Concentration of Antifoulant Herbicide, Diuron in the Vicinity of Port Klang, Malaysia

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Abstract:

Diuron is one of the alternative compounds that had been introduced by the paint manufacturer to be used in the coating paints. It is used to replace organotin-based paint that is prohibited to be used due to its deleterious effects on non-target organisms. However, a significant amount of Diuron that been released resulted from shipping moved was accumulated and contaminated the coastal waterline. Thus, environmental samples (sediment, porewater and surface seawater) were collected from the largest Malaysia shipping port, Port Klang area and extracted quantified for Diuron concentration by using an LC-MS/MS. Results showed the range of mean concentration in sediments (2.24 µg/kg to 19.28 µg/kg) hold the highest reading followed by porewater (0.88 µg/L to 12.91 µg/L) and followed by surface seawater samples (N.D to 0.53 µg/L). Recovery of samples ranged from 79.72 to 86.56 %. Vessels moored, rapid industrialization, active fishing activities, rich flushing zone are the point sources of Diuron input in the Port Klang area. In conclusion, the founded concentrations exceed previous reported of Diuron concentration. Continues study is suggested to report and monitor the level of Diuron in the marine environment.

Keywords: Diuron; antifouling; sediment; seawater; porewater; Port Klang

I. INTRODUCTION

Antifoulant in the coating paint is used to prevent any settlement of fouling organisms on submerged structures such as ship's hull, buoys, oil rig support and fish cages [1;2]. Ship and maritime industries together with paint manufacturer have developed several coating paints to reduce the effects of this paint towards marine environment. In 2008, organotin-based antifoulant has been banned worldwide suggested by IMO due to its irrevocable effects on aquatic organisms. Leaching of this Organotin compound led to imposex and deformation shell events [3], which causes the alteration of aquatic food web ecosystem. Thus, alternative biocides have been introduced by paint manufacturer to replace the existed Organotin-based compound. Alternatives biocide paint is a paint of copper-based with added of several booster biocides (e.g Diuron, Irgarol, Zinc pyrithione etc.) that significantly optimize the production efficiency. Biocides, Diuron is one of the Persistent Organic Pollutant (POPs) and has long half-lives sinking in the sediment that could last up to years. Due to its low water solubility, Diuron strongly bonds to particulate matters thus, leads to the deposition and accumulation in sediments [4;5;6]. Furthermore, its release to the environment is augmented with the increase of shipping activities on the waterline. Concerning this issue, this study has been conducted to assess the level of booster biocide, Diuron in the marine environment of Port Klang, Malaysia collected from three types of environmental samples.

II. MATERIALS AND METHODS

a. Study area description

Located strategically at the west coast of Peninsular Malaysia and in the middle of the Straits of Malacca, Port Klang is listed amongst Top 20's World Busiest Port with the 11,887 TEUs recorded [7], thus made the surrounding water bodies highly potential to be polluted by sea-sources and terrestrial pollutant. Near to the cosmopolitan area of Kuala Lumpur, vigorous of shipping activities are expected since the presence of railway station and historically tin mining at peninsular Malaysia during colonial decades. Three ports are extensively located represent the Port Klang area which are Northport, Southport and Westport. Northport and Westport are focusing on the good trade meanwhile Southport is used for jetty and passengers purpose.

b. Samples collection

Three types of samples were collected during sampling dated on 29 September 2016. Sediments sample were collected by Ekman grab (Wildco, Florida) and scoop, porewater was collected as it has been trapped in the sediment and surface seawater samples were collected by horizontal water sampler (Hydrobios, Germany). Collected samples were transported back to the laboratory in an ice box and stored in the refrigerator under 4˚C and kept free from light prior to laboratory experiment. All the procedures of sample preservation are as reported [8].

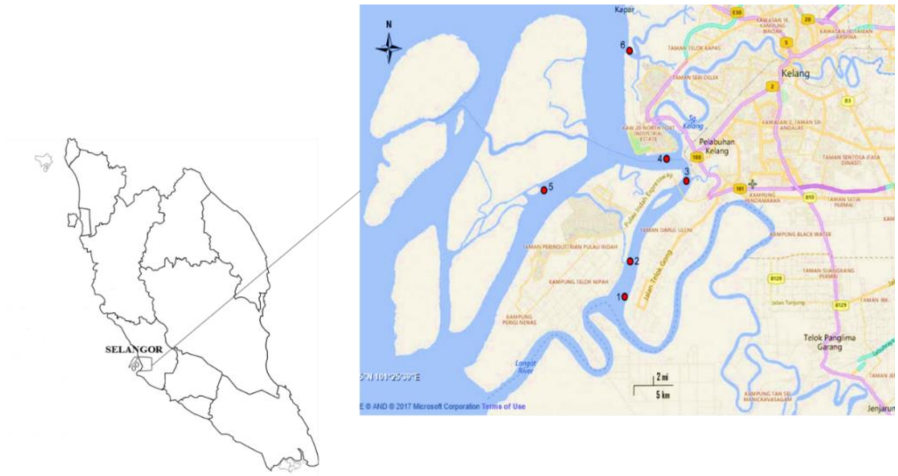

Fig. 1: Map of study site at Port Klang, Malaysia

c. Extraction procedure

Samples were recommended to be extracted within a week after collecting period. Liquid-liquid extraction (LLE) technique have been employed to extract desired compound, Diuron from samples and been clean-up to free the extracted samples from any other undesired compounds [9] [10][11]. The samples were mixed with acetone (J.T Baker, ACS Grade, USA), shake and centrifuge to get the supernatant. The process was then continued by changing the solvent carrier, dichloromethane (Macron Fine chemicals, ACS reagent, USA). The last carrier solvent of Diuron is methanol (J.T Baker, ACS Grade, USA). The analyte was concentrated up to 1 ml of nitrogen gas with the addition of 100 µl (1 mg/L) atrazine-d5 (PESTANAL grade, Sigma Aldrich, USA) as the internal standard. Diuron (≥ 98% purity assay, Sigma Aldrich, USA) has been used in spiked samples.

d. Samples analyzed

LC (Agilent UPLC 1290) connected with Mass Spectrometer (AB Sciex 5500) was used supported by an autosampler. Analyte separation was performed in C18 column (2 x 50 mm, 4 µm) (Synergi Fusion-RP 80A) and using helium as a carrier gas during the operation. A sample volume of 10 µL was injected into the instruments. MRM mode for quantification and confirmation was applied. The chosen ion for quantification are 233.01 (precursor ion) and 72.00 (product ion) meanwhile for qualification are 233.01 (precursor ion) and 160.00 (product ion).

e. Validation of method

Instrument calibration was performed by using ten different concentrations (0.1, 0.25, 0.5, 0.75, 1.0, 5.0, 10, 25, 50 and 100 µg/L). Recoveries of three types of samples were conducted by sample spiked at ranges 1, 10 and 100 µg/L (Table 1).

Table 1: Spiking rate for each samples type with their respective recovery rate (%)

Samples	Spiked volume	Spiked concentration	Recovery rates (%)
Sediment	5 g	1, 10,100 ppb	86.56
Porewater	5 ml		79.72
Surface seawater	5 ml		83.54

f. Statistical analysis

One-way ANOVA (Analysis of Variances, Ver. 22.0) was performed for all set of data. Post-hoc test was conducted to compare the mean within and between the samples.

III. RESULTS AND DISCUSSION

Diuron was found higher in sediments at Station 6 amongst all sampling stations as it has a significant difference with Station 2 ($p < 0.05$). Station 6 is the representation of the Northport area and of the input originating from the estuaries nearby. Runoff from the industrialization activities, residential areas and landfill areas provide the input into the river and consequently increase Diuron concentrations in the water column. Northport also is one of the efficient port as it is well-established container terminal which handles Dry Bulk, Breakbulk and Liquid Bulk Cargoes [12]. Experienced in handling the huge mass vessel of minimum 200 m in length, the increment of Diuron leaches in the water bodies of Port Klang is undeniable. It is due to the rule announced in the UK to only allow the antifouling paint to be applied to the vessel more than 25 m in length [2][13]. High records of vessel movement in the Port Klang coastal area, with the rampant development of factories in especially in manufacturing of herbicides are the point sources pollutant, Diuron [12]. Data revealed the mean concentration of Diuron in sediment is 19.28 µg/kg and the least is found at Station 2 (2.24 µg/kg) by referring to Table 2. Station 2 referring to the area of mangrove where there is only small- and moderate-sized vessels can pass through the waterways. Diuron is presence due to the ocean current that washes the area with the condition of pre-monsoon seasons. For all, the data collected revealed it has a significant increment of Diuron in sediment compared to the previous record (Table 3).

Table 2: Mean concentration ± standard deviation (s.d) of Diuron for environmental samples according to their stations

Sampling Stations	Mean Concentration ± S.D		
	Sediment (µg/kg)	**Porewater (µg/L)**	**Surface Seawater (µg/L)**
Station 1	8.03 ± 4.31	0.88 ± 0.52	N.D
Station 2	2.24 ± 1.32	1.84 ± 1.14	N.D
Station 3	4.92 ± 7.89	2.24 ± 1.67	0.54 ± 1.39
Station 4	6.55 ± 6.11	12.91 ± 1.16	N.D
Station 5	13.54 ± 12.88	11.75 ± 1.17	N.D
Station 6	19.28 ± 11.87	11.31 ± 3.45	N.D

Table 3: Concentration of Diuron in water and sediment samples from previous records (Noted: N.D = no data)

Location	Description/ Sampling Date	Samples		References
		Water (ng/L)	**Sediment µg/kg**	
Malaysia	2007		<0.04-4.8	[10]
Straits of Johor	2005		<0.02-9.9	
Melaka	2005		<0.02-4.1	[17]
Peninsular Malaysia	2005		<0.02-4.8	
Kemaman, Terengganu	November 2011-April 2012	N.D to 42		
Redang Island, Terengganu	November 2011-April 2012	21-63		
Bidong Island, Terengganu	November 2011-April 2012	8-41		[16]
Port Klang, Selangor	November 2011-April 2012	3-274		
Pasir Gudang, Johor	November 2011-April 2012	1-285		
Present study	2016	N.D. to 540	2.24-19.28	

Diuron concentration in porewater varies by referring to Table 2 with the highest at station 4 (12.91 µg/L) and the lowest belonging to station 1 (0.88 µg/L), while both stations are significantly different ($p< 0.05$). The valued data are lower compared to sediment data as the porewater is an interstitial water, which resides between the pore of sediment particle. It contains the uncomplex/free phase of pollutants meanwhile sediment particle is the binding site of the complex phase of Diuron [14][15]. The result clearly proved that station 4 which is the intermediate waterline between Northport and Westport has been polluted with the high free phase of Diuron. Before the modern Port Klang is well-established, Southport was the centre of all shipping activities. Highly toxic antifoulant other than Diuron also have been introduced into the water column. The runoff water from the Klang River estuaries has added pollutants that sink ultimately in the sediment of Southport. The porewater from Station 4 proved the real-time condition of pollutant and showed the worst-case scenario at Port Klang effects.

Surface seawater of Port Klang has also been contaminated with the presence of Diuron. Water is the first primary media to be intact with the pollutant through the friction with the vessel surface. A previous study conducted by [16] at from anthropogenic activities (urbanization, industrialization, etc) that contained pollutants (toxic). Port Klang was assessed at 3 ng/L up to 273 ng/L. Surprisingly, present data collected was only detectable at Station 3 (0.54 µg/L) and it is possibly due to the windy, cloudy weather creating unstable water conditions and rainfall variations during the sampling session as it occurred the monsoon season (September- February). Thus, this pollutant was dispersed and carried to other areas while at the same time sank deep into water bodies faster than usual. In fact, Diuron is potentially undetectable in surface water as it is already broken down naturally to its primary metabolite (DCA) caused by the photolysis process. This current Diuron concentration exceeds the safe limit of Diuron and it is shown an increasing value for Diuron from its past record (Table 3).

IV. CONCLUSION

Concentration of Diuron found at Port Klang area follow following pattern which is [Sediment] > [Porewater] > [Surface seawater]. All collected data from three different types of samples were above the permitted concentration limit of Diuron to be applied on ships at 430 ng/L. Furthermore, level of Diuron in Malaysian samples are higher compared to the previous record in coastal water of Malaysia and this is the first data for porewater recorded in Malaysia. Continuous assessment of Diuron in Port Klang water bodies is highly recommended to monitor the water condition to ensure the continuity of aquatic production.

ACKNOWLEDGEMENT

This study was jointly supported by the Fundamental Research Grant Scheme (FRGS) (Ref. No.:1/2014/STWN01/UPM/02/4) from the Malaysian Ministry of Higher Education and the Core-to-Core Program by the Japan Society for the Promotion of Science (JSPS).

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Isu-Isu Terkini Penyelidikan Saintifik Sains Marin Di Malaysia

Vol. 1

Disunting oleh

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Pusat Pengajian Sains Sekitaraan dan Sumber Alam (PPSSSA)
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Cetakan / Printing

Diterbitkan oleh

Pusat Pengajian Sains Sekitaraan dan Sumber Alam,
Fakulti Sains dan Teknologi,
Universiti Kebangsaan Malaysia
43600 UKM Bangi, Selangor, Malaysia

ISBN 978-983-41358-3-6

ISU – ISU TERKINI PENYELIDIKAN SAINTIFIK SAINS MARIN DI MALAYSIA VOL 1.

UNIVERSITI KEBANGSAAN MALAYSIA
The National University of Malaysia

PUSAT PENGAJIAN SAINS SEKITARAAN DAN SUMBER ALAM (PPSSSA)
UNIVERSITI KEBANGSAAN MALAYSIA

Diterbitkan oleh
Pusat Pengajian Sains Sekitaraan & Sumber Alam

ISBN 978-983-41358-3-6