than the values obtained in Langkawi Island (Zn: ~132.20 mg/kg, Cu: 38.24 mg/kg; Zahir *et al.,* 2012; Cr: ~91.53 mg/kg, Fe: 318.11 g/kg; Mokhtar *et al.,* 2019), Port Klang area (Fe: >3000 g/kg, Al: >6000 g/kg, Mn: >400 mg/kg, Cr: > 27 mg/kg, Zn: > 20 mg/kg, Ni: >5.00 mg/kg; Sany *et al.,* 2013), East Coast of Peninsular Malaysia (Cr: 79.2 mg/kg, Ni: ~20 mg/kg, Cu: ~17 mg/kg; Saraee *et al.,* 2011; Co: 9.30 mg/kg; Shaari *et al.,* 2015), and Klang coastal area (Zn: 32 – 388 mg/kg, Fe: ~20 g/kg, Zn: ~20 g/kg; Hamzan *et al.,* 2015). The average concentrations of Cd were almost similar to Langkawi Island (~1.00 mg/kg; Zahir *et al.,* 2012) and slightly higher than (~0.3 g/kg) Hamzan *et al.* (2015), but seemed to be higher than (0.11 mg/kg) Mokhtar *et al.* (2019).

Summary

This paper presented some preliminary data of heavy metals and TOC concentrations in the coastal area between Sematan and Tanjung Datu, which can be used for conservation and sustainable resource management. Throughout this study, nine metals and TOC were analysed and correlation between them were also reported. Overall, the concentrations of heavy metals and TOC in this study were lower than other locations, except for Cd, suggesting that sediments at this study area were not polluted by heavy metals. The main possible sources of metals were atmospheric inputs (*e.g.* dust) and land-based input (*e.g.* bauxite ex-mining, human habitation area and human activities). Detailed work needs to be done to obtain more information on sediment pollution especially after the recent opening of the Telok Melano beach to the public.

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Tanjung Datu National Park to Samunsam

This proceeding contains an overview of inventory works performed at Tanjung Datu National Park to Samunsam Sanctuary in the year 2018 to 2019, encompassing the organisms of terrestrial and aquatic ecosystems. Simultaneously, the status of local ecotourism, fisheries and pollution were also reported. This wide coverage of findings is very useful to complement the current and future development of the Tanjung Datu – Santubong Marine and Coastal Conservation Master Plan. With the construction of the Pan Borneo coastal highway, the impacts on marine environment and socio-economic are very important to be monitored. Thus, this book can be used as the main reference for future research in that area by scientists, policymakers and stakeholders, especially the relevant state and federal agencies in Sarawak. Environmental consultancy companies can also use the baseline data for Environmental Impact Assessment purposes.

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